Reactions of quinones with aromatic ethers.

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REACTIONS OF QUINONES WITH AROMATIC ETHERS

by

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A thesis submitted to the University of Aberdeen
for the degree of Doctor of Philosophy.

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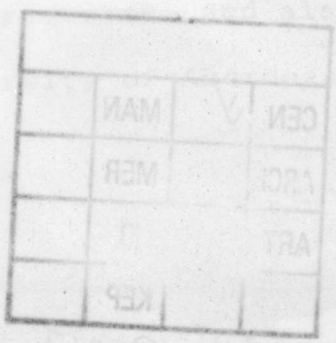


PREFACE

I hereby declare that the work presented in this thesis has been performed by myself and that it has not been previously presented for any degree. All sources of information have been specifically acknowledged by reference to the authors. The work was carried out in the School of Chemistry, Robert Gordon's Institute of Technology, Aberdeen, between January, 1968 and December, 1970.

I wish to express my gratitude to Dr. O.C. Musgrave for his help and guidance throughout this research, and to Dr. M.B. Watson for numerous helpful suggestions. I also wish to thank my colleagues for valuable discussions, and members of the Technical staff of both Robert Gordon's Institute of Technology and the University of Aberdeen for analytical results and other assistance. I am also grateful to Professor R.H. Thomson and to Professor H.G.H. Erdtman for providing authentic samples. Further thanks are due to Mrs Margaret Riddoch for typing this thesis.

Finally I am indebted to the Governors of Robert Gordon's Institute of Technology for the opportunity to do this research, and also for part payment of fees to the University of Aberdeen.

CONTENTS

Page

SUMMARY

The reactions between quinones and aromatic compounds in the presence of acids are surveyed; and a summary of the methods used for preparing triphenylenes is outlined.

Mono- and di-arylquinones have been prepared by the arylation of benzoquinones with diazotised 3,4-dimethoxyaniline (Meerwein reaction). The structures of the arylquinones are determined spectroscopically and by conversion to known compounds.

The aluminium chloride-catalysed reaction between benzoquinones and either veratrole or 3',4'-dimethoxyphenylbenzoquinones gives derivatives of triphenylene-1,4:5,8-diquinone.

2-(3',4'-dimethoxyphenyl)-3-arylbenzoquinones have been cyclised in the presence of Lewis or protic acids to triphenylene-1,4-quinones. The reaction between concentrated hydrochloric acid and either 2,3-di(3',4'-dimethoxyphenyl)-benzoquinone or 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)-benzoquinone gives 5-chloro-substituted triphenylene-1,4-quinones.

A new synthesis of 2-hydroxytriphenylenes is developed

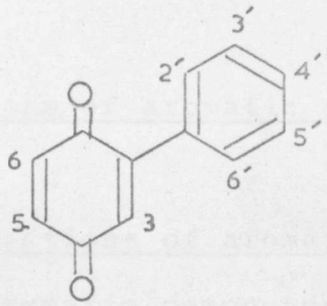
by treating veratrole with chlorobenzoquinones in aqueous sulphuric acid.

An attempted reaction between veratrole and 1,4-naphthaquinone in the presence of aluminium chloride gave only products derived from 1,4-naphthaquinone, one of these is a new dinaphofuran derivative, viz. 8-hydroxydinaphtho-[1,2-b:2',1'-d]furan-5,6-quinone.

The structures of all compounds have been determined by both physical and chemical techniques, and mechanisms have been suggested and discussed for new reactions.

NOMENCLATURE

The nomenclature used throughout this thesis follows the I.U.P.A.C. 1957 rules as far as possible. In some cases however simplicity, clarity, and ease of cross-reference have necessitated a departure from the rules. "Benzoquinone" refers to 1,4-benzoquinone except where otherwise stated. Arylquinones are numbered as follows:-



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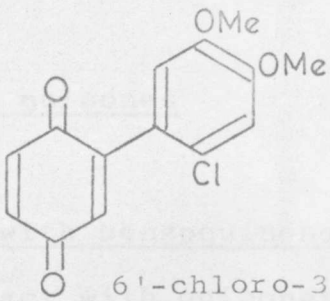
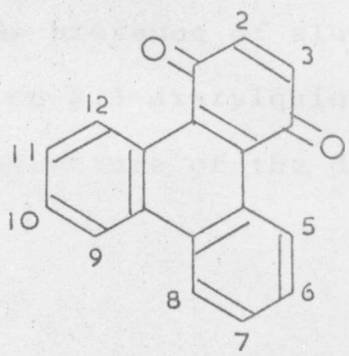
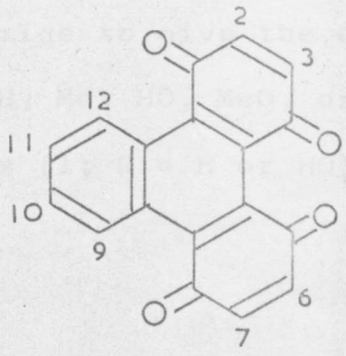


6'-chloro-3',4'-dimethoxyphenylbenzoquinone

Triphenylene-quinones and -diquinones are numbered thus:-





CHAPTER 1

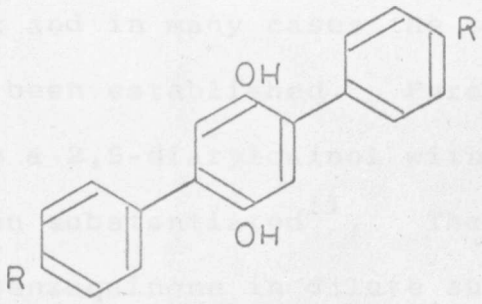
Introduction

This thesis is concerned with reactions between aromatic compounds and quinones to give arylquinones and triphenylene derivatives. A survey of the known reactions of quinones with aromatic compounds under acid conditions, and a summary of the previous methods used for preparing triphenylenes are therefore appropriate.

Reactions of aromatic compounds with quinones

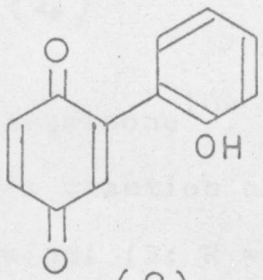
1. Reactions of aromatic compounds with benzoquinone

Aromatic compounds generally react with quinones in the presence of Lewis or protic acids to give mono- or diarylquinols or the corresponding quinones. Benzene, toluene, phenol, anisole, and phenetole each react with benzoquinone in the presence of aluminium chloride to give the corresponding 2,5-diarylquinol (1; R = H, Me, HO, MeO, or EtO).[1-4] The structure of the diarylquinols (1; R = H or HO) has been



(1)

confirmed by Kögl and Postowsky[5,6] who converted derivatives of the diarylquinols into p-terphenyl by zinc dust distillation. Phenol reacts with benzoquinone in the presence of aqueous sulphuric acid or boron trifluoride etherate to give a mixture of the arylquinones (2) and (3).[7] The reaction of benzoquinone with p-xylene is not readily



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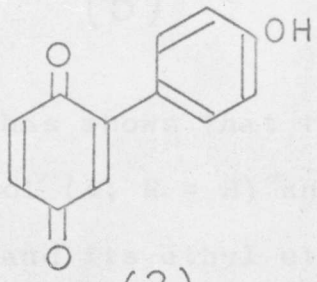

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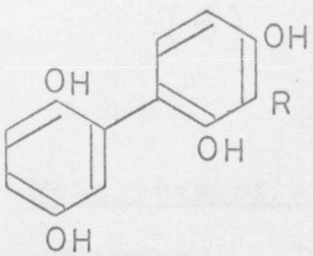
effected[2], but the reactions with m-xylene[8] and with mesitylene[9] both give good yields of the 2,5-diarylquinols.

Reactions with substituted phenols or aromatic ethers are more complex and in many cases the structure of the product has not been established. Pyrogallol was originally reported to give a 2,5-diarylquinol with benzoquinone[10], but this has not been substantiated[11]. The reaction between pyrogallol and benzoquinone in dilute sulphuric acid has been shown recently[12] to give a complex mixture containing the biphenyl (4; R = HO) and the terphenyl (5; R = HO), together with self-condensation products from pyrogallol. A diarylquinol was isolated from the reaction of resorcinol



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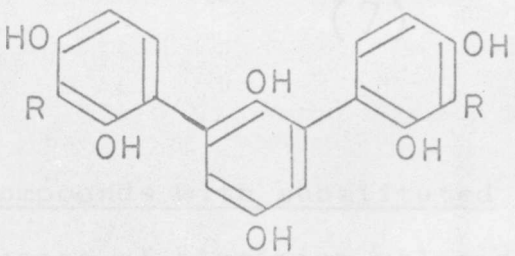

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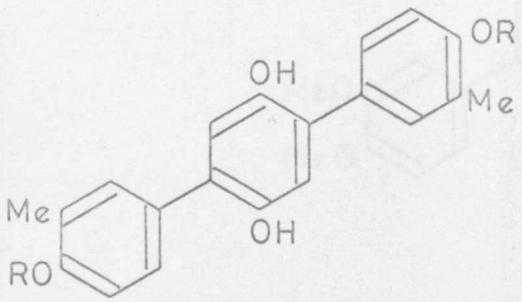
and benzoquinone[10]. Later work[13] has shown that the products from this reaction are the arylquinol (4; R = H) and the diarylquinol (5; R = H). o-Cresol and its ethyl ether react readily with benzoquinone to give diarylquinols to which structures (6; R = H and Et) have been assigned[14]. The

reaction with m-cresol is more difficult and no product was obtained from p-cresol[14]. It is claimed, without supporting evidence, that p-methoxytoluene gives the diarylquinol (7)[14]. The reaction between veratrole and benzoquinone[14] is of particular interest and is discussed in Section 3.



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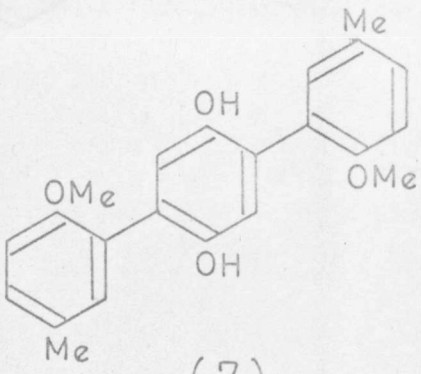

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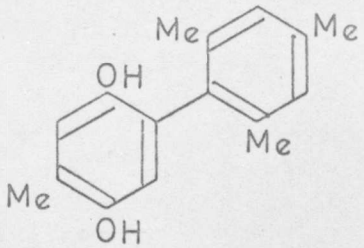
2. Reactions of aromatic compounds with substituted benzoquinones. In the presence of aluminium chloride, methylbenzoquinone reacts with mesitylene[15] to give the arylquinol (8), and with 1-methyl-2,5-dimethoxybenzene[16] to give the arylquinol (9; R = Me). Similarly chlorobenzoquinone



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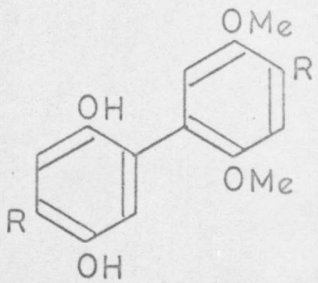
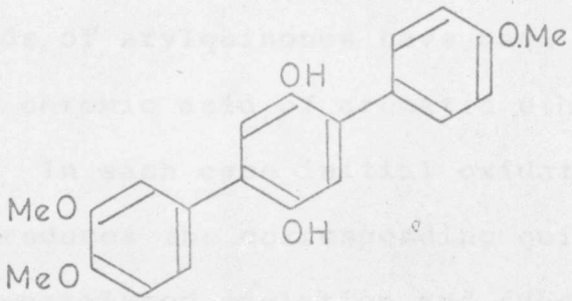


(9)

reacts with 1-chloro-2,5-dimethoxybenzene[16] to give the arylquinol (9; R = Cl). Attempts to prepare the diarylquinol (10) from either 4'-methoxyphenylbenzoquinone and veratole, or 3',4'-dimethoxyphenylbenzoquinone and



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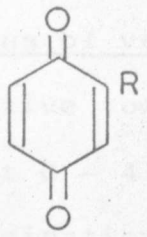
anisole, in the presence ofaluminium chloride, have been unsuccessful[17]. Reactions of 1,4-naphthaquinone with resorcinol, pyrogallol, and with naphthol give mono-aryl-naphthols[10]. The negatively substituted benzoquinones (11; R = $COCH_3$ or $COOCH_3$) react readily with aromatic hydrocarbons, ethers, amines, or phenols to furnish the 3-arylbenzoquinones (12; R = $COCH_3$ or $COOCH_3$) or the corresponding quinols[79]. These reactions are catalysed by formic acid, acetic acid or trifluoroacetic acid.



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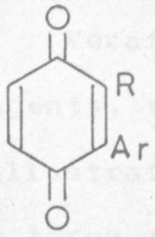

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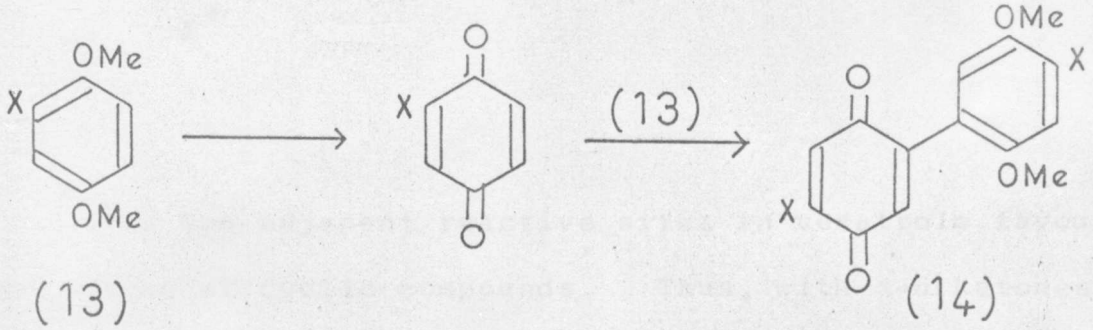
High yields of arylquinones have been obtained by the oxidation with chromic acid of aromatic ethers of the type (13).[16,18-22] In each case initial oxidative demethylation of the ether produces the corresponding quinone which then undergoes acid-catalysed arylation and subsequent oxidation to the arylquinone (14). The oxidation of 2-methoxy-naphthalene to the quinone (15) with peroxoformic acid follows a similar course.[23]



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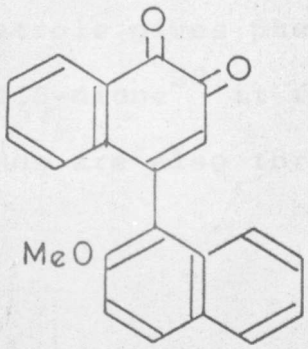

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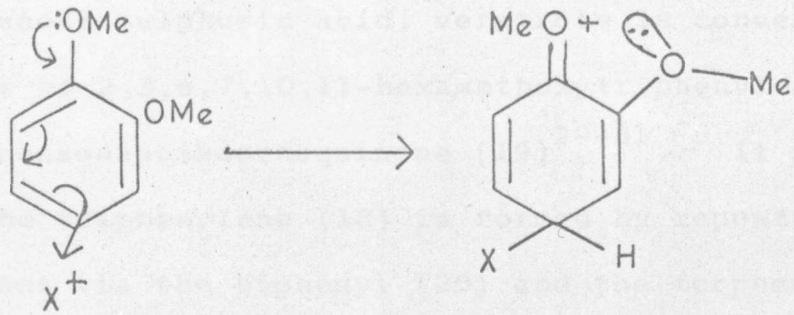
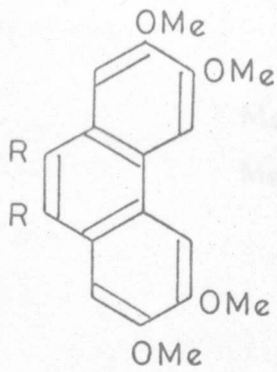
3. Reactions of veratrole with quinones. Veratrole is highly reactive towards electrophilic reagents, substitution occurring at C - 4 and C - 5. This is illustrated by the rate of bromination of veratole, which is three times faster than that of anisole[24]. The C - 4 position in veratrole is brominated 100 times faster than the C - 3 position[25,26]. This great reactivity has been attributed to interaction between the oxygen atoms of the methoxy-groups, which facilitates the formation of the oxonium ion in the transition state[24]:-



The two adjacent reactive sites in veratrole favour the formation of cyclic compounds. Thus, with α-diketones[27,80] in acidic media, veratrole gives phenanthrene derivatives (16), while with hexane - 2,5-dione[28] it forms the dihydroanthracene (17). Cyclic compounds are also formed when veratrole is oxidised



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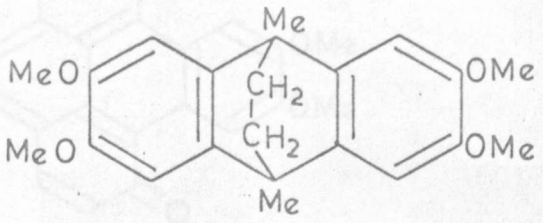
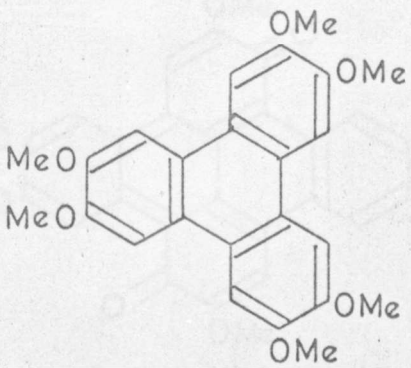


(17)

by high potential quinones. In the presence of chloranil and aqueous sulphuric acid, veratrole is converted into a mixture of 2,3,6,7,10,11-hexamethoxytriphenylene (18) and the dibenzonaphthacenequinone (19)[29-31]. It is suggested that the triphenylene (18) is formed by repeated Scholl reactions via the biphenyl (20) and the terphenyl (21), dehydrogenation being brought about by the chloranil[22]. The polycyclic quinone (19) is suggested to be formed[22] by the



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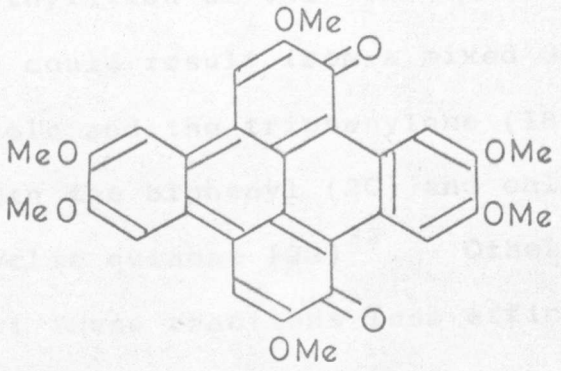
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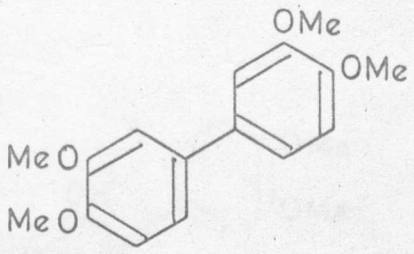
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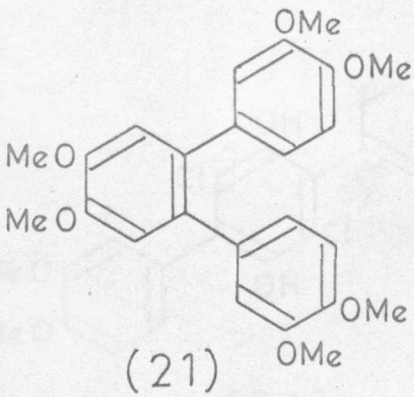
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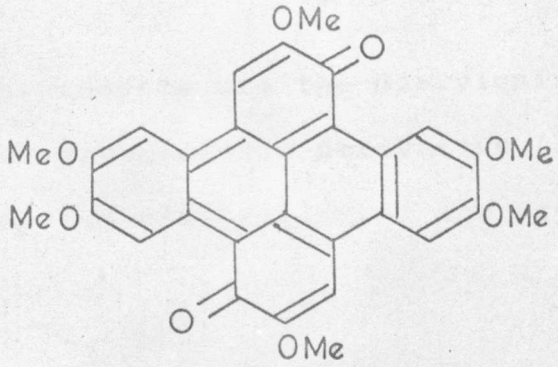
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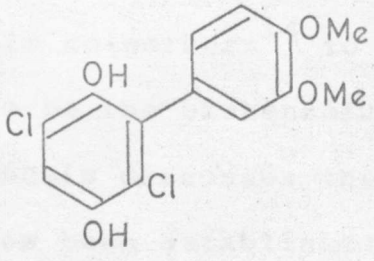
(22)

oxidative demethylation of the corresponding octamethoxy-compound which could result from a mixed Scholl reaction between veratrole and the triphenylene (18). A similar reaction between the biphenyl (20) and chloranil gives the related polycyclic quinone (22)[32]. Other high potential quinones effect these reactions less efficiently[31].

The reaction between veratrole and 2,5-dichlorobenzoquinone gives, in addition to the triphenylene (18) and the polycyclic quinone (19), the mono- and di-arylquinols (23) and (24)[33]. When an excess of 2,5-dichlorobenzoquinone is



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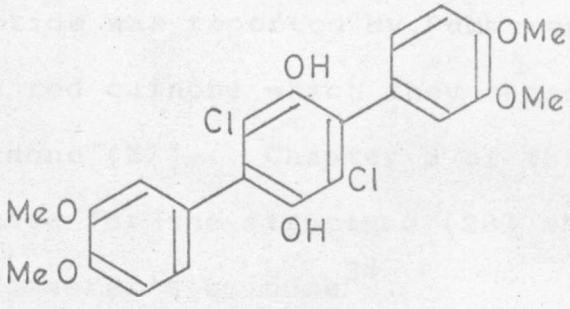

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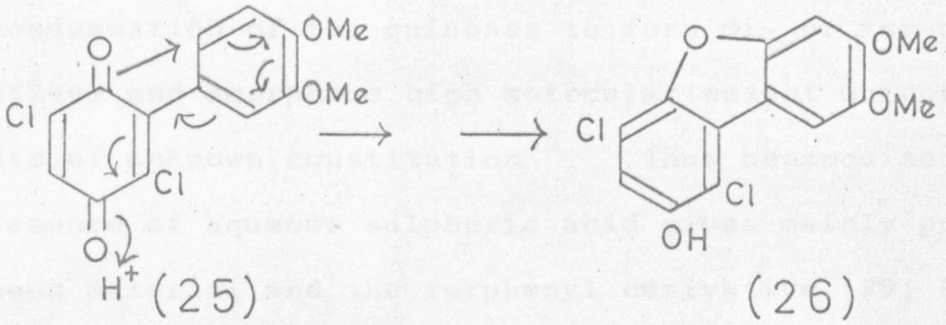
used, the main products are the diarylquinone corresponding to (24) and the dibenzofuran derivative (26)[33], the latter being formed by the cyclisation of the arylquinone (25):-



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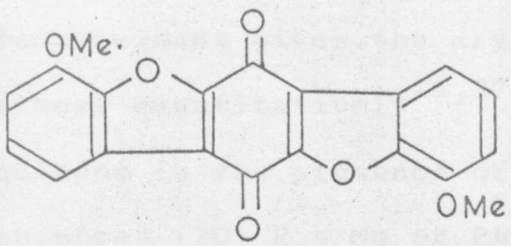
Analogous products are obtained when 2,6-dichlorobenzoquinone is used[33].

The reaction of veratrole with benzoquinone in the presence of aluminium chloride was reported by Pummerer and his co-workers[14] to give a red quinone which they considered to be the bisbenzofuranquinone (27). Chapter 3 of this thesis discusses the evidence for the structure (28) which has now been established for Pummerer's quinone[34].



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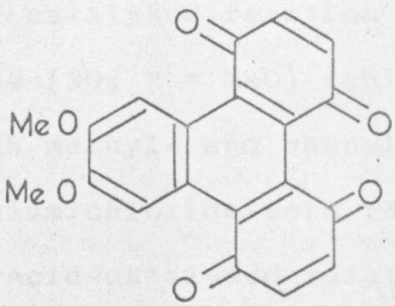
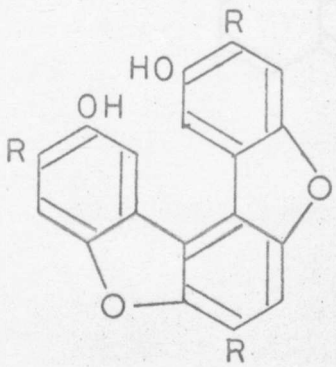


(28)

4. Self-condensation reactions of quinones. Many acid-catalysed reactions involving quinones are complicated by the self-condensation of the quinones to form di- or ter-phenyl derivatives and amorphous high molecular weight quinonoid products of unknown constitution[35]. Thus benzoquinone in the presence of aqueous sulphuric acid gives mainly polymeric amorphous material and the terphenyl derivative (29; R = H)[36,81]. Similarly methyl- and ethyl- benzoquinone yield the terphenyls



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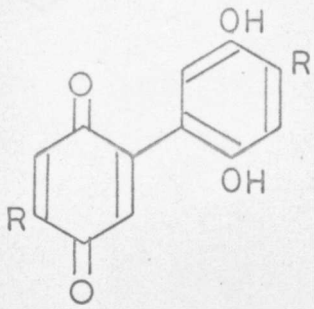
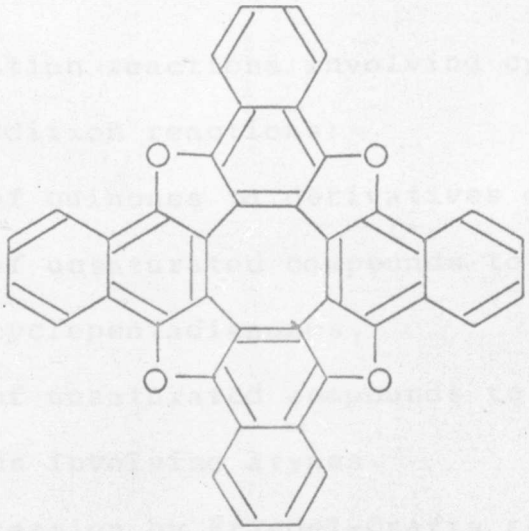


(30)

(29; R = Me or Et) together with the arylquinones (30; R = Me or Et)[35]. In contrast, the acid-catalysed reaction of methoxy-benzoquinone gives the arylquinone (30; R = MeO) rapidly and almost quantitatively[18,37]. Both methyl- and phenyl - benzo-quinone in the presence of aluminium chloride form the aryl-quinones (30; R = Me or Ph)[38]. Acid-catalysed reactions of

1,4-naphthaquinone yield mainly the cyclo-octatetraene derivative (31)[39-41, 81].



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Syntheses of triphenylenes.

The methods for the synthesis of triphenylenes are summarised in Elsevier's Encyclopaedia of Organic Chemistry[42]

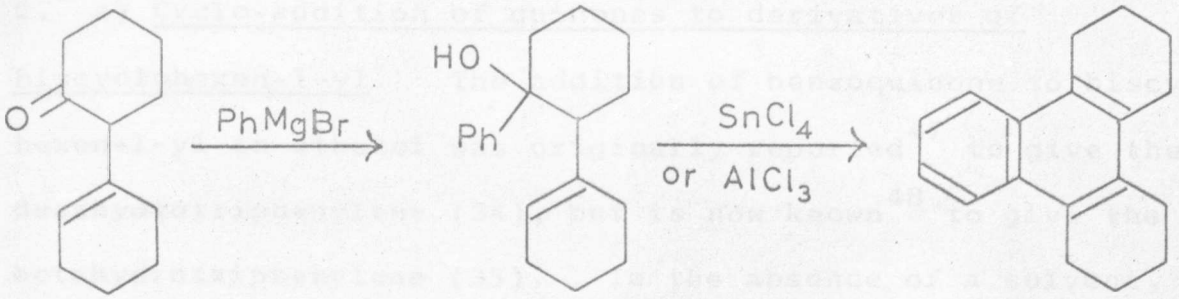
up to 1946, and in Chemical Reviews[43] up to 1959. The following summary deals mainly with the methods developed since 1959, the earlier methods being mentioned only briefly.

The syntheses of triphenylenes may be classified as follows:

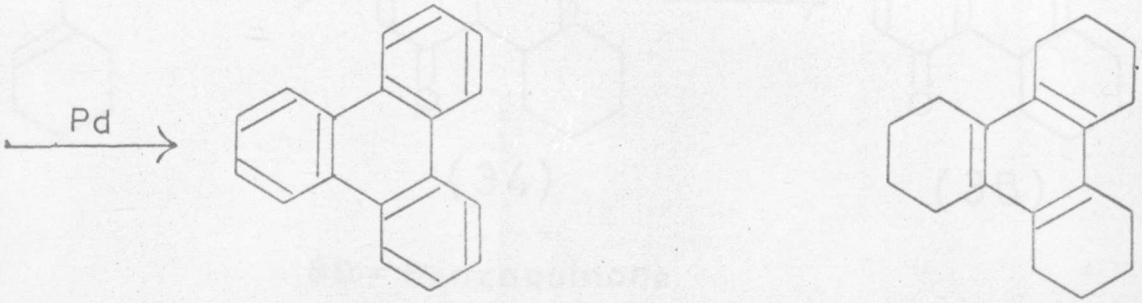
1. Condensation reactions involving cyclohexanones.
2. Cyclo-addition reactions:-
   (a) of quinones to derivatives of biscyclohexen-1-yl,
   (b) of unsaturated compounds to substituted cyclopentadienones,
   (c) of unsaturated compounds to dibenzocalicenes
3. Reactions involving arynes.
4. Ring extension by Friedel-Crafts reactions.
5. Dehydrogenation reactions.
6. Rearrangement reactions.

1. Condensation reactions involving cyclohexanones.

Cyclohexanone undergoes self-condensation in the presence of a wide variety of reagents to give the polyhydrotriphenylene (33). The best yield (13%) has been obtained using a mixture of aluminium and thorium oxides as the condensing agent.[44] Rapson[45] synthesised triphenylene by the following series of reactions:-



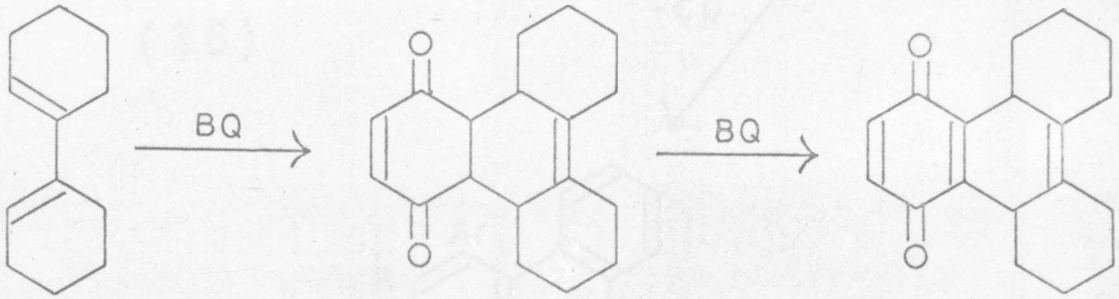
(32)



(33)

This synthesis is improved by epoxidation of the intermediate (32) followed by cyclisation with a mixture of acetic and hydrobromic acids[44]. In this way, triphenylene has been obtained from (32) in 50% yield[44]. Similarly by using the appropriately substituted Grignard reagent, 1- and 2-methyl-[44], 1- and 2-methoxy-[45], 2-hydroxy-[45,46], and 1,2-benzo-[44] triphenylenes have been prepared.

2. a) Cyclo-addition of quinones to derivatives of biscyclohexen-1-yl. The addition of benzoquinone to biscyclohexen-1-yl in ethanol was originally reported[47] to give the decahydrotriphenylene (34), but is now known[48] to give the octahydrotriphenylene (35). In the absence of a solvent,

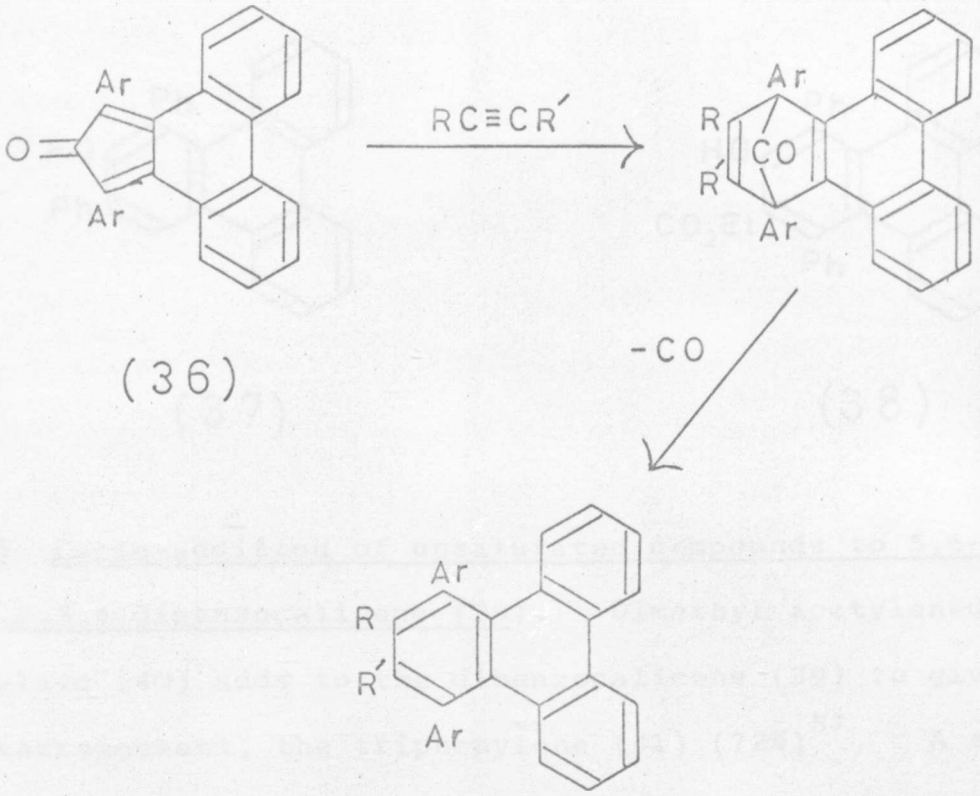


(34) (35)

BQ = Benzoquinone

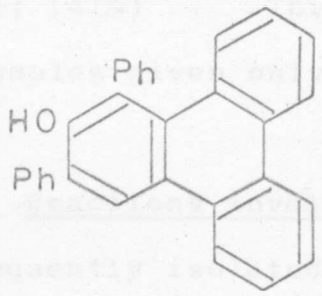
and using equimolar quantities of reacants, (34) is formed. This reaction has been applied to methylbenzoquinone, and to the 4,4'-dimethyl-, dimethoxy-, and dicyclohexyl- and the 3,3',5,5'-tetramethyl- derivatives of biscyclohexen-1-yl[48]. The yields of the adducts range from 14-85%, and the polyhydrotriphenylenes have been dehydrogenated using palladium-charcoal catalysts in satisfactory yields (42-74%).

b) Cyclo-addition of unsaturated compounds to substituted cyclopentadienones. 1,4-Diaryltriphenylenes may be prepared by the Diels-Alder addition of acetylenes[49-52] or ethylenes[52-54] to cyclopentadienones of the type (36):

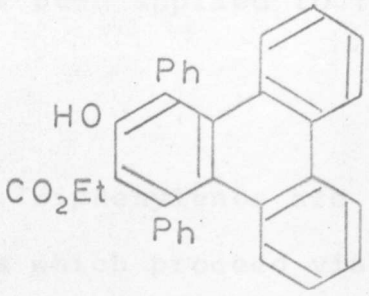


(36)

The substituted cyclopentadienones (36) are readily prepared by condensing phenanthraquinone with dibenzyl ketones[55]. The yields of the Diels-Alder adducts depend mainly on the reactivity of the dienophile. Similar reactions involving the addition of diazomethane and of ethyl diazo acetate give the triphenylenes (37) and (38) in excellent yields[56].

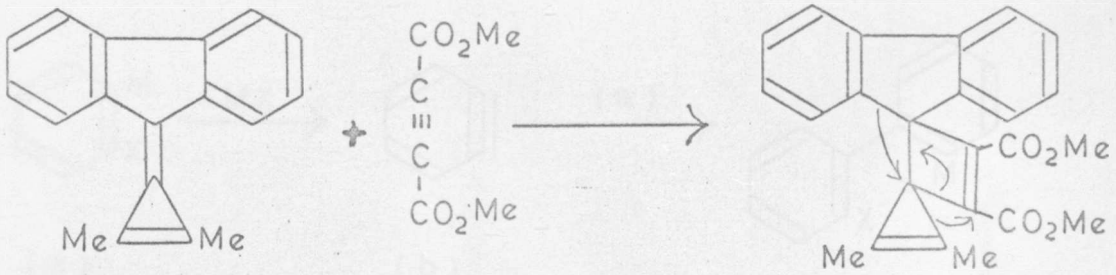


(37)

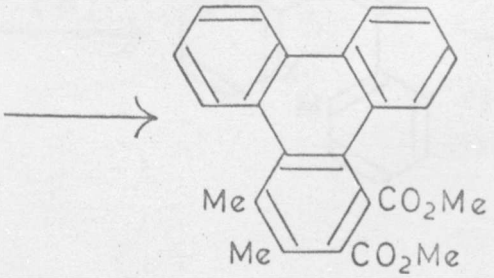


(38)

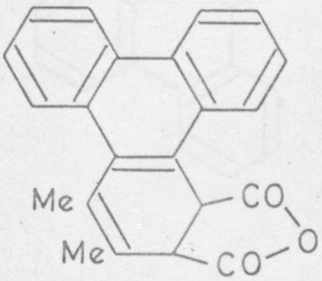
c) Cyclo-addition of unsaturated compounds to 5,6-dimethyl-1,2,3,4-dibenzocalicene (39). Dimethyl acetylenediacarboxylate (40) adds to the dibenzocalicene (39) to give, after rearrangement, the triphenylene (41) (72%)[57]. A similar reaction with maleic anhydride gives the dihydrotriphenylene



(39) (40)



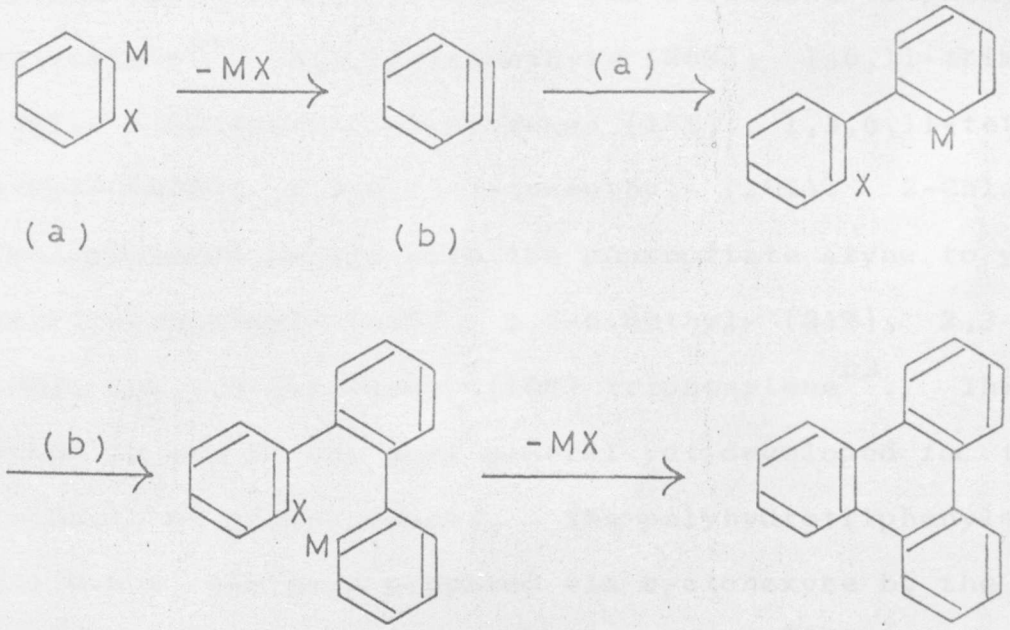
(41)



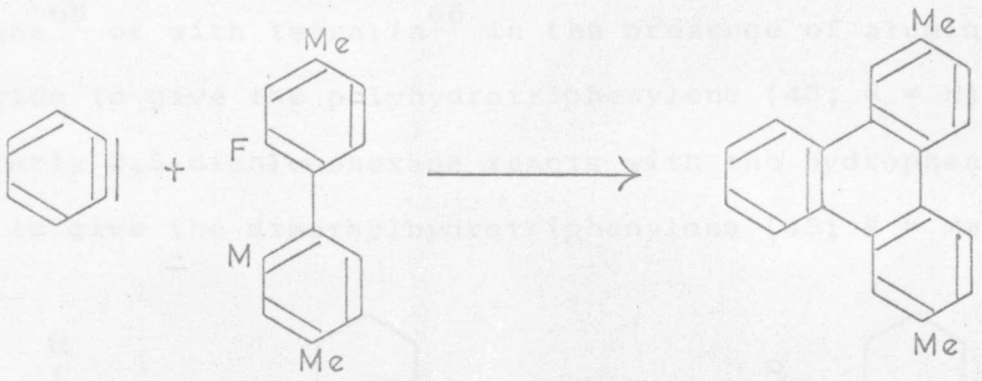
(42)

(42) (47%)[57]. This synthesis has been applied to the examples given only.

3. Reactions involving arynes. Triphenylenes are frequently isolated from reactions which proceed via an aryne intermediate[58], the best yields being obtained from reactions involving organo-metallic compounds. Triphenylene is formed in 59% yield from the reaction of o-bromoiodobenzene with lithium[59] and in 85% yield from o-fluorobromobenzene and magnesium[60,61], but the yields of substituted triphenylenes obtained from substituted arynes are considerably lower[62]. A stepwise mechanism has been suggested for such reactions:[61]



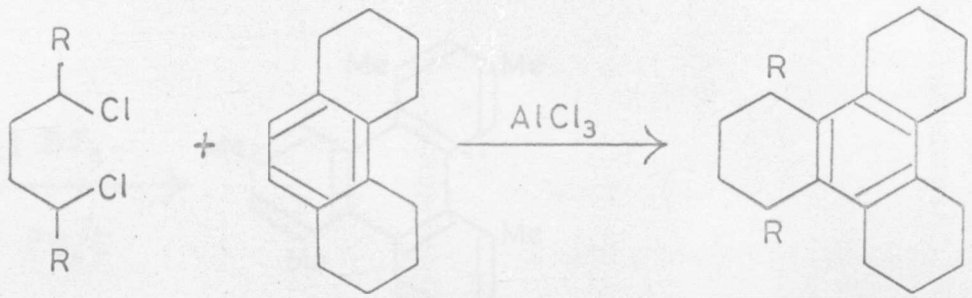
This is supported by the successful synthesis of triphenylenes by the action of arynes on suitably substituted biphenyls[61]. Reaction of the biphenyl (43; M = Li) with benzyne gives 2,7-dimethyltriphenylene (50%)[61]:



(43)

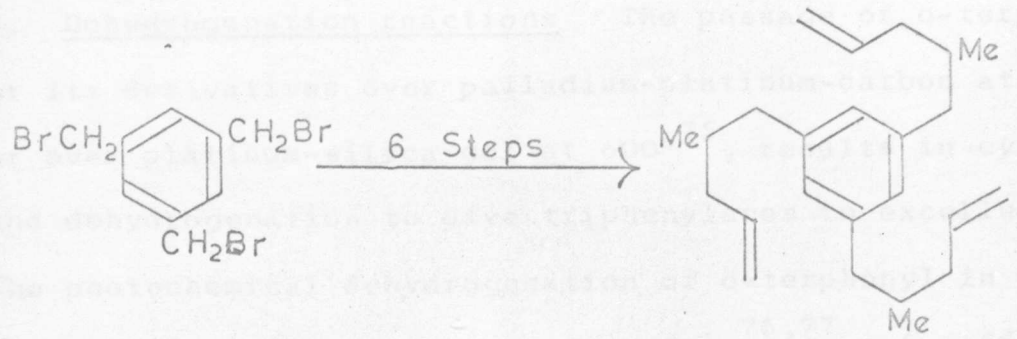
Similar reactions between the biphenyl (43; M = Li or MgI) and the appropriate aryne give the following triphenylene derivatives[61]: 2,6,11-trimethyl- (26%); 1,6,11-trimethyl- (13%); 6,11-dimethyl-2-methoxy- (15%); 1,3,6,11-tetramethyl- (60%); 2,3,6,11-tetramethyl- (20%). 2-Chloro-2'-lithiobiphenyl reacts with the appropriate aryne to yield 2-trifluoromethyl- (11%), 1,3-dimethyl- (21%), 2,3-dimethyl- (10%), and 2,3-dimethoxy- (10%) triphenylene[63]. This method is one of the most general yet developed for the synthesis of triphenylenes. The polyhydrotriphenylene (45; R = H) has been prepared via cyclohexyne by the action of magnesium on 1,2-dibromocyclohex-1-ene[64].

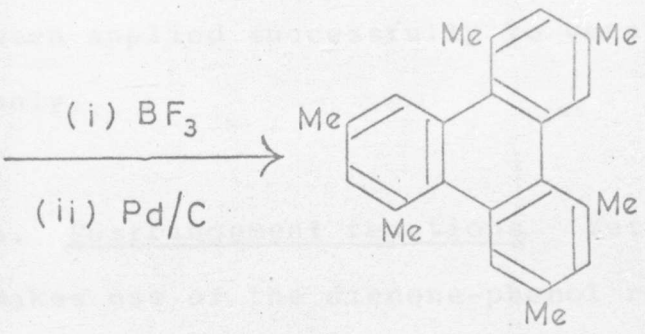
4. Ring extension by Friedel-Crafts reactions Several triphenylenes have been prepared by adding ring systems to an existing benzene, naphthalene or phenanthrene nucleus by a Friedel-Crafts reaction. 1,4-Dichlorobutane reacts with benzene[65] or with tetralin[66] in the presence of aluminium chloride to give the polyhydrotriphenylene (45; R = H). Similarly 2,5-dichlorohexane reacts with the hydrophenanthrene (44) to give the dimethylhydrotriphenylene (45; R = Me):[67]



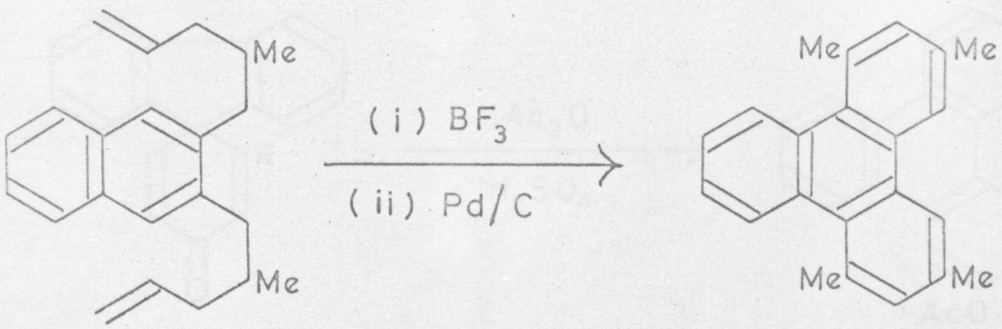
(44) (45)

Triphenylene may be prepared by the succinoylation of naphthalene[68,69], or of 1,2,3,4-tetrahydrophenanthrene[70], and subsequent cyclisation and dehydrogenation. The polymethyltriphenylenes (46) and (47) have been obtained by the sequences shown on p. 23 . Many of these syntheses involve several steps and the overall yields from readily available starting materials are often low.


BrCH2
CH2Br
CH2Br
6 Steps
Me
Me
Me


(i) BF3
(ii) Pd/C
Me
Me
Me
Me
Me
Me

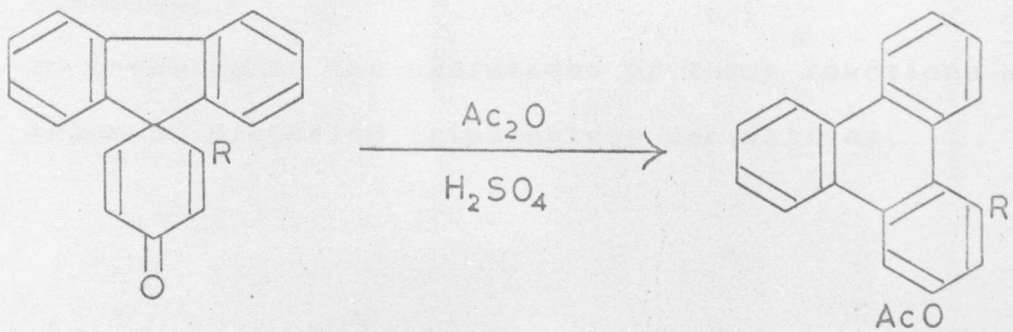
(46)


Me
Me
(i) BF3
(ii) Pd/C
Me
Me
Me
Me

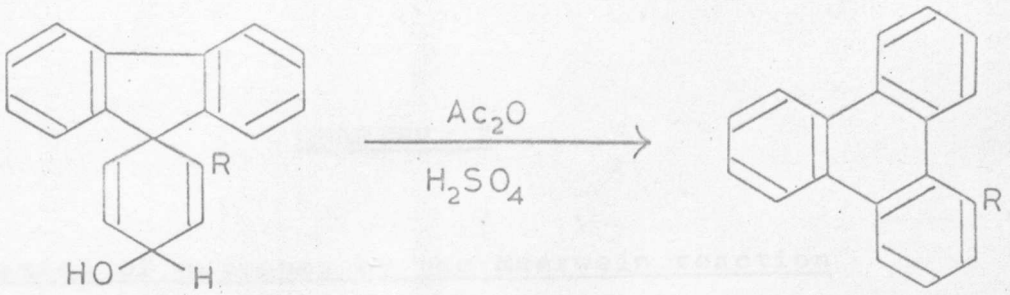
(47)

5. Dehydrogenation reactions The passage of o-terphenyl or its derivatives over palladium-platinum-carbon at 490°[73,74], or over platinum-silica gel at 600°[75], results in cyclisation and dehydrogenation to give triphenylenes in excellent yields. The photochemical dehydrogenation of o-terphenyl in the presence of iodine is also successful.[76,77] A different type of dehydrogenation, namely the oxidation of veratrole by chloranil in aqueous sulphuric acid gives 2,3,6,7,10,11-hexamethoxytriphenylene (18) (65%).[29-31] This reaction has been applied successfully to veratrole and o-diethoxybenzene[31] only.

6. Rearrangement reactions Yet another route to triphenylenes makes use of the dienone-phenol rearrangement[78]. The dienones (48; R = H or CO_2Me) and the corresponding dienols (49) rearrange in acetic anhydride/sulphuric acid to give triphenylenes in good yields (68-83%):



(48)



(49)

Although a number of methods are available for preparing triphenylenes, many syntheses are of limited range, and suitable starting materials are not always readily accessible. New methods for preparing triphenylenes are therefore desirable.

Objects of this study

The objects of the present work were:

(a) to establish the structure of Pummerer's quinone;[14]

(b) to extend the reactions between aromatic compounds and quinones;

(c) to investigate the usefulness of these reactions as a means of preparing triphenylene derivatives.

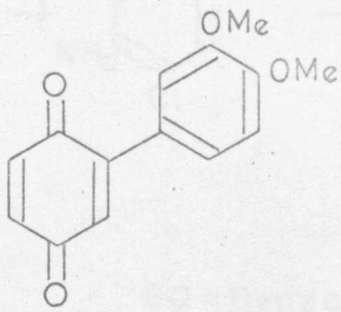
CHAPTER 2

Arylation of quinones by the Meerwein reaction

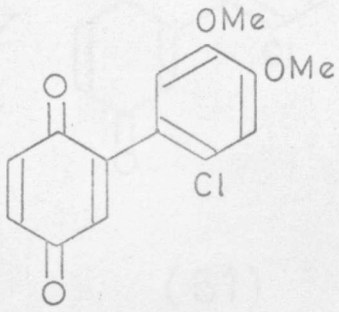
During the course of these investigations, a number of arylbenzoquinones were required either as starting materials, or to confirm the identities of products formed by the acid-catalysed arylation of various benzoquinones. The preparation of mono- and di-arylbenzoquinones and of the corresponding chloro-compounds by the Meerwein reaction[91] are now discussed. The Meerwein reaction provides a simple method for the arylation of quinones by diazonium salts, although the yields are often low.

Arylation of benzoquinone with diazotised 3,4-dimethoxyaniline

The reduction of 3,4-dimethoxynitrobenzene with granulated tin, tin (II) chloride, and concentrated hydrochloric acid gave a crude product (70%), m.p. 78-83°, which on crystallisation afforded pure 3,4-dimethoxyaniline (50%), m.p. 84-86° . When the pure amine was diazotised and treated with benzoquinone, 3',4'-dimethoxyphenylbenzoquinone (50) was obtained. Diazotisation of the crude amine followed



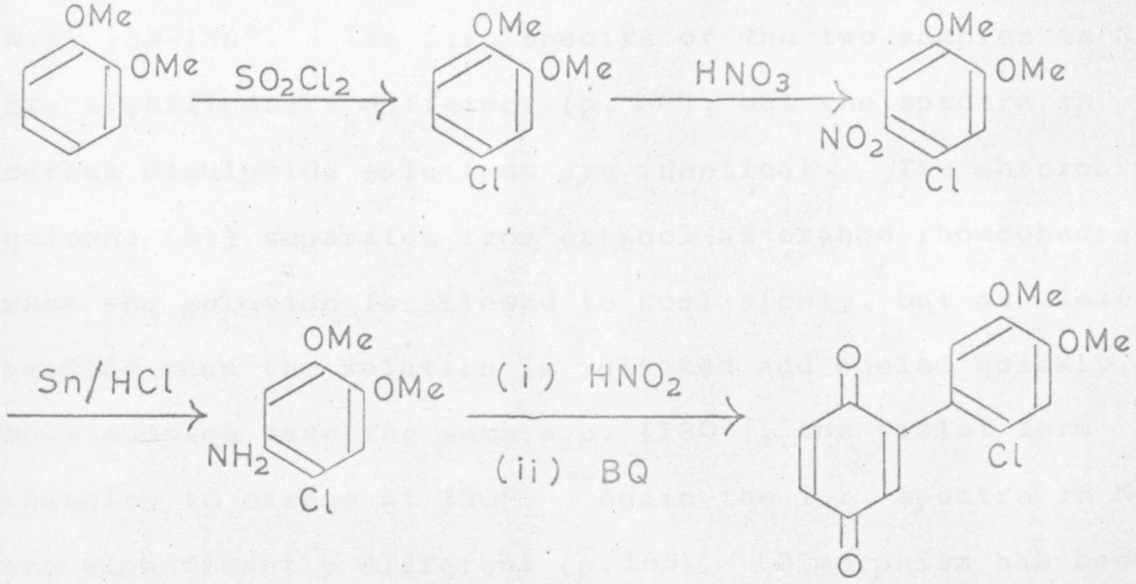
(50)



(51)

by treatment with benzoquinone gave the arylquinone (50) together with a second quinone ($C_{14}H_{11}Cl\ O_4$). The n.m.r. spectrum of the latter, which showed the presence of two methoxy-groups and of five aromatic or quinonoid protons, suggests the compound is 6'-chloro-3',4'-dimethoxyphenylbenzoquinone (51). This is presumably formed from diazotised 6-chloro-3,4-dimethoxyaniline present in the crude amine. The

structure of the chloroarylquinone was confirmed by preparing an authentic sample as follows:



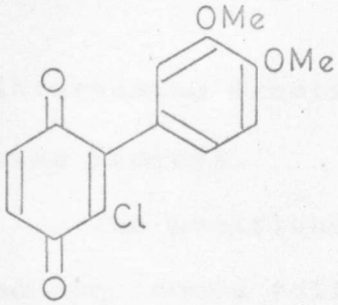
BQ = Benzoquinone (51)

Chlorination frequently occurs during the reduction of aromatic nitro-compounds in the presence of metal and hydrochloric acid.[92] The reduction of 4-ethoxynitrobenzene by tin and hot, concentrated hydrochloric acid gives 2-chloro-4-ethoxyaniline in high yield (90%), but when dilute hydrochloric acid is used, 4-ethoxyaniline is the only product.[93]

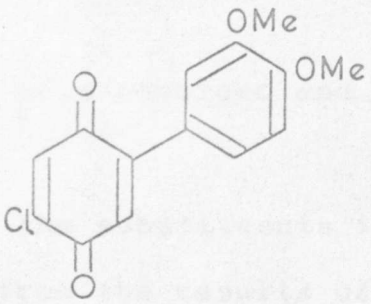
The arylquinones (50) and (51) show dimorphism. The first crystallises from ethanol as red rhombohedra, m.p. 133-134°, which sublime to give a red microcrystalline solid, m.p. 135-136°. The i.r. spectra of the two samples in Nujol are significantly different (p.163), but the spectra in carbon disulphide solutions are identical. The chloroarylquinone (51) separates from ethanol as orange rhombohedra when the solution is allowed to cool slowly, but as violet needles when the solution is agitated and cooled quickly. Both samples have the same m.p. (130°), the violet form changing to orange at 120°. Again the i.r. spectra in Nujol are significantly different (p.165). Dimorphism has been observed previously in diarylbenzoquinones.[1,2]

Arylation of chlorobenzoquinone with diazotised 3,4-dimethoxyaniline.

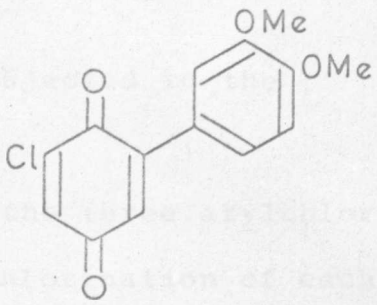
The reaction of chlorobenzoquinone with diazotised 3,4-dimethoxyaniline gave a mixture of the three expected products; the 2- aryl-3-chloroquinone (52), the 2-aryl-5-chloroquinone (53), and the 2-aryl-6-chloroquinone (54), the proportions being approximately 2:1:1 respectively. From this mixture p.l.c. readily afforded the pure 2,3-disubstituted



(52)



(53)



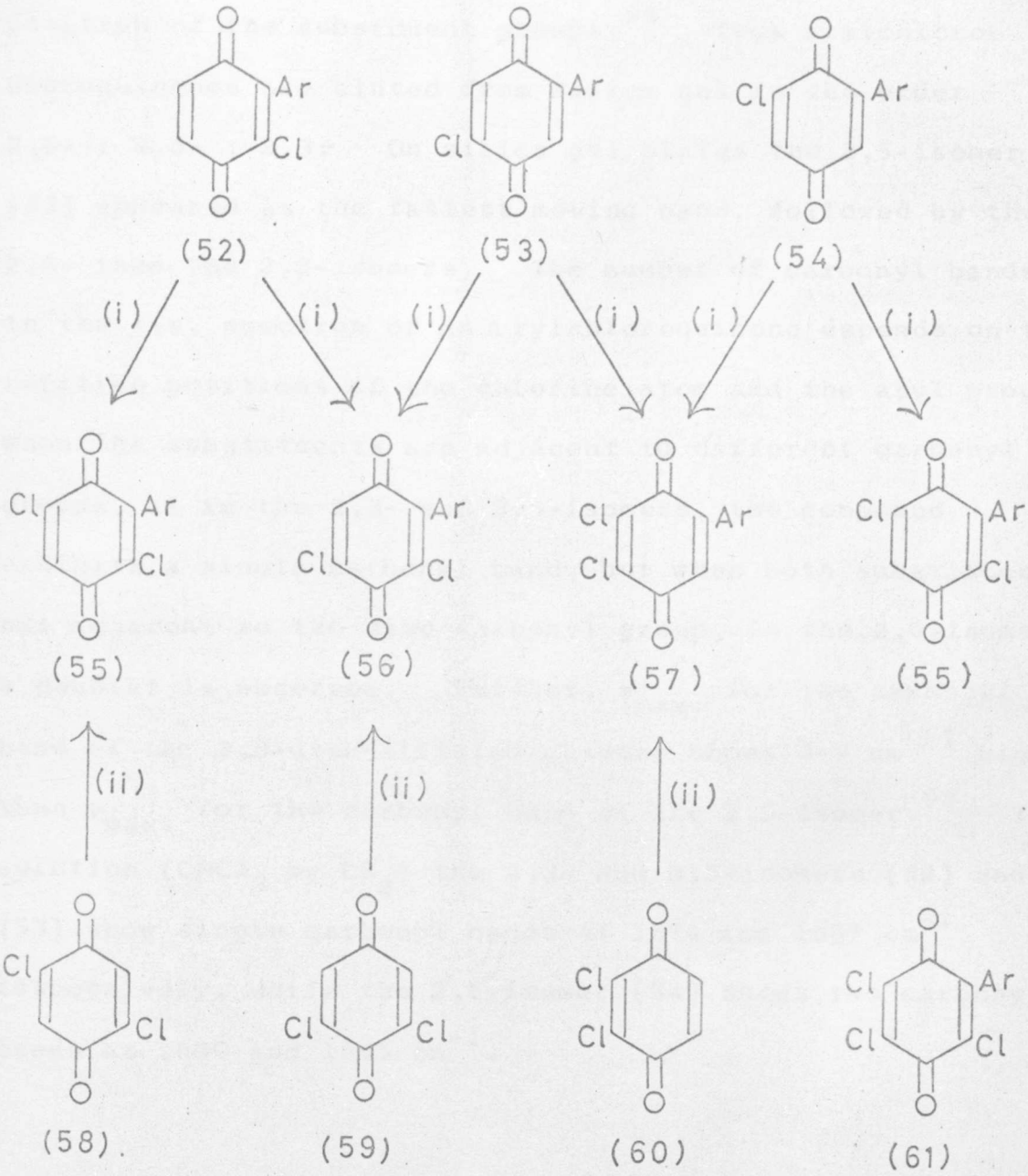
(54)

quinone (52), but the separation of the remaining 2,5- and 2,6-quinones proved to be very difficult. The mixed 2,5- and 2,6-isomers was subjected to multiple p.l.c. for 70 developments as described on p.161, only one broad band was obtained. The upper darker portion of this band gave the 2,5-isomer, but the lower part of the band was a mixture of the 2,5- and 2,6-isomers, together with decomposition products. This method of separation was wasteful and a modified p.l.c. tecnhique was used instead. The mixture was subjected to multiple p.l.c. for 7 developments and the upper and lower parts of the band were removed and each was subjected to further p.l.c. The resulting bands were again split and the process was repeated until the product from the upper part of the band showed no i.r. absorption due to the 2,6-isomer, and the product from the lower part of the band showed no i.r. absorption due to the 2,5-isomer. The

intervening fractions were combined and subjected to the same process.

The positions of the substituents in the three arylchlorobenzoquinones follow from the results of chlorination of each isomer (p. 32). The 2,3-isomer (52), on treatment with concentrated hydrochloric acid followed by oxidation with iron (III) chloride gave a (1:7) mixture of the 2-aryl-3,6-dichloroquinone (55) and the 2-aryl-3,5-dichloroquinone (56). The 2,5-isomer (53) and the 2,6-isomer (54) similarly gave the dichloroquinones (56) and (55) respectively, along with the 2-aryl-5,6-dichloroquinone (57) as the main product in each case. The 2-aryl-3,5,6-trichloroquinone (61) was also produced in small amounts in each of the above chlorinations. Authentic samples of the aryldichloroquinones (55), (56), and (57) were prepared by treating diazotised 3,4-dimethoxyaniline with the corresponding dichlorobenzoquinones (58), (59), and (60).

The structures of the arylchloroquinones (52), (53), and (54) were confirmed by chromatographic and spectroscopic evidence. The order of elution of arylchlorobenzoquinones from a column of silica gel is known to be dependent on the



Ar = 3,4-$(MeO)_2C_6H_3$-.

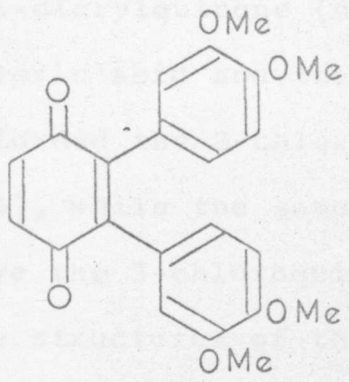
(i) HCl, then $FeCl_3$.

(ii) ArN_2^+.

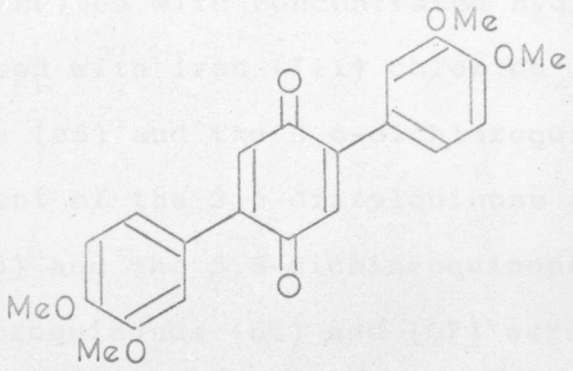
position of the substituent groups.[94] Thus arylchloro-benzoquinones are eluted from silica gel in the order 2,5- : 2,6- : 2,3- On silica gel plates the 2,5-isomer (53) appeared as the fastest moving band, followed by the 2,6- then the 2,3-isomers. The number of carbonyl bands in the i.r. spectrum of an arylchloroquinone depends on the relative positions of the chlorine atom and the aryl group.[95] When the substituents are adjacent to different carbonyl groups, as in the 2,3- and 2,5-isomers, the compound exhibits a single carbonyl band, but when both substituents are adjacent to the same carbonyl group, in the 2,6-isomer, a doublet is observed. Further, $\nu_{max.}$ for the carbonyl band of the 2,3-disubstituted quinone shows 5-9 $cm.^{-1}$ higher than $\nu_{max.}$ for the carbonyl band of the 2,5-isomer.[95] In solution ($CHCl_3$ or CS_2) the 2,3- and 2,5-isomers (52) and (53) show single carbonyl bands at 1674 and 1667 cm^{-1} respectively, while the 2,6-isomer (54) shows two carbonyl bands at 1680 and 1645 cm^{-1}.

Arylation of 3',4'-dimethoxyphenylbenzoquinone with diazotised 3,4-dimethoxyaniline.

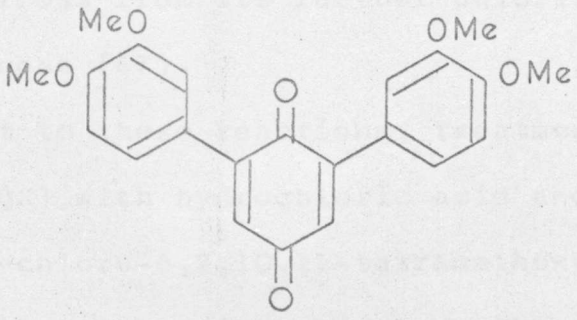
The reaction of 3',4'-dimethoxyphenylbenzoquinone (50) with diazotised 3,4-dimethoxyaniline in 50% aqueous acetone gave the three possible diarylbenzoquinones (62), (63), and (64). The same products together with the arylquinone (50)



(62)



(63)

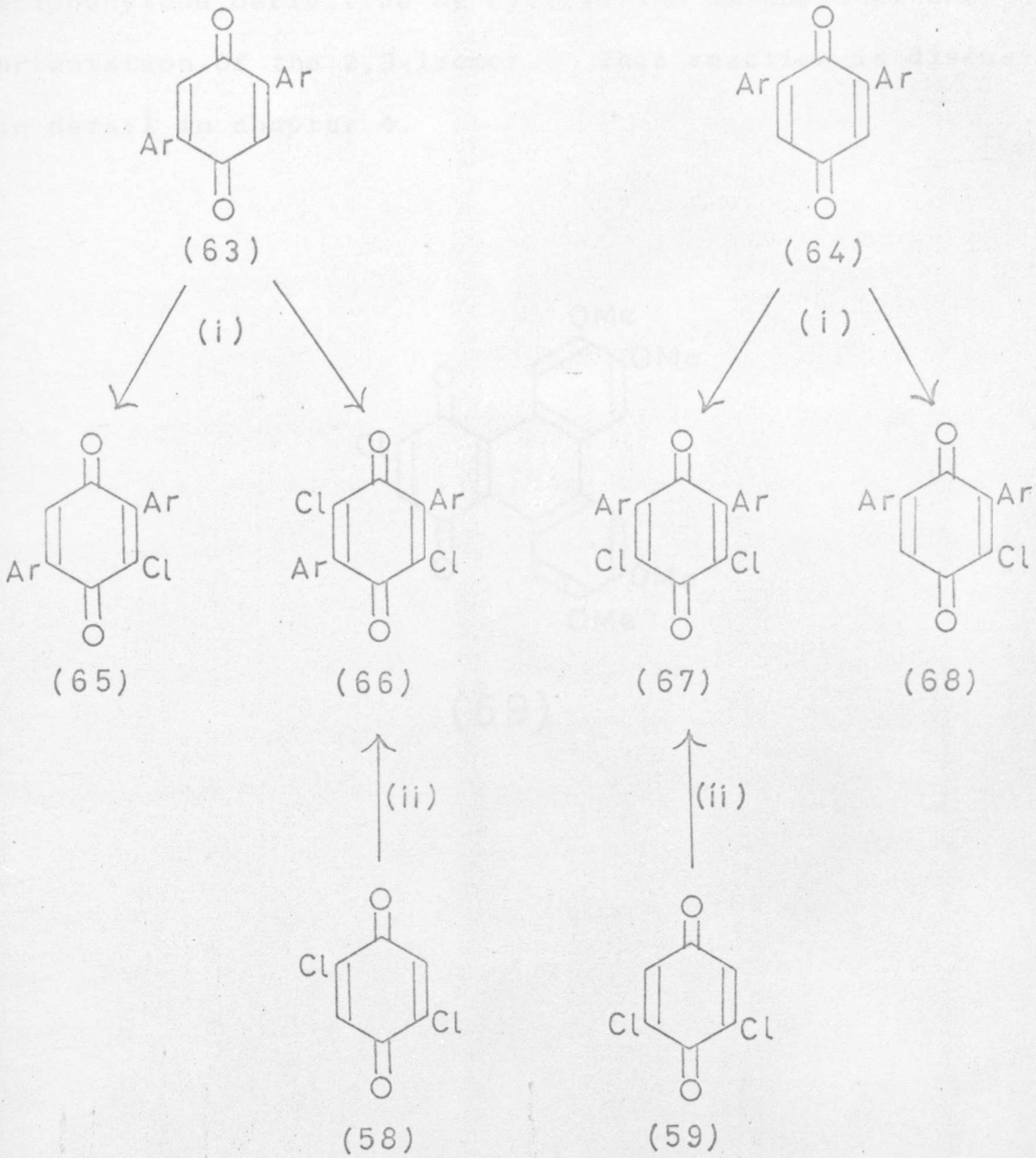


(64)

were obtained from a similar reaction with benzoquinone. In both reactions the products were separated by p.l.c., the proportions of the three diarylquinones (2,3-: 2,5-: and 2,6-) being approximately 10:1:4. The arylation of (50) with diazotised 3,4-dimethoxyaniline in aqueous acetic acid was less efficient and gave only the 2,3- and 2,6-isomers.

The positions of the aryl groups in the three diarylquinones were determined by the following procedures. The 2,5-diarylquinone (63) when heated with concentrated hydrochloric acid and then oxidised with iron (III) chloride afforded the 3-chloroquinone (65) and the 3,6-dichloroquinone (66), while the same treatment of the 2,6-diarylquinone (64) gave the 3-chloroquinone (68) and the 3,5-dichloroquinone (67). The structures of the dichloroquinones (66) and (67) were established by their synthesis from diazotised 3,4-dimethoxyaniline and 2,5-dichlorobenzoquinone (58), and 2,6-dichlorobenzoquinone (59) respectively. The structure of the chloroquinone (68) follows from its further chlorination to give the dichloroquinone (67).

In contrast to these reactions, treatment of the 2,3-diarylquinone (62) with hydrochloric acid and then iron (III) chloride gave 2-chloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (69) as the main product. The formation of the

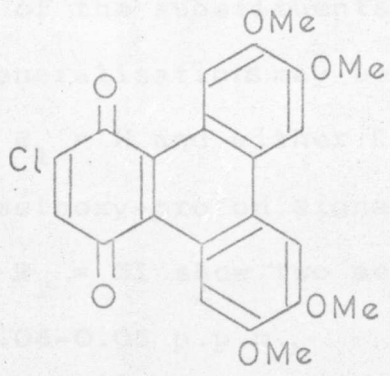


Ar = 3,4-$(MeO)_2C_6H_3$-.

(i) HCl, then $FeCl_3$.

(ii) ArN_2^+.

triphenylene derivative by cyclisation establishes the orientation of the 2,3-isomer. This reaction is discussed in detail in chapter 4.



(69)

Chemical shifts of the methoxy-protons in the arylbenzoquinones

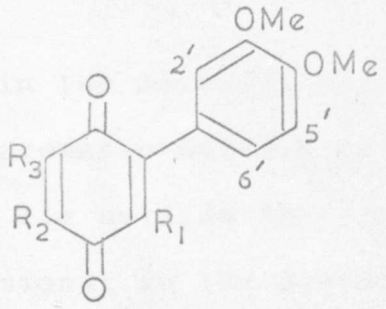
The chemical shifts of the methoxy-protons for a range of arylquinones of the type (70) are listed in Table 1. In these compounds the methoxy-proton resonances depend on the nature and position of the substituents in the quinone nucleus, and the following generalisations may be made:

a) compounds with R_1 = H and either R_2 or R_3 = H show no separation of methoxy-proton signals,

b) compounds with R_1 = Cl show two methoxy-proton signals separated by 0.04-0.05 p.p.m.,

c) compounds in which R_1 is an aromatic nucleus show two methoxy-proton signals separated by 0.23-0.29 p.p.m.

This behaviour may be rationalised by examining the steric features of the various structures. When R_1 is small (eg. hydrogen), the dimethoxyphenyl ring can be coplanar with the quinone ring and the magnetic environment of the two methoxy-groups will be similar. When R_1 is larger (eg. chlorine) the dimethoxyphenyl ring will not be coplanar with the quinone ring and there will be a slight difference in the environment of the two methoxy-groups. However, when R_1 is an aromatic nucleus, molecular models show that the C-3'



(70)

Table 1 Chemical shifts of the methoxy-protons in the arylquinones (70)

Substituents			Chemical Shifts		
R_1	R_2	R_3	$\tau(CH_3O)$	$\tau(CH_3O)$	Δ
H	H	H	6.09	6.09	0.0
H	H	Cl	6.07	6.07	0.0
H	Cl	H	6.10	6.10	0.0
H	H	Ar	6.08	6.08	0.0
H	Ar	H	6.07	6.07	0.0
H	Cl	Cl	6.08	6.10	0.02
Cl	Ar	H	6.06	6.10	0.04
Cl	H	Ar	6.06	6.10	0.04
Cl	H	H	6.06	6.11	0.05
Cl	H	Cl	6.07	6.12	0.05
Cl	Cl	H	6.09	6.14	0.05
*Ar	H	H	6.16	6.39	0.23
*Ar	Cl	Cl	6.14	6.37	0.23
*Ar'	Cl	Cl	6.15	6.42	0.27
*Ph	Cl	Cl	6.15	6.44	0.29

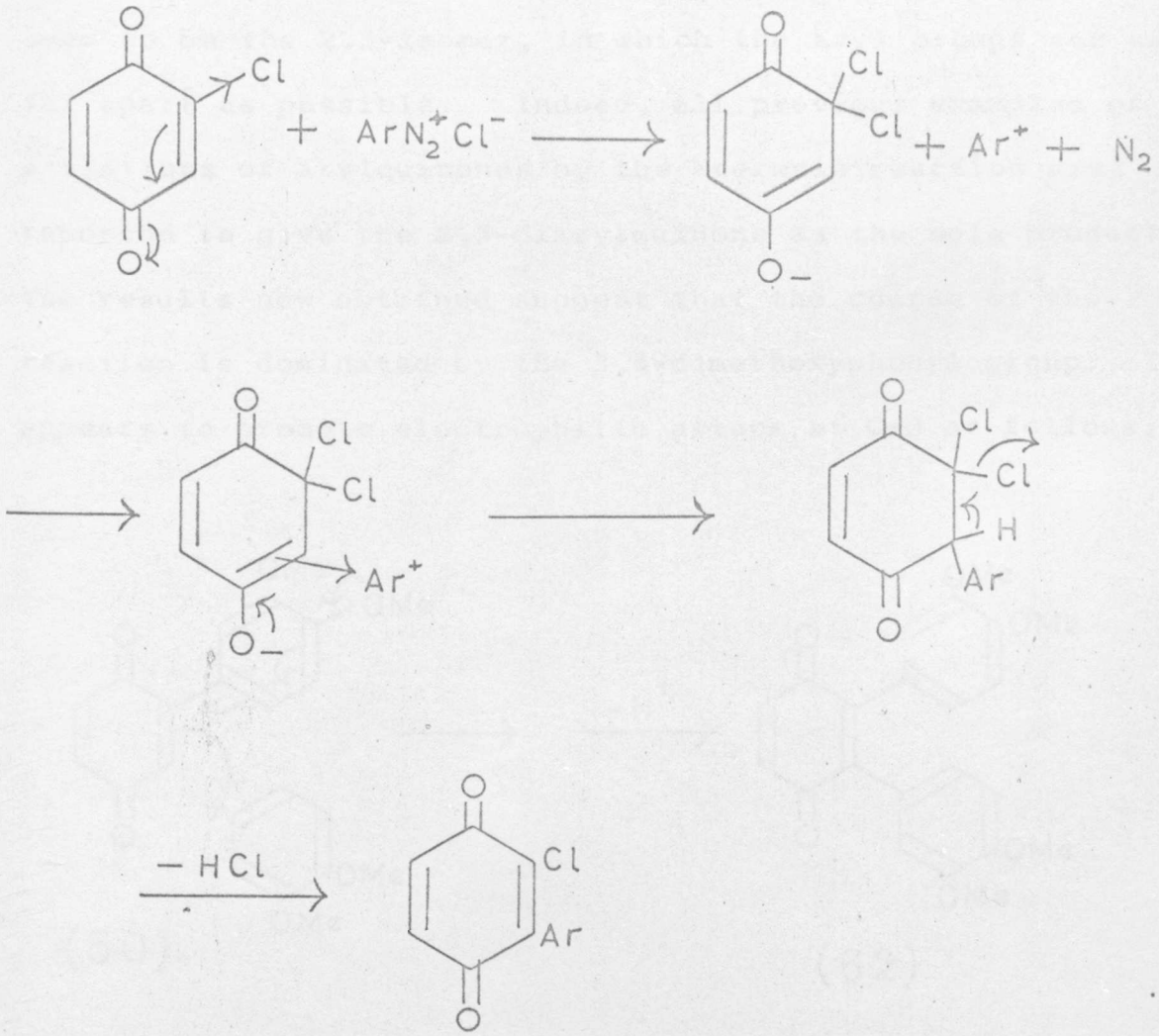
Ar = 3,4-$(MeO)_2C_6H_3$- ; Ar' = 3-$(MeO)C_6H_4$-

* Compounds described in Chapter 4

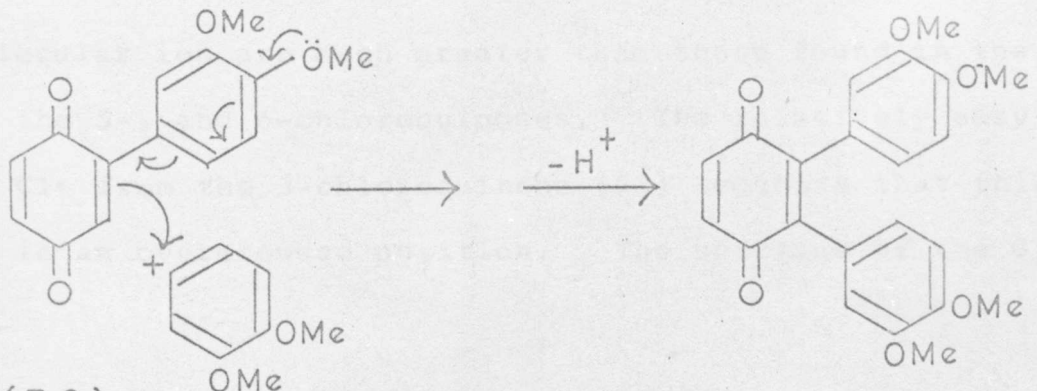
methoxy-protons lie in the shielded region caused by the ring current of the aromatic nucleus at R_1, whereas the C-4' methoxy-protons lie outside this region. Thus the C-3' methoxy-proton signal in the 2,3-diarylbenzoquinones is observed at a considerably higher field than the C-4' methoxy-proton signal. This provides a simple method for distinguishing these 2,3-diarylbenzoquinones from the 2,5- and 2,6-isomers.

Mechanism of the Meerwein arylation reaction.

The decomposition of a diazonium salt is largely governed by the pH of the mixture. Under basic conditions the reaction follows a free radical pathway,[96] but in aqueous acid the reaction is ionic.[97] The following mechanism has been proposed for the arylation of chlorobenzoquinone under aqueous acid conditions.[94]



This accounts for the formation of the 2-aryl-3-chlorobenzoquinone as the predominant product in the arylation of chlorobenzoquinone by diazonium salts. However, in 3',4'-dimethoxyphenylbenzoquinone (50), the dimethoxyphenyl ring would tend to deactivate the C-2 position towards nucleophilic attack. Thus this mechanism does not explain the results of the arylation of the quinone (50). Here the main product is the 2,3-diarylquinone (62) but the 2,5- and 2,6-isomers are also obtained. On steric grounds, the favoured product would seem to be the 2,5-isomer, in which the aryl groups are as far apart as possible. Indeed, all previous examples of arylations of arylquinones by the Meerwein reaction are reported to give the 2,5-diarylquinone as the sole product.[91] The results now obtained suggest that the course of the reaction is dominated by the 3,4-dimethoxyphenyl group. This appears to promote electrophilic attack at C-3 as follows:



(50) (62)

Further study of this reaction is necessary to ascertain the effects of different aryl groups in the quinone, and of different diazonium salts on the nature of the products.

Mass spectra of the arylbenzoquinones.

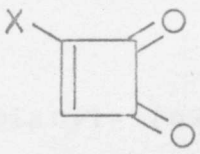
The ions (excluding isotopes) with relative abundances $>5\%$ obtained from the chloro-3',4'-dimethoxyphenylbenzoquinones are recorded in Table 2. The spectra of the 5-, and 6-chloroquinones (53) and (54) are similar. In each case the base peak is the molecular ion (m/e 278) and the metastable transitions show that fragmentation of this ion involves loss of MeO· followed by loss of CO. In addition loss of Me· and the fragment (71; X = Cl) occurs to give the ions with m/e 263 and 162 respectively. The latter ion is not present in the spectrum of the 3-chloroquinone (52). This isomer loses CH≡CH; the abundances of the ions with m/e 247 and 243 formed by loss of MeO· and of Cl· from the molecular ion are much greater than those found in the spectra of the 5-, and 6-chloroquinones. The relatively easy loss of Cl· from the 3-chloroquinone (52) suggests that this atom is in an overcrowded position. The spectrum of the 3,5,6-

Table 2. Mass spectra of the chloroarylbenzoquinones

Substituted 3',4'-dimethoxyphenylbenzoquinones	Principal ions and relative abundances (%)
5-Chloro- (53)	m/e 278(100), 263(5), 247(13), 219(5), 215(6), 162(5); 249* (278→263), 219.5* (278→247), 194.5*(247→219)
6-Chloro- (54)	m/e 278(100), 263(9), 247(12), 235(7), 219(6), 215(5), 207(6), 172(7), 162(7), 91(5), 83(6), 81(5), 76(7), 53(7), 50(6); 249*(278→263), 219.5*(278→247) 194.5*(247→219).
3-Chloro- (52)	m/e 278(100), 263(7), 252(13), 247(47), 243(12), 235(6), 219(10), 200(10), 215(7), 207(6), 179(6), 171(5), 126(9), 115(6), 75(9), 58(9), 54(6); 219.5*(278→247), 212.5* (278→243), 194.5*(247→219).
3,5,6-Trichloro- (61)	m/e 346(100), 331(6), 315(34), 311(11), 303(7), 287(11), 268(12), 240(6), 189(6), 146(5), 145(6), 110(8), 89(5), 87(15); 287*(346→315), 279.5*(346→311) 261.5*(315→287).
6'-Chloro- (51)	m/e 278(77), 243(100), 215(53), 196(16), 181(10), 82(8), 75(7), 54(12); 212.5*(278→243), 190.5*(243→215).

*Metastable transition.

trichloroquinone (61) resembles that of the 3-chloroquinone (52), showing ready loss of MeO· and Cl· from the molecular ion. The 6'-chloroquinone (51) in which the chlorine is attached to the aromatic ring undergoes fragmentation in a different manner and may be readily distinguished from the above chloroquinones. Here the molecular ion readily loses Cl· to give the base peak (m/e 243) which then loses CO.



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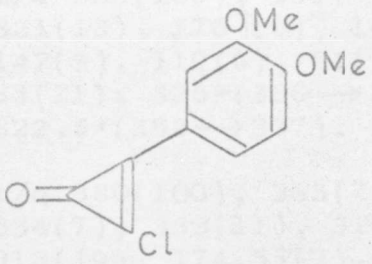

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Mass spectra of the diarylbenzoquinones

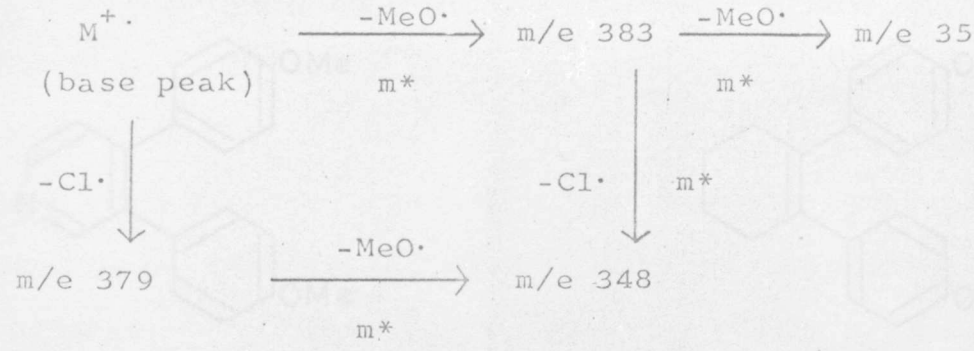
The salient ions obtained from the diarylquinones are recorded in Table 3. The 2,5- and 2,6-diarylquinones (63) and (64) show the successive loss of CO and Me·, and both also lose the fragment [71; X = 3,4-$(MeO)_2C_6H_3$-] to give abundant ions at m/e 162. The successive loss of two methoxy-radicals from the molecular ion of the 2,5-isomer gives

Table 3 Mass spectra of the diarylbenzoquinones

Di(3',4'-dimethoxyphenyl-benzoquinones	Principal ions and relative abundances (%)
2,5-Diaryl- (63)	m/e 380(100), 352(5), 349(41), 337(5), 334(5), 321(12), 318(47), 174.5†(10), 162(31), 159†(8), 147(12), 145.5†(8), 119(7), 91(9), 76(8); 320.5*(380 → 349), 289.5*(349 → 318).
2,6-Diaryl- (64)	m/e 380(100), 352(9), 337(11), 321(13), 176†(6), 162(26), 147(9), 119(6), 91(7), 85(7), 83(11); 326*(380 → 352), 322.5*(352 → 337).
2,3-Diaryl- (62)	m/e 380(100), 365(7), 349(7), 334(7), 333(11), 319(5), 318(19), 174.5†(7), 159†(6), 83(5); 350.5*(380 → 365), 320.5*(380 → 349), 304* (365 → 333), 289.5*(349 → 318).
3-Chloro-2,5-diaryl- (65)	m/e 414(100), 383(19), 379(12), 352(50), 348(95), 333(5), 207†(8), 191.5†(10), 189(22), 176†(11), 165(9), 162(11), 149(6), 147(6), 119(6), 91(8), 76(6); 354.5*(414 → 383), 323*(383 → 352), 319*(379 → 348), 316*(383 → 348).
3-Chloro-2,6-diaryl- (68)	m/e 414(100), 386(5), 383(6), 379(7), 371(5), 355(25), 351(7), 193†(6), 189(12), 165(6); 354.5*(414 → 383), 347*(414 → 379), 329.5*(383 → 355).

*Metastable transition. †Doubly-charged ion.

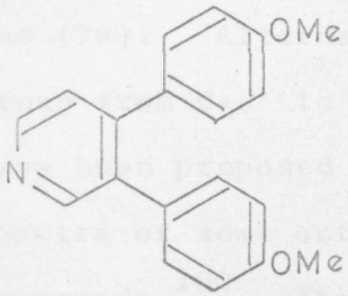
abundant ions at m/e 349 and 318, but the corresponding ions from the 2,6-isomer are of low abundance. The fragmentation of the 3-chloro-2,6-diarylquinone (68) is similar to that of the parent compound (64), and the 3-chloro-2,5-diarylquinone (65) gives abundant ions due to loss of MeO· and Cl· as shown in the following scheme:



Both the arylchloroquinones (65) and (68) lose the fragment (72) to give the ion m/e 189. The 2,3-diarylquinone (62) undergoes either the successive loss of 2MeO· from the molecular ion, or the loss of MeO· followed by the loss of MeOH. The second of these fragmentation pathways is not apparently available to the corresponding 2,5- and 2,6-isomers.

The loss of MeO· from the molecular ions of the aryl-quinones (52), (53), (54), and (61), and the successive loss of 2MeO· from the 2,3- and 2,5-diarylquinones (62), (63), and (65) is unusual.[98] Methoxystilbenes and the methoxyphenyl

derivatives (73) and (74) have been shown[98] to undergo fragmentation by loss of MeO·, but the relative abundances of the $(M-MeO)^+$ ions are considerably lower than those of the above arylquinones.



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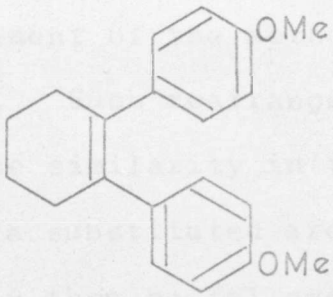

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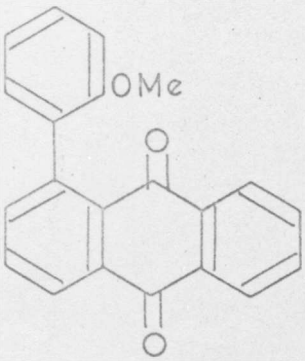

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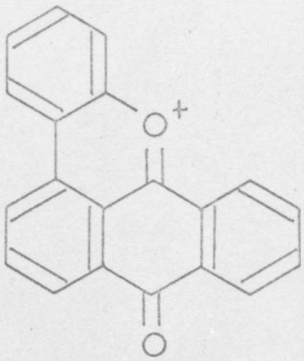
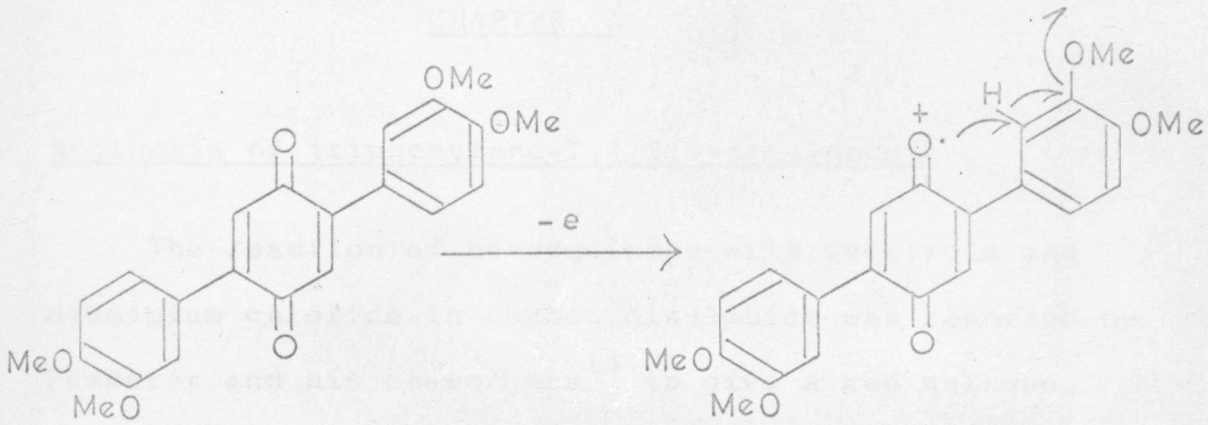


(76)

A methoxy-radical is readily lost from ions which can subsequently undergo cyclisation. Thus the molecular ion from the arylquinone (75) loses MeO· to give the ion (76) which isthe base peak.[99] A possible sequence for the fragmentation of the 2,5-diarylquinone (63) is shown on p. 50 . The loss of MeO· may occur by concerted processes as shown on p. 50 to give the resonance stabilised ions (77) and (78). Alternatively, rearrangement of the methoxy-group from C-3' to C-2' could occur. Such rearrangements have been proposed to account for the similarity in the mass spectra of some ortho, meta, and para substituted aromatic compounds.[100] The rearrangement may then be followed by loss of MeO· and subsequent cyclisation. The sequence shown on p. 50 is also applicable to the 2,3- but not to the 2,6-diarylquinones. It is significant that the latter quinones do not show appreciable loss of MeO·.

Fragmentation of 2,5-di(3',4'-dimethoxyphenyl)benzoquinone



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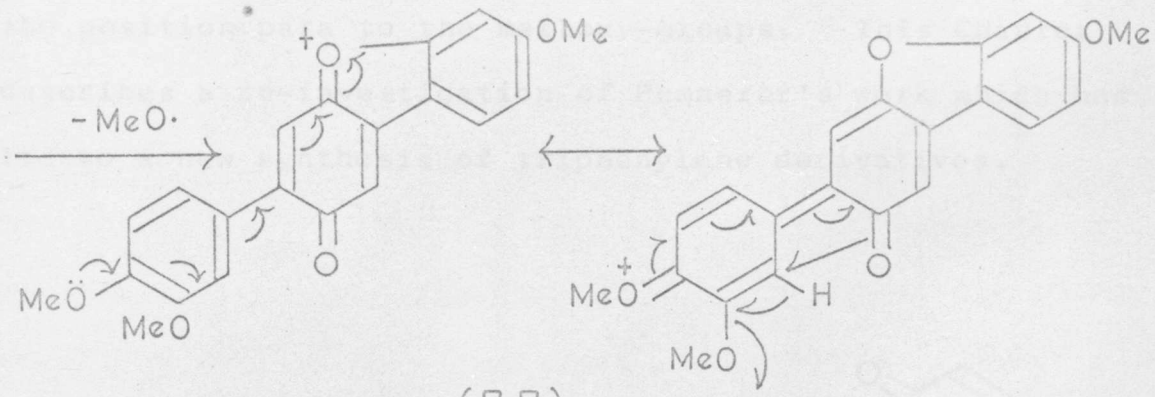

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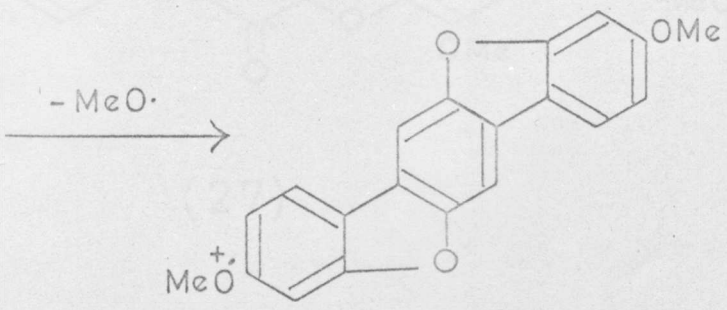
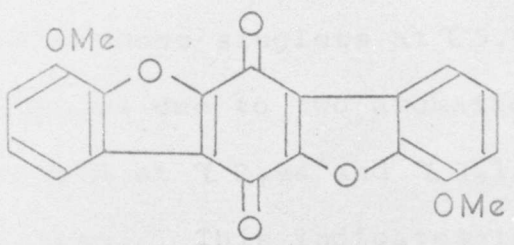


(78)

CHAPTER 3

Synthesis of triphenylene-1,4:5,8-diquinones.

The reaction of benzoquinone with veratrole and aluminium chloride in carbon disulphide was reported by Pummerer and his co-workers[14] to give a red quinone, $(MeO)_2C_{18}H_6O_4$, which was formulated as the bisbenzofuranoquinone (27). This structure appeared to be unsatisfactory because veratrole undergoes substitution predominantly at the positions para to the methoxy-groups. This Chapter describes a re-investigation of Pummerer's work which has led to a new synthesis of triphenylene derivatives.



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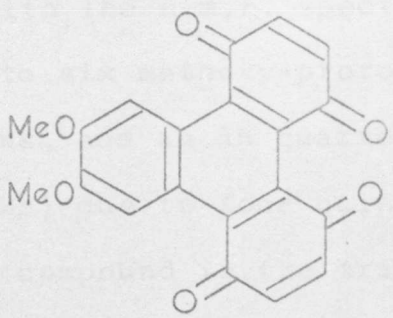

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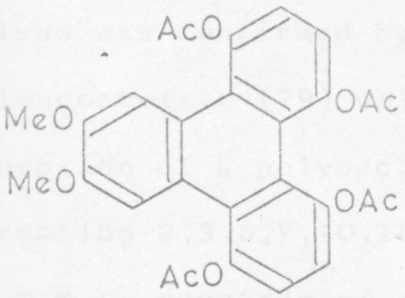
Reaction of benzoquinone with veratrole.

Benzoquinone reacted with veratrole in the presence of aluminium chloride to give a mixture of quinol, chloroquinol, and a red quinone. The chloroquinol was formed by reaction between benzoquinone and the hydrochloric acid used to decompose the aluminium chloride complex. The red quinone crystallised from toluene as dark red rhombohedra which contained toluene of crystallisation. The pure quinone, $(MeO)_2C_{18}H_6O_4$, m.p. 250-255° (decomp.), was obtained by heating a finely powdered sample at 140°/0.1 Torr. The red quinone, m.p. 290°, obtained by Pummerer under identical reaction conditions turned brown at 245°.[14] The quinone shows the presence of two types of carbonyl band in its i.r. absorption ($\nu_{max.}$ 1675 and 1650 cm^{-1}), which suggests an unsymmetrically substituted quinone. Pummerer's proposed structure (27) is not consistent with the n.m.r. spectrum which shows singlets at τ 5.92 due to six methoxy-protons, and at τ 1.04 due to two aromatic protons, and an AB quartet centred at τ 2.94 and τ 3.13 (J 10Hz) due to four quinonoid protons. This indicates that the compound is the triphenylene-1,4:5,8-diquinone (28) (Pummerer's quinone). The triphenylene



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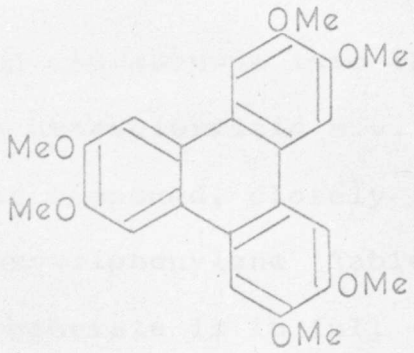


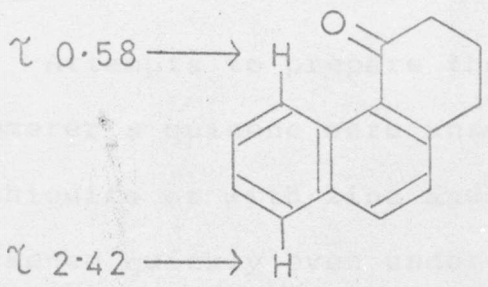
(18)

Table 4 U.v. absorptions of the triphenylenes (79) and (18)

Triphenylene (79)		Hexamethoxytriphenylene (18)[31]	
$\lambda_{max.}(CHCl_3)$(nm)	log ε	$\lambda_{max.}(CHCl_3)$(nm)	log ε
-	-	263*	4.66
275*	4.75	272*	4.79
279	4.77	281	4.89
305*	4.12	309	4.38
317*	4.07	320*	4.22
326*	4.01	330*	3.97
350*	3.45	346	3.49
372	3.33	361	2.43

* Inflection.

nucleus was confirmed by converting the quinone into the bisleucoacetate (79) which had the characteristic u.v. absorption of a polycyclic aromatic compound, closely resembling 2,3,6,7,10,11-hexamethoxytriphenylene (Table 4). The n.m.r. spectrum of the bisleucoacetate is in full agreement with the proposed structure. It shows six acetoxy-protons at τ 7.76 and six at τ 7.56, six methoxy-protons at τ 5.95, four aromatic protons at τ 2.70, and two at τ 1.54. The low field signals of the aromatic protons at C-9 and C-12 in the quinone (τ 1.04) and in the bisleucoacetate (τ 1.54) result from the presence of the substituents at C-1 and C-8. N.m.r. studies on polycyclic compounds have shown that peri-substituents generally cause considerable deshielding of aromatic protons[101] as in the polycyclic ketones[102] (80) and (81). The structure of Pummerer's quinone was confirmed



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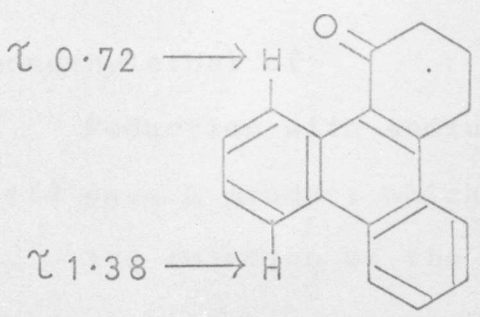
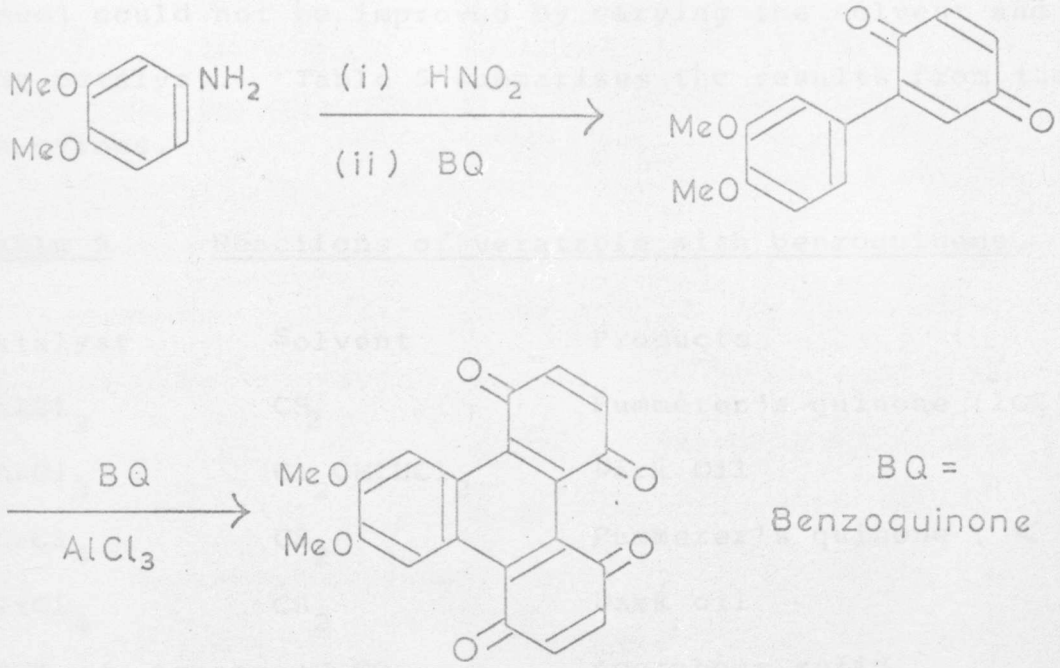


(81)

chemically by its synthesis from 3,4-dimethoxyaniline by the following route:



(28)

Attempts to prepare the bisleucomethylether of Pummerer's quinone were unsuccessful. Reduction with sodium dithionite or with zinc and acetic acid gave a product which darkened quickly even under nitrogen. The reaction of the reduction product with either dimethyl sulphate or diazomethane

gave only decomposition products.

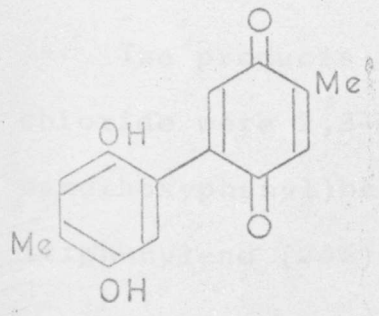
The yield of Pummerer's quinone (10% based on the amount of veratrole consumed, excess benzoquinone being used) could not be improved by varying the solvent and the catalyst. Table 5 summarises the results from these reactions.

Table 5 Reactions of veratrole with benzoquinone

Catalyst	Solvent	Products
$AlCl_3$	CS_2	Pummerer's quinone (10%)
$AlCl_3$	$Cl_2CHCHCl_2$	Dark Oil
$ZrCl_4$	CS_2	Pummerer's quinone (< 1%)
$TiCl_4$	CS_2	Dark oil
70% v/v aqueous H_2SO_4		Amorphous solid
Polyphosphoric acid		Black solid

Attempted reactions of methylbenzoquinone, phenylbenzoquinone, 1,4-naphthaquinone, and 4,4'-diphenoquinone with veratrole.

Attempts to prepare triphenylenediquinones by treating veratrole with methylbenzoquinone, phenylbenzoquinone, or 1,4-naphthaquinone, in the presence of aluminium chloride were unsuccessful. In each case, most of the veratrole was recovered, and the only products isolated resulted from the reduction or self-condensation of the quinone. The reaction with methylbenzoquinone gave methylquinol and 2-methyl-5-(2',5'-dihydroxy-4'-methylphenyl)benzoquinone[38] (82). The latter compound was identified by its conversion into the tetra-acetate (83) and also into the diquinone (84). The n.m.r. spectrum of the diquinone showed the presence of six methyl protons coupled with the adjacent quinonoid protons, and two unperturbed quinonoid protons. The reaction of veratrole with phenylbenzoquinone gave only unchanged reactants



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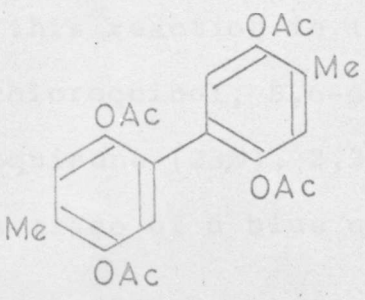

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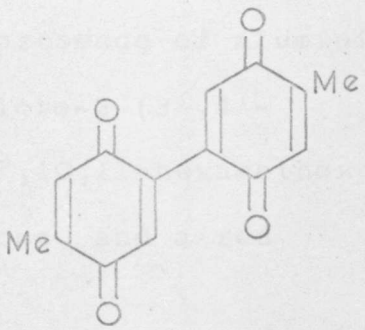
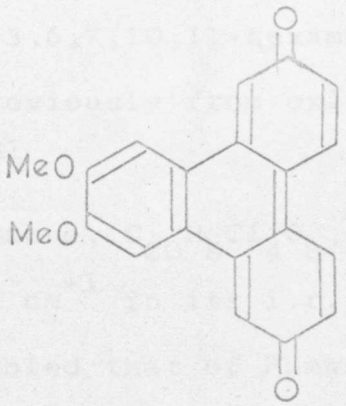


(84)

and phenylquinol, but that with 1,4-naphthaquinone gave 1,4-dihydroxynaphthalene, the binaphthaquinone (152), the dinaphthofuranquinone (155), and the tetrameric self-condensation product (31). This reaction is discussed in Chapter 6. Attempts to prepare the triphenylenequinone (85) by treating veratrole with 4,4'-diphenoquinone in the presence of aluminium chloride or aqueous sulphuric acid gave only unchanged reactants and 4,4'-dihydroxybiphenyl.



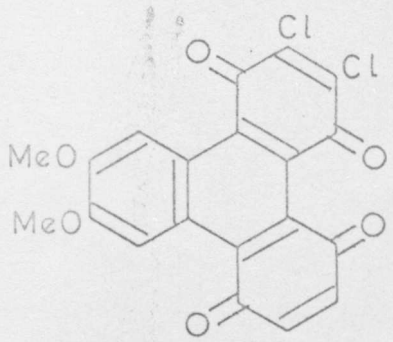
(85)

Reaction of 2,3-dichlorobenzoquinone with veratrole

The products of this reaction in the presence of aluminium chloride were 2,3-dichloroquinol, 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone (23%), 2,3,6,7,10,11-hexamethoxytriphenylene (24%), a trace of a blue quinone, and a red

quinone (0.25%), the yields being based on the amount of veratrole consumed. The 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone was identical with the product obtained from the reaction between 2,3-dichlorobenzoquinone and diazotised 3,4-dimethoxyaniline (Chapter 2). There was insufficient blue quinone to permit purification, but its u.v. absorption, and behaviour on silica gel suggest that it is the dibenzonaphthacenequinone (19). This compound, together with 2,3,6,7,10,11-hexamethoxytriphenylene, have been obtained previously from oxidations of veratrole by chloroquinones.[31]

The red quinone, $C_{20}H_8Cl_4O_6$, showed two carbonyl bands at 1690 and 1678 cm^{-1} in its i.r. spectrum, and its u.v. absorption resembled that of Pummerer's quinone (28), and also that of the 2,3-dichlorodiquinone (86) (Figure 2 p. 79). It follows that the red quinone is 2,3,6,7-tetrachloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (87). Because of the small amount available no further work was done on this product.



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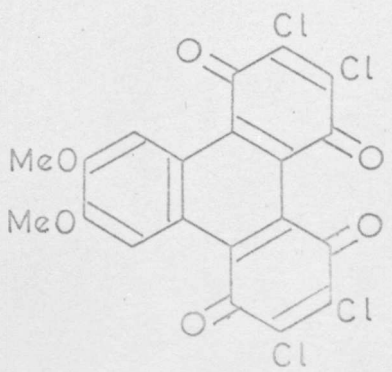
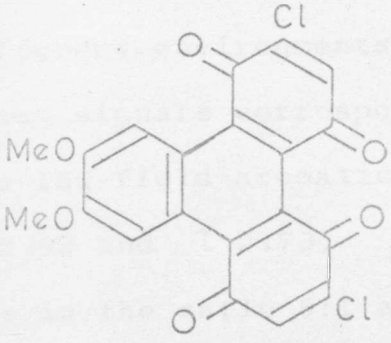


(87)

Reaction of chlorobenzoquinone with veratrole.

The products from this reaction were chloroquinol and a mixture (7.5% based on the veratrole consumed) of the three dichlorotriphenylenediquinones (88), (89), and (90). The complete separation of the mixture could not be effected,



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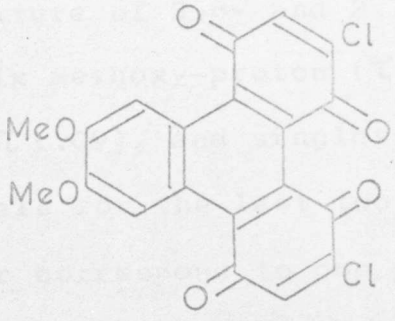

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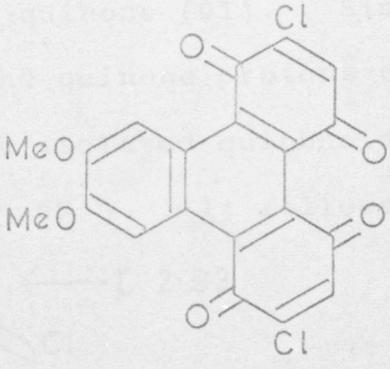
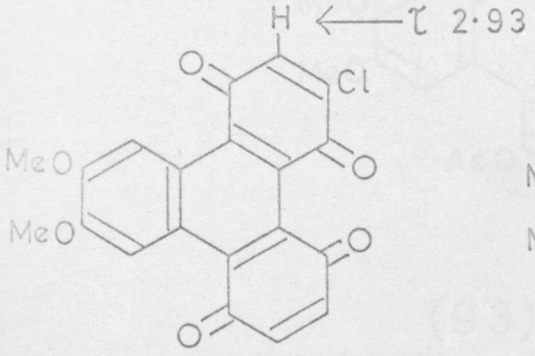


(90)

the products being a small amount of the pure 2,6-dichloro-quinone (88), and a 6:1- mixture of the 3,6- and 2,7-isomers (89) and (90). The quinones show u.v. absorptions resembling that of Pummerer's quinone (Figure 3 p. 80). The n.m.r. spectrum of the 2,6-isomer (88) shows six methoxy-protons (τ 5.92), two low-field aromatic protons (τ 1.09), and two quinonoid protons (τ 2.94 and τ 2.78) which must be in different environments. The mixture of 3,6- and 2,7-isomers shows signals corresponding to six methoxy-proton (τ 5.91), two low-field aromatic protons (τ 1.09), and singlets at τ 2.92 and τ 2.73. The integrals for the last two signals are in the ratio 6:1 and together correspond to one proton, indicating a 6:1- mixture of the two isomers. The signal at τ 2.92 is attributed to the quinone protons of the 3,6-isomer (89) by analogy with the isolated quinonoid proton (τ 2.93) of the quinone (91). Similarly that at τ 2.73 is attributed to the quinone protons of the 2,7-isomer (90) by analogy with the isolated quinonoid proton (τ 2.72) of the quinone (92) (p. 69). It follows that in the 2,6-dichloro-



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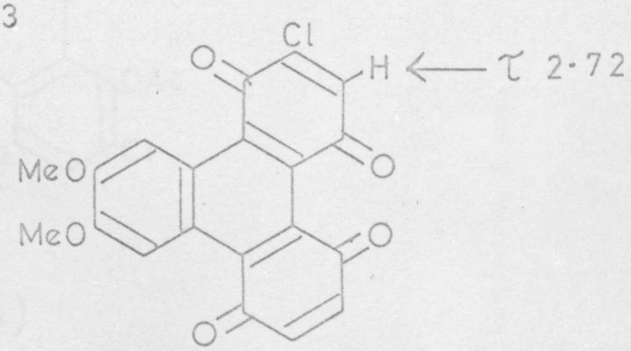
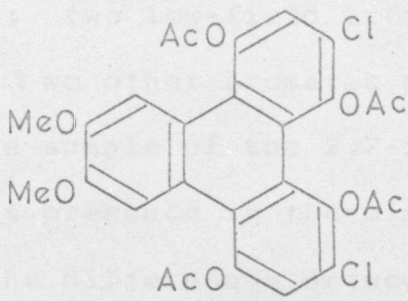


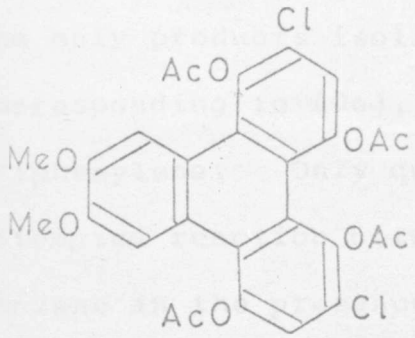
(92)

diquinone (88) the signal at τ 2.94 corresponds to the C-7 proton, and that at τ 2.78 to the C-3 proton.

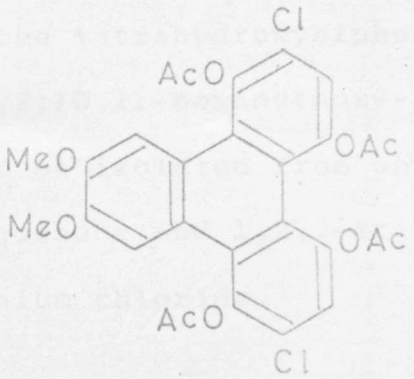
When the reaction was repeated on a larger scale small amounts of the three chloroarylquinones (52), (53), and (54) (p. 30) were also obtained. In this second experiment, an attempt was made to isolate the triphenylenes as their bis-leucoacetates. Reductive acetylation of a mixture of the three dichlorotriphenylenediquinones gave the mixed dichloro-triphenylenes (93), (94), and (95). Preparative t.l.c. enabled the 3,6-isomer (93) to be separated; this isomer was also obtained by reductive acetylation of a 7:1-mixture of the 3,6- and 2,7-dichlorodiquinones (89) and (90). Repeated crystallisation of the mixed 2,7- and 2,6-dichloro-triphenylenes (95) and (94) afforded only one of the pure components, this being identified as the unsymmetrical 2,6-isomer (94) by its n.m.r. spectrum. The latter shows



(93)



(94)

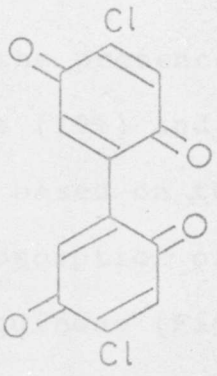


(95)

signals corresponding to the protons of four acetoxy-groups (τ 7.83 , 7.62, 7.55, and 7.55), and two methoxy-groups (each at τ 5.98); two low-field aromatic protons (τ 1.69. and τ 1.57), and two other aromatic protons (τ 2.61 and τ 2.46). A pure sample of the 2,7-isomer (95) could not be isolated, but its presence in the mixture was established by considering the differences between the n.m.r. spectra of

the pure 2,6-isomer and of the mixture of the 2,6- and 2,7-isomers (Table 8).

It was not possible to prepare the 2,7-dichlorodiquinone (90) by the reaction of veratrole with the diquinone (96). The only products isolated were the tetrahydroxybiphenyl corresponding to (96), and 2,3,6,7,10,11-hexamethoxy-triphenylene. Only quinol could be isolated from an attempted reaction between benzoquinone and 1,2,3-trimethoxy-benzene in the presence of aluminium chloride.



(96)

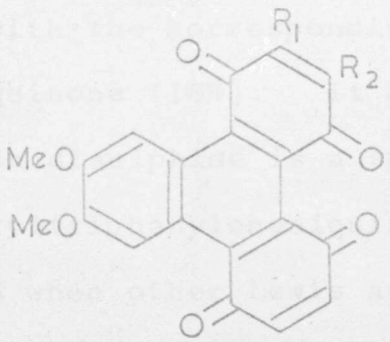
Reactions of benzoquinones with 3',4'-dimethoxyphenylbenzoquinones.

The isolation of arylchlorobenzoquinones from reactions between chlorobenzoquinones and veratrole suggested that such arylbenzoquinones might be intermediates in the formation of the triphenylenediquinones. The reactions between various benzoquinones and 3',4'-dimethoxyphenylbenzoquinones were therefore examined.

1. Benzoquinone and 3',4'-dimethoxyphenylbenzoquinone (50)

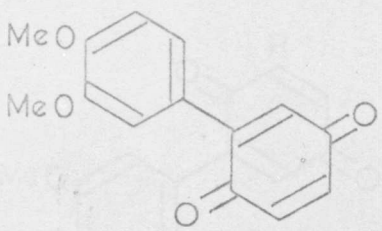
These reacted in the presence of aluminium chloride to give Pummerer's quinone (19%) and a red crystalline solid (15%); the yields are based on the amount of the arylquinone consumed. The u.v. absorption of the red solid is similar to that of Pummerer's quinone (Figure 4) (p. 81), and its n.m.r. spectrum shows the presence of four different methoxy-groups (τ 6.03, 6.00, 5.93, and 5.91), two different low-field aromatic protons (τ 1.03 and 0.95), and six aromatic and quinonoid protons (τ 3.13-2.62). The molecular formula, $C_{28}H_{20}O_8$, corresponds to two dimethoxyphenylbenzo-quinone units ($2 \times C_{14}H_{12}O_4$) less four hydrogen atoms, and

the product is therefore either the 2- or the 3-aryltriphenylenediquinone (97) or (98), or a mixture of these; it clearly results from the self-condensation of two molecules of the arylquinone (50). Although attempted p.l.c. separation of the red solid gave only one band, the i.r. spectra obtained

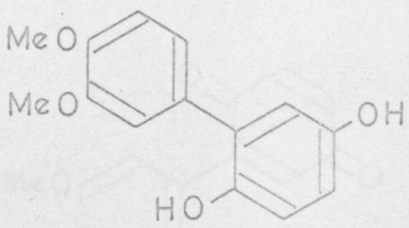


(97) $R_1 = 3,4\ (MeO)_2\ C_6H_3^-$; $R_2 = H$.

(98) $R_1 = H$; $R_2 = 3,4\text{-}(MeO)_2\ C_6H_3^-$.



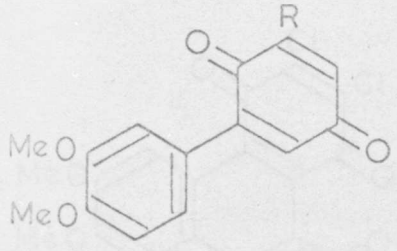
(50)



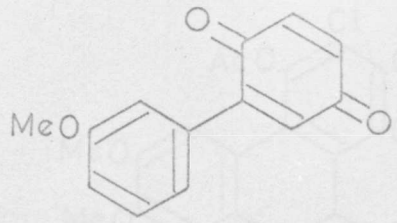
(99)

from different parts of the band showed slight differences in the relative intensities of the peaks. This suggested that the red solid is not a single compound, but is a mixture of the two isomers (97) and (98).

The same product (6%) was obtained when the arylquinone (50) was treated with aluminium chloride, but the reaction of benzoquinone with the corresponding arylquinol (99) gave only Pummerer's quinone (18%). It appears that aluminium chloride in carbon disulphide is a specific reagent for the preparation of aryltriphenylenediquinones, as these compounds were not obtained when other Lewis acids were used (Table 6). An attempted synthesis of the 2-aryltriphenylenediquinone (97), by the reaction between benzoquinone and the 2,6-diarylquinone (64) gave only unchanged starting material. Likewise benzoquinone and 3'-methoxyphenylbenzoquinone (100) failed to react.



(64) R = 3,4-$(MeO)_2$ C_6H_3-.



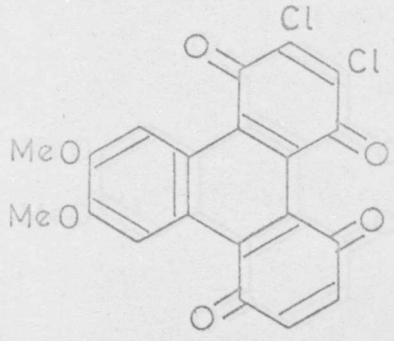
(100)

Table 6 Reactions of 3',4'-dimethoxyphenylbenzoquinone (50) with Lewis acids.

Catalyst	Solvent	Products
$AlCl_3$	CS_2	Aryltriphenylenediquinones (97) and (98)
$AlCl_3$	C_6H_6	Unchanged arylquinone (50)
$AlCl_3$	CH_3NO_2	Black solid
$ZrCl_4$	CS_2	Unchanged arylquinone (50)
BF_3	Et_2O	Black solid
$SnCl_4$	C_6H_6	Unchanged arylquinone (50)

2. 2,3-Dichlorobenzoquinone and 3',4'-dimethoxyphenylbenzoquinone

These reacted to give 2,3-dichloroquinol, the aryltriphenylenediquinones (97) and (98) (11%), and the 2,3-dichlorotriphenylenediquinone (86) (4.5%). The last compound was obtained in a much higher (44%) yield by treating



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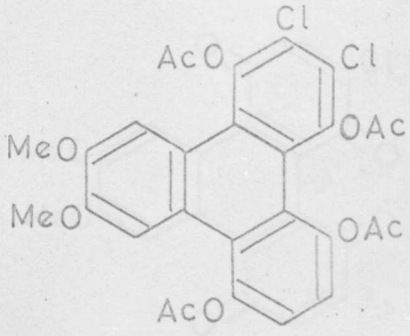
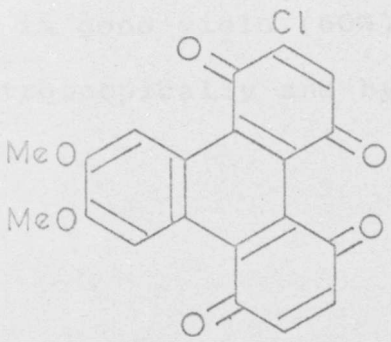


(101)

benzoquinone with 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-benzoquinone (57). The structure of the 2,3-dichloro-triphenylenediquinone (86) was confirmed by its reductive acetylation to give the triphenylene (101) which has a u.v. absorption (Table 9) (p.82) similar to that of the bisleuco-acetate (79) obtained from Pummerer's quinone. The n.m.r. spectrum of the triphenylene (101) shows the presence of four acetoxy-groups (τ 7.84, 7.60, 7.60, and 7.50), two methoxy-groups (τ 5.98), two low-field aromatic protons (τ 1.67 and 1.57), and two other aromatic protons (τ 2.66, broad signal).

3. Chlorobenzoquinone and 3',4'-dimethoxyphenylbenzoquinone

These reacted to give a mixture (13%) of the aryltriph-enylenediquinones (97) and (98), together with a mixture (10%) of the 2- and 3-chlorotriphenylenediquinones (92) and (91). A similar mixture of chlorotriphenylenediquinones was obtained



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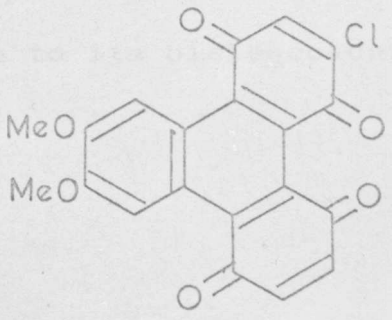
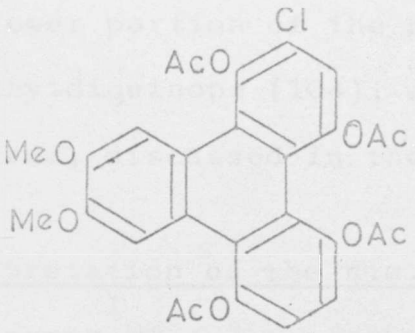


(91)

by treating benzoquinone with an equal mixture of 6- and 5-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (54) and (53), but the yield was much higher (58%). The mixed chlorotriphenylenediquinones could not be separated neither could the corresponding mixture of the bisleucoacetates (102) and (103). The components of the latter mixture were identified by their u.v. (Table 9) and n.m.r. (Table 8) spectra. The reaction



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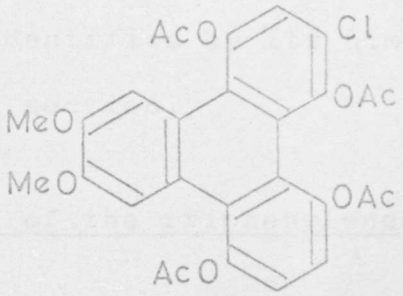


(103)

between benzoquinone and 5-chloro-2-(3',4'-dimethoxyphenyl)-benzoquinone gave the expected 3-chlorotriphenylenediquinone (91) in good yield (60%). The compound was identified spectroscopically and by conversion to its bisleucoacetate (103).

4. Methylbenzoquinone and 3',4'-dimethoxyphenylbenzoquinone

The reaction of methylbenzoquinone and 3',4'-dimethoxyphenylbenzoquinone in the presence of aluminium chloride gave the dihydroxyarylquinone (82) (p.57) and a mixture of the 2- and 3-methyltriphenylenediquinones (105) and (104). The mixture was identified by its u.v. absorption (Figure 4) (p. 81), and its partial separation was effected by p.l.c. The lower portion of the broad band obtained gave mainly the 3-methyldiquinone (104), which was identified by its n.m.r. spectrum, discussed in the following section.

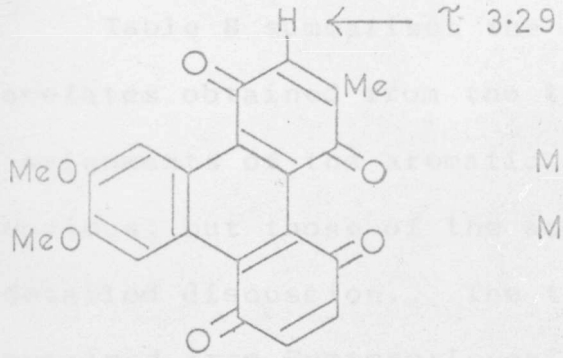
Interpretation of the n.m.r. spectra of the triphenylenediquinones

The n.m.r. spectra of the triphenylenediquinones are summarised in Table 7. Assignments of the methoxy-proton and aromatic proton signals are obvious in each case, but the quinonoid proton signals require more information and the assignments are made as follows. Pummerer's quinone (28) shows an AB quartet centred at τ 3.13 and τ 2.94 (J 10Hz) due to the two pairs of quinonoid protons. Now the signals of the isolated quinonoid protons in the 3- and 2-chlorotriphenylenediquinones (91) and (92) occur at τ 2.93 and τ 2.72

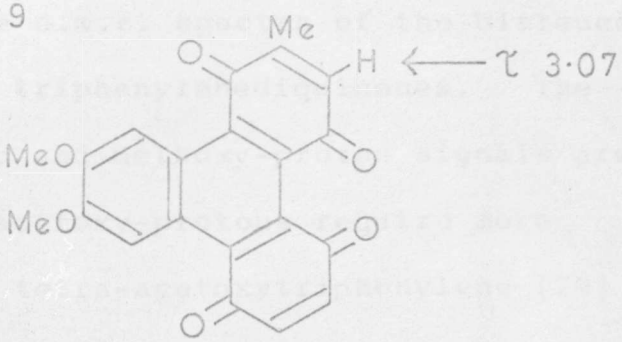
respectively (p. 61). Because a chlorine atom is known to deshield the cis-proton of a chloro-olefin by 0.19 p.p.m.,[104] the unchlorinated triphenylenediquinone would be expected to give a C-2 proton signal at ca. τ 3.12 and a C-3 signal at ca. τ 2.91. Thus the signals in Pummerer's quinone at τ 3.13 and τ 2.94 clearly correspond to the resonances of the C-2 and C-3 protons respectively.

One of the two methyltriphenylenediquinones shows signals corresponding to two coupled quinonoid protons (τ 3.11 and τ 2.95, ABq, J 10Hz), and to one isolated quinonoid proton (τ 3.29, q, J 2Hz) weakly coupled to a methyl group (τ 7.76, d, J 2Hz). As expected, irradiation at τ 7.76 caused the quartet at τ 3.29 to collapse to a singlet. The spectrum of the other isomer shows two coupled quinonoid protons (τ 3.11 and τ 2.94, ABq, J 10Hz), and one isolated quinonoid proton (τ 3.07, q, J 2Hz) weakly coupled with the protons of the methyl group (τ 7.79, d, J 2Hz). Again irradiation at τ 7.79 converted the quartet into a singlet. Comparison of the isolated quinonoid proton signals at τ 3.29 and τ 3.07 with those of the C-2 and C-3 protons (τ 3.13 and τ 2.94) in Pummerer's quinone indicates that the first methyltriphenylenediquinone is the 3-isomer (104) and the second is the 2-isomer (105).

The spectra of the dichlorotriphenylenediquinones are discussed on p. 61.



(104)



(105)

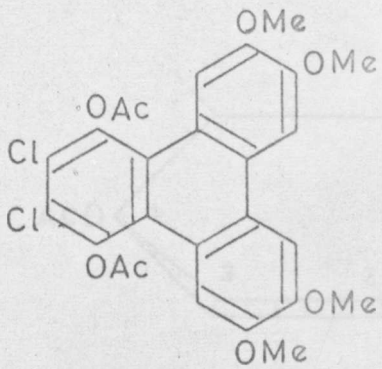
Table 7 N.m.r. spectra of the triphenylenediquinones

Compound	Chemical Shifts (τ)					
	CH_3O	C-9 and C-12	C-2	C-3	C-6	C-7
(28)(p. 51)	5.92	1.04	3.13	2.94	2.94	3.13
(91)(p. 69)	5.92	0.97,1.02	2.93	-	2.95	3.11
*(92)(p. 69)	5.92	1.06,1.10	-	2.72	2.95	3.11
*(104)(p. 73)	5.90	0.98,1.02	3.29	7.76(CH_3)	2.95	3.11
*(105)(p. 73)	5.90	1.02	7.79(CH_3)	3.07	2.94	3.11
(88)(p. 60)	5.92	1.09	-	2.78	-	2.94
*(89)(p. 60)	5.91	1.09	2.92	-	-	2.92
*(90)(p. 60)	5.91	1.09	-	2.73	2.73	-

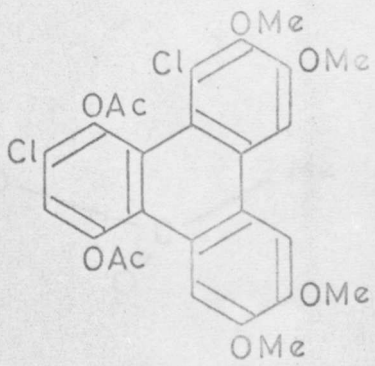
* Chemical shifts obtained from spectra of mixtures.

Interpretation of the n.m.r.spectra of the tetra-acetoxytriphenylenes

Table 8 summarises the n.m.r. spectra of the bisleuco-acetates obtained from the triphenylenediquinones. The assignments of the aromatic and methoxy-proton signals are obvious, but those of the acetoxy-protons require more detailed discussion. The tetra-acetoxytriphenylene (79) obtained from Pummerer's quinone shows six acetoxy-protons at τ 7.76 and six at τ 7.56; the higher field signal (τ 7.76) is attributed to the groups at C-4 and C-5. Molecular models show that, due to steric hinderence, the favoured conformation of the acetoxy-groups at C-4 and C-5 is as shown in Figure 1a. Here the acetoxy-protons lie within the shielded region caused by the ring current. These protons will thus resonate at higher field than the corresponding protons at C-1 and C-8, which are virtually outside the influence of the ring current (Figure 1b). The n.m.r. spectra of the diacetoxytriphenylenes (106) and (107) provide support for this explanation. The triphenylene (106) shows a singlet at τ 7.53 due to the



(106)



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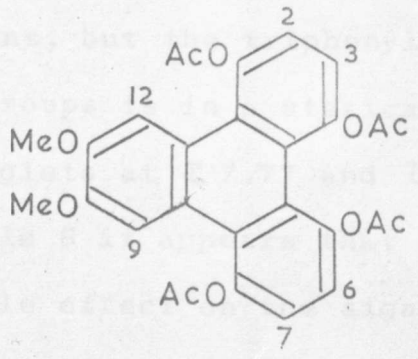


(79)

Figure 1a Conformation of the acetoxy-groups at C-4 and C-5 of the tetra-acetoxytriphenylenes

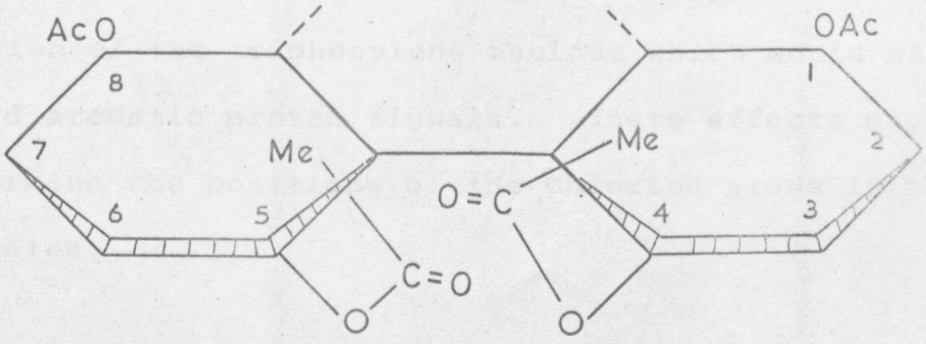
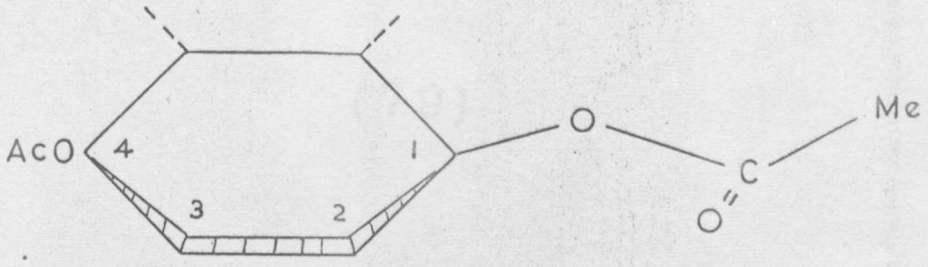
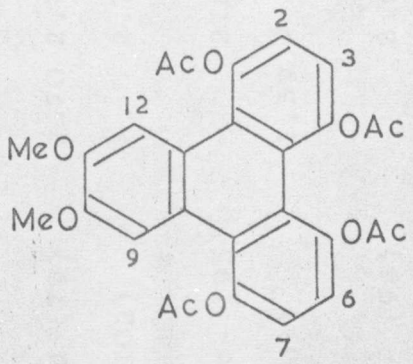


Figure 1b Conformation of the acetoxy-groups at C-1 and C-8 of the tetra-acetoxytriphenylenes



acetoxy-protons, but the triphenylene (107) in which one of the acetoxy-groups is in a sterically hindered position, shows two singlets at τ 7.77 and τ 7.49 (Chapter 4).

From Table 8 it appears that chlorine atoms at C-2 and C-7 have little effect on the signals of the C-4 and C-5 acetoxy-protons, or the C-9 and C-12 aromatic protons, but that chlorine atoms at C-3 and C-6 shift both these signals somewhat. The overcrowding caused by the presence of the bulky chlorine atoms on C-3 and C-6 must affect the conformation of the C-4 and C-5 acetoxy-groups, and may also cause some distortion of the triphenylene nucleus which would shift the low-field aromatic proton signals. These effects may be used to determine the positions of the chlorine atoms in the bisleucoacetates.



(79)

Table 8 N.m.r. spectra of the tetra-acetoxytriphenylenes

Substituted 1,4,5,8-tetra-acetoxy-10,11-dimethoxytriphenylene	Chemical shifts (τ)							
	C-2	C-3	C-6	C-7	C-9 C-12	C-10 C-11 (CH_3O)	C-1 C-8 (CH_3CO_2)	C-4 C-5 (CH_3CO_2)
Unsubstituted (79)	2.70	2.70	2.70	2.70	1.54	5.95	7.56	7.76
*2-Chloro- (102)	-	2.73	2.70 or 2.58	2.58 or 2.70	1.57	5.98	7.57	7.77
*2,7-Dichloro- (95)	-	2.61	2.61	-	1.57	5.98	7.55	7.77
3-Chloro- (103)	2.59	-	2.62 or 2.77	2.77 or 2.62	1.57 1.64	5.98	7.57 7.55	7.62 7.84
2,6-Dichloro- (94)	-	2.61 or 2.46	-	2.46 or 2.61	1.57 1.69	5.98	7.55	7.62 7.83
2,3-Dichloro- (101)	-	-	2.66	2.66	1.57 1.67	5.98	7.50 7.60	7.60 7.84
3,6-Dichloro- (93)	2.57	-	-	2.57	1.67	5.98	7.57	7.69

* Chemical shifts obtained from spectra of mixtures.

U.v. absorptions of the triphenylenediquinones and their bisleucoacetates

The close similarity between the u.v. absorptions of the triphenylenediquinones is shown in Figures 2,3, and 4. All show a characteristic band between 488 and 468 nm and another band of similar intensity between 418 and 384 nm. These bands provide a simple method for confirming the presence of the triphenylenediquinone nucleus. The spectra of the bisleucoacetates (Table 9) all show the fine structure which is typical of polycyclic aromatic compounds.

Figure 2 U.v. absorptions (in $CHCl_3$) of the di- and tetra-chlorotriphenylenediquinones (86) and (87)

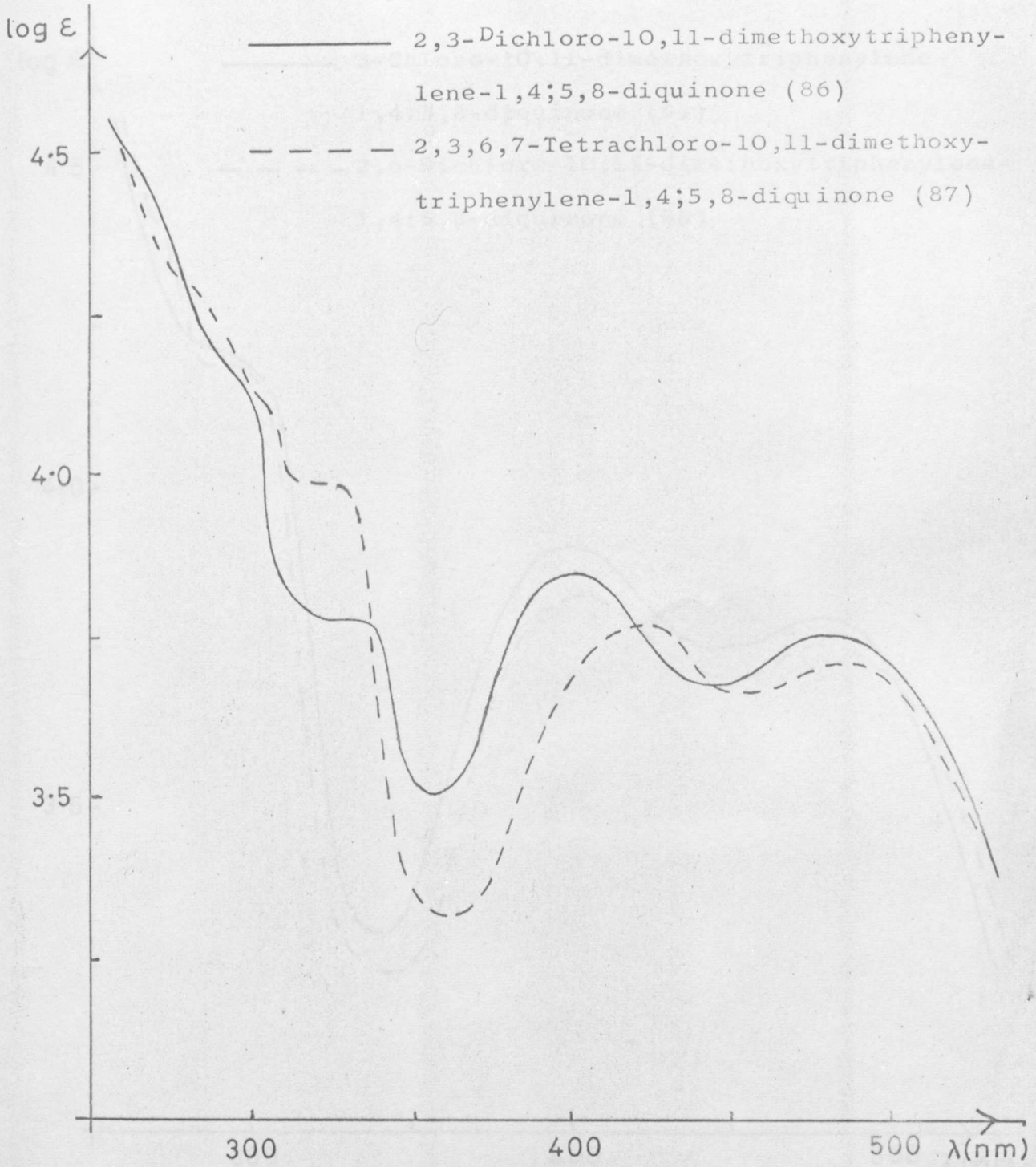


Figure 3 U.v. absorptions (in $CHCl_3$) of the mono- and di-chlorotriphenylenediquinones (91) and (88)

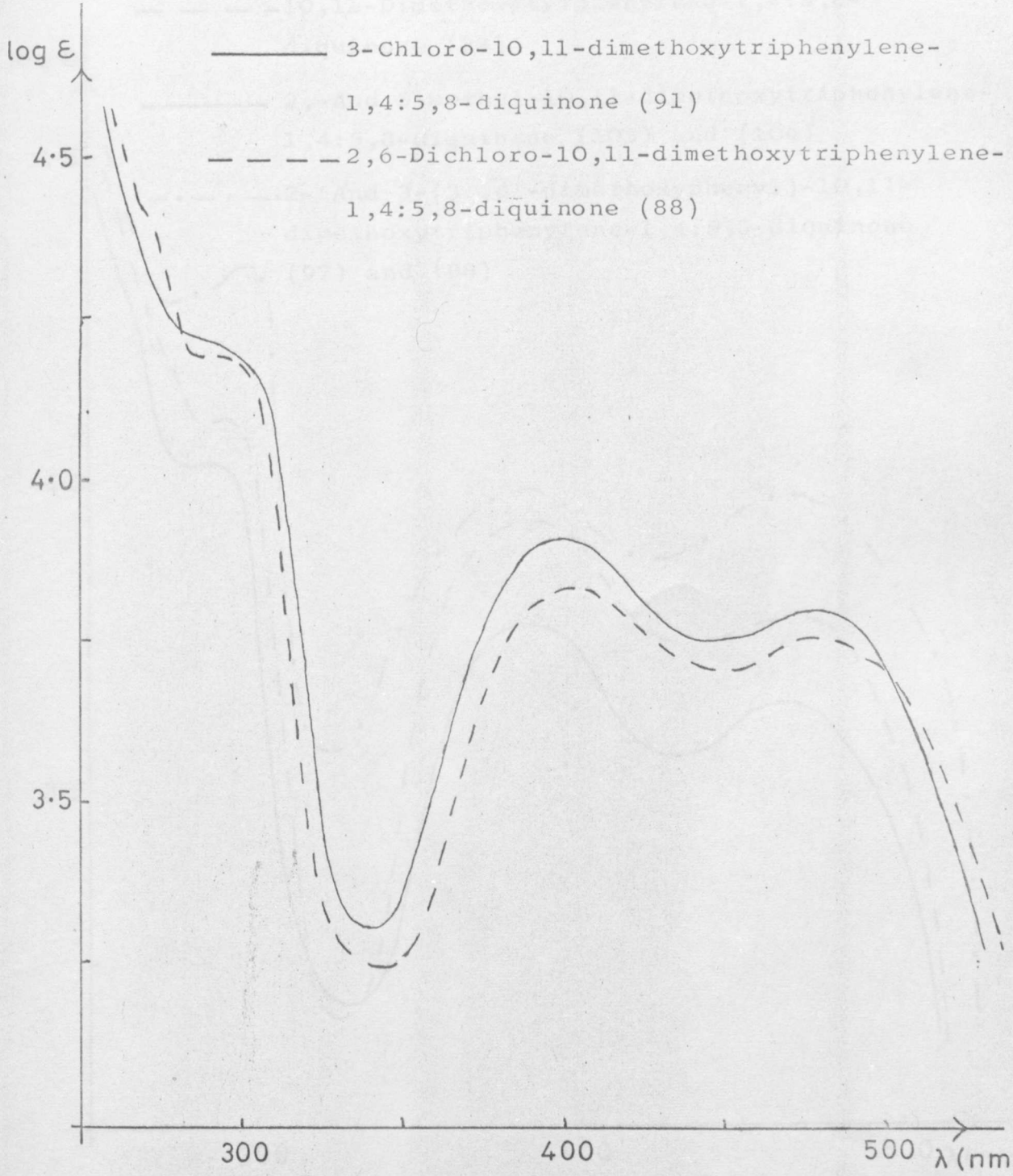


Figure 4 U.v. absorption (in $CHCl_3$) of Pummerer's quinone and its methyl- and aryl-derivatives

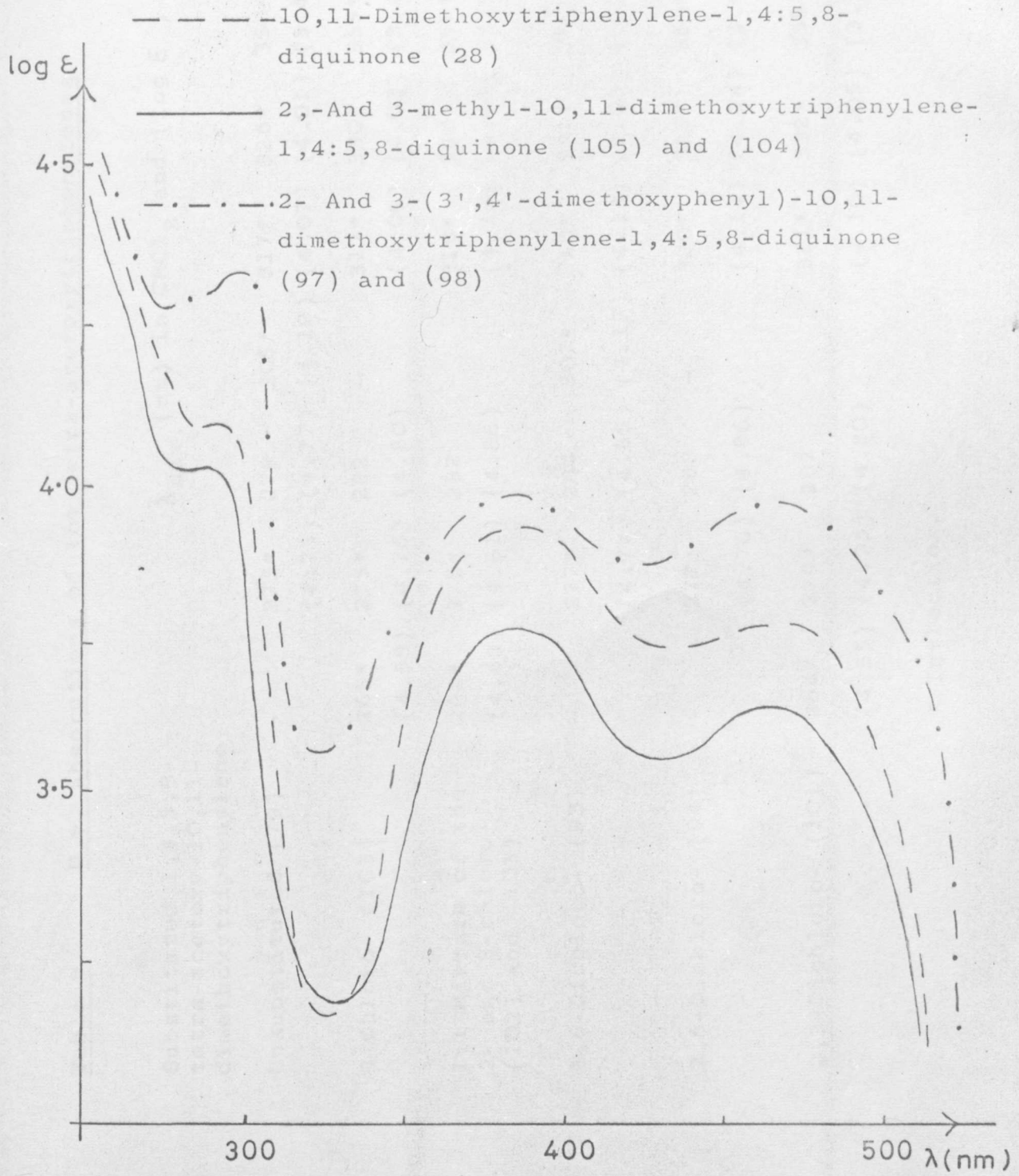


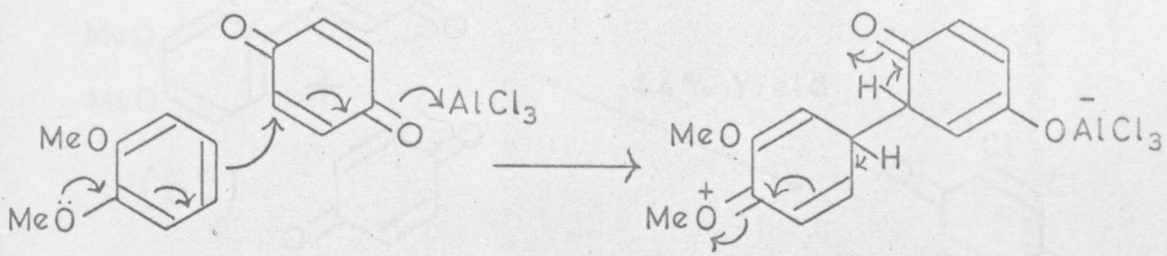
Table 9 U.v. absorptions of the tetra-acetoxytriphenylenes

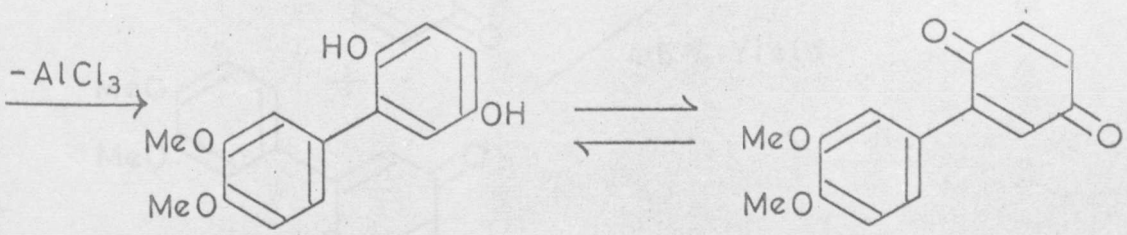
Substituted 1,4,5,8-tetra-acetoxy-10,11-dimethoxytriphenylene	$\lambda_{max.}$ (nm) in $CHCl_3$ and (log ε)							
Unsubstituted (79)	-	275* (4.75)	279 (4.77)	305* (4.12)	317* (4.07)	326* (4.01)	350* (3.45)	372 (3.33)
3-Chloro- (103)	265* (4.58)	275* (4.76)	282 (4.80)	-	317* (4.09)	330* (4.03)	355* (3.49)	375 (3.38)
1:1 Mixture of the 2- and 3-chloro- (102) and (103)	264* (4.62)	275* (4.81)	282 (4.86)	-	318* (4.13)	330* (4.06)	356* (3.52)	375 (3.36)
3,6-Dichloro- (93)	-	277* (4.77)	284 (4.85)	307* (4.17)	318* (4.13)	331* (4.05)	364 (3.52)	381 (3.49)
2,6-Dichloro- (94)	-	277* (4.76)	288 (4.86)	-	320* (4.14)	335* (4.04)	360* (3.49)	381 (3.38)
2,3-Dichloro- (101)	264* (4.55)	279* (4.75)	287 (4.80)	-	321* (4.10)	332* (4.05)	358* (3.53)	379 (3.35)

* Inflection.

Mechanism of the formation of the triphenylenediquinones

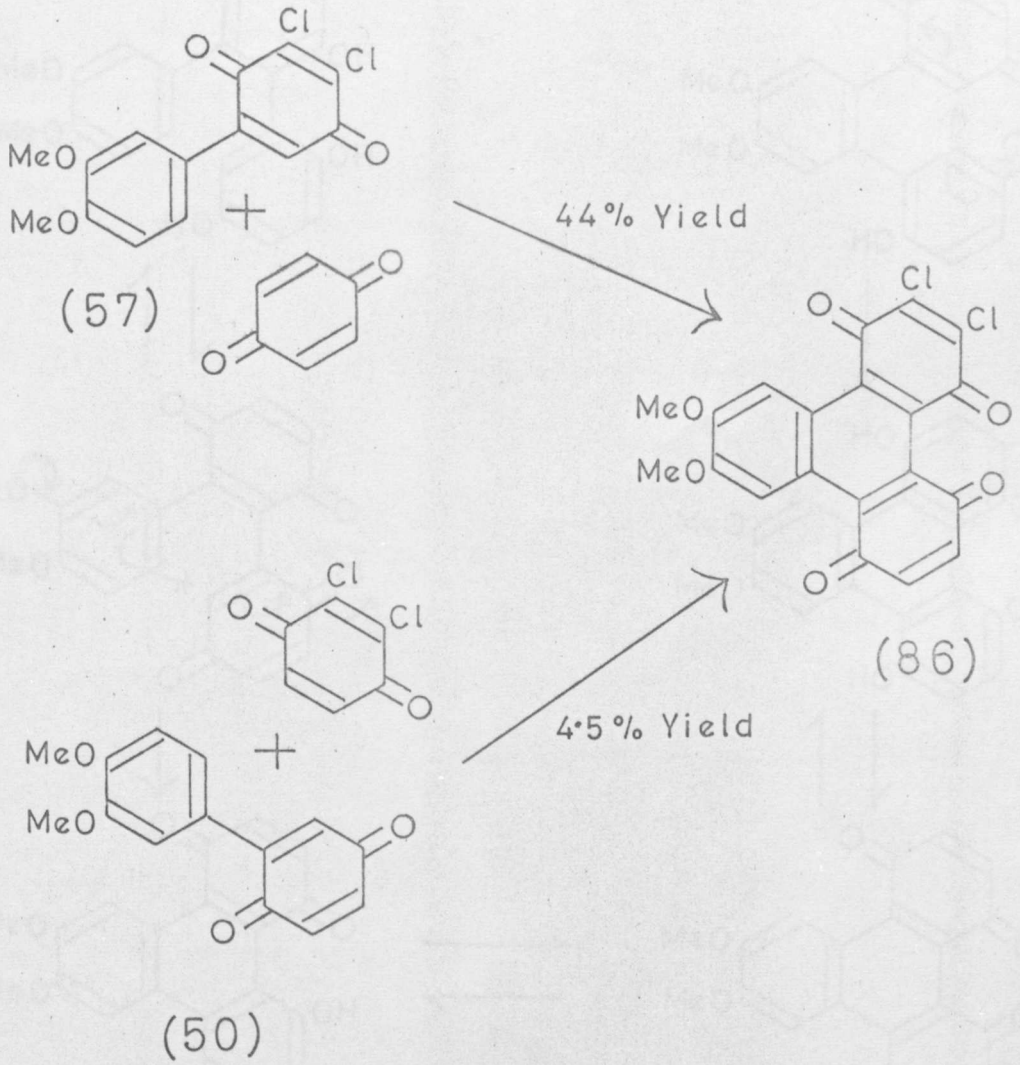
As has been shown above, arylquinones are intermediates in the formation of triphenylenediquinones from veratrole and benzoquinones. The reaction of an aromatic compound with a quinone in the presence of aluminium chloride to form arylquinols or arylquinones involves an electrophile formed from the quinone and the catalyst.[105] The first stage of the reaction between veratrole and benzoquinone may be written thus:

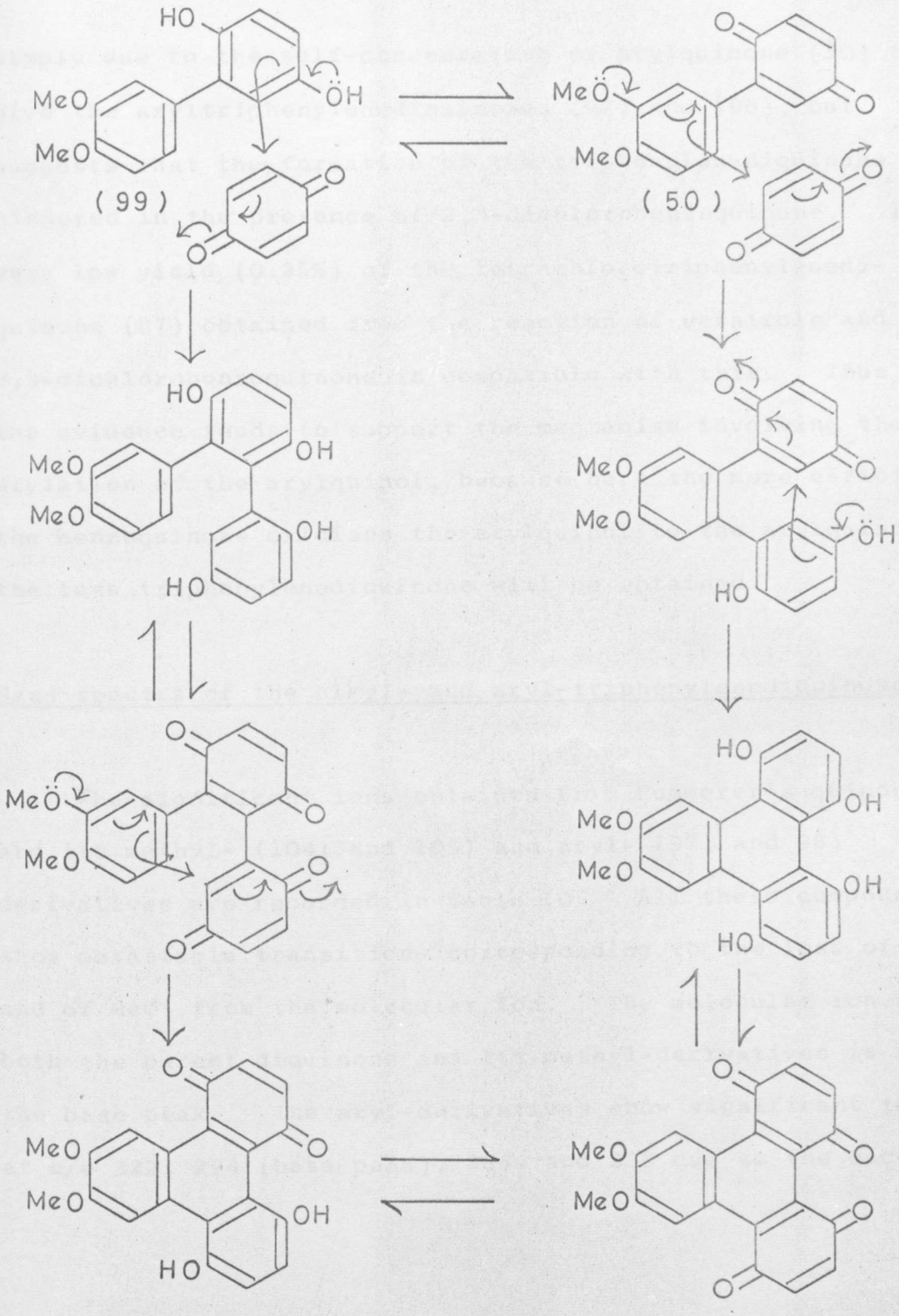




(99) (50)

The formation of the triphenylene system could involve arylation of the arylquinol (99) followed by cyclisation, or arylation of the quinone (50) and subsequent cyclisation as illustrated on p. 85. The dichlorotriphenylenediquinone (86) could be prepared by the two routes shown below but the yields were significantly different. This difference is not




HO
MeO
MeO
ÖH
(99)
(50)
OH
(28)

simply due to the self-condensation of arylquinone (50) to give the aryltriphenylenediquinones (97) and (98), but suggests that the formation of the triphenylenediquinone is hindered in the presence of 2,3-dichlorobenzoquinone. The very low yield (0.25%) of the tetrachlorotriphenylenediquinone (87) obtained from the reaction of veratrole and 2,3-dichlorobenzoquinone is compatible with this. Thus the evidence tends to support the mechanism involving the arylation of the arylquinol, because here the more efficiently the benzoquinone oxidises the arylquinol to the arylquinone, the less triphenylenediquinone will be obtained.

Mass spectra of the alkyl- and aryl-triphenylenediquinones

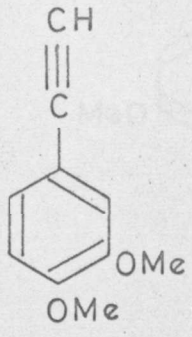
The significant ions obtained from Pummerer's quinone, and its methyl- (104; and 105) and aryl- (97; and 98) derivatives are recorded in Table 10. All these compounds show metastable transitions corresponding to the loss of CO and of MeO· from the molecular ion. The molecular ion in both the parent diquinone and its methyl-derivatives is also the base peak. The aryl-derivatives show significant ions at m/e 322, 294 (base peak), 266, and 238 due to the successive

Table 10 Mass spectra of the alkyl- and aryl-triphenylenediquinones

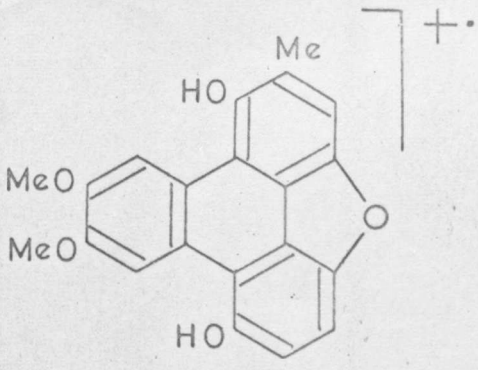
Substituted 10,11-dimethoxy-triphenylene-1,4:5,8-diquinone	Principal ions and relative abundances (%)
Unsubstituted (28)	m/e 348(100), 320(32), 317(26), 305(12), 294(10), 289(6), 277(15), 266(1), 262(14), 249(6), 238(17), 234(7), 221(6), 206(10), 195(7), 178(6), 167(6), 165(5), 152(9), 150(14), 139(8), 124(9), 98(8); 294*(348→320), 291.5*(320→305), 288.5*(348→317), 241*(294→266), 213*(266→238).
Mixture of 2- and 3-methyl- (105; and 104)	m/e 362(100), 348(38), 347(16), 334(16), 333(7), 331(14), 319(5), 308(9), 305(6), 303(9), 294(22), 238(8), 163(7), 142(5), 128(9), 127(6); 308*(362→334), 303*(362→331).
Mixture of 2- and 3-, 3',4'-dimethoxyphenyl- (97; and 98).	m/e 484(90), 470(9), 456(12), 454(4), 453(12), 425(4), 323(8), 322(43), 296(4), 294(100), 266(3), 242(4), 239(5), 238(28), 195(4), 139(4); 430.5*(484→456), 424*(484→453), 397*(453→425), 214*(484→322), 268.5*(322→294), 241*(294→266), 213*(266→238).

*Metastable transition

loss of the acetylene (108) and three molecules of CO from the molecular ion (m/e 484). Similar fragmentations occur with Pummerer's quinone and its methyl derivatives, but here the relative abundances of the corresponding ions are much lower. The methyl- and aryl-diquinones show low abundance $(M+4)^{+\cdot}$ ions due to the diquinols formed by reaction of the diquinones with water or other source of hydrogen in the mass spectrometer.[106] The ions at m/e 348 in the methyl-diquinones, and at m/e 470 in the aryldiquinones may be formed by the loss of H_2O from the corresponding $(M+4)^{+\cdot}$ ions to give radical ions such as (109). A similar type of fragmentation is observed in the spectra of the tetra-acetoxytriphenylenes discussed on p.91.



(108)

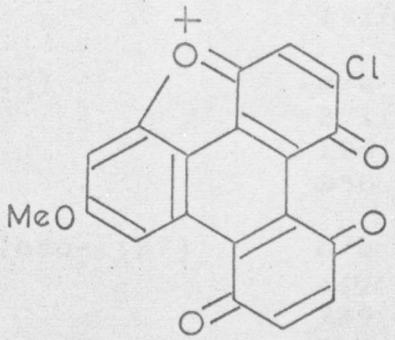


m/e 348

(109)

Mass spectra of the chlorotriphenylenediquinones

The more important ions (excluding isotopes) obtained from the chlorotriphenylenediquinones are recorded in Table 11. In each of the spectra, the molecular ion is the base peak and fragmentation results in the successive loss of CO and Cl·. Each compound forms an abundant ion resulting from the loss of MeO· from the base peak. This presumably occurs because of the formation of a relatively stable ion such as (110) by processes similar to those described earlier (p. 49) for the methoxyarylquinones.



m/e 351

(110)

Table 11 Mass spectra of the chlorotriphenylenediquinones

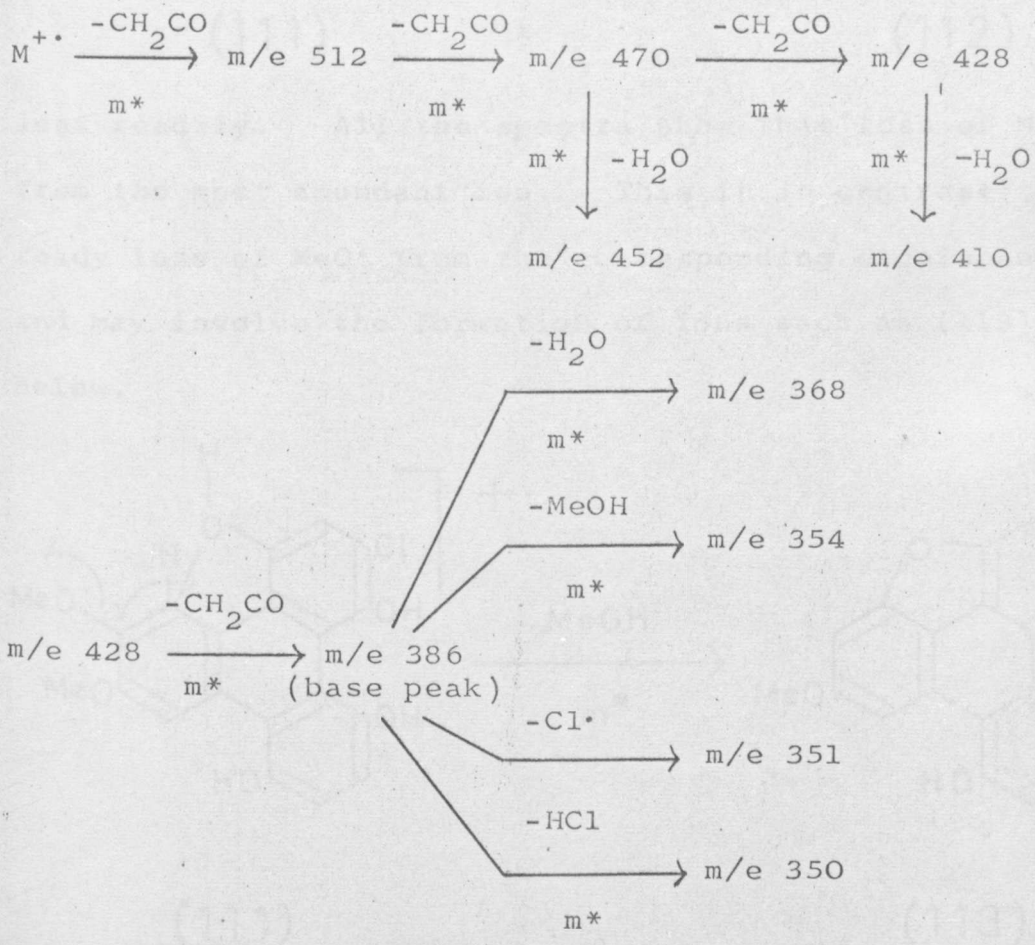
Substituted 10,11-dimethoxy-triphenylene-1,4:5,8-diquinone	Principal ions and relative abundances (%)
3-Chloro- (91)	m/e 382(100), 354(11), 351(33), 347(11), 319(28), 314(6), 312(9), 296(6), 278(6), 238(5), 149(9), 128(23), 127(11); 328*(382→354), 323*(382 → 351), 287*(354 → 319).
2,6-Dichloro- (88)	m/e 416(100), 388(29), 385(45), 381(17), 353(45), 345(6), 337(6), 330(8), 274(5), 272(7), 195(5), 183(5), 123(8), 122(8), 98(8); 363*(416 → 388), 356.5*(416 → 385) 349.5*(416 → 381), 321.5* (388→353).
Mixture of 3,6- and 2,7-dichloro- (89 and 90)	m/e 416(100), 388(20), 385(57), 381(20), 353(50), 337(7), 330(7), 272(7), 195(5), 194(6), 178(6), 164(6), 123(8), 122(8), 120(6), 98(7); 363*(416 → 388), 356.5*(416 → 385), 349.5* (416 → 381), 321.5*(388→353).
2,3-Dichloro- (86)	m/e 416(100), 388(17), 385(28), 381(13), 353(54), 330(5), 195(7), 194(7); 363*(416 → 388), 356.5*(416 → 385).
2,3,6,7-Tetrachloro- (87)	m/e 484(100), 456(31), 453(42), 449 (19), 428(8), 421(67), 229(10), 220(11), 218(11), 216(17), 157(10), 122(14), 98(11), 87(19).

*Metastable transition

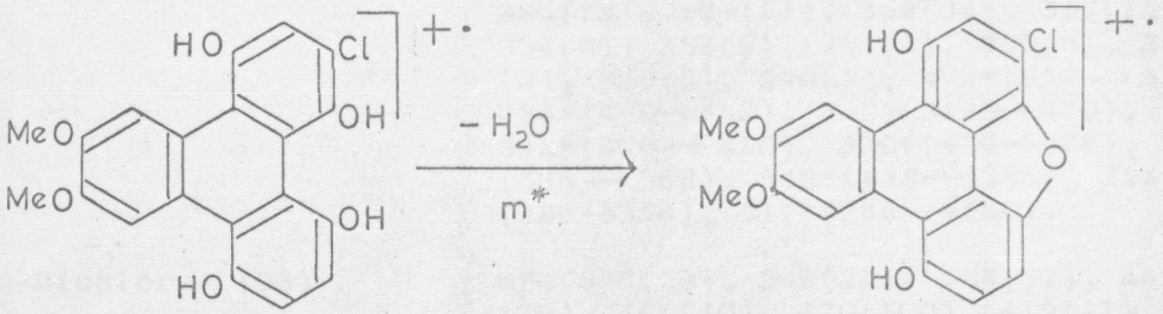
Mass spectra of the tetra-acetoxytriphenylenes

Table 12 records the ions (excluding isotopes) with relative abundances $>5\%$ obtained from the tetra-acetoxytriphenylenes. In each case, the base peak corresponds to the molecular ion less four molecules of ketene and is presumably derived from a diquinol derivative such as (111). The fragmentation of the monochloro-compound is summarised in the scheme below. The most abundant ion with m/e 386 readily

Fragmentation of the 3-chlorotetra-acetoxytriphenylene (103)

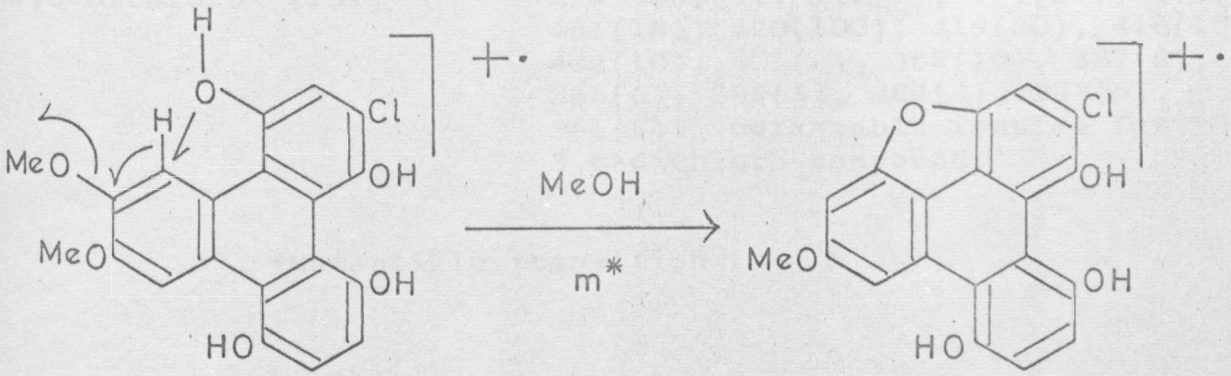


loses water. This is presumably because the hydroxy groups of the ion (111), at C-4 and C-5 can easily eliminate H_2O to form the stable ion (112). The dichloro-compounds fragment in a similar fashion but here the loss of H_2O occurs



(111) (112)

less readily. All the spectra show that loss of MeOH occurs from the most abundant ion. This is in contrast to the ready loss of MeO· from the corresponding diquinones (Table 11) and may involve the formation of ions such as (113) as shown below.



(111) (113)

Table 12 Mass spectra of the tetra-acetoxytriphenylenes

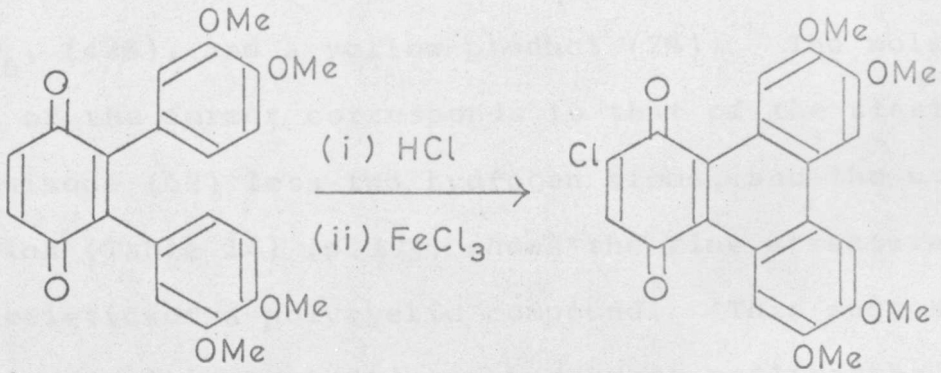
Substituted 1,4,5,8-tetra-acetoxy-10,11-dimethoxy-triphenylene	Principal ions and relative abundances (%)
3-Chloro- (103)	m/e 554(14), 512(16), 470(38), 452(8), 428(62), 427(9), 410(11), 386(100), 385(15), 384(11), 368(54), 367(15), 354(8), 353(6), 351(5), 350(9), 349 (8), 325(5), 290(5); 472*(554 → 512), 434*(470 → 452), 431*(512 → 470), 392*(428 → 410), 390*(470 → 428), 350* (386 → 368), 348*(428 → 386), 324.5* (386 → 354), 317*(386 → 350).
3,6-Dichloro- (93)	m/e 588(23), 546(31), 504(52), 462 (76), 461(10), 420(100), 419(11), 418(9), 402(5), 401(5), 388(7), 387(6), 386(9), 385(7), 384(9), 383 (10); 507.5*(588 → 546), 465*(546 → 504), 423.5*(504 → 462), 382*(462 → 420), 384*(420 → 402), 358.5*(420 → 388), 351*(420 → 384,385).
2,6-Dichloro- (94)	m/e 588(19), 546(19), 504(40), 462(69), 461(10), 420(100), 419(13), 418(10), 402(5), 401(5), 388(7), 387(4), 386(5), 385(6), 384(9), 383(8); metastable ions as for the 3,6-dichloro-compound.
2,3-Dichloro- (101)	m/e 588(13), 546(9), 504(30), 462(39), 461(12), 420(100), 419(20), 418(16), 402(10), 401(8), 388(10), 387(8), 386(6), 385(5), 384(8), 383(6), 361(5); metastable ions as for the 3,6-dichloro-compound.

*Metastable transition

CHAPTER 4

Synthesis of triphenylene-1,4-quinones

The structures of the three di(3',4'-dimethoxyphenyl) benzoquinones were established using their reactions with concentrated hydrochloric acid and subsequent oxidation with iron (III) chloride (Chapter 2). The 2,3-diaryl-quinone (62) was found to undergo cyclisation giving the triphenylenequinone (69) as the main product. This



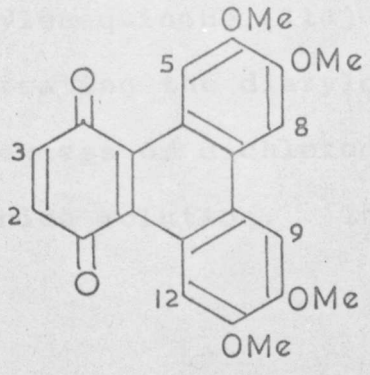
(62) (69)

suggested that triphenylene-1,4-quinones might be synthesised simply by treating suitably substituted 2,3-diarylbenzo-quinones with an acid, and oxidising the resulting quinol.

Because the reaction of the diarylquinone (62) with hydrochloric acid gave a complex mixture of chlorotriphenylene-quinones which could not be completely separated, the less complicated cyclisation reactions of 2,3-diarylquinones with aluminium chloride, and with aqueous sulphuric acid are described first.

Cyclisation of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone

The reaction of the diarylquinone (62) with aluminium chloride in carbon disulphide, and subsequent oxidation of the product by iron (III) chloride, gave a violet quinone, $C_{22}H_{18}O_6$, (42%), and a yellow product (7%). The molecular formula of the former corresponds to that of the starting diarylquinone (62) less two hydrogen atoms, and the u.v. absorption (Table 14) (p.116) shows the fine structure characteristic of a polycyclic compound. This suggested that the diarylquinone (62) had undergone cyclisation with the formation of 6,7,10,11-tetramethoxytriphenylene-1,4-quinone (114). The n.m.r. spectrum of this compound



(114)

confirmed its structure, showing singlets at τ 5.92 (six methoxy-protons), τ 5.89 (six methoxy-protons), τ 3.18 (two quinonoid protons), τ 2.42 (two aromatic protons), τ 1.01 (two aromatic protons). The low field signal at τ 1.01 may be assigned to the aromatic protons at C-5 and C-12 which are peri to the quinone carbonyl groups.[101]

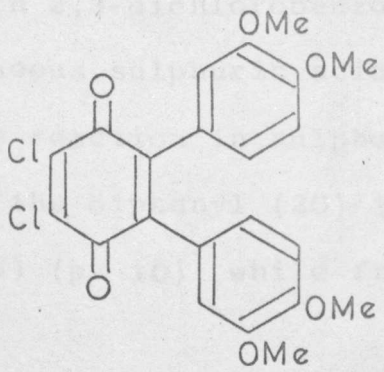
The yellow product which had m.p. > 350° contains two carbonyl groups ($\nu_{max.}$ 1688 and 1662 cm^{-1}). Mass spectra could only be obtained using an ion source at 290°, and consistent results could not be obtained. The most abundant peaks occurred at m/e 754, which corresponds to two of the triphenylene (114) molecules less two hydrogens, and at m/e 758, which corresponds to two of the diarylquinone (62) molecules less two hydrogens. Less abundant ions appeared at higher m/e values. This product appears to be a high molecular weight compound formed by the oxidation of the initial diarylquinone, but no definite structure can be assigned to it, and the lack of material has prevented further investigation.

The triphenylenequinone (114) was obtained in improved yield (50%) by treating the diarylquinone (62) with aluminium chloride and an excess of dichlorodicyanobenzoquinone (D.D.Q.) in carbon disulphide solution. The starting material was

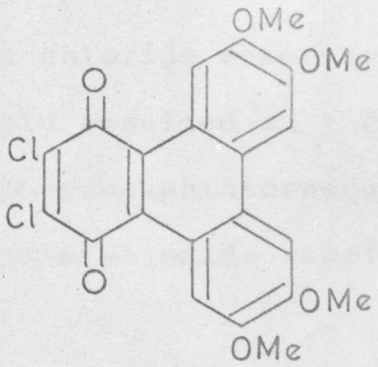
recovered unchanged from an attempted reaction between the diarylquinone (62) and D.D.Q. in benzene. Treatment of the diarylquinone (62) with aqueous sulphuric acid followed by oxidation of the product with iron (III) chloride gave a poor yield (5%) of the triphenylenequinone (114), together with more of the unidentified yellow product (15%); and the reaction between the diarylquinone (62), aqueous sulphuric acid and chloranil gave only a small amount of the yellow product.

Cyclisation of 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)-benzoquinone.

The diarylquinone (115) which was prepared by the arylation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone with diazotised 3,4-dimethoxyaniline, underwent cyclisation in the presence of aqueous sulphuric acid and chloroanil to give the triphenylenequinone (116) in very good yield (88%). Reductive acetylation of the resulting quinone furnished the

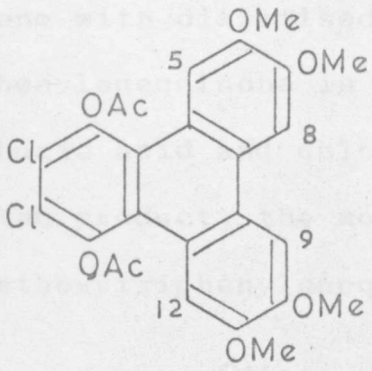


(115)

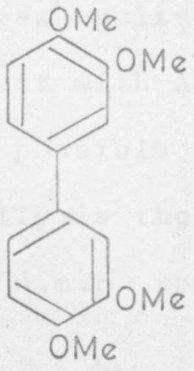


(116)

diacetoxytriphenylene (106) which shows n.m.r. signals at τ 7.53 (six acetoxy-protons), τ 5.96 (six methoxy-protons), τ 5.92 (six methoxy-protons), τ 2.30 (two aromatic protons) and τ 1.54 (two aromatic protons). The low field signal at τ 1.54 is attributed to the protons at C-5 and C-12, each of which is peri to an acetoxy-group.[101] The u.v. absorption



(106)



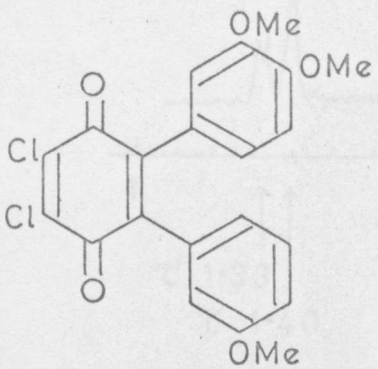
(20)

of the leucoacetate (106) again shows the fine structure expected for a polycyclic compound and resembles that of 2,3,6,7,10,11-hexamethoxytriphenylene. Attempts to prepare the triphenylenequinone (116) by treating the biphenyl (20) with 2,3-dichlorobenzoquinone in the presence of either aqueous sulphuric acid or aluminium chloride were unsuccessful. The reaction in sulphuric acid merely resulted in the oxidation of the biphenyl (20) to give the dibenzonaphthacenequinone[32] (22) (p. 10), while from the aluminium chloride reaction only

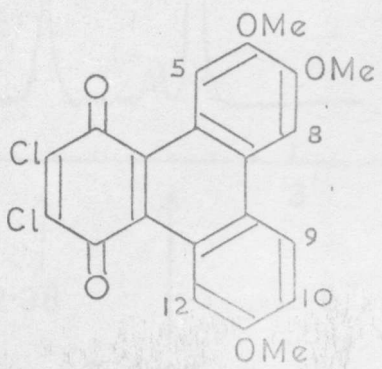
unchanged starting material was isolated.

Cyclisation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-3-(3'-methoxyphenyl)benzoquinone.

The diarylquinone (117), which was prepared by the arylation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone with diazotised 3-methoxyaniline, was cyclised to a triphenylenequinone in 67% yield by treatment with aqueous sulphuric acid and chloranil. Of the two possible structures for the product, the more favoured sterically is the 6,7,11-trimethoxytriphenylenequinone (118). The n.m.r. spectrum



(117)

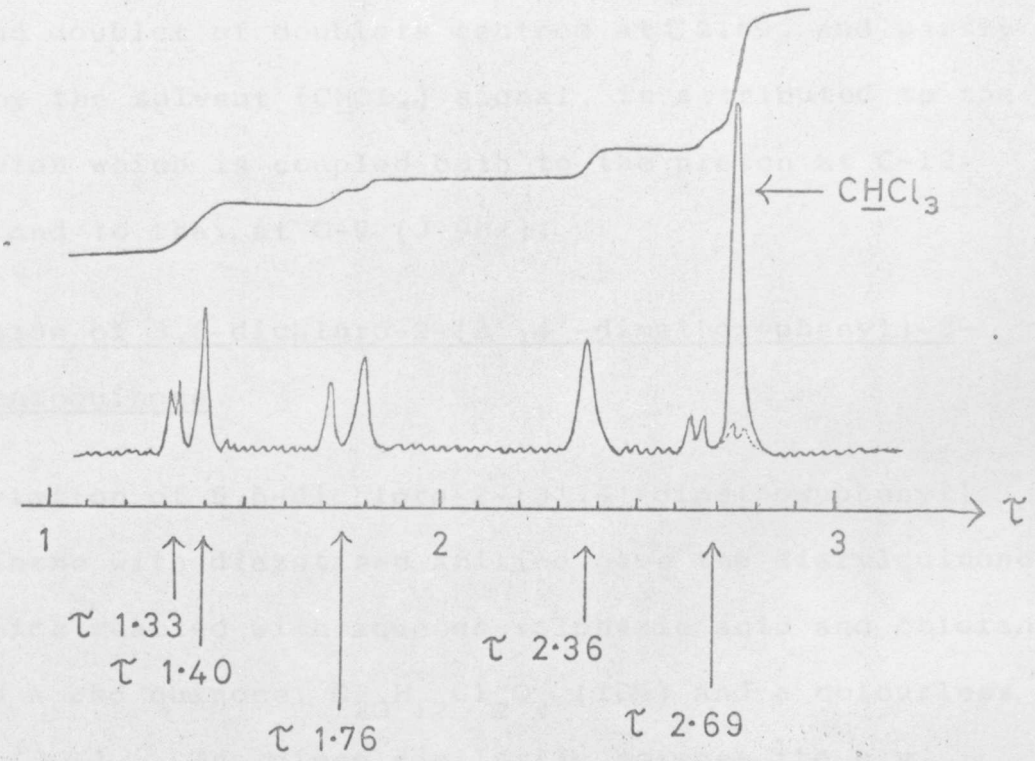


(118)

of the product is in full accord with this structure, showing signals at τ 6.02, τ 5.95, and τ 5.89, (three methoxy-protons in each case), and between τ 2.75 and τ 1.30 (five aromatic

protons). The aromatic proton signals are shown in Figure 5. The low field singlet at τ 1.40 is assigned to the

Figure 5 Aromatic proton signals of the triphenylenequinone (118)

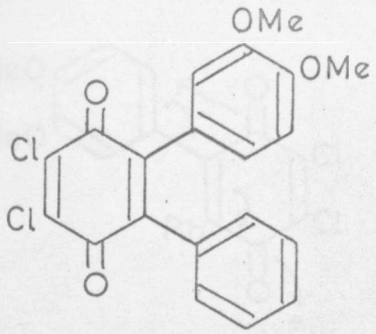


C-5 proton which is peri to one of the carbonyl groups, and the singlet at τ 2.36 is attributed to the C-8 proton. The doublet (J 3Hz) centred at τ 1.33 is assigned to the C-12

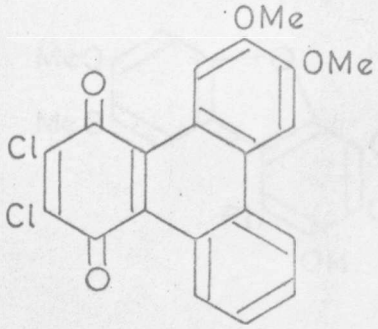
proton which is peri to the second carbonyl group, and which is coupled to the C-10 proton. Irradiation of the proton at τ 2.69 produced a singlet at τ 1.33, and irradiation of the proton at τ 1.33 affected the doublet at τ 2.69. The doublet (J 9Hz) centred at τ 1.76 is assigned to the C-9 proton which is coupled to the adjacent proton at C-10. The remaining doublet of doublets centred at τ 2.69, and partly masked by the solvent ($C\underline{H}Cl_3$) signal, is attributed to the C-10 proton which is coupled both to the proton at C-12 (J 3Hz) and to that at C-9 (J 9Hz).

Cyclisation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-3-phenylbenzoquinone.

Arylation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl) benzoquinone with diazotised aniline gave the diarylquinone (119) which reacted with aqueous sulphuric acid and chloranil to yield a red quinone, $C_{20}H_{12}Cl_2O_4$ (10%) and a colourless product (50%). The close similarity between the u.v. absorption of the red quinone and that of the triphenylene-quinone (118) (Table 14) (p.116) confirms that this compound is 2,3-dichloro-6,7- dimethoxytriphenylene-1,4-quinone (120).

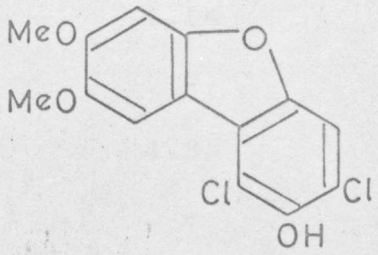


(119)



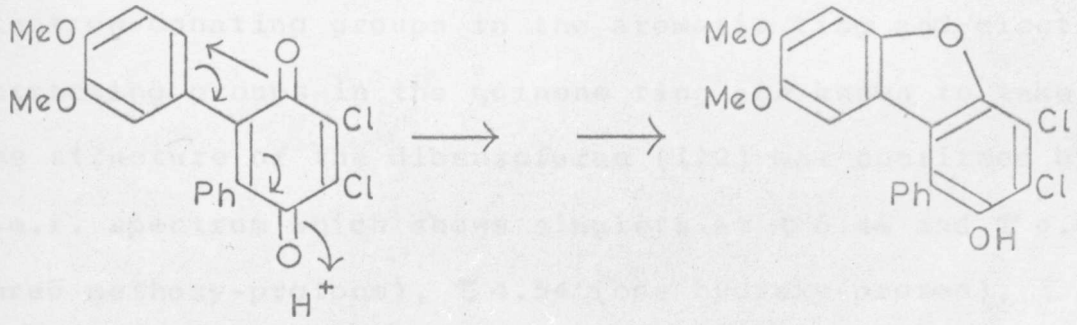
(120)

The colourless product, $C_{20}H_{14}Cl_2O_4$, is isomeric with the starting quinone (119). Its i.r. spectrum shows the presence of a phenolic OH group ($\nu_{max.}$ 3530 cm^{-1}), while its u.v. absorption resembles that of the dibenzofuran (121) (Table 13). This suggests that the compound is 1,2-dichloro-



(121)

3-hydroxy-6,7-dimethoxy-4-phenyldibenzofuran (122) formed by cyclisation of the diarylquinone thus:



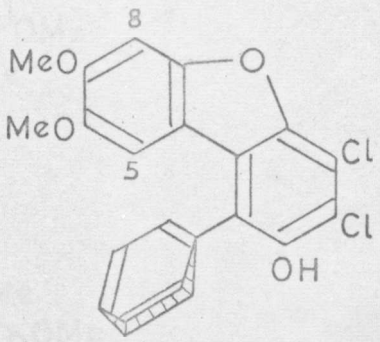
(119) (122)

Table 13 U.v. absorption of the dibenzofuran (121), and of the compound $C_{20}H_{14}Cl_2O_4$

Compound $C_{20}H_{14}Cl_2O_4$		Dibenzofuran (121)[107]	
$\lambda_{max.}$ (EtOH)(nm)	log ε	$\lambda_{max.}$ (EtOH)(nm)	log ε
221*	4.46	223	4.48
250	4.23	242*	4.28
262*	4.14	265	4.08
-	-	278	3.86
319	4.35	315	4.40
-	-	324*	4.32

*Inflection

Such acid-catalysed cyclisations of arylquinones containing electron-donating groups in the aromatic ring and electron-attracting groups in the quinone ring are known to take place.[33] The structure of the dibenzofuran (122) was confirmed by its n.m.r. spectrum which shows singlets at τ 6.44 and τ 6.08 (both three methoxy-protons), τ 4.54 (one hydroxy-proton), τ 3.64 and τ 2.90 (both one aromatic proton), and a broad signal between τ 2.66 and τ 2.46 (five phenyl protons). The aromatic proton signal at relatively high field (τ 3.64) is attributed to the C-5 proton. Because of steric effects the plane of the phenyl group is perpendicular to that of the dibenzofuran nucleus (122a). Thus the C-5 proton lies above the plane of



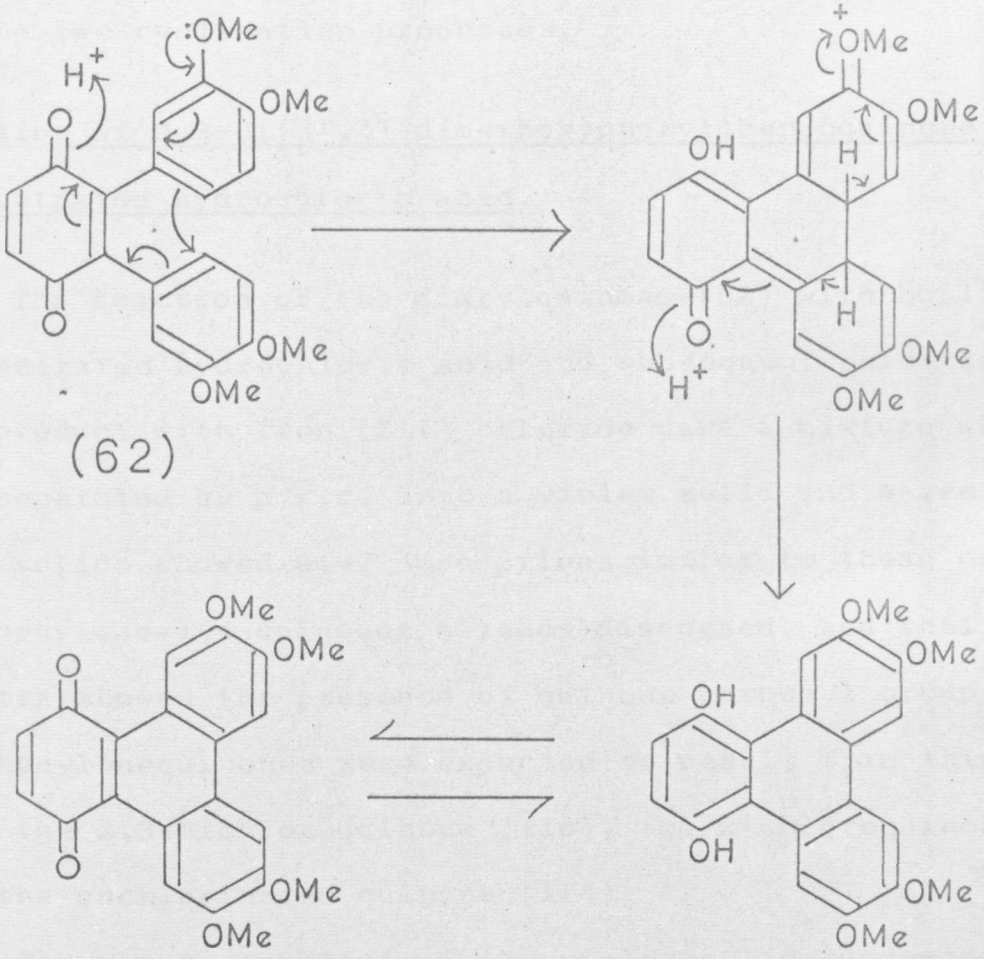
(122a)

the phenyl group, and, because of the ring current in the latter, is more shielded than is the C-8 proton.

Mechanism of the formation of the triphenylene-1,4-quinones

A possible mechanism for the formation of the above triphenylenequinones is given below. This requires that one of the aromatic rings in the 2,3-diarylquinone should

Formation of the triphenylene-1,4-quinone (114)

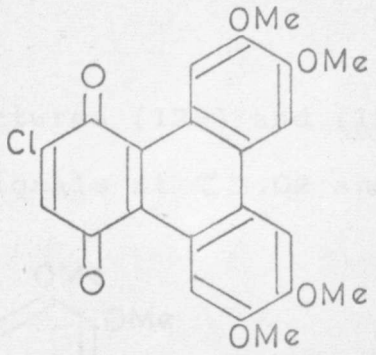


be activated towards electrophilic attack at C-6'. This particular position is strongly activated in all the diarylquinones which have been used in this work.[24] It is not immediately obvious why the diarylquinones (62), (115), and (117) give only triphenylenequinones, but the diarylquinone (119) gives a dibenzofuran as the major product. Further studies will be necessary to determine the relative rates of the two cyclisation processes.

Reaction of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone with concentrated hydrochloric acid.

The reaction of the diarylquinone (62) with boiling concentrated hydrochloric acid and subsequent oxidation of the product with iron (III) chloride gave a mixture which was separated by p.l.c. into a violet solid and a red solid. Both solids showed u.v. absorptionssimilar to those of the triphenylene-1,4-quinones already discussed, and their i.r. spectra showed the presence of quinone carbonyl groups. Three triphenylenequinones were expected to result from this reaction, viz. the 2,3-dichloroquinone (116), the 2-chloroquinone (69), and the unchlorinated quinone (114).

The n.m.r. spectrum of the violet solid suggested that this was the 2-chlorotriphenylenequinone (69), showing signals

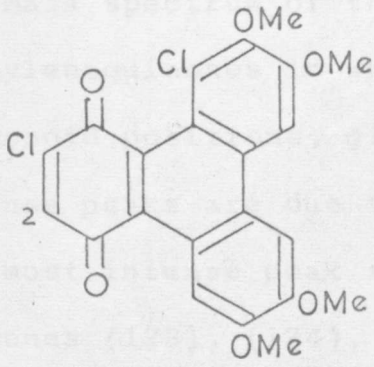


(69)

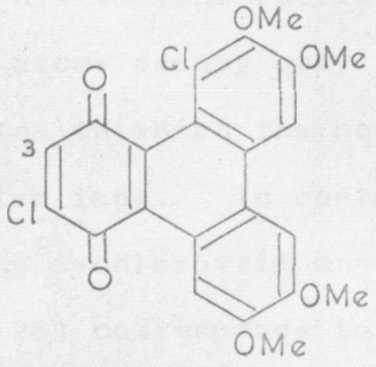
at τ 6.02 (three methoxy-protons), τ 6.00 (nine methoxy-protons), τ 3.22 (one quinonoid proton), τ 2.82 (two aromatic protons), τ 1.42 (one aromatic proton), and τ 1.36 (one aromatic proton). Small signals present in the spectrum indicated the presence of impurities, but these could not be removed by crystallisation or by p.l.c. The mass spectrum of this product confirmed that it was a mixture of the 2-chloroquinone (69) (86.5%), the 2,3-dichloroquinone (116) (3.5%) and the unchlorinated quinone (114) (10%).

The red product also appeared from its n.m.r. spectrum to be a tetramethoxytriphenylenequinone, but it showed only one aromatic proton signal at low-field (τ 0.98). As the low field signals in these triphenylene-1,4-quinones are given by the protons at C-5 and C-12, this indicated that one of these positions in the red product is occupied by an atom other than hydrogen. The mass spectrum indicated that the product contained two atoms of chlorine and was compatible

with the structures (123) and (124). The n.m.r. spectrum also showed signals at τ 3.02 and τ 2.83, each corresponding

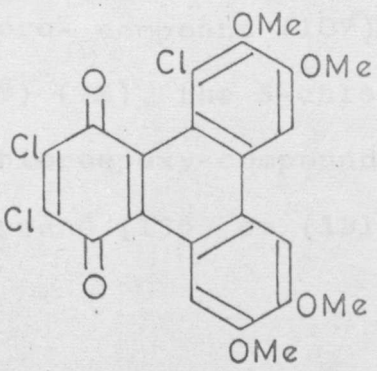


(123)

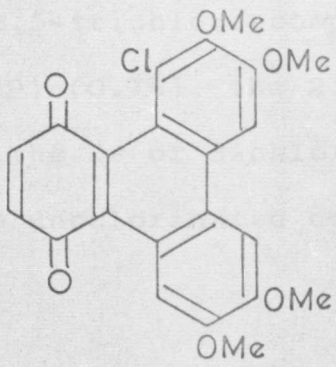


(124)

to about 0.5 proton, which may be assigned to the quinonoid protons at C-2 and C-3. An approximately (1:1) mixture of the compounds (123) and (124) therefore appeared to be present. The mass spectrum of the red product confirmed that the main components were the 2,5- and 3,5-dichlorotriphenylenequinones (93.5%), but also showed ions derived from the 2,3,5-trichloroquinone (125) (4.5%) and to the 5-chloroquinone (126) (2%). Further support for the presence



(125)



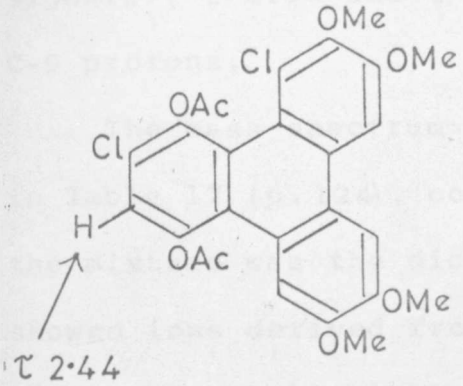
(126)

of a chlorine atom at C-5 in each of the compounds (123), (124), (125), and (126) was obtained from the analysis of the mass spectrum of the mixture. All the chlorotriphenylenequinones in which chlorine atoms occupy only quinonoid positions, give mass spectra in which the most intense peaks are due to the molecular ions. In contrast, the most intense peak for each of the 5-chlorotriphenylenequinones (123), (124), (125), and (126) corresponds to the $(M-Cl)^+$ ion. The ready loss of Cl· during fragmentation indicates that in each of these compounds one chlorine atom is located in a position in which it causes steric strain in the molecule.

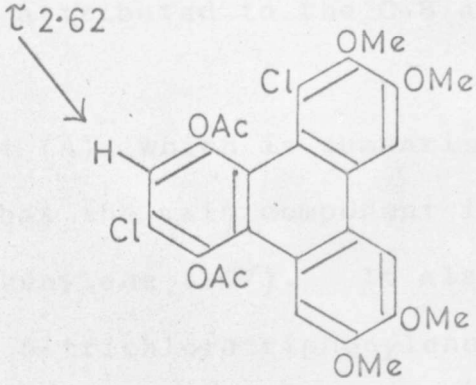
The above mixture of 5-chlorotriphenylenequinones could not be separated into its components and was therefore converted into the corresponding mixture of leucoacetates. A partial separation into two products (A) and (B) was achieved by p.l.c. On the basis of its n.m.r. and mass spectra (see below) product (A) appeared to be a mixture of the 3,5-dichloro- compound (107) (83%), the 2,3,5-trichloro-compound (128) (7%), the 5-chloro-compound (129) (0.7%), the 2,3-dichloroepoxy-compound (134) (1.0%), the 2- or 3-chloroepoxy-compound (136) or (131) (7%), and the unchlorinated epoxy-

compound (135) (1.0%). Likewise product (B) was a mixture of the 2,5-dichloro-compound (127) (90%), the 2,3,5-trichloro-compound (128) (0.3%), the 5-chloro-compound (129), (1.5%), the 2- or 3-chloroepoxy-compound (136) or (131) (7%), and the unchlorinated epoxy-compound (135) (0.5%).

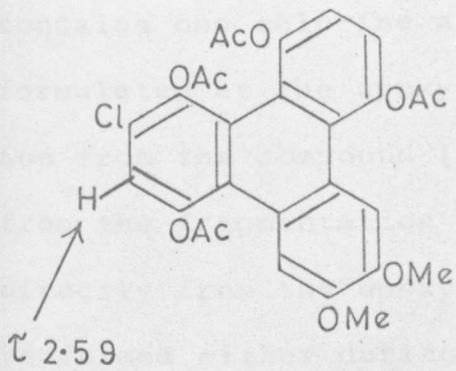
The n.m.r. spectrum of the mixture (A) showed signals from only the main component, the 3,5-dichlorotriphenylene (107). These occurred at τ 7.77 and τ 7.49 (each three acetoxy-protons), τ 6.06, τ 5.94, τ 5.92, and τ 5.90 (each three methoxy-protons), and τ 2.44, τ 2.40, τ 2.34, and τ 1.58 (each one aromatic proton). The spectrum of (B) was identical with that of (A) except that the aromatic proton signal at τ 2.44 was here found at τ 2.62. In these spectra the signal at τ 2.44 is attributed to the C-2 proton of the 3,5-dichloro-compound (107) by analogy with the signal at τ 2.59 given by the C-2 proton of the triphenylene (103) (p.111). Similarly the signal at τ 2.62 is attributed to the C-3 proton of the 2,5-dichloro-compound (127) by analogy with the signal at τ 2.73 given by the C-3 proton of the triphenylene (102) (p.111). In each compound (107) and (127), the low-field signal (τ 1.58) is assigned to the C-12 proton which is peri to an acetoxy-group, and the remaining aromatic



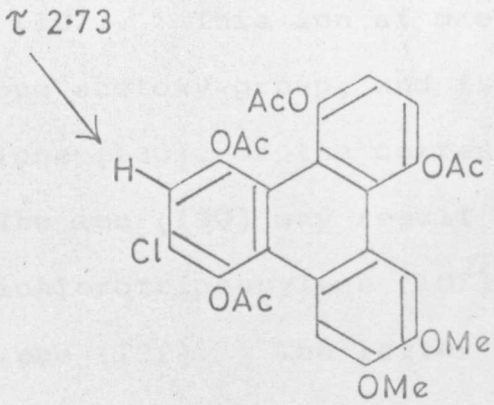
(107)



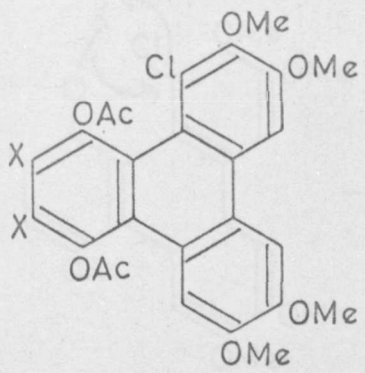
(127)



(103)

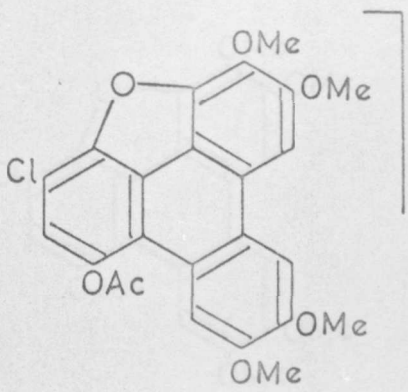


(102)



(128 ; X = Cl)

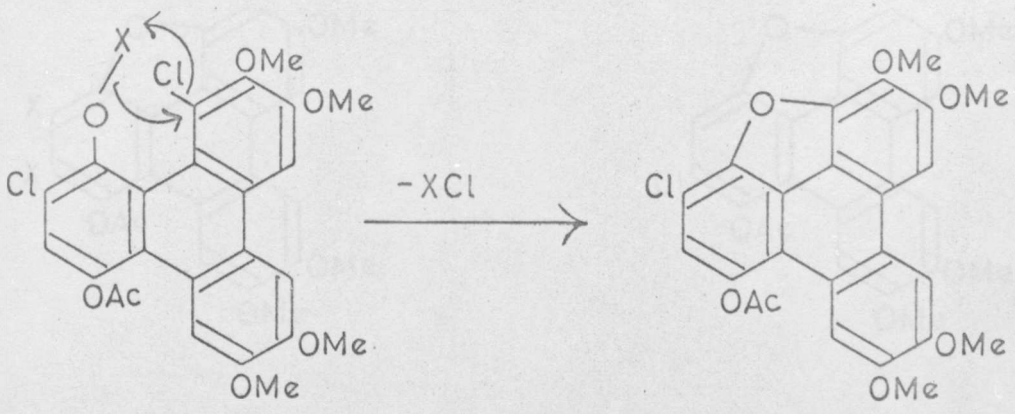
(129 ; X = H)



(130)

signals (τ 2.34 and τ 2.40) are attributed to the C-8 and C-9 protons.

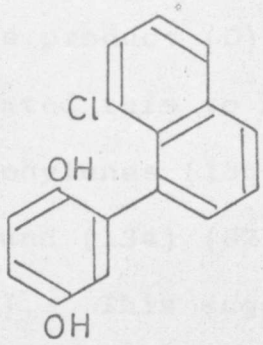
The mass spectrum of product (A), which is summarised in Table 17 (p.124), confirmed that the main component in the mixture was the dichlorotriphenylene (107). It also showed ions derived from the 2,3,5-trichlorotriphenylene (128) and the 5-chlorotriphenylene (129). An abundant ion (m/e 454) corresponds to the loss of CH_2CO and HCl from the molecular ion of the dichlorotriphenylene (107). This ion at m/e 454 contains one chlorine atom and one acetoxy-group, and is formulated as the epoxytriphenylene (130), or the corresponding ion from the compound (136). The ion (130) may result either from the fragmentation of the dichlorotriphenylene (107) or, directly from the epoxytriphenylene (131). The latter could be formed either during the reductive acetylation, or during the chromatographic purification on silica gel:



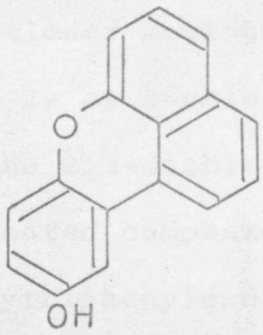
X = H or Ac

(131)

Such elimination reactions are known to take place under basic conditions eg. the chloroquinol (132) gives the pyran derivative (133) on being treated with aqueous sodium dithionite and potassium hydroxide.[108] The mass spectrum of the mixture (A) also showed the presence of ions derived

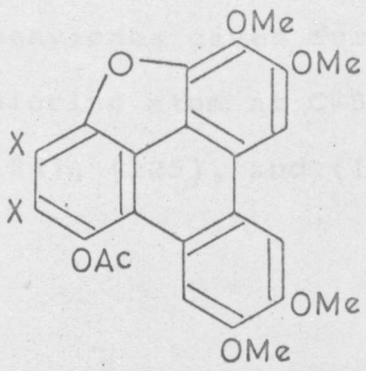


(132)

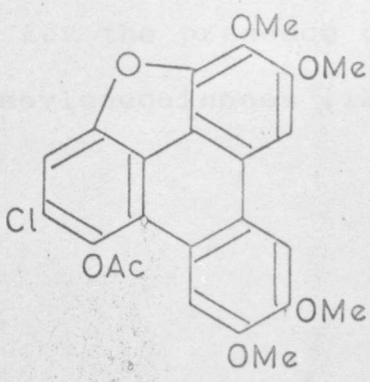


(133)

from the dichloroepoxytriphenylene (134) and the unchlorinated compound (135).



(134; X = Cl)
(135; X = H)



(136)

When the mixture (A) was subjected to further p.l.c. on silica gel, two bands were obtained. The faster moving band gave a product (C), the mass spectrum of which showed it to be a mixture similar to (A), containing rather more of the epoxytriphenylenes (Table 17). The mass spectrum of the product (D) isolated from the slower moving band indicated this to be a mixture of the 2- or 3-chloroepoxy-triphenylenes (136) or (131) (86%), the 2,3-dichloro-compound (134) (8%), and the unchlorinated compound (135) (5.5%). This suggests that the epoxytriphenylenes are formed at least in part during the chromatographic treatment. The composition of the product (B), which is summarised on p.110 , has been determined from its mass spectrum (Table 17) by arguements similar to those used for product (A). The lack of material prevented the further investigation of these compounds. However, the ready formation of the epoxytri-phenylenes gives further evidence for the presence of a chlorine atom at C-5 in the triphenylenequinones (123), (124), (125), and (126).

Reaction of 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)-benzoquinone (115) with concentrated hydrochloric acid.

The reaction of the diarylquinone (115) with concentrated hydrochloric acid and subsequent oxidation of the product with iron (III) chloride gave the 2,3-dichlorotriphenylenequinone (116) (32%) and a small amount (ca. 2%) of the 2,3,5-trichlorotriphenylenequinone (125). The latter was identified (a) by its u.v. absorption (Table 14) which is very similar to that of the 2,3-dichlorotriphenylenequinone (116), and (b) by its mass spectrum (Table 16) which shows the expected molecular ion at m/e 480 with the characteristic isotope pattern of a trichloro-compound, and a base peak at m/e 445 corresponding to the $(M-Cl)^+$ ion.

Attempts to prepare the 5-chlorotriphenylenes by the reaction of boiling concentrated hydrochloric acid on either the 2,3-dichlorotriphenylenequinone (116) or the corresponding unchlorinated compound (114), or by the reaction of hydrogen chloride on the dichloro-compound (116) in benzene solution were unsuccessful. In each case most of the starting quinone was recovered unchanged.

Table 14 U.v. absorption of the triphenylene-1,4-quinones

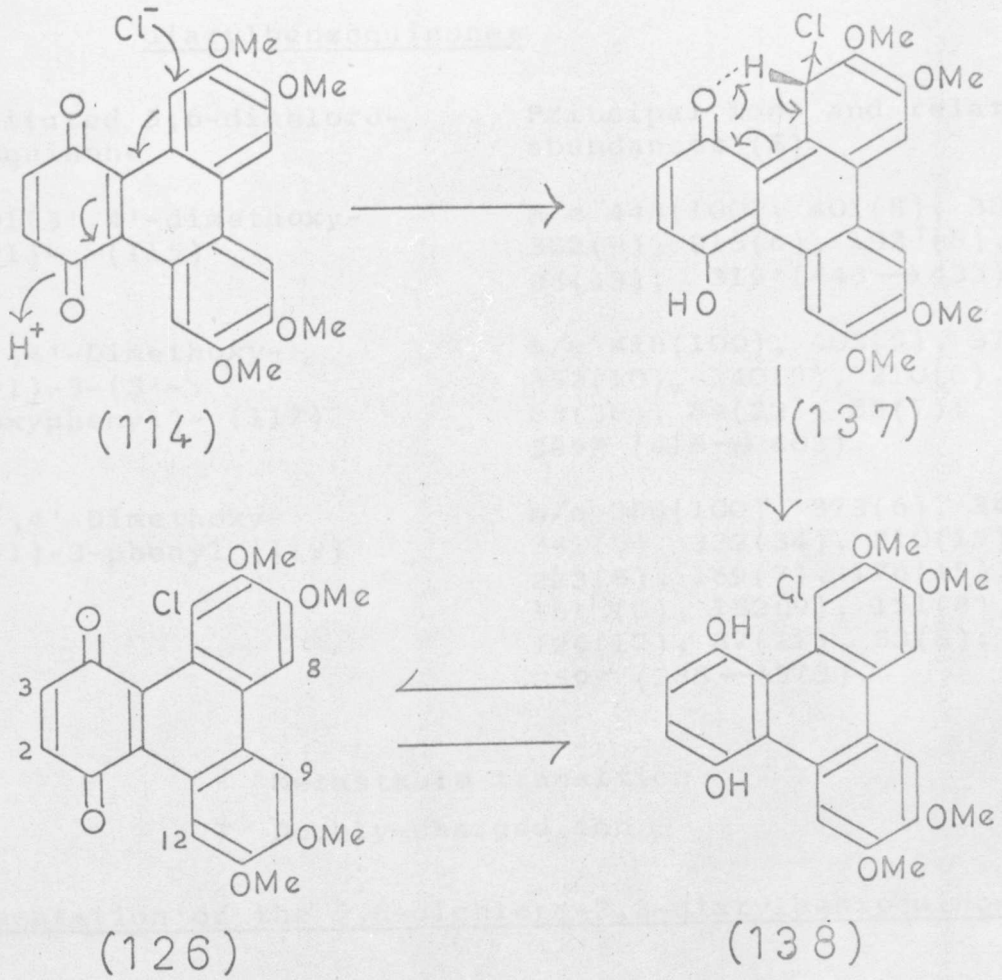
Substituted triphenylene-1,4-quinone	$\lambda_{max.}$ (nm) in $CHCl_3$ and (log ε)								
6,7,10,11-Tetramethoxy- (114)	-	-	271 (4.77)	298* (4.23)	304* (4.15)	312* (3.92)	326 (3.62)	346 (3.40)	498 (3.76)
† 2-Chloro-6,7,10,11-tetramethoxy- (69)	-	-	274 (4.85)	300* (4.40)	-	316* (3.95)	328* (3.72)	351 (3.57)	517 (3.80)
2,3-Dichloro-6,7,10,11-tetramethoxy- (116)	-	-	276 (4.84)	300* (4.39)	-	317* (4.06)	329* (3.84)	350 (3.61)	532 (3.80)
2,3,5-Trichloro-6,7,10,11-tetramethoxy- (125)	-	-	278 (4.54)	-	305* (4.13)	320* (3.93)	335* (3.81)	354* (3.51)	490 (3.54)
2,3-Dichloro-6,7,11-trimethoxy- (118)	-	268* (4.75)	273 (4.81)	292* (4.38)	305* (4.24)	322* (3.90)	-	354* (3.44)	536 (3.61)
2,3-Dichloro-6,7-dimethoxy- (120)	250* (4.46)	264* (4.72)	268 (4.75)	291* (4.29)	309* (4.06)	320* (3.92)	-	354* (3.32)	514 (3.62)

* Inflection † Compound described in Chapter 5

Mechanism of the formation of the 5-chlorotriphenylene-1,4-quinones

The substitution of one of the aromatic hydrogen atoms by chlorine as a result of the treatment of the 2,3-diaryl-quinones with hydrochloric acid was unexpected. It is unlikely that an electrophilic chlorination reaction takes place, because, under the conditions used, free chlorine or the chlorine cation cannot be formed. Furthermore, electrophilic substitution would be expected to occur at C-8 or C-9 as well as at C-5, but there was no evidence of such chlorotriphenylenequinones in the reaction mixtures. This suggests that the 5-chloro-compounds are formed by 1,6-addition of the elements of hydrogen chloride to the triphenylenequinone as illustrated below for the formation of the 5-chlorotriphenylene-quinone (126). The driving force for this process may be the stabilisation of the intermediate (137) by weak hydrogen bonding, and the ease with which a proton may be transferred to the adjacent carbonyl group during aromatisation (137) $\longrightarrow$ (138). The fact that there was no reaction between hydrochloric acid and the pure triphenylenequinones (114) or (116) may have been due to the lack of solubility of the pure quinone in the acid.

Formation of the 5-chlorothriphenylene-1,4-quinone (126)



Mass spectra of the 5,6-dichloro-2,3-diarylbenzoquinones

The ions (excluding those resulting from ^{37}Cl) with relative abundances > 5% are recorded in Table 15. All the spectra resemble that of the unchlorinated 2,3-diarylbenzoquinone (62) which is discussed in Chapter 2. The fragmentation of a typical dichlorodiarylbenzoquinone (119) is summarised below.

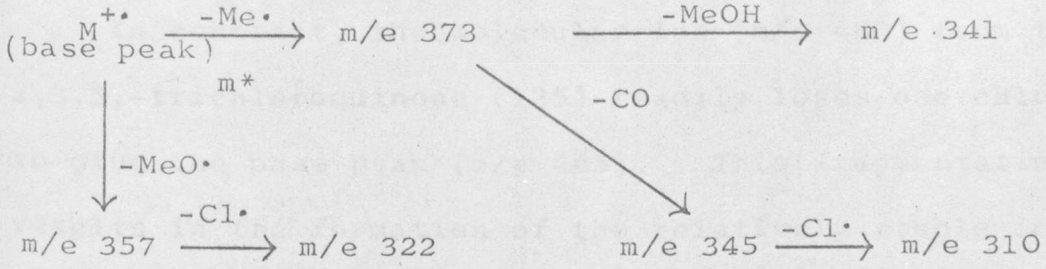
Table 15 Mass spectra of the 5,6-dichloro-2,3-diarylbenzoquinones

Substituted 5,6-dichloro-benzoquinone	Principal ions and relative abundances (%)
2,3-Di(3',4'-dimethoxy-phenyl)- (115)	m/e 448(100), 401(8), 386(8), 382(9), 315(6), 193†(5), 83(20), 84(13); 319*(448 → 433).
2-(3',4'-Dimethoxy-phenyl)-3-(3'-methoxyphenyl)- (117)	m/e 418(100), 403(5), 371(11), 352(10), 340(9), 210(6), 176†(5), 83(36), 84(22), 85(7); 389* (418 → 403).
2-(3',4'-Dimethoxy-phenyl)-3-phenyl (119)	m/e 388(100), 373(6), 345(6), 341(5), 322(34), 310(15), 239(7), 223(8), 169(7), 176(15), 165(13), 161†(8), 152(19), 151(8), 150(7), 126(17), 87(11), 83(8); 359* (388 → 373).

* Metastable transition

† Doubly-charged ion

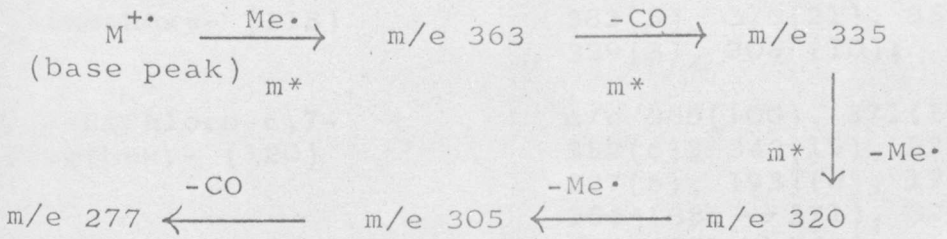
Fragmentation of the 5,6-dichloro-2,3-diarylbenzoquinone (119)



Mass spectra of the triphenylene-1,4-quinones

Table 16 records the principal ions obtained from the triphenylene-1,4-quinones. With the exception of the 5-chloro-substituted quinone (125), the molecular ion in each case is the base peak, and there is a significant peak due to the doubly-charged molecular ion. The only other important ion corresponds to the successive loss of Me• and CO; the fragmentation sequence is illustrated below for the tetramethoxyquinone (114).

Fragmentation of the tetramethoxytriphenylenequinone (114)



In contrast, the molecular ion (m/e 480) from the 2,3,5,-trichloroquinone (125) readily loses one chlorine atom to give the base peak (m/e 445). This fragmentation probably results in the formation of the relatively stable ion (139). The presence of an abundant $(M-Cl)^+$ ion supports the view that one of the chlorine atoms occupies a position peri to one of the quinone carbonyl groups.

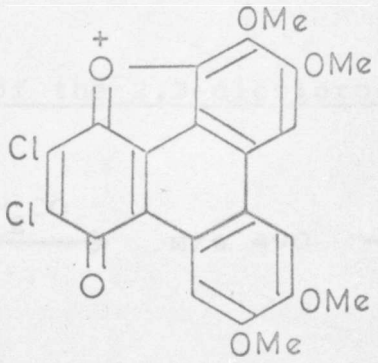
Table 16 Mass spectra of the triphenylene-1,4-quinones

Substituted triphenylene-1,4-quinone	Principal ions and relative abundances (%)
6,7,10,11-Tetramethoxy- (114)	m/e 378(100), 363(2.5), 347(2.5), 335(24), 320(2.5), 305(2.5), 277(2.5) 249(2), 189†(10); 349*(378 → 363); 309*(363 → 335), 306*(335 → 320).
2,3-Dichloro-6,7,10,11-tetramethoxy- (116)	m/e 446(100), 431(2), 415(3), 403(27) 388(3), 373(3), 359(3), 345(4), 329(3), 317(3), 223† (7); 417* (446 → 431), 376*(431 → 403), 374*(403 → 388).
‡2-Chloro-6,7,10,11-tetramethoxy- (69)	m/e 412(100), 397(1.5), 381(2), 378(2), 369(21), 354(2), 339(2), 325(2), 311(2.5), 295(2), 283(1.5), 206† (8); 383* (412 → 397), 342*(397 → 369), 339*(369 → 354).
2,3-Dichloro-6,7,11-trimethoxy- (118)	m/e 416(100), 401(2), 385(3), 382(5), 373(21), 358(3), 330(3), 329(3), 208†(10); 386* (416 → 401).
2,3-Dichloro-6,7-dimethoxy- (120)	m/e 386(100), 371(1.5), 355(7), 352(6), 343(15), 328(5), 272(6), 237(6), 193†(8), 174(15), 150(7); 356*(386 → 371), 326*(386 → 355), 317*(371 → 343), 314*(343 → 328).
2,3,5-Trichloro-6,7,10,11-tetramethoxy- (125)	m/e 480(10), 445(100), 415(4), 411(6), 401(7), 222.5†(6); 414*(480 → 445).

* Metastable transition

† Doubly-charged ion

‡ Compound described in Chapter 5

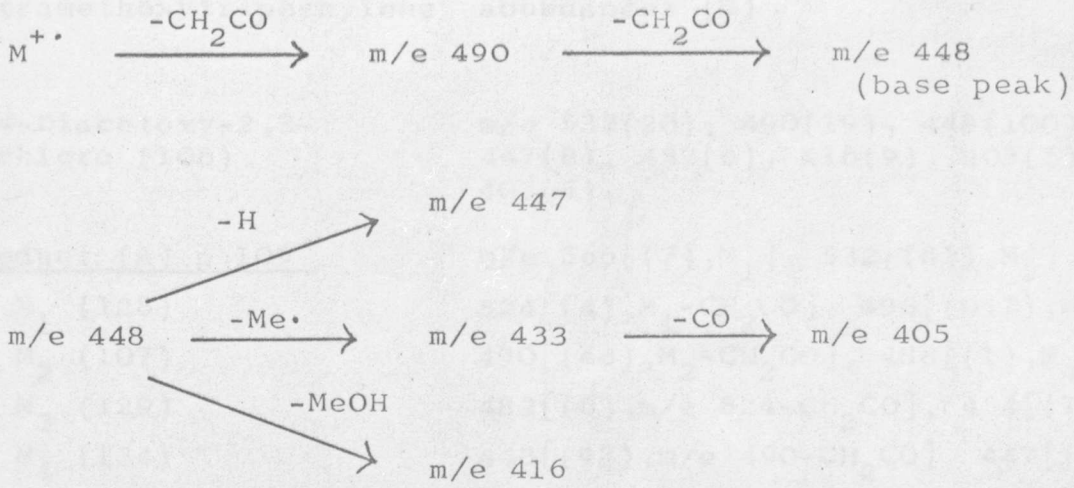


(139)

Mass spectra of the acetoxytriphenylenes

The principal ions obtained from these are recorded in Table 17. The base peak (m/e 448) in the spectrum of the 1,4-diacetoxy-2,3-dichlorotriphenylene (106) corresponds to the molecular ion (m/e 532) less two molecules of ketene. In contrast, the base peak from each of the triphenylenes containing a 5-chloro substituent corresponds to the molecular ion (Table 17; M_1, M_2, and M_3) less two molecules of ketene and one atom of chlorine. Further fragmentation of all the 1,4-diacetoxytriphenylenes occurs in a similar manner. The salient features of the fragmentation of the 2,3- and 3,5-dichlorodiacetoxytriphenylenes are illustrated on p. 123. The base peak of the 1-acetoxy-epoxytriphenylenes results from the molecular ion (Table 17; M_4, M_5, and M_6) by the loss of one ketene molecule. Thereafter there is the successive loss of Me·, CO, and MeO·.

Fragmentation of the 2,3-dichloro-1,4-diacetoxytriphenylene (106)



Fragmentation of the 3,5-dichloro-1,4-diacetoxytriphenylene (107)

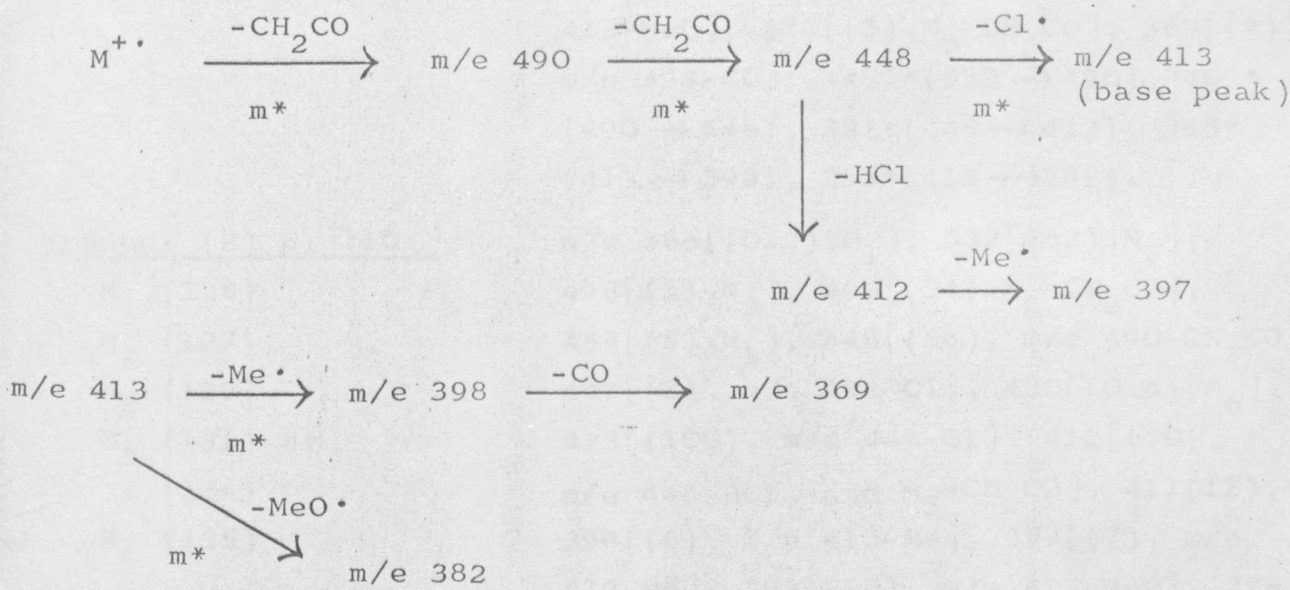


Table 17 Mass spectra of the acetoxytriphenylenes

Substituted 6,7,10,11-tetramethoxytriphenylene	Principal ions and relative abundances (%)
1,4-Diacetoxy-2,3-dichloro (106)	m/e 532(20), 490(19), 448(100), 447(8), 433(6), 416(9), 405(5), 403(5).
Product (A) p.109 M_1 (128) M_2 (107) M_3 (129) M_4 (134) M_5 (131) or (136) M_6 (135)	m/e 566[(7),M_1], 532[(81),M_2], 524[(4),M_1-CH_2CO], 498[(0.7),M_3], 490[(46),M_2-CH_2CO], 488[(1),M_4], 482[(8),m/e 524-CH_2CO], 454[(7),M_5], 448[(93),m/e 490-CH_2CO], 447[(22), m/e 482-Cl], 420[(1),M_6], 413[(100), m/e 448-Cl], 412[(61), m/e 448-HCl, and M_5-CH_2CO], 398[(7), m/e 413-Me], 397[(8), m/e 412-Me], 382[(21), m/e 413-MeO], 378[(5),M_6-CH_2CO], 369[(9), m/e 398-CO]; 451*(532 → 490), 409*(490 → 448), 381*(448 → 413), 383*(413 → 398), 353*(413 → 382).
Product (B) p. 110 M_1 (128) M_2 (127) M_3 (129) M_5 (131) or (136) M_6 (135)	m/e 566[(0.2),M_1], 532[(62),M_2], 498[(1),M_3], 490[(54),M_2-CH_2CO], 454[(5),M_5], 448[(56), m/e 490-CH_2CO] 447[(8), m/e 482-Cl], 420[(0.4),M_6], 413[(100), m/e 448-Cl], 412[(50), m/e 448-HCl, and M_5-CH_2CO], 411(11), 398[(6), m/e 413-Me], 397[(7), m/e 412-Me], 382[(15), m/e 413-MeO], 378 [(2.5), M_6-CH_2CO]; 451*(532 → 490), 409*(490 → 448), 381*(448 → 413), 353*(413 → 382).

Table 17 continued

Substituted 6,7,10,11-tetramethoxytriphenylene	Principal ions and relative abundances (%)
Product (C) p. 114	m/e 566[(0.2),M_1], 532[(16),M_2], 498[(2),M_3], 490(18), 488[(0.6),M_4], 482(0.5), 454[(21),M_5], 448(36), 447(6), 420[(7),M_6], 413(75), 412(100) 398(16), 397(21), 382(14), 379(11), 378(32), 369(8); 451*(532 → 490), 409*(490 → 448), 383*(412 → 397), 381*(448 → 413), 374*(454 → 412), 353*(413 → 382).
M_1 (128)	
M_2 (107)	
M_3 (129)	
M_4 (134)	
M_5 (131) or (136)	
M_6 (135)	
Product (D) p. 114	m/e 488[(3),M_4], 454[(32),M_5], 446[(11),M_4-CH_2CO], 431[(4), m/e 446-Me], 420[(2),M_6], 412[(100), M_5-CH_2CO], 411[(14), m/e 446-Cl], 397 [(45), m/e 412-Me], 378[(9), M_6-CH_2CO], 369[(6), m/e 397-CO], 338[(12), m/e 369-MeO], 334[(12), m/e 369-Cl]; 383*(412 → 397).
M_4 (134)	
M_5 (131) or (136)	
M_6 (135)	

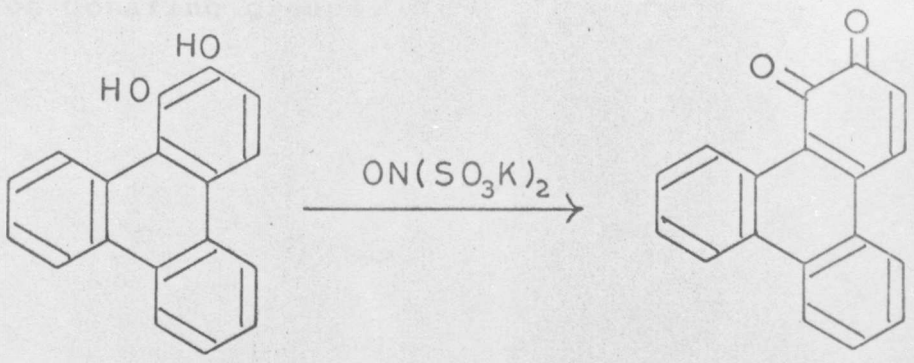
* Metastable transition

Mass spectrum of the dibenzofuran

The principal ions obtained from the dibenzofuran (122) are: m/e 388(100), 373(8), 345(5), 341(8), 329(9), 310(23), 274(7), 210(5), 194†(5); 358*(388 $\longrightarrow$ 373), 311*(388 $\longrightarrow$ 341). (*denotes metastable transition and $\dagger$, doubly-charged ion). The molecular ion (m/e 388) is very stable and there is a significant peak (m/e 194) corresponding to the doubly charged molecular ion. The only other salient ion (m/e 310) is that corresponding to the molecular ion less C_6H_6.

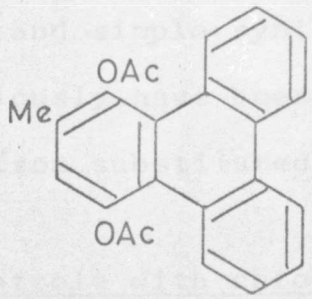
Conclusion

Only one triphenylenequinone (141), has been reported previously,[109] this was prepared by the oxidation of 1,2-dihydroxytriphenylene (140) using potassium nitrosodisulphonate:



(140) (141)

A compound thought to be a triphenylene-1,4-quinone was obtained during the attempted purification of the 1,4-diacetoxytriphenylene (142) by chromatography on alumina.[48] The product showed strong carbonyl absorption at 1655 cm^{-1}



(142)

but was not further investigated. The work described in the last two Chapters shows that triphenylene mono- and di-quinones may be obtained simply from mono- and di-arylquinones provided that the aromatic nuclei are suitably activated by electron donating groups.

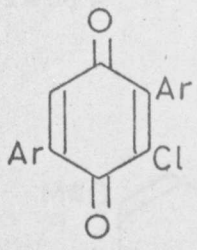
CHAPTER 5

Synthesis of 2-hydroxytriphenylenes

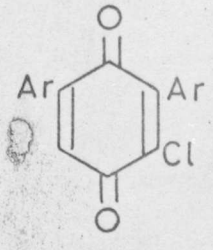
Among the products obtained when veratrole reacts with some chlorobenzoquinones in the presence of aqueous sulphuric acid are 2-hydroxytriphenylene derivatives. This furnishes a new and simple synthesis for 2-hydroxytriphenylenes which previously have been obtained by the Rapson synthesis[45] or from substituted cyclopentadieneones.[56]

Reaction of veratrole with chlorobenzoquinone in aqueous sulphuric acid

Veratrole reacted with chlorobenzoquinone in the presence of aqueous sulphuric acid to give a dark blue solid from which was isolated the 3-, 5-, and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones (52), (53), and (54), a mixture of the 2,5- and 2,6-diarylchlorobenzoquinones (65) and (68), a blue product, and a colourless compound



(65)

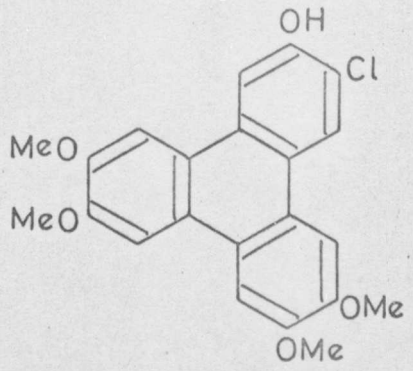


(68)

Ar = $3,4(MeO)_2C_6H_3$-

(3% from veratrole). The small quantity of the blue product prevented its further purification, but a qualitative u.v. spectrum showed $\lambda_{max.}(CHCl_3)$ at 277, 316, and 560 nm, suggesting that it may be related to the blue dibenzonaphthacenequinone (19) (p. 10). The latter [$\lambda_{max.}$ $(CHCl_3)$ 281, 294, 317, 560, 655, and 715 nm] results from the oxidation of veratrole by high potential quinones in the presence of aqueous sulphuric acid.[31]

The colourless compound $C_{22}H_{19}Cl\ O_5$, has the properties of a phenol ($\nu_{max.}$ 3430 cm^{-1}). Its u.v. absorption (Table 18) has the fine structure typical of a polycyclic compound, and closely resembles that of 2,3,6,7,10,11-hexamethoxytriphenylene. The n.m.r. spectrum shows singlets corresponding to twelve methoxy-protons at τ 5.91, one aromatic proton each at τ 2.37, τ 2.23, τ 2.01, and τ 1.66, two aromatic protons at τ 2.27, and one hydroxy-proton at τ 0.28. The phenol is accordingly formulated as the triphenylene (143).

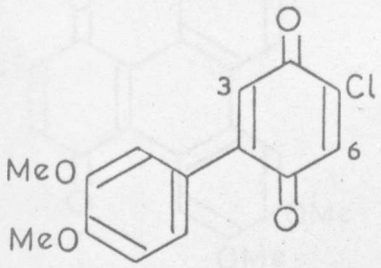


(143)

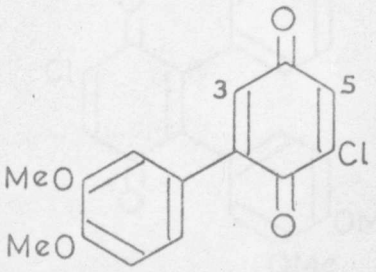
Table 18 U.v. absorptions of the phenol $C_{22}H_{19}ClO_5$ and of 2,3,6,7,10,11-hexamethoxytriphenylene

Phenol $C_{22}H_{19}ClO_5$		2,3,6,7,10,11-hexamethoxy-triphenylene[31]	
$\lambda_{max.}(CHCl_3)$(nm)	logε	$\lambda_{max.}(CHCl_3)$(nm)	logε
262*	4.56	263*	4.66
269	4.74	272*	4.79
278	4.88	281	4.89
308	4.25	309	4.38
315*	4.21	-	-
321*	4.13	320*	4.22
331*	3.79	330*	3.97
347	3.34	346	3.49
364	3.01	361	2.43

* Inflection.



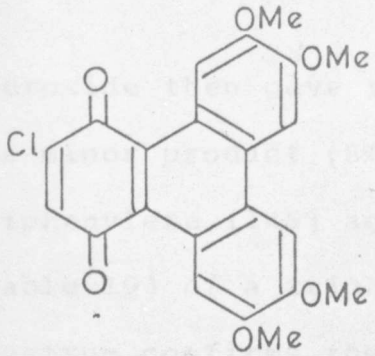
(53)



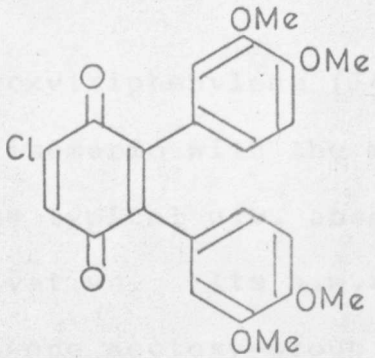
(54)

Reaction of veratrole with a mixture of 5- and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones in aqueous sulphuric acid.

To confirm the structure of the triphenylene (143), an alternative synthesis from veratrole and the 5-chloro-2-arylquinone (53) was desirable. However, because of the difficulty of separating the 5-chloro-2-arylquinone (53) from the corresponding 6-chloro-2-aryl-compound (54) (Chapter 2), the reaction had to be performed with a (1:1) mixture of the compounds. The resulting crude product on being oxidised with iron (III) chloride gave a mixture of the 2,5- and 2,6-diaryl-3-chlorobenzoquinones (65) and (68), the 2-chlorotriphenylene-1,4-quinone (69) formed by the cyclisation of the 2,3-diarylquinone (144), crude 3-chloro-2-hydroxy-6,7,10,11-tetramethoxytriphenylene (143) (23% from

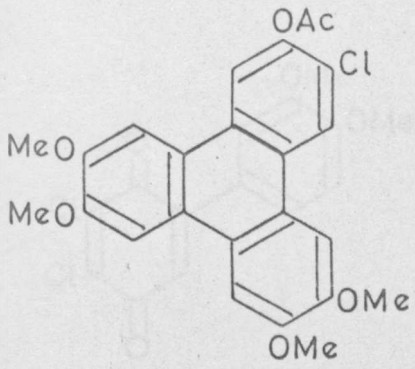


(69)

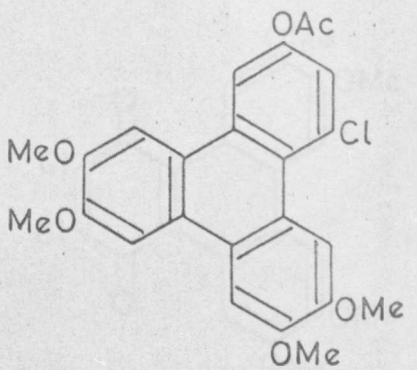


(144)

the arylquinones), and a trace of a blue solid. The u.v. spectrum of the blue solid showed this to be identical with the blue product obtained from the reaction between veratrole and chlorobenzoquinone described earlier. Acetylation of the crude hydroxytriphenylene (143) and subsequent chromatography gave two products. The more abundant of these, the 2-acetoxytriphenylene (145) (65%), was identified by its u.v. absorption (Table 19) which is very similar to that of 2,3,6,7,10,11-hexamethoxytriphenylene. Its n.m.r. spectrum, which shows that there is no measurable coupling between the various aromatic protons, is in full agreement with the structure (145). Hydrolysis of this compound with aqueous ethanolic potassium



(145)

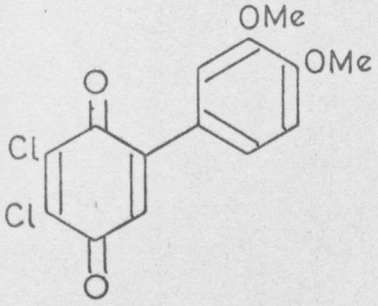


(146)

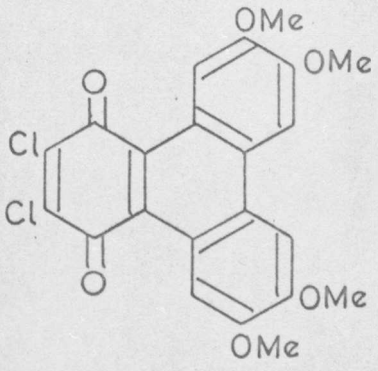
hydroxide then gave the pure hydroxytriphenylene (143). The minor product (8%) which was isomeric with the acetoxytriphenylene (145) again shows the typical u.v. absorption (Table 19) of a triphenylene derivative. Its n.m.r. spectrum confirms the presence of one acetoxy-group and four methoxy-groups, but the signals from the aromatic protons were too weak to permit accurate integration. The available evidence suggests that this product is the 2-acetoxy-4-chlorotriphenylene (146) formed from the corresponding hydroxycompound, which in turn results from the reaction between veratrole and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (54).

Reaction of veratrole with 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone in aqueous sulphuric acid.

To provide a simple and alternative synthesis for the triphenylenequinone (116) (Chapter 4) the dichloroarylquinone (57) was treated with veratrole in the presence of aqueous sulphuric acid. This reaction gave the expected

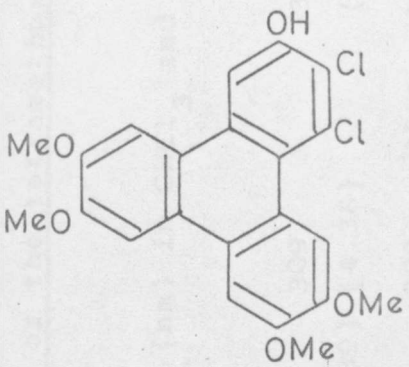


(57)

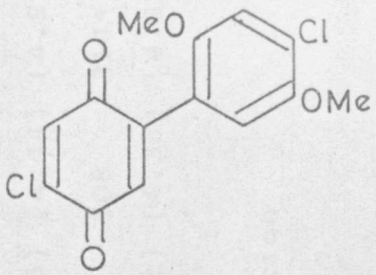


(116)

triphenylenequinone (116) (14%) together with 2,3,6,7,10,11-hexamethoxytriphenylene (12%) formed by the oxidation of the veratrole,[31] and a hydroxytriphenylene derivative (18%). The u.v. absorption (Table 19) and the n.m.r. spectrum of the last compound are in full agreement with the structure (147). In contrast, a reaction between veratrole and



(147)



(148)

3',4'-dimethoxyphenylbenzoquinone (50) in aqueous sulphuric acid gave no crystalline material, while veratrole and the arylquinone (148) failed to react under similar conditions.

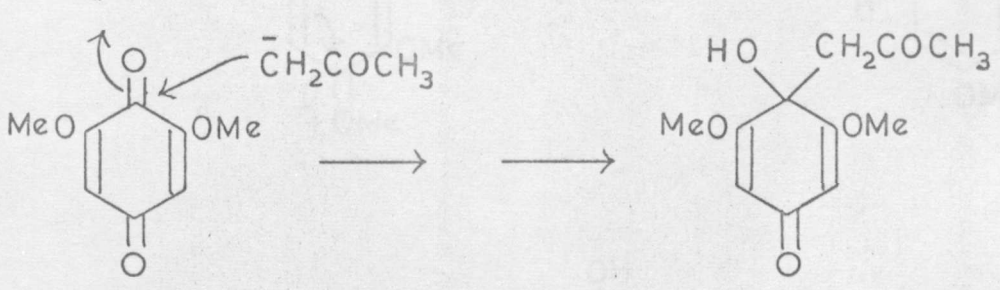
Table 19 U.v. absorptions of the tetramethoxytriphenylenes

Substituted 6,7,10,11-tetramethoxy-triphenylene	$\lambda_{max.}$ (nm) in $CHCl_3$ and (log ε)								
2,3-Dimethoxy-[31] (18)	263* (4.66)	272* (4.79)	281 (4.89)	309 (4.38)	-	320* (4.22)	330* (3.97)	346 (3.49)	361 (2.43)
2-Hydroxy-3-chloro (143)	262* (4.66)	269 (4.84)	278 (4.96)	308 (4.36)	315* (4.32)	321* (4.24)	331* (3.91)	346 (3.50)	365 (3.07)
2-Acetoxy-3-chloro (145)	260* (4.56)	269 (4.75)	278 (4.91)	305 (4.32)	313* (4.25)	319* (4.16)	329* (3.77)	346 (3.40)	364 (2.98)
2-Acetoxy-4-chloro (146)	264* (4.64)	273* (4.81)	281 (4.95)	304 (4.44)	314* (4.33)	-	334* (3.78)	350 (3.59)	369 (3.38)
2-Hydroxy-3,4-dichloro (147)	-	273* (4.74)	282 (4.92)	308 (4.38)	314* (4.37)	-	-	356* (3.33)	374 (3.09)

* Inflection

Mechanism of the formation of the 2-hydroxytriphenylenes.

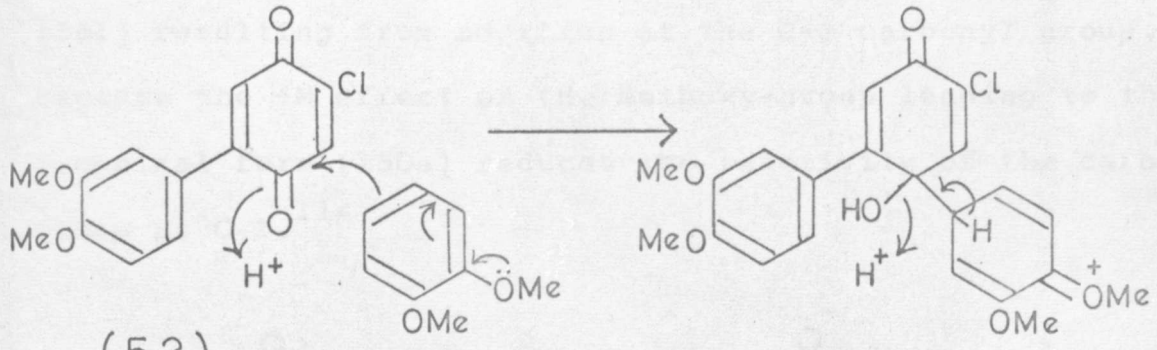
The formation of the hydroxytriphenylenes must involve the 1,2- addition of veratrole to the C-1 carbonyl group of the arylquinone, followed by dehydration and cyclisation as shown on p.137 for the conversion of the arylquinone (53) into the triphenylene (143). The reaction of a nucleophile with a benzoquinone normally results in 1,4-addition to the C=C-C=O system. 1,2-Addition to the carbonyl group of the quinone is unusual and few examples have been recorded.[110-114] 2,6-Dimethoxybenzoquinone reacts with acetone in the presence of potassium carbonate[111,112] or alumina[113] to give the aldol condensation product (149), but no reaction occurs with



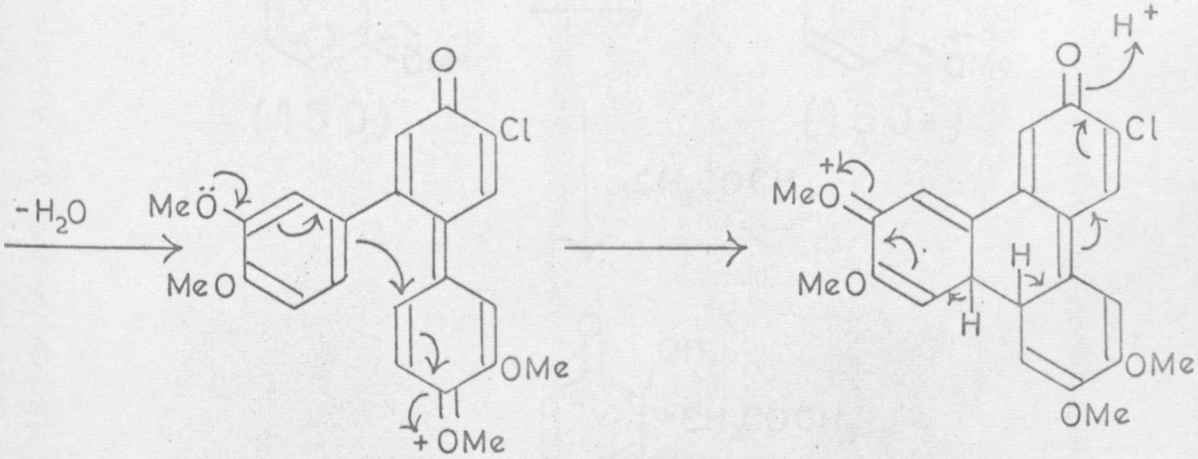
(149)

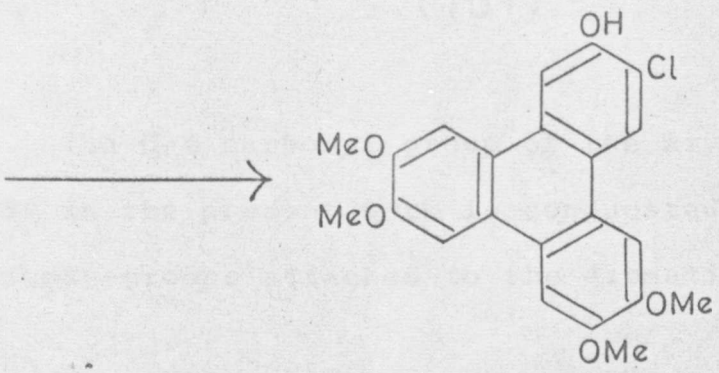
2,5-dimethoxybenzoquinone.[112] Substituted ortho benzoquinones undergo similar addition reactions,[114] the inductive and mesomeric effects of the substituents determining which

Formation of the 2-hydroxytriphenylene (143)



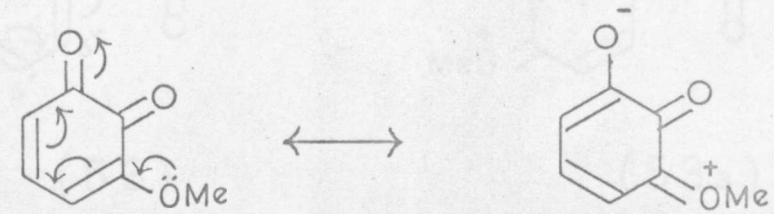
(53)



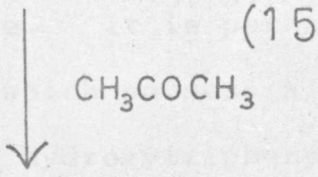


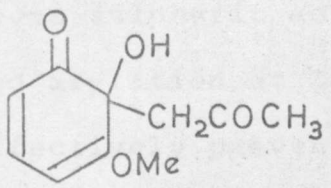
(143)

carbonyl group is attacked by the nucleophile. For example, 3-methoxy-1,2-benzoquinone (150) gives the product (151) resulting from addition at the C-2 carbonyl group, because the +M effect of the methoxy-group leading to the canonical form (150a) reduces the reactivity of the carbonyl group at C-1.[114]



(150) (150a)

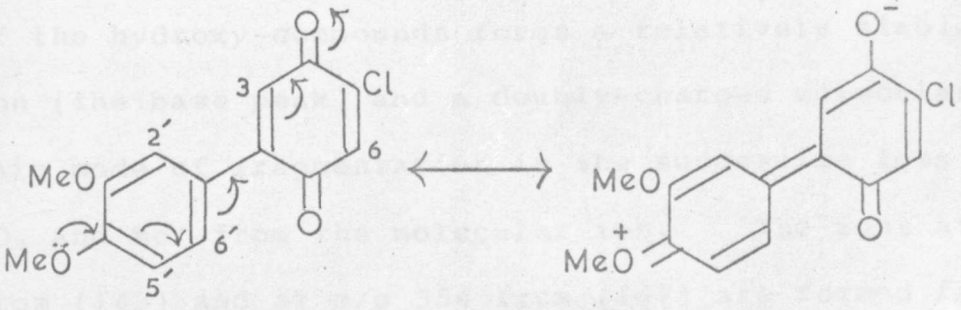




(151)

The C-4 carbonyl group of the arylquinones (eg. 53) used in the present work is conjugated with one of the methoxy-groups attached to the aromatic ring. The +M effect

of this methoxy-group leads to the canonical form (53a) and so reduces the reactivity of the carbonyl group at C-4. This allows the other carbonyl group at C-1 to



(53) (53a)

behave more like a ketone. It is perhaps significant that those arylquinones which possess a chlorine atom at C-3, do not give rise to hydroxytriphenylenes when treated with veratrole and aqueous sulphuric acid, but form dibenzofurans or undergo arylation at C-5 or C-6.[33] The chlorine atom at C-3 effectively prevents these molecules from becoming coplanar and mesomerism of the type (53) ⟷ (53a) is no longer possible. The formation of the 2-hydroxytriphenylenes thus appears to be limited to those arylquinones (see 53) which possess an electron-attracting group at C-5 or C-6 and an electron-donating group at C-3' and C-4'.

Mass spectra of the 2-hydroxy- and 2-acetoxy-triphenylenes.

The more significant ions obtained from the 2-hydroxy- and 2-acetoxy-triphenylenes are recorded in Table 20. Each of the hydroxy-compounds forms a relatively stable molecular ion (the base peak) and a doubly-charged molecular ion. The main mode of fragmentation is the successive loss of Me·, CO, and Me· from the molecular ion. The ions at m/e 320 from (143) and at m/e 354 from (147) are formed from the $(M-Me)^+$ ions by the loss of ClCO·. This fragmentation resembles that of a simple phenol, the molecular ion of which is known to lose HCO·;[115] deuterium labelling has revealed that part of the lost hydrogen comes from the aromatic ring.[115,116] The base peak in the spectrum of each of the 2-acetoxytriphenylenes corresponds to the loss of one ketene molecule from the molecular ion. Thereafter the fragmentation is similar to that of the 2-hydroxy-compound (143).

Table 20 Mass spectra of the 2-hydroxy- and 2-acetoxy-triphenylenes

Substituted 6,7,10,11-tetramethoxytriphenylene	Principal ions and relative abundances (%)
2-Hydroxy-3-chloro- (143)	m/e 398(100), 383(7), 355(12), 340(7), 325(5), 324(5), 320(13), 297(4), 199†(11), 160†(6); 368*(398 → 383), 326*(355 → 340), 268*(383 → 320).
2-Hydroxy-3,4-dichloro- (147)	m/e 432(100), 417(8), 389(16), 374(5), 359(4), 358(5), 354(9), 346(5), 331(5), 216†(11), 177†(5), 173†(5); 404*(432 → 417), 361* (389 → 374), 300*(417 → 354).
2-Acetoxy-3-chloro- (145)	m/e 440(53), 398(100), 383(10), 355(9), 340(6), 325(5), 324(5), 320(11); 369*(398 → 383), 360*(440 → 398), 326*(355 → 340), 268*(383 → 320).
2-Acetoxy-4-chloro- (146)	m/e 440(80), 398(100), 383(16), 355(13), 340(5), 325(4), 324(5), 320(12), 312(8); 369*(398 → 383), 360*(440 → 398), 268*(383 → 320).

* Metastable transition

† Doubly-charged ion

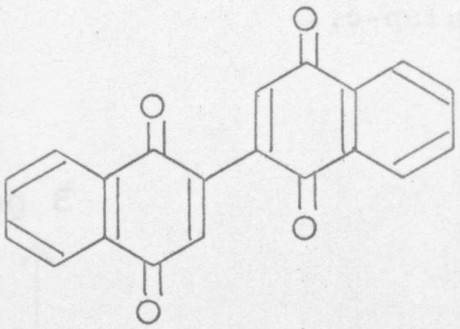
CHAPTER 6

Self-condensation of 1,4-naphthaquinone in the presence of aluminium chloride

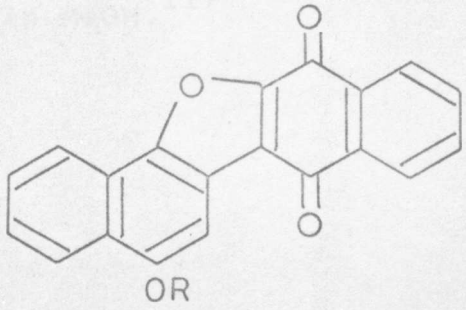
The attempted reaction between veratrole, 1,4-naphthaquinone and aluminium chloride in carbon disulphide gave only products derived from naphthaquinone, most (87%) of the veratrole being recovered unchanged. The products isolated were 1,4-dihydroxynaphthalene, the binaphthaquinone (152), the tetramethoxynaphthocyclo-octatetraene (31) (p.14), and a violet solid (16%). The binaphthaquinone (152) and the cyclo-octatetraene derivative (31) were identical with authentic specimens prepared from 1,4-naphthaquinone.[90,40]

The violet solid separated during the working-up of the reaction mixture, it could not be purified by crystallisation. The i.r. spectrum of the crude material showed the presence of a hydroxy-group ($\nu_{max.}$ 3400 cm^{-1}) and quinonoid carbonyl groups ($\nu_{max.}$ 1660 cm^{-1}). Acetylation gave a red mono-acetate, $C_{20}H_9O_3 \cdot OCOCH_3$, the i.r. absorption of which shows both arylacetate and quinonoid carbonyl groups. This suggested that the violet product was a dehydro dimer of

1,4-naphthaquinone ($C_{10}H_6O_2$) containing a quinonoid system and a phenolic group. The binaphthaquinone (152) is known to cyclise readily to the dinaphthofuranquinone (153),[37] but the m.p.[37] and the u.v. spectrum[117] of the acetate (154) were different from those of the red acetate described above.



(152)



(153; R=H)

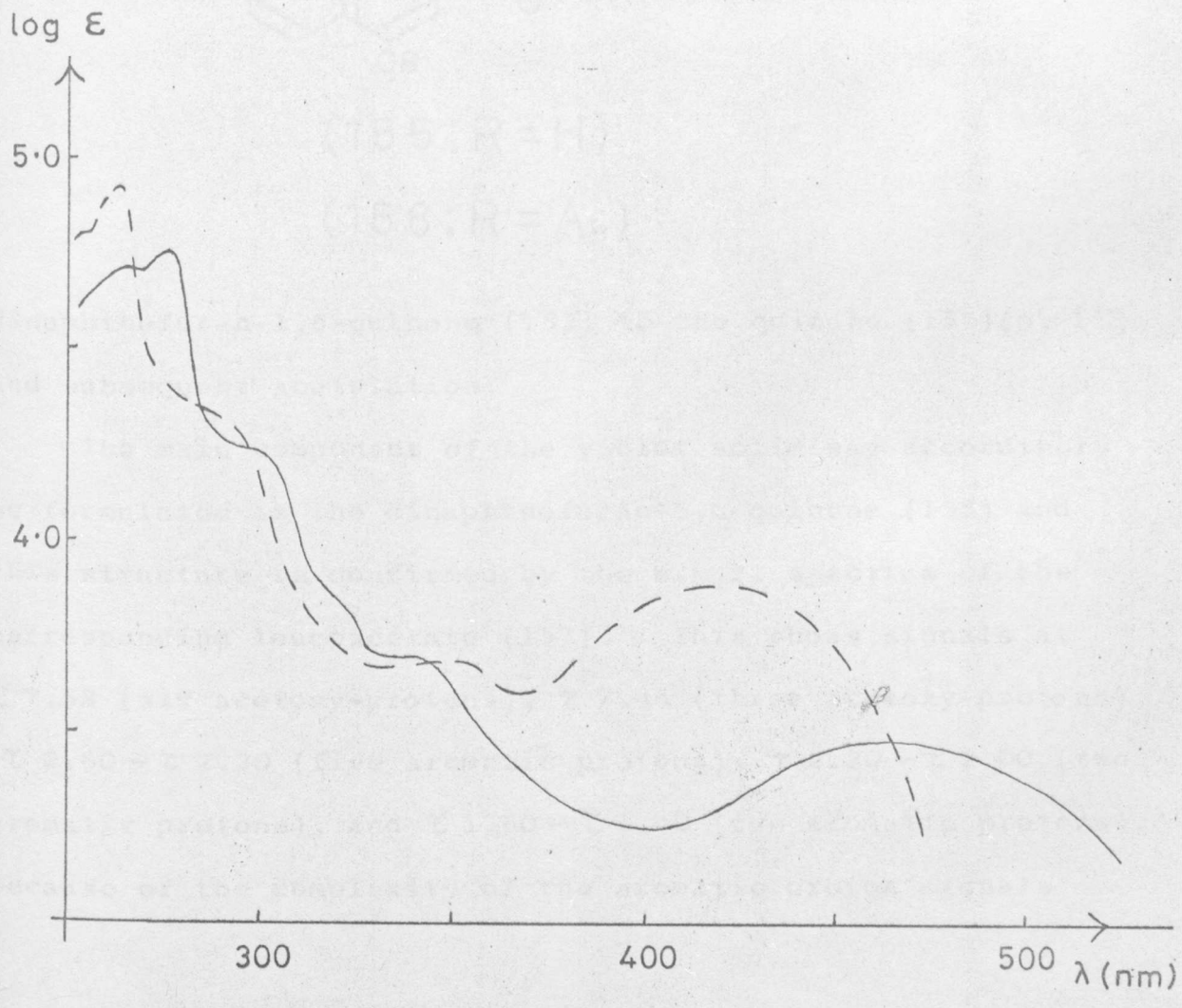
(154; R=Ac)

The u.v. spectrum of the acetate (154) resembles that of the red acetate, but the absorption maximum in the visible region of the latter compound is at longer wavelength (Figure 6). The i.r. spectrum of the red acetate shows two main carbonyl bands at $\nu_{max.}$ 1665 and 1650 cm^{-1}, and a weak band at $\nu_{max.}$ 1698 cm^{-1}. Now the i.r. spectrum of a 1,2-naphthaquinone often shows a band or shoulder between 1700 and 1680 cm^{-1} which is not present in the spectrum of the corresponding 1,4-naphthaquinone.[118,119] Furthermore the visible absorption of a 1,2-quinone often shows a bathochromic

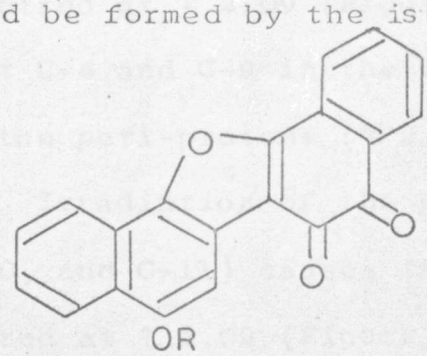
Figure 6 U.v absorptions of the acetoxydinaphthofuran-quinones (156) and (154)

———— 8-Acetoxydinaphtho[1,2-b:2',1'-d] furan-5,6-quinone (156) in EtOH

— — — 8-Acetoxydinaphtho[1,2-b:2',3',-d]furan-1,6-quinone (154) in MeOH.[117]



displacement with respect to that of the corresponding 1,4-quinone.[119,120] The above spectra therefore suggest that the red acetate is a derivative of 1,2-naphthaquinone, namely the dinaphthofuran-5,6-quinone (156). Such a compound could be formed by the isomerisation of the



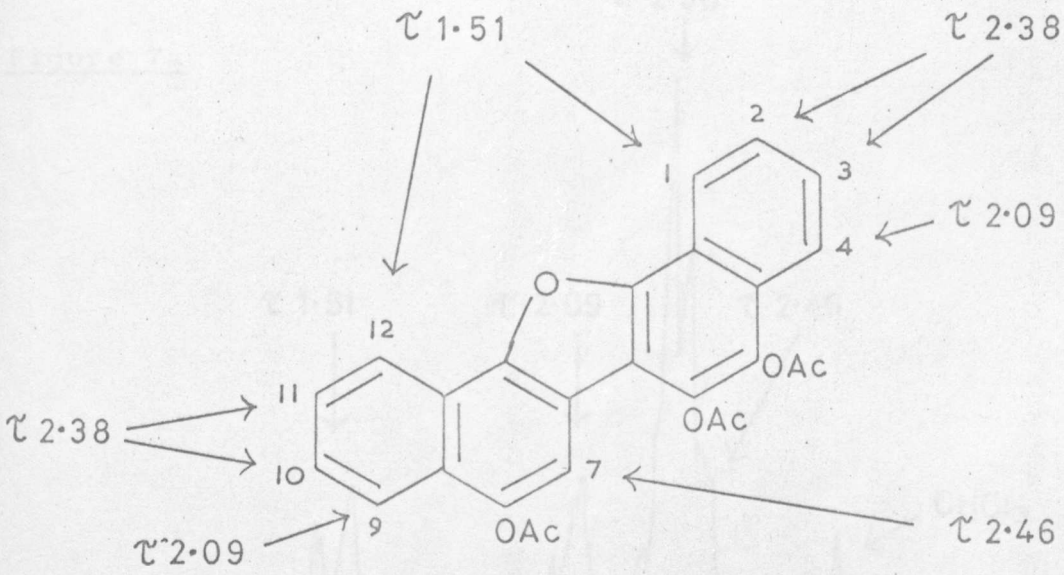
(155; R = H)

(156; R = Ac)

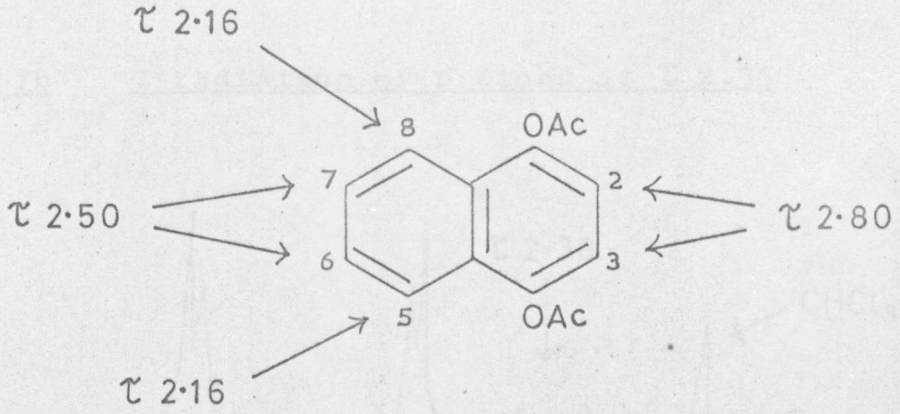
dinaphthofuran-1,6-quinone (153) to the quinone (155)(p. 152), and subsequent acetylation.

The main component of the violet solid may accordingly be formulated as the dinaphthofuran-5,6-quinone (155) and this structure is confirmed by the n.m.r. spectrum of the corresponding leucoacetate (157). This shows signals at τ 7.52 (six acetoxy-protons), τ 7.46 (three acetoxy-protons), τ 2.60 – τ 2.20 (five aromatic protons), τ 2.20 – τ 2.00 (two aromatic protons), and τ 1.60 – τ 1.40 (two aromatic protons). Because of the complexity of the aromatic proton signals

(Figure 7a), a complete analysis of the spectrum was not possible. However, the chemical shifts were deduced by analogy with the aromatic proton resonances of 1,4-diacetoxynaphthalene (158) and by spin decoupling experiments. The signal centred at τ 2.09 (Figure 7a) is attributed to the protons at C-4 and C-9 in the leucoacetate (157) by analogy with the peri-protons (τ 2.16) in 1,4-diacetoxy-naphthalene. Irradiation of the protons at τ 2.38 (i.e. at C-2, C-3, C-10, and C-11) causes the partial collapse of the multipletcentred at τ 2.09 (Figure 7b), and irradiation at τ 2.09 affects the signal near τ 2.38 (Figure 7c). The low-field signal centred at τ 1.51 is assigned to the protons at C-1 and C-12. These, being situated peri to the rigidly orientated electron pair of the furan oxygen atom, would be deshielded to a greater extent than the protons at C-4 and C-9. Irradiation at τ 2.38 tends to collapse the signal centred at τ 1.51 (Figure 7b), and irradiation at τ 1.51 produces a singlet at τ 2.38 (Figure 7d). By analogy with the C-6 and C-7 protons of 1,4-diacetoxynaphthalene (158), the signals near τ 2.38 are attributed to the protons at C-2, C-3, C-10, and C-11 in the leucoacetate (157). These signals show complex splitting and are somewhat modified by irradiation either at τ 2.09 or τ 1.51 (Figures 7c and 7d).


τ 1·51
τ 2·38
τ 2·09
τ 2·38
τ 2·09
τ 2·46
OAc
OAc
OAc
1
2
3
4
7
9
10
11
12
O

(157)


τ 2·16
τ 2·50
τ 2·80
τ 2·16
OAc
OAc
2
3
5
6
7
8

(158)

Aromatic proton signals of the triacetoxydinaphthofuran (157)

Figure 7a

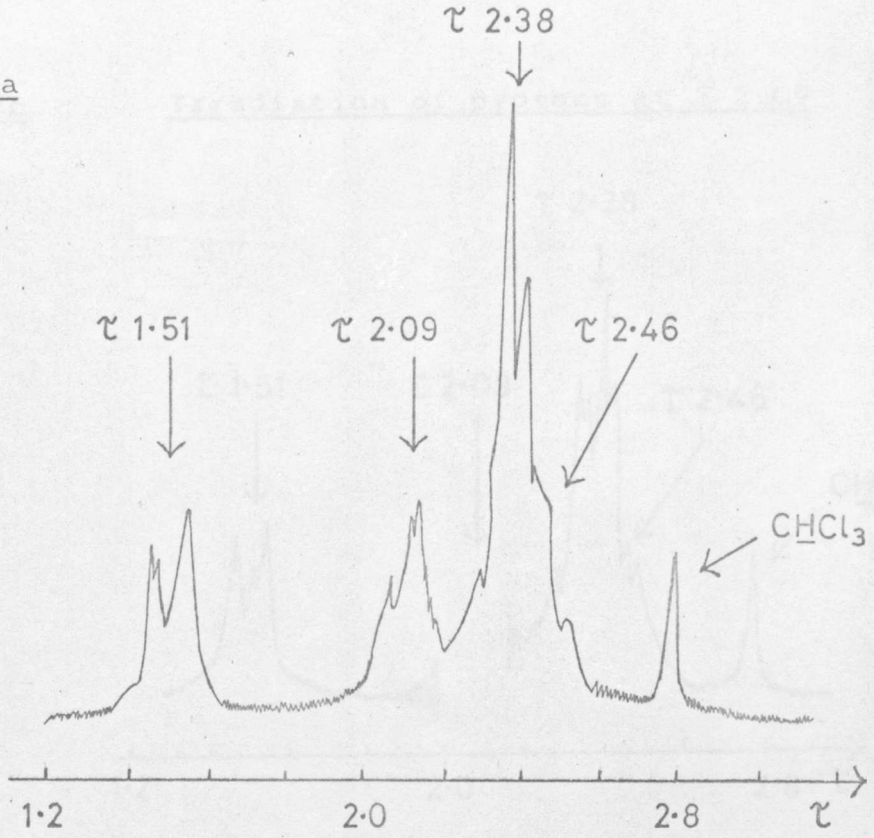
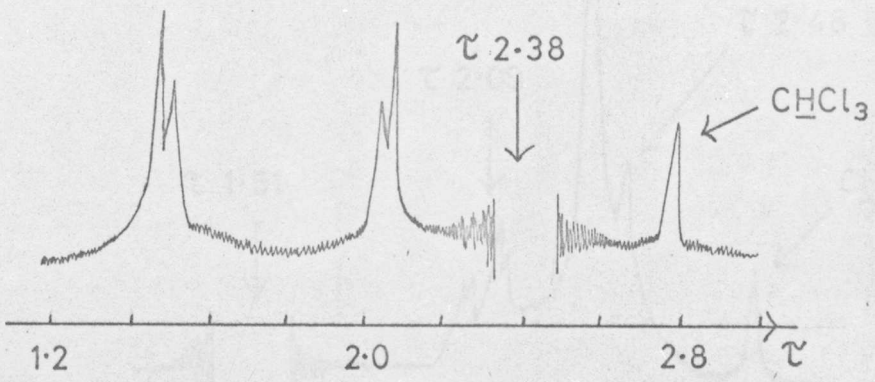


Figure 7b Irradiation of protons at τ 2.38



Aromatic proton signals of the triacetoxydinaphthofuran (157)

Figure 7c Irradiation of protons at τ 2.09

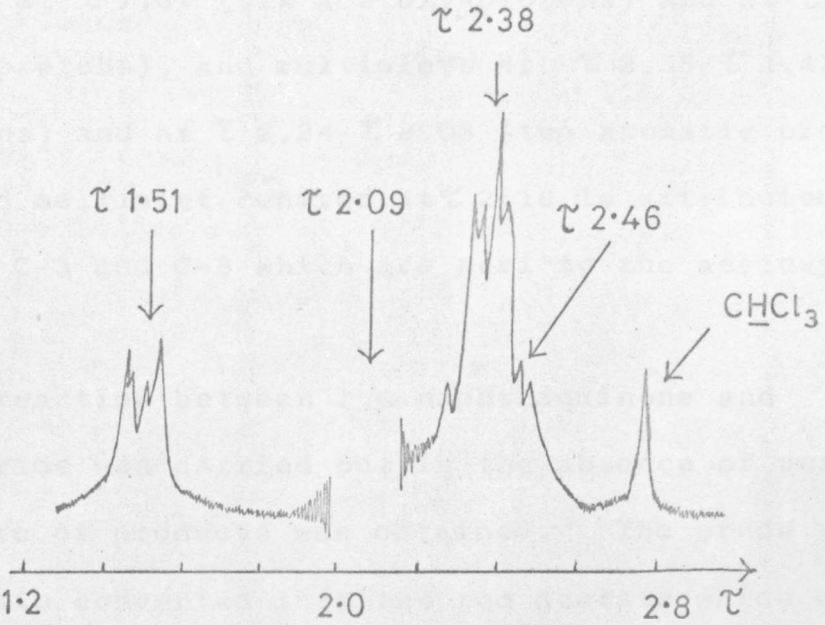
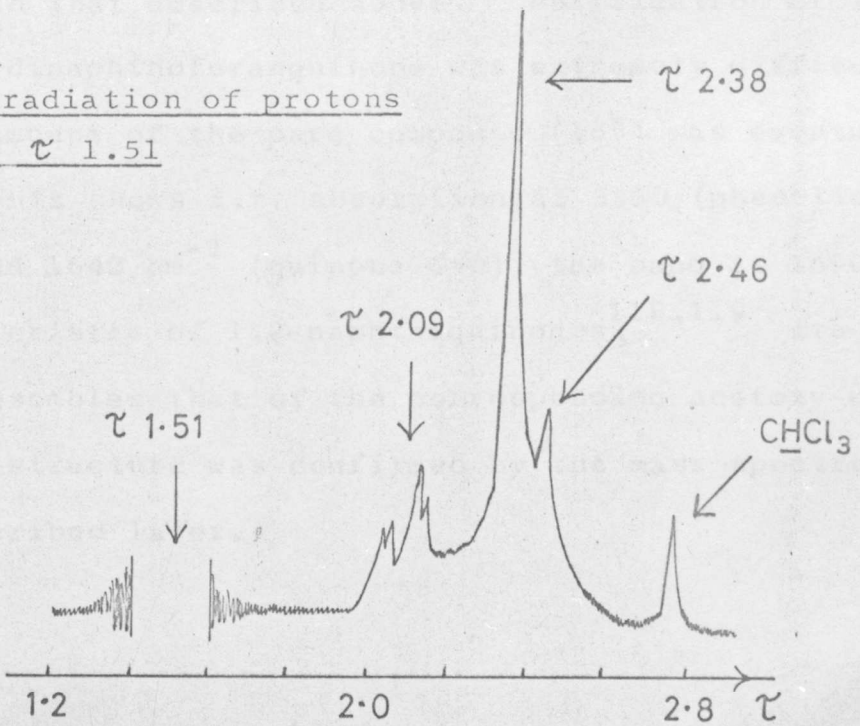


Figure 7d. Irradiation of protons at τ 1.51

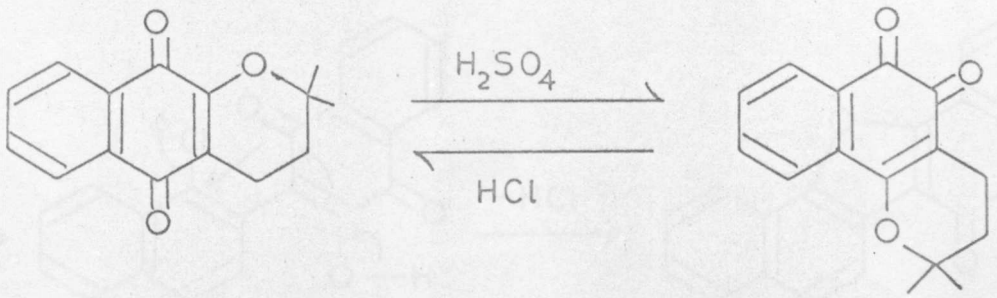


The signal at τ 2.46 is unaffected by such irradiation and is attributed to the isolated proton at C-7. The 1,4-diacetoxynaphthalene (158) was prepared by the reductive acetylation of 1,4-naphthaquinone. Its n.m.r. spectrum shows singlets at τ 7.61 (six acetoxy-protons) and at τ 2.80 (two aromatic protons), and multiplets at τ 2.58-τ 2.42 (two aromatic protons) and at τ 2.24-τ 2.08 (two aromatic protons). The lower-field multiplet centred at τ 2.16 is attributed to the protons at C-5 and C-8 which are peri to the acetoxy-groups.

When the reaction between 1,4-naphthaquinone and aluminium chloride was carried out in the absence of veratrole, the same mixture of products was obtained. The crude violet product was again converted into the red acetate which was identical with that described above. Purification of the crude hydroxydinaphthofuranquinone was extremely difficult but a small amount of the pure compound (155) was eventually obtained. This shows i.r. absorption at 3350 (phenolic OH), 1690, 1655 and 1642 cm^{-1} (quinone C=O), the band at 1690 cm^{-1} being characteristic of 1,2-naphthaquinones;[118,119] its u.v. absorption resembles that of the corresponding acetoxy-compound (156). The structure was confirmed by the mass spectrum which is described later.

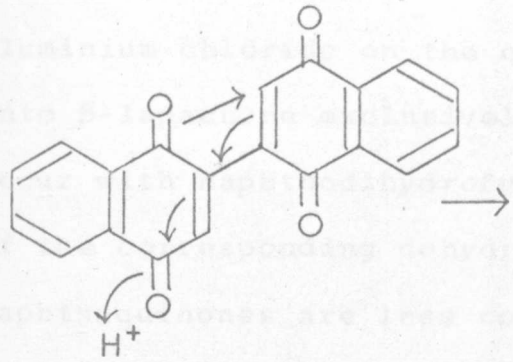
Mechanism of the formation of the hydroxydinaphthofuran-5,6-quinone

A possible reaction sequence from the binaphthaquinone (152) to the dinaphthofuran-5,6-quinone (155) is given on p.152 . The binaphthaquinone (152) readily cyclises under the influence of heat[90] or light[37,117] to the dinaphthofuran-1,6-quinone (153). Other diquinones[127] are known to cyclise in acid to dibenzofuranquinones. The conversion of the 1,6-quinone (153) to the 5,6-quinone (155) may take place during the treatment with hydrochloric acid, as a number of analogous isomerisations occur in the presence of proton acids. Thus α-lapachone (159) is converted into the β-isomer (160) in the presence of concentrated sulphuric acid, and the process is reversed in concentrated hydrochloric acid.[123] The chloro-dihydrolapachol (161) is an intermediate in the latter conversion.[123] Treatment of either of the lapachones with

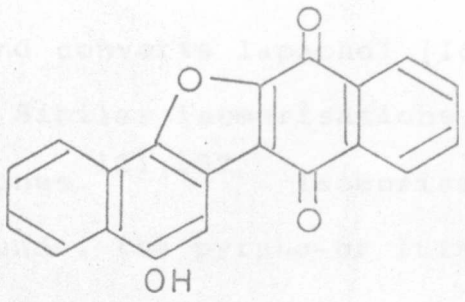


(159) (160)

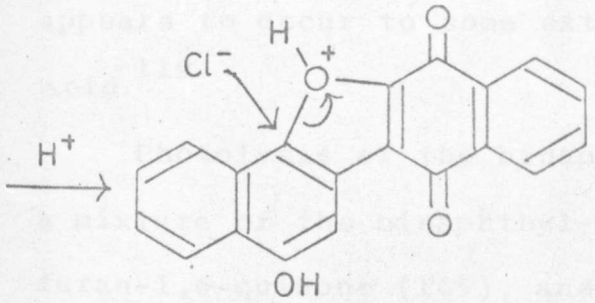
Formation of the dinaphthofuran-5,6-quinone (155)

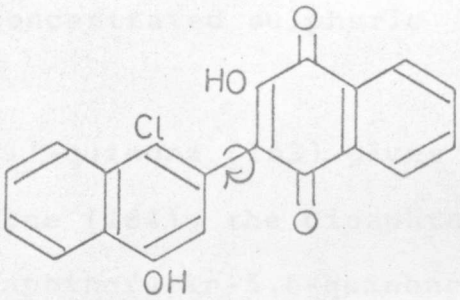


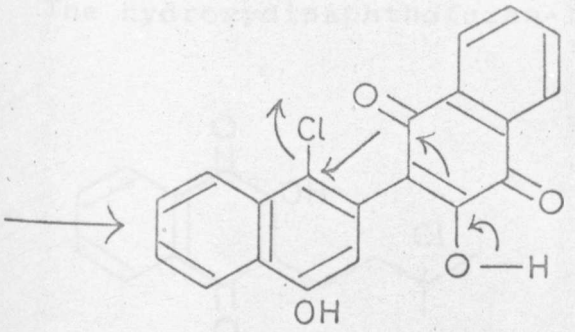
(152)

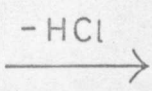


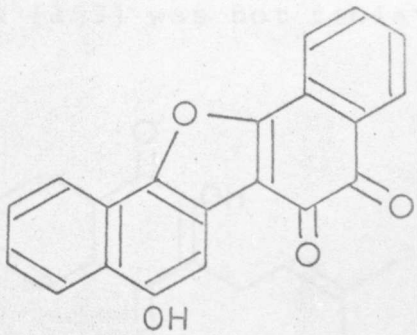
(153)







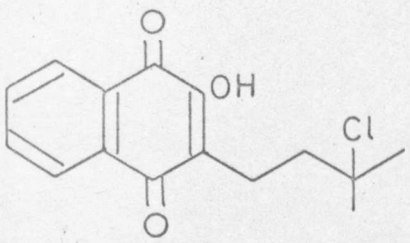




(155)

aqueous sulphuric acid (< 62%) gives α-lapachone, but at higher concentrations (> 75%), β-lapachone is obtained.[124] Aluminium chloride on the other hand converts lapachol (162) into β-lapachone exclusively.[125] Similar isomerisations occur with naphthodihydrofuranquinones.[121,122] Isomerisations of the corresponding dehydro-compounds, the pyrano-or furano-naphthaquinones are less common. Dehydro-β-lapachone is converted into the α-isomer in the presence of a little acid,[119] and the conversion of dehydro-α-lapachone into the β-isomer appears to occur to some extent in concentrated sulphuric acid.[119]

Photolysis of the binaphthyl-1,1'-quinone (163) gives a mixture of the binaphthyl-1,4-quinone (164), the dinaphthofuran-1,6-quinone (165), and the dinaphthofuran-5,6-quinone (166).[126] The last compound only appears after prolonged irradiation of the binaphthyl-1,1'-quinone (163), and is probably formed by the isomerisation of the quinone (165). The hydroxydinaphthofuran-1,6-quinone (153) was not isolated



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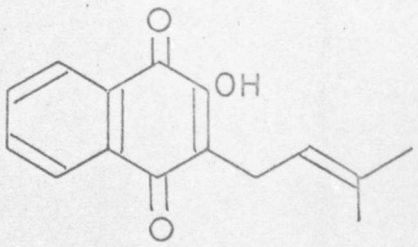
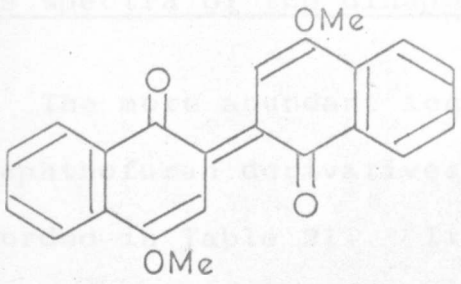
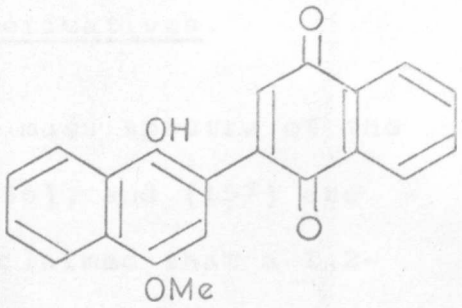


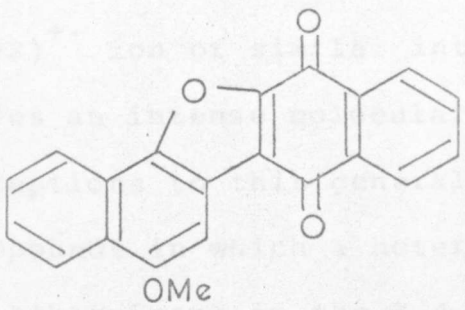
(162)



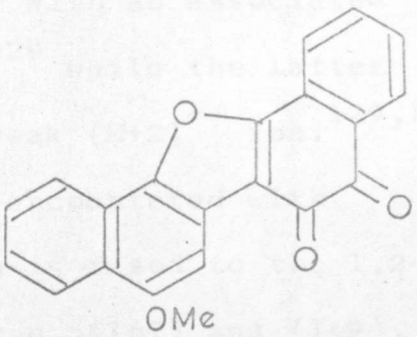
(163)



(164)



(165)



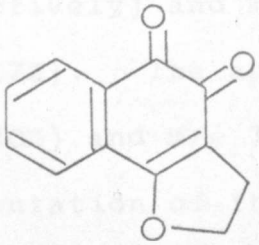
(166)

from the reaction between 1,4-naphthaquinone and aluminium chloride, and an investigation of the effects of acids on the quinone (153) is obviously necessary.

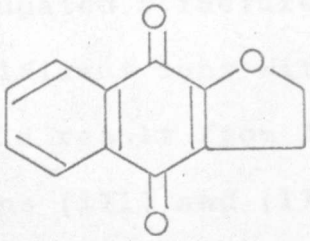
Mass spectra of the dinaphthofuran derivatives.

The more abundant ions from the mass spectra of the dinaphthofuran derivatives (155), (156), and (157) are recorded in Table 21. It has been claimed that a 1,2-naphthaquinone and a 1,4-naphthaquinone may be distinguished mass spectrometrically.[128,129] The former gives a relatively weak molecular ion (I. < 35%) together with an associated $(M+2)^{+\cdot}$ ion of similar intensity,[128,129] while the latter gives an intense molecular ion and a weak $(M+2)^{+\cdot}$ ion.[129,130] Exceptions to this generalisation are encountered with compounds in which a heterocyclic ring is fused to the 1,2-naphthaquinone in the 3,4-positions, e.g. (167) and (169). Such compounds show relatively abundant molecular ions and the $(M+2)^{+\cdot}$ ions are not of comparable intensity. These exceptions may be due to the rearrangement of the 1,2-naphthaquinone to the corresponding 1,4-naphthaquinone in the mass spectrometer.[129] The mass spectra of such 1,2- and 1,4-naphthaquinones are however different in other ways. Each of the 1,2-naphthaquinones (167)[129] and (169)[131] gives, as the base peak, the $(M-CO)^{+\cdot}$ ion, while each of the corresponding 1,4-isomers (168) and (170) gives, as the base peak, the molecular ion. This difference in ion abundance has been attributed to the greater stability of the 1,4-

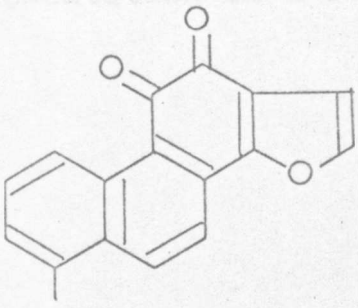
naphthaquinones.[131]



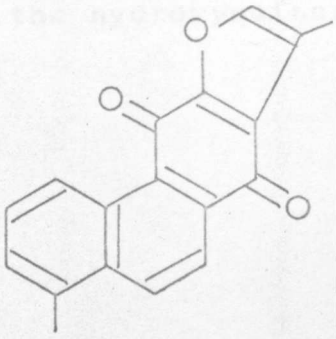
(167)



(168)



(169)



(170)

In the present work, the mass spectrum of the hydroxy-dinaphthofuran-5,6-quinone (155) has, as the base peak, the $(M-CO)^{+\cdot}$ ion. This ion then loses either three molecules of carbon monoxide to give m/e 202, or one molecule of carbon monoxide and two formyl radicals to give m/e 200. A feasible, fragmentation sequence is shown on p. 158. The ions with

m/e 202 and 200 are relatively stable (I = 34% and 31% respectively) and may have the conjugated structures (171) and (172). The appearance of significant ions with m/e 101 (I = 20%) and m/e 100 (I = 12%) could result from further fragmentation of the symmetrical ions (171) and (172) respectively. The acetoxydinaphthofuranquinone (156) and the triacetoxydinaphthofuran (157) lose one and three molecules of ketene respectively, and then appear to undergo fragmentation in a similar fashion to the hydroxyquinone (155).

Fragmentation of the dinaphthofuran-5,6-quinone (155)

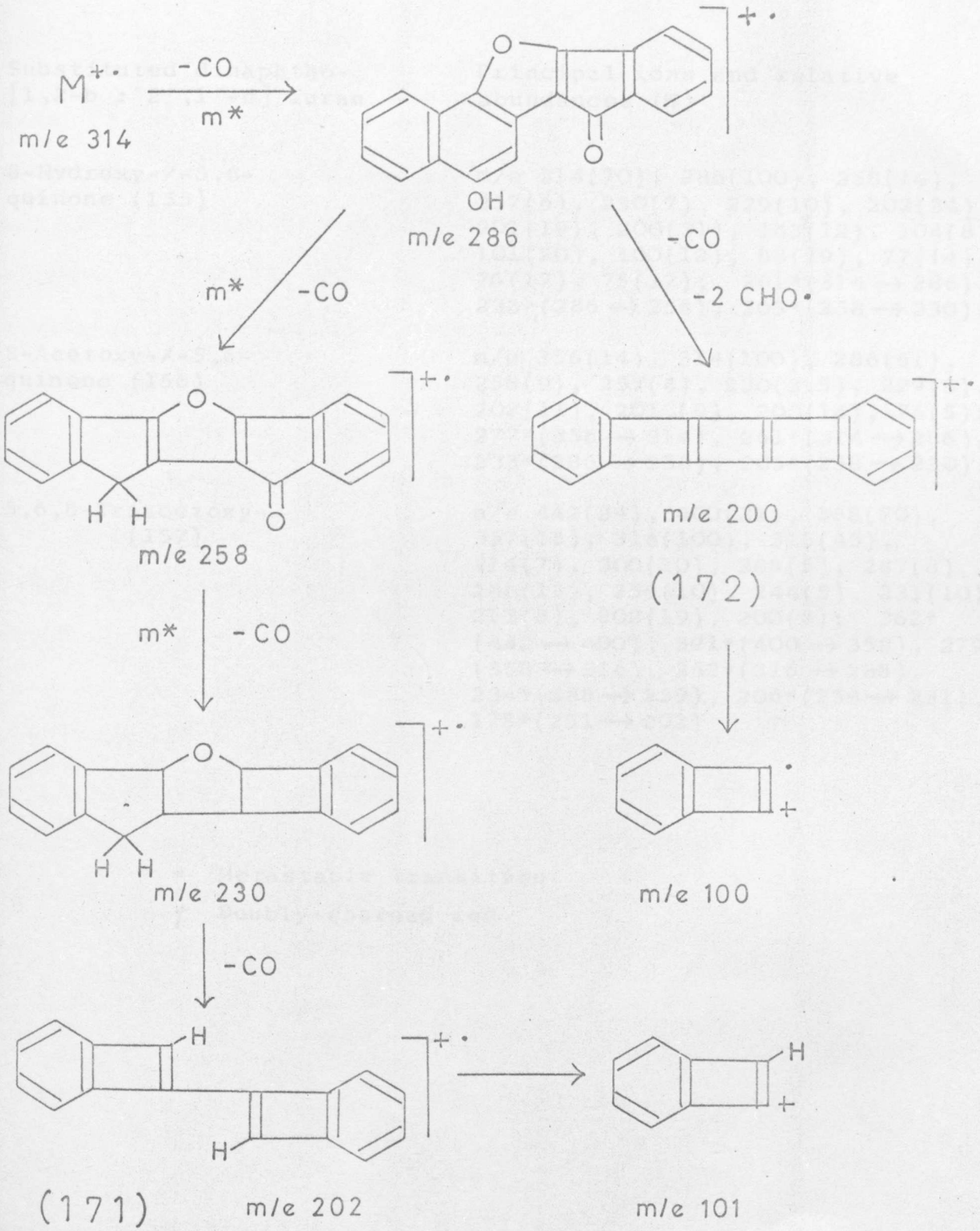


Table 21 Mass spectra of the dinaphthofurans

Substituted dinaphtho-[1,2-b : 2',1'-d] furan	Principal ions and relative abundances (%)
8-Hydroxy-/-5,6-quinone (155)	m/e 314(70), 286(100), 258(14), 257(6), 230(7), 229(10), 202(34), 201(19), 200(31), 143†(12), 104(8), 101(20), 100(12), 88(19), 77(14), 76(17), 75(17); 261*(314 → 286), 233*(286 → 258), 205*(258 → 230).
8-Acetoxy-/-5,6-quinone (156)	m/e 356(14), 314(100), 286(61), 258(9), 257(4), 230(3.5), 229(5), 202(11), 201(9), 200(14), 76(5); 277*(356 → 314), 261*(314 → 286), 233*(286 → 258), 205*(258 → 230).
5,6,8-Triacetoxy- (157)	m/e 442(24), 400(21), 358(70), 357(18), 316(100), 315(43), 314(7), 300(10), 288(5), 287(8), 286(13), 259(10), 244(5), 231(10), 213(8), 202(19), 200(8); 362* (442 → 400), 321*(400 → 358), 279* (358 → 316), 262*(316 → 288), 234*(288 → 259), 206*(259 → 231), 178*(231 → 202)

* Metastable transition.

† Doubly-charged ion.

Experimental

The following general conditions and procedures were used: anhydrous aluminium chloride was fresh and finely powdered; A.R. carbon disulphide was dried over phosphorous pentoxide; organic solutions were dried over anhydrous magnesium sulphate, and all solvents and other volatile compounds were evaporated under reduced pressure using a rotary evaporator. The identity of a compound with an authentic specimen was established by way of their i.r. spectra and t.l.c. behaviour. The additional methods of identification also used have been indicated after the name of the compound, using the abreviations mixed m.p., u.v., and n.m.r. U.v. absorption spectra were measured using a Unicam S.P. 800 spectrophotometer, and i.r. absorption spectra were obtained with Unicam S.P. 200 and 200 G spectrophotometers. N.m.r. spectra were recorded using Varian Associates A 60 and HA 100 spectrometers with tetramethylsilane (τ = 10.0) as internal standard. Molecular weights were measured mass spectrometrically by P.C.M.U. at Aldermaston using an AEI MS9 instrument. M.p. were determined with an Electrothermal m.p. apparatus. The silica gel for column chromatography was Hopkins and

Williams MFC grade, and for t.l.c. Merck Kieselgel GF_{254} was used. Unless otherwise stated, light petroleum refers to the fraction b.p. 40-60°. New compounds are underlined when first mentioned.

Preparative thin layer chromatography (p.l.c.)

This was performed on glass plates (20 x 20 cm) covered by u.v.-sensitised silica gel (Merck Kieselgel GF_{254}). A solution of the mixture (5-50 mg) to be separated in the minimum volume of chloroform was applied manually to each plate using a dropping pipette. Development was continued until the solvent front had reached the top of the plate. When separation of the component was particularly difficult, multiple development was carried out in the following manner.

The plate was developed, removed from the developing tank and allowed to dry in air (ca. 15 min), and the dried plate was replaced in the tank. This process was repeated until separation of the bands had been effected. Bands are recorded in the order of their speed of movement on the silica gel, the fastest being given first. To isolate a compound the appropriate band was removed from the plate and the silica gel was extracted with chloroform. The chloroform solution was filtered through sintered glass and the solvent was evapoarated.

CHAPTER 2

3,4-Dimethoxynitrobenzene.[82]

Veratrole (20 g) was added slowly to a stirred mixture of concentrated nitric acid (13 ml.) and water (18 ml.). The mixture was stirred at room temperature for 30 min., poured into water and the resulting precipitate was collected and crystallised from ethanol to give 3,4-dimethoxynitrobenzene as yellow needles (20 g) m.p. 94-95° (lit.,[83] m.p. 96°).

Reduction of 3,4-dimethoxynitrobenzene

3,4-Dimethoxynitrobenzene (20 g) was mixed with granulated tin (20 g), tin (II) chloride (19 g), and concentrated hydrochloric acid (200 ml.).

After the initial vigorous reaction, the mixture was heated on a steam bath for 15 min. and kept for 1 h. A saturated solution of sodium hydroxide was added until the mixture had a pH $>$ 10. The alkaline solution was shaken with ether to give an extract which on being concentrated gave crude 3,4-dimethoxyaniline (11.6 g) m.p. 78-83°. Crystallisation of the crude product from ether gave pure 3,4-dimethoxyaniline (8.3 g) m.p. 84-86° (lit.,[83] m.p. 86°).

Arylation of benzoquinone

(a) With diazotised 3,4-dimethoxyaniline.

A cooled solution of sodium nitrite (1.8 g) in water (20 ml.) was added dropwise to a solution of 3,4-dimethoxyaniline (3.5 g) (m.p. 84-86°) in 2M-hydrochloric acid (35 ml.) at 0-4°. The resulting solution was added to a vigorously stirred suspension of benzoquinone (3.25 g) and sodium acetate trihydrate (8.5 g) in water (225 ml.) at 14°. Evolution of nitrogen began immediately and the mixture was stirred for 2 h then kept overnight at room temperature. The resulting red solid was collected (4.6 g), and the aqueous filtrate was extracted with ether to give more of the red solid (1.5 g). This was dissolved in benzene and filtered through a column of silica gel using chloroform-benzene (1:5). Unchanged benzoquinone was eluted first, followed by a red solid which crystallised from ethanol-acetone to give 3',4'-dimethoxyphenylbenzoquinone as red rhombohedra (3.1 g) m.p. 133-134° (lit.,[84] 134-135°); τ ($CDCl_3$) 6.09 (s, 6H, CH_3O), 3.20 (s, 3H, quinone-H), and 3.05-2.75 (m, 3H, Ar-H); $\nu_{max.}$(Nujol) 1645, 1600, 1590, 1518, 1340, 1280, 1258, 1220, 1160, 1140, 1090, 1028, and 897 cm^{-1}. A portion of the red solid from the

column was sublimed (90°/0.1 Torr) to give 3',4'-dimethoxyphenylbenzoquinone m.p. 135-136°; $\nu_{max.}$(Nujol) 1655, 1602, 1593, 1522, 1340, 1280, 1265, 1220, 1165, 1145, 1090, 1030, 922, 862, and 780 cm^{-1}. The i.r. absorptions of both specimens in carbon disulphide solution were identical; $\nu_{max.}$ (2% in CS_2) 1653 (quinone C = O) and 1260 cm^{-1} (ether C - O).

(b) With diazotised crude 3,4-dimethoxyaniline

The above experiment was repeated using crude 3,4-dimethoxyaniline (3.5 g), (m.p. 78-83°). This gave a red solid which crystallised from chloroform-ethanol to give 3',4'-dimethoxyphenylbenzoquinone (1.5 g) m.p. 133-134°. Evaporation of the solvent from the mother liquor gave a crude product (1.5 g) which was shown by t.l.c. to be a mixture. A portion (0.5 g) of the crude product on being subjected to p.l.c. using benzene-light petroleum (2:1) gave an orange band and a red band. The red band afforded 3',4'-dimethoxyphenylbenzoquinone (180 mg), and the orange band gave a solid which crystallised from ethanol to give 6'-chloro-3',4'-dimethoxyphenylbenzoquinone (51) as orange rhombohedra (240 mg), m.p. 130° (Found: M, 278.0349. $C_{14}H_{11}{}^{35}ClO_4$ requires M, 278.0346), $\lambda_{max.}$(EtOH) 244 (log ε 4.39), 283 (3.81), and 427 nm (3.04),

$\lambda_{infl.}$(EtOH) 324 (log ε 3.01) and 345 nm (2.98); τ ($CDCl_3$) 6.14 and 6.10 (both s, 3H, CH_3O), 3.29 (s, 1H), 3.18 (s, 1H), 3.15 (s, 2H), and 3.05 (s, 1H); $\nu_{max.}$(Nujol) 1660, (quinone C = O), 1602, 1520, 1285, 1270 (ether C - O), 1215, 1175, and 883 cm^{-1}. This compound separated from ethanol as violet needles when the solution was agitated and cooled quickly, $\nu_{max.}$(Nujol) 1658, 1610, 1595, 1527, 1325, 1260, 1220, 920, and 860 cm^{-1}. The violet form changed to the orange form at 120°.

(c) With diazotised 6-chloro-3,4-dimethoxyaniline

A cooled solution of sodium nitrite (140 mg) in water (2 ml.) was added to a solution of 6-chloro-3,4-dimethoxyaniline (375 mg) (prepared by Dr. C.J. Webster[31]) in 3M-hydrochloric acid (3 ml.) at 0-4°. The resulting solution was added to a vigorously stirred mixture of benzoquinone (250 mg), sodium acetate (0.7 g), and water (100 ml.) at 10°, and stirring was continued for 3 h at room temperature. The precipitate was collected and crystallised from ethanol to give 6'-chloro-3',4'-dimethoxyphenylbenzoquinone as orange rhombohedra (275 mg) m.p. 130-130.5° (Found: C, 60.4; H, 4.0; Cl, 12.6; MeO, 22.6%. Calc. for $C_{14}H_{11}ClO_4$: C, 60.35; H, 4.00; Cl, 12.75; 2MeO, 22.25%), mixed m.p. 130° with the

sample from the previous experiment.

Chlorobenzoquinone

A mixture of chloroquinol (30 g) (m.p. 99-100°), manganese dioxide (40 g) and 1M-sulphuric acid (150 ml.) was steam-distilled. The steam volatile solid crystallised from ethanol to give chlorobenzoquinone (15 g) m.p. 50-54°, contaminated with dichlorobenzoquinones. This (5 g) was chromatographed on a column of silica gel using benzene-light petroleum (1:9) as eluant. The dichlorobenzoquinones were eluted first, followed by chlorobenzoquinone which crystallised from ethanol as yellow rhombohedra (2 g) m.p. 56-57° (lit.,[85] 57°).

Arylation of chlorobenzoquinone with diazotised 3,4-dimethoxyaniline

A cooled solution of sodium nitrite (1.725 g) in water (15 ml.) was added dropwise to a solution of 3,4-dimethoxyaniline (3.83 g) in 3M-hydrochloric acid (32 ml.) at 0-5°. The diazonium solution was added to a vigorously stirred mixture of chlorobenzoquinone (3.6 g), sodium acetate (7.7 g), and water (500 ml.) at 10°. Stirring was continued for 1 h

at 10° and then at room temperature for 12 h. The resulting red-violet solid (3.0 g) was collected, and the filtrate was extracted with ether to give more of the red-violet solid (2.0 g). A portion (0.5 g) of this solid on being subjected to p.l.c. using benzene-light petroleum (4:1) gave a violet band and a red band. The violet band afforded a mixture (1:1) (170 mg). m.p. 144-148° of 5- and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones (Found M, 278.0335. $C_{14}H_{11}{}^{35}ClO_4$ requires M, 278.0346). The slower moving band gave a red solid which crystallised from chloroform-ethanol to give 3-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone as clusters of red needles (170 mg), m.p. 200.5-201.5° (Found: M, 278.0339. $C_{14}H_{11}{}^{35}ClO_4$ requires M, 278.0346), $\lambda_{max.}$(EtOH) 250 (log ε 4.29) and 448 nm (3.22), $\lambda_{infl.}$(EtOH) 279 (log ε 3.86) and 308 nm (3.20); $\nu_{max.}$(Nujol) 1672 and 1658 (both quinone C = O), 1256 cm^{-1} (ether C - O), $\nu_{max.}$(2% $CHCl_3$), 1674 cm^{-1}, $\nu_{max.}$ (2% CS_2), 1674 and 1260 cm^{-1}. τ ($CDCl_3$) 6.11 and 6.06 (both s, 3H, CH_3O), and 3.17-2.86 (m, 5H, Ar-H and quinone -H).

Separation of the mixture of 5- and 6-chloro-2-(3',4'-dimethoxyphenyl)-benzoquinones

(a) The mixture (270mg) was subjected to p.l.c. using benzene-light petroleum (3:7) (70 developments over 10 days). One broad

violet band was obtained, the top of which was darker than the rest. The top part of the band gave 5-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (40 mg) m.p. 150-151°, the i.r. spectrum of which showed no bands due to the 2,6-isomer. The remainder of the band gave a crude mixture of the 2,5- and 2,6-quinones.

(b) The mixture of quinones (650 mg) was subjected to p.l.c. using benzene-light petroleum (4:1). The top part of the resulting band gave a solid (A) (270 mg) which was mainly the 2,5-isomer. The other part of the band gave a solid (B) (370 mg) which was mainly the 2,6-isomer. This p.l.c. separation was repeated on the solid (A), and again the top part of the resulting band gave a soild (C) (120 mg) m.p. 150-151° which showed no i.r. absorption bands due to the 2,6-isomer. The other part of the band gave a mixture of the isomers. Another p.l.c. separation on (C) gave an apparently uniform violet band. The lower half of the band gave a violet solid of which the i.r. absorption was that of the 2,5-quinone containing a trace of the 2,6-isomer. The top half of the band gave a solid which crystallised from ethanol to give 5-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone as violet

needles (66 mg) m.p. 151-152° (Found: M, 278.0344. $C_{14}H_{11}{}^{35}ClO_4$ requires M, 278.0346), $\lambda_{max.}$(EtOH) 253 (log ε 4.27) and 468 nm (3.45), $\lambda_{infl.}$(EtOH) 274 (log ε 4.09) and 309 nm (3.52); $\nu_{max.}$ (Nujol) 1655 (quinone C = O), and 1260 cm^{-1} (ether C - O), $\nu_{max.}$ (2% $CHCl_3$), 1667 cm^{-1}, $\nu_{max.}$(2% CS_2) 1667 and 1265 cm^{-1}; τ($CDCl_3$) 6.10 (s, 6H, CH_3O), 3.06 (s, 2H, quinone - H) and 3.18-2.81 (m, 3H, Ar-H)

The solid (B) (370 mg) was subjected to repeated p.l.c. using benzene-light petroleum (4:1). Each time the lower portion of the band was removed, and finally the lower portion of the resulting band was crystallised from carbon disulphide to give 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone as violet needles (120 mg) m.p. 157.5-158.5° (Found: M, 278.0355. $C_{14}H_{11}{}^{35}ClO_4$ requires M, 278.0346), $\lambda_{max.}$(EtOH) 254 (log ε 4.28) and 464 nm (3.43), $\lambda_{infl.}$(EtOH) 273 (log ε 4.11) and 313 nm (3.36); $\nu_{max.}$(Nujol) 1675 and 1642 (both quinone C = O), 1273 and 1262 cm^{-1}(both ether C - O), $\nu_{max.}$ (2% $CHCl_3$) 1680 and 1645 cm^{-1}, $\nu_{max.}$ (2% CS_2) 1680, 1645, and 1260 cm^{-1}; τ ($CDCl_3$) 6.07 (s, 6H, CH_3O), 3.17 (d, J3Hz, 1H, quinone -H), 3.01 (d, J3Hz, 1H, quinone -H), and 3.01-2.81 (m, 3H, Ar-H).

Chlorination of 3-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone

3-Chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (100 mg) was heated under reflux for 1.5 h with concentrated hydrochloric acid (10 ml.), cooled, and poured into water with vigorous stirring. The mixture was shaken with chloroform, and the extract was washed with water and dried. The dried chloroform solution was shaken with anhydrous iron (III) chloride (250 mg), washed with 2M-hydrochloric acid, and with water, and dried. Evaporation of the chloroform gave a violet solid (118 mg) which was subjected to p.l.c. using benzene-light petroleum (2:1). Three coloured bands were obtained, a dark violet band (A), a violet band (B), and a light violet band (C).

The product from band (A) was crystallised from light petroleum (b.p. 60-80°) to give 3,5,6-trichloro-2-(3',4'-dimethoxyphenyl)benzoquinone as long dark-violet needles (7 mg) m.p. 166-167.5° (Found: M, 345.9573. $C_{14}H_9{}^{35}Cl_3O_4$ requires M, 345.9567), $\lambda_{max.}$(EtOH) 283 (log ε 4.27), 341 (3.25) and 495 nm (3.17), $\lambda_{infl.}$(EtOH) 265 nm (log ε 4.13); $\nu_{max.}$ (Nujol) 1685 (quinone C = O) and 1263 cm^{-1}(ether C - O).

Band (B) gave a violet solid which crystallised from chloroform-

ethanol to give 3,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone as clusters of red-violet needles (30 mg) m.p. and mixed m.p. 174-176° (lit.,[86] m.p. 177-178°), τ($CDCl_3$) 6.12 and 6.07 (both s, 3H, CH_3O), 3.17-3.07 (m, 3H, Ar-H), and 2.82 (s, 1H, quinone-H). Evaporation of the mother liquor gave more violet crystals (10 mg) which showed the i.r. absorption of a mixture (1:1) of 3,6- and 3,5-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinones. Authentic samples of 3,6- and 3,5-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinones were supplied by Dr. C.J. Webster. These were prepared by the reaction of diazotised 3,4-dimethoxyaniline on 2,5- and 2,6-dichlorobenzoquinone respectively.[86,89] The light violet band (C) gave unchanged 3-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (2 mg).

Chlorination of 5-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone

5-Chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (50 mg) was heated under reflux for 1·5 h. with concentrated hydrochloric acid (8 ml.), cooled, and poured into water. The resulting mixture was extracted with chloroform and treated with iron (III) chloride (250 mg) as in the previous

experiment. Evaporation of the chloroform gave a solid which was subjected to p.l.c. using benzene-light petroleum (2:1). Three violet bands were obtained (A), (B), and (C).

Band (A) gave 3,5,6-trichloro-2-(3',4'-dimethoxyphenyl)-benzoquinone (5 mg). Band (B) afforded a solid (22 mg) which crystallised from ethanol to give 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone as violet needles (15 mg) m.p. 203-204°, mixed m.p. 203-204° with an authentic sample prepared by the reaction of diazotised 3,4-dimethoxyaniline on 2,3-dichloro-benzoquinone. Evaporation of the mother liquor gave violet crystals which showed the i.r. absorption of crude 3,5-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone. Band (C) gave unchanged 5-chloro-2-(3',4'-dimethoxyphenyl)benzo-quinone (12 mg).

Chlorination of 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone

6-Chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (54 mg) was heated under reflux for 1.25 h with concentrated hydrochloric acid (12 ml.), cooled, poured into water, and the mixture was extracted with chloroform, and treated with iron (III) chloride (250 mg) as in the previous experiment. Evaporation of the chloroform gave a violet solid which on

being subjected to p.l.c. using benzene-light petroleum (2:1) gave three violet bands (A), (B), and (C).

Band (A) gave 3,5,6-trichloro-2-(3',4'-dimethoxyphenyl)-benzoquinone (9 mg). Band (B) yielded a solid (36 mg) which crystallised from chloroform-ethanol to give 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone as violet needles (20 mg) m.p. and mixed m.p. 203-204°. Partial evaporation of the mother liquor gave 3,6-dichloro-2-(3',4'-dimethoxyphenyl)-benzoquinone (5 mg) m.p. and mixed m.p. 172-174° (lit.,[86] 177-178°), while complete evaporation afforded crude 3,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone. Band (C) gave unchanged 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (3.5 mg).

Chlorination of quinol[85]

Dry chlorine was passed through a suspension of quinol (40 g) in glacial acetic acid (200 ml.) at 40° for 2 days (weight increase: 25 g). The solution was evaporated, and the resulting solid was crystallised from water (charcoal) to give two crops of crystals. The first crop (15 g) (m.p. 145-150°), which was mainly 2,5-dichloroquinol, was steam-distilled in the presence of manganese dioxide (20 g) and 1M-sulphuric

acid (100 ml.). The steam volatile solid crystallised from ethanol to give 2,5-dichlorobenzoquinone containing the 2,3-isomer as impurity. The second crop (13 g) (m.p. 120-125°) crystallised from benzene to give 2,3-dichloroquinol (7 g) m.p. 140° (lit.,[85] m.p. 143°). This was steam-distilled in the presence of manganese dioxide (10 g) and 1M-sulphuric acid (50 ml.) to give 2,3-dichlorobenzoquinone which crystallised from ethanol as yellow needles (3 g) m.p. 97-99° (lit.,[85] m.p. 100-101°).

Arylation of 2,3-dichlorobenzoquinone with diazotised 3,4-dimethoxyaniline

A cooled solution of sodium nitrite (0.55 g) in water (5 ml.) was added dropwise to a solution of 3,4-dimethoxyaniline (1.2 g) in 3M-hydrochloric acid (12 ml.) at 0-4°. The resulting solution was added together with a solution of sodium acetate (2.3 g) in water (8 ml.) to a vigorously stirred solution of 2,3-dichlorobenzoquinone (0.55 g) in acetone (70 ml.) at 0°. The mixture was stirred for 2h at 4° and for 1 h at room temperature. Water (70 ml.) was added and the resulting precipitate was collected and crystallised from chloroform-ethanol to give 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzo-

quinone as violet needles (210 mg) m.p. 205-206° (Found: C, 53.5; H, 3.3; Cl, 22.68; MeO, 20.5%. $C_{14}H_{10}Cl_2O_4$ requires C, 53.70; H, 3.20; 2Cl, 22.65; 2MeO, 19.85%), $\lambda_{max}(CHCl_3)$ 278 (log ε 4.14), 337 (3.56), and 510 nm (3.46); $\nu_{max.}$ (Nujol) 1675 and 1650 (both quinone C = O), 1272 and 1260 cm^{-1} (both ether C - O); τ ($CDCl_3$) 6.10 and 6.08 (both s, 3H, CH_3O), and 3.05-2.92 (m, 4H, Ar-H and quinone-H). The filtrate was concentrated to 100 ml., shaken with chloroform, and the extract was washed with water and dried. Evaporation of the chloroform gave a red solid which on being subjected to p.l.c. using benzene-ethyl acetate (20:1) gave one main band. This afforded a violet solid which crystallised from chloroform-ethanol to give more 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-benzoquinone (100 mg) m.p. 204-205°.

Arylation of benzoquinone with diazotised 3,4-dimethoxy-aniline in aqueous acetone

A cooled solution of sodium nitrite (1.725 g) in water (15 ml.) was added dropwise to a solution of 3,4-dimethoxy-aniline (3.83 g) in 3M-hydrochloric acid (32 ml.) at 0-5°. This mixture was added together with a solution of sodium acetate (7 g) in water (25 ml.) to a vigorously stirred solution

of benzoquinone (2.7 g) in acetone (125 ml.) at 10°, and the stirring was continued for 2 h. Water (100 ml.) was added and the resulting precipitate (A) was collected. The filtrate was concentrated to 200 ml., and shaken with chloroform to give an extract which was washed with water, dried, and evaporated to an oily solid which was combined with (A), and chromatographed on a column of silica gel. Benzene eluted a red solid which crystallised from ethanol to give 3',4'-dimethoxyphenylbenzoquinone (1.92 g) m.p. 133-134°.

Elution with benzene-chloroform (1:1) gave a violet solid which was subjected to p.l.c. using benzene-ethyl acetate (20:1). A red band (B) and two violet bands (C) and (D) were obtained. Band (B) gave a red solid which crystallised from chloroform-ethanol to give 2,5-di(3',4'-dimethoxyphenyl)benzoquinone as orange needles (60 mg) m.p. 194-195° (Found: M, 380.1255. $C_{22}H_{20}O_6$ requires M, 380.1260), $\lambda_{max.}(CHCl_3)$ 288 (log ε 4.29) and 440 nm (3.79), $\lambda_{infl.}(CHCl_3)$ 283 (log ε 4.27) and 367 nm (3.50); $\nu_{max.}$(Nujol) 1648 (quinone C = O) and 1260 cm^{-1} (ether C - O), $\nu_{max.}$ (2% $CHCl_3$) 1652 cm^{-1}; τ ($CDCl_3$) 6.07 (s, 12H, CH_3O), 3.10 (s, 2H, quinone-H), and 3.15-2.69 (m, 6H, Ar-H). Band (C) gave a solid which crystallised from ethanol to give 2,6-di(3',4'-dimethoxyphenyl)benzoquinone as violet needles (250 mg) m.p. 168-169.5° (Found: M, 380.1263.. $C_{22}H_{20}O_6$

requires M, 380.1260), $\lambda_{max.}$($CHCl_3$) 281 (log ε 4.26) and 460 nm (broad)(3.72), $\lambda_{infl.}$ 285 (log ε 4.24) and 354 nm (3.30); $\nu_{max.}$ (Nujol) 1647 (quinone C = O) and 1260 cm^{-1} (ether C - O), $\nu_{max.}$ (2% $CHCl_3$) 1665 and 1647 cm^{-1}; τ ($CDCl_3$) 6.08 (s, 12H, CH_3O), 3.15 (s, 2H, quinone-H), and 3.12-2.72 (m, 6H, Ar-H). Band (D) gave a violet solid which crystallised from chloroform-ethanol to give 2,3-di(3',4'-dimethoxyphenyl)benzoquinone as clusters of dark red rhombohedra (600 mg) m.p. 199-200.5° (Found: M, 380.1263. $C_{22}H_{20}O_6$ requires M, 380.1260), $\lambda_{max.}$ ($CHCl_3$) 283 (log ε 4.02) and 483 nm (broad)(3.38), $\lambda_{infl.}$ ($CHCl_3$) 286 (log ε 4.01); $\nu_{max.}$ (Nujol) 1660 and 1652 (both quinone C = O), and 1260 cm^{-1} (ether C - O), $\nu_{max.}$ (2% $CHCl_3$) 1658 cm^{-1}; τ ($CDCl_3$) 6.39 and 6.16 (both s, 6H, CH_3O), 3.09 (s, 2H, quinone-H), and 3.49-3.27 (m, 6H, Ar-H).

Arylation of 3',4'-dimethoxyphenylbenzoquinone with diazotised 3 ,4 -dimethoxyaniline.

(a) In acetic acid

A solution of sodium nitrite (0.3 g) in water (3 ml.) was added dropwise to a solution of 3,4-dimethoxyaniline (0.7 g) in 3M-hydrochloric acid (6 ml.) at 0-5°. The resulting solution was added to a vigorously stirred mixture of 3',4'-

dimethoxyphenylbenzoquinone (0.8 g), sodium acetate trihydrate (1.7 g), and glacial acetic acid (25 ml.), and stirring was continued for 3 h at 40°. Water (100 ml.) was added, the resulting precipitate (A) was collected and the filtrate was shaken with ether. The ether extract was washed with 10% aqueous sodium carbonate and with water, dried, and evaporated to give a red solid which was combined with (A). The following compounds were isolated by p.l.c. using benzene-ethyl acetate (20:1) as in the previous experiment: unchanged 3',4'-dimethoxyphenylbenzoquinone (200 mg); 2,6-di(3',4'-dimethoxyphenyl)benzoquinone (60 mg), and 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (80 mg).

(b) In aqueous acetone

A cooled solution of sodium nitrite (0.3 g) in water (3 ml.) was added dropwise to a solution of 3,4-dimethoxyaniline (0.7 g) in 3M-hydrochloric acid (6 ml.) at 0-5°. This solution was added to a vigorously stirred mixture of 3',4'-dimethoxyphenylbenzoquinone (0.73 g), sodium acetate (1.4 g), acetone (100 ml.), and water (100 ml.) at -5°. The mixture was kept at -5° for 30 min, stirred at room temperature for 2 h, concentrated to 100 ml., and shaken with chloroform. The chloroform extract was washed with water, dried, and

evaporated to give an oily precipitate from which the following compounds were obtained by p.l.c. as in the previous experiment: unchanged 3',4'-dimethoxyphenylbenzoquinone (170 mg); 2,5-di(3',4'-dimethoxyphenyl)benzoquinone (10 mg); 2,6-di(3',4'-dimethoxyphenyl)benzoquinone (40 mg); and 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (110 mg).

Chlorination of 2,5-di(3',4'-dimethoxyphenyl)benzoquinone

A mixture of 2,5-di(3',4'-dimethoxyphenyl)benzoquinone (43 mg) and concentrated hydrochloric acid (20 ml.) was boiled under reflux for 1.5 h, cooled, and poured into water (150 ml.) with vigorous stirring. The resulting mixture was shaken with chloroform, and the extract was washed with water and dried. The chloroform solution was shaken with iron (III) chloride (250 mg), washed with 2M-hydrochloric acid, and with water, and dried. Evaporation gave a red solid which on being subjected to p.l.c. using benzene-ethyl acetate (20:1) gave three coloured bands (A), (B), and (C).

Band (A) gave a red solid which crystallised from chloroform-ethanol to give 3,6-dichloro-2,5-di(3',4'-dimethoxyphenyl)-benzoquinone as golden crystals (2 mg) m.p. 300-301° (mixed m.p. 300-301° with an authentic sample prepared by the reaction

of 2,5-dichlorobenzoquinone with diazotised 3,4-dimethoxyaniline[86]). The product from band (B) crystallised from chloroform-ethanol to give 3-chloro-2,5-di(3',4',-di-methoxyphenyl)benzoquinone as a mixture of red needles and orange plates (15 mg) m.p. 208-209.5°. The red needles changed to orange above 130° (Found: M, 414.0866. $C_{22}H_{19}{}^{35}Cl\ O_6$ requires M, 414.0871), $\lambda_{max.}(CHCl_3)$ 260 (log ε 4.37), 283 (4.28), and 461 nm (3.67), $\lambda_{infl.}(CHCl_3)$ 360 nm (log ε 3.40); $\nu_{max.}$(Nujol) 1665 and 1643 cm^{-1} (both quinone C = O), and1260 cm^{-1} (ether C - O); τ ($CDCl_3$) 6.10 (s, 3H, CH_3O), 6.06 (s, 9H, CH_3O), and 3.08-2.81 (m, 7H, Ar-H and quinone-H). Band (C) gave unchanged 2,5-di(3',4'-dimethoxyphenyl)benzoquinone (10 mg).

Chlorination of 2,6-di(3',4'-dimethoxyphenyl)benzoquinone

A mixture of 2,6-di(3',4'-dimethoxyphenyl)benzoquinone (70 mg) and concentrated hydrochloric acid (20 ml.) was boiled under reflux for 1.5 h, cooled, and poured into water (100 ml.). The mixture was extracted with chloroform and treated with iron (III) chloride (250 mg) as in the previous experiment. Evaporation of the chloroform solution afforded a solid which on being subjected to p.l.c. using benzene-ethyl acetate (10:1) gave three violet bands (A), (B), and (C).

Band (A) afforded a violet solid which crystallised from chloroform-ethanol to give 3,5-dichloro-2,6-di(3',4'-dimethoxyphenyl)benzoquinone as deep violet micro-needles (6 mg) m.p. 212-213.5° (mixed m.p. 212.5-213° with an authentic specimen prepared by the reaction of 2,6-dichlorobenzoquinone with diazotised 3,4-dimethoxyaniline[89]). The product from band (B) crystallised from chloroform-ethanol to give 3-chloro-2,6-di(3',4'-dimethoxyphenyl)benzoquinone as dark-violet clusters (43 mg) m.p. 174.5-177° (Found: M, 414.0869. $C_{22}H_{19}{}^{35}ClO_6$ requires M, 414.0871, $\lambda_{max.}$ ($CHCl_3$) 257 (log ε 4.40), 280 (4.30), and 490 nm (3.66), $\lambda_{infl.}$ ($CHCl_3$) 318 (log ε 3.50); $\nu_{max.}$ (Nujol) 1658 (quinone C = O) and 1262 cm^{-1} (ether C - O); τ ($CDCl_3$) 6.10 (s, 6H, CH_3O), 6.06 (s, 6H, CH_3O) and 3.20-2.82 (m, 7H, Ar-H and quinone-H). Band (C) gave unchanged 2,6-di(3',4'-dimethoxyphenyl)benzoquinone (6 mg).

Chlorination of 3-chloro-2,6-di(3',4'-dimethoxyphenyl)-benzoquinone

A mixture of 3-chloro-2,6-di(3',4'-dimethoxyphenyl)benzoquinone (35 mg) and concentrated hydrochloric acid (20 ml.) was boiled under reflux for 0.5 h, cooled, and poured into

water (100 ml.). The mixture was extracted with chloroform, and the chloroform solution was treated with iron (III) chloride (250 mg) as in the previous experiment. Evaporation of the solution gave a solid which on being subjected to p.l.c. using benzene-ethyl acetate (9:1) gave two bands (A) and (B). The product from band (A) crystallised from chloroform-ethanol to give 3,5-dichloro-2,6-di(3',4'-dimethoxyphenyl)benzoquinone (5 mg). Band (B) gave unchanged 3-chloro-2,6-di(3',4'-dimethoxyphenyl)benzoquinone (20 mg).

CHAPTER 3

Reaction of benzoquinone with veratrole.

(a) Using aluminium chloride and carbon disulphide (Pummerer's reaction conditions[14]). A solution of veratrole (13.8 g) in carbon disulphide (50 ml.) was added dropwise to a stirred suspension of benzoquinone (16.2 g) and anhydrous aluminium chloride (26.6 g) in carbon disulphide (175 ml.) and the mixture was stirred for 26 h at room temperature. Ice (150 g) and 5M-hydrochloric acid (150 ml.) were added and the resulting mixture was stirred for 2 h and filtered to give a black

precipitate (A) and a dark brown filtrate. The filtrate was steam-distilled to remove carbon disulphide and unchanged veratrole (10 g). The residual brown precipitate (B) was collected, and the aqueous filtrate was shaken with ether to give extract (C). Steam distillation of the precipitate (A) gave benzoquinone (1.0 g), and an involatile residue which was collected and combined with (B), the aqueous filtrate was shaken with e ther and the extract was combined with (C).

The brown solid (B) was extracted successively with cold acetone (100 ml.), boiling acetone (30 ml.), and boiling toluene (150 ml.). The toluene solution was filtered hot, cooled, filtered to remove some brown amorphous material, and concentrated. The red solid (0.1 g) which separated, crystallised from toluene to give 10, 11-dimethoxytriphenylene-1,4:5,8-diquinone (28) (Pummerer's quinone) containing toluene of crystallisation, as clusters of dark red rhombohedra m.p. (evacuated capillary) 230-240° (decomp.) (lit.,[14] darkens at 245°, m.p. 290°) (Found: C, 72.2; H, 3.9; MeO, 15.4%. $C_{20}H_{12}O_6 + \frac{1}{2}C_7H_8$ requires C, 71.55; H, 4.1; 2MeO, 15.75%), $\lambda_{max.}(CHCl_3)$ 292 (log ε 3.91), 387 (3.74), and 467 nm (3.58), $\lambda_{infl.}(CHCl_3)$ 280 (log ε 3.95) and 494 nm (3.49); $\nu_{max.}$ (KCl) 1675 and 1650 (both quinone C = O), 1610 (C = C), and 1253 cm^{-1} (ether C - O); $(CDCl_3)$ 7.65 (s, 1.5H, CH_3 of toluene), 2.78

(s, 2.5H, Ar-H of toluene), 5.92 (s, 6H, CH_3O), 1.09 (s, 2H, Ar-H at C - 9 and C - 12) and an AB quartet centred at τ 2.94 and τ 3.13 (J 10Hz, 4H, quinone-H). The toluene of crystallisation was removed by heating a finely powdered sample at 140° and 0.1 Torr when the pure diquinone was obtained m.p. 250-255° (decomp.) (Found: C, 68.8; H, 3.5; MeO 19.9%; M, 348.0634. $C_{20}H_{12}O_6$ requires C, 68.95; H, 3.45; 2MeO, 17.8%; M, 348.0634), $\lambda_{max.}(CHCl_3)$ 293 (log ε 4.10), 386 (3.93), and 468 nm (3.78), $\lambda_{infl.}(CHCl_3)$ 279 (log ε 4.14) and 492 nm (3.70); $\nu_{max.}$(Nujol) 1675 and 1650 (both quinone C = O), 1615 (C = C) and 1258 cm^{-1} (ether C - O); τ ($CDCl_3$) 5.92 (s, 6H, CH_3O), 1.04 (s, 2H, Ar-H at C - 9 and C - 12), and an AB quartet centred at τ 2.94 and τ 3.13 (J10Hz, 4H, quinone-H). Combustions for C and H analysis were done slowly with vanadium pentoxide as catalyst. Examination of the acetone-soluble material by t.l.c. using benzene-ethyl acetate (10:3) showed the presence of more of the triphenylene diquinone, and a small amount was obtained by extraction with chloroform. No other crystalline material could be isolated.

Removal of the solvent from the ether extract (C) gave a mixture of phenols (9.7 g). Examination by t.l.c. using benzene-chloroform (1:4) showed the presence of two substances one of which corresponded to quinol. The mixture crystallised

from boiling chloroform giving quinol, m.p. 170° (lit.,[87] m.p. 170°). The motherliquor was filtered through a column of silica gel which was eluted with chloroform. Evaporation of the chloroform gave chloroquinol m.p. 106-107° (lit.,[88] m.p. 106°).

(b) Using aluminium chloride, carbon disulphide and excess benzoquinone.

A solution of veratrole (6.9 g) in carbon disulphide (50 ml.) was added slowly to a stirred mixture of benzoquinone (37.8 g), anhydrous aluminium chloride (33.4 g) and carbon disulphide (350 ml.). Stirring was continued for 26 h at room temperature and then ice (150 g) and 1M-sulphuric acid (200 ml.) were added. The resulting mixture was stirred for 2 h. The following compounds were isolated as in the previous experiment: Pummerer's quinone (0.55 g), quinol (20 g), veratrole (4.7 g), and benzoquinone (8 g).

(c) Using aluminium chloride and tetrachloroethane.

A solution of veratrole (3.45 g) in dry tetrachloroethane (25 ml.) was added slowly to a stirred suspension of benzoquinone (18.9 g) and anhydrous aluminium chloride (13.35 g) in dry tetrachloroethane (100 ml.). The mixture was stirred at

room temperature for 48 h. Ice (75 g) and 5M-hydrochloric acid (75 ml.) were added, and the resulting mixture was stirred for 2 h. Steam-distillation left an involatile, dark oil from which no crystalline material could be isolated.

(d) Using zirconium (IV) chloride and carbon disulphide

A mixture of veratrole (1 g), benzoquinone (5 g), anhydrous zirconium (IV) chloride (5 g), and carbon disulphide (100 ml.) was shaken for 1 h and kept in a stoppered flask at room temperature for 1 day. Ice (50 g) and 1M-sulphuric acid (50 ml.) were added and the mixture was steam-distilled. The distillate gave a mixture (1.7 g) of veratrole and benzoquinone. The involatile residue was extracted with chloroform and the resulting red solution was examined by t.l.c. using benzene-ethyl acetate (10:3). A spot corresponding to Pummerer's quinone was obtained, but there was insufficient material to isolate the compound.

(e) Using titanium (IV) chloride and carbon disulphide.

Anhydrous titanium (IV) chloride (2 ml.) was added to a suspension of veratrole (1 g) and benzoquinone (5 g) in carbon disulphide (100 ml.). The mixture, which became very dark, was shaken for 1 h and kept in a stoppered flask at room

temperature for 1 day. Ice (50 g) and 1M-sulphuric acid (50 ml.) were added and the resulting mixture was steam-distilled. The distillate gave veratrole (1 g) but no benzoquinone, while the dark oily residue gave no crystalline material.

(f) Using aqueous sulphuric acid

A mixture of veratrole (3.45 g), benzoquinone (13.6 g), and 70% aqueous sulphuric acid (100 ml.) was shaken for 2 h, kept in a stoppered flask at room temperature for 1 week, and diluted with water (250 ml.). After being kept for 1 day, the grey-green precipitate was collected and steam-distilled when veratrole (1 g) but no benzoquinone was obtained. The involatile amorphous precipitate showed a strong broad band at 3400 cm^{-1} (phenolic-OH) in the i.r., but could not be crystallised.

(g) Using polyphosphoric acid

A mixture of veratrole (2.3 g), benzoquinone (9 g), and polyphosphoric acid (100 g) was stirred at 70° for 6 h. The resulting black syrup was poured into water (500 ml.) and left overnight. Filtration gave a dark solid which was extracted with acetone and chloroform. Evaporation of the extracts gave black solids from which no crystalline material could be obtained.

Reductive acetylation of 10,11-dimethoxytriphenylene-1,4:5,8-diquinone

10,11-Dimethoxytriphenylene-1,4:5,8-diquinone (105 mg) was boiled under reflux for 45 min with acetic anhydride (5 ml), zinc dust (210 mg), and triethylamine (0.2 ml). The pale yellow mixture was poured into hot water, stirred vigorously for 10 min, and shaken with chloroform. The chloroform extract was washed with 10% aqueous sodium carbonate, and with water, and dried. Evaporation of the solution gave a pale yellow solid (100 mg) which crystallised from toluene and then from chloroform-ethanol to give 1,4,5,8-tetra-acetoxy-10,11-dimethoxytriphenylene (79) as needles m.p. 247-249° (Found: C, 64.3; H, 4.3; MeO, 12.2; AcO, 46.2%. $C_{28}H_{24}O_{10}$ requires C, 64.6; H, 4.65; 2MeO, 11.9; 4AcO 45.4%), $\lambda_{max.}$ ($CHCl_3$) 279 (log ε 4.77) and 372 nm (3.33), $\lambda_{infl.}$ ($CHCl_3$) 275 (log ε 4.75), 305 (4.12), 317 (4.07), 326 (4.01) and 350 nm (3.45), $\lambda_{max.}$ (EtOH) 219 (log ε 4.40), 275 (4.86), and 368 nm (3.42), $\lambda_{infl.}$ (EtOH) 269 (log ε 4.84), 304 (4.19), 313 (4.14), 325 (4.07), and 348 nm (3.59); $\nu_{max.}$ (KCl) 1748 (acetate C=O) and 1200 cm^{-1} (acetate C-O), τ ($CDCl_3$) 7.76 (s, 6H, CH_3CO_2 at C-4 and C-5), 7.56 (s, 6H, CH_3CO_2 at C-1 and C-8), 5.95 (s, 6H, CH_3O), 2.70 (s, 4H, Ar-H at C-2, C-3, C-6, and C-7), and 1.54 (s, 2H, Ar-H at C-9 and C-12).

Attempted reductive methylation of 10,11-dimethoxytriphenylene-1,4:5,8-diquinone

(a) Using sodium dithionite and dimethyl sulphate

10,11-Dimethoxytriphenylene-1,4:5,8-diquinone (260 mg) was ground with sodium dithionite (3.6 g), water (10 ml), and acetone (5 ml) until the red colour of the quinone had disappeared. The mixture was poured into water (100ml) and shaken with chloroform to give an extract which was washed with water and dried in an atmosphere of nitrogen. Evaporation yielded a brown solid which was mixed with freshly fused potassium carbonate (1.0 g), acetone (50 ml), and redistilled dimethyl sulphate (6 ml). The mixture was heated under reflux for 4 h in an atmosphere of nitrogen, the acetone was evaporated under reduced pressure, and the brown oily residue was shaken for 30 min with 2M-sodium hydroxide (50 ml). Extraction with chloroform gave a small amount of dark oily solid from which crystalline material could not be obtained.

(b) Using zinc-acetic acid and diazomethane

A mixture of 10,11-dimethoxytriphenylene-1,4:5,8-diquinone (100 mg), zinc dust (450 mg), glacial acetic acid (5 ml), and water (0.5 ml) was boiled under reflux in an atmosphere of

nitrogen for 30 min, and the resulting pale yellow mixture was poured into water. The aqueous suspension was shaken with ether and the extract was washed with water and dried in an atmosphere of nitrogen, and added to an ethereal solution of diazomethane. Next day the ether was evaporated to give a dark brown solid which could not be crystallised.

(c) Using sodium dithionite and alkaline dimethyl sulphate.

A mixture of 10,11-dimethoxytriphenylene-1,4:5,8-diquinone (230 mg), chloroform (50 ml) and 10% aqueous sodium dithionite (10 ml) was shaken until the red colour of the quinone had disappeared. The chloroform was evaporated by passing a stream of nitrogen through the mixture, and dimethyl sulphate (2.5 ml) was added followed by 50% aqueous sodium hydroxide. The mixture was stirred at room temperature for 5 h under an atmosphere of nitrogen, and ice (50 g) was added. Extraction with chloroform gave a dark oil from which no crystalline material could be obtained.

Attempted reaction of methylbenzoquinone with veratrole.

A solution of veratrole (5.52 g) in carbon disulphide (50 ml) was added dropwise to a stirred suspension of methylbenzoquinone (24.4 g) and anhydrous aluminium chloride (26.7 g) in carbon disulphide (200 ml). Stirring was continued for

48 h at room temperature, then ice (150 g) and 5M-hydrochloric acid (150 ml) were added. The resulting mixture was stirred for 2 h and filtered to give a dark violet precipitate (A) and a filtrate. Steam distillation of the filtrate removed carbon disulphide, and veratrole (4 g). The residual aqueous solution was shaken with ether to give extract (B). Steam distillation of the precipitate (A) removed unchanged veratrole and methylbenzoquinone (2 g). The residual violet solid (C) was collected (13 g), and the aqueous filtrate was shaken with ether and the ethereal extract was combined with (B). Evaporation of the ethereal extract (B) gave crude methylquinol. The violet solid (C) showed $\nu_{max.}$ (Nujol) at 3340 (phenolic OH) and 1640 cm^{-1} (quinone C=O), and was 2-methyl-5-(2',5'-dihydroxy-4'-methylphenyl)benzoquinone[38] (82).

A portion (0.5 g) of the violet solid (C) was heated under reflux for 1 h with acetic anhydride (20 ml), zinc dust (1 g), and triethylamine (0.25 ml). The mixture was poured into hot water (100 ml), stirred vigorously for 15 min, and extracted with chloroform. The extract was washed with 10% aqueous sodium carbonate and water, dried, and evaporated. The residue crystallised from ethanol to give 2,5,2',5'-tetra-acetoxy-4,4'-dimethylbiphenyl (83) as needles (0.5 g) m.p. 138-139° (lit.,[103] m.p. 137°).

Another portion (3.0 g) of the violet solid (C) was added, with vigorous stirring, to concentrated nitric acid (5 ml) at room temperature. Water (100 ml) was added and the resulting solid was collected, washed thoroughly with water, and crystallised from ethanol to give 4,4'-dimethoxybiphenyl-2,5:2',5'-diquinone (84) as golden needles (1.5 g) m.p. 168-170° (decomp.) [lit.,[37] m.p. 168-169°(decomp.)], $\nu_{max.}$(Nujol) 1660 cm^{-1} (quinone C=O); τ ($CDCl_3$) 7.93 (d, J 1.5Hz, 6H, CH_3), 3.31 (q, J 1.5Hz, 2H, quinone-H), and 3.2 (s, 2H, quinone-H).

Attempted reaction of phenylbenzoquinone with veratrole

A mixture of phenylbenzoquinone (12.9 g), veratrole (1.38g), anhydrous aluminium chloride (6.67 g), and carbon disulphide (300 ml) was stirred for 48 h at room temperature. Ice (100 g) and 1M-sulphuric acid (50 ml) were added, and the resulting mixture was stirred for 1 h, then steam-distilled to give unchanged veratrole (1 g). The residue was examined by t.l.c. using benzene-chloroform (1:4). Only two spots were observed, one corresponding to phenylbenzoquinone and the other to phenylquinol.

Attempted reaction of 1,4-naphthaquinone with veratrole

(see p. 256).

Attempted reaction of 4,4'-diphenoquinone with veratrole.

(a) In the presence of aluminium chloride

A mixture of 4,4'-diphenoquinone (4.5 g), veratrole (4 g), anhydrous aluminium chloride (8.4 g) and carbon disulphide (250 ml) was stirred at room temperature for 24 h. Ice (100 g) and 5M-hydrochloric acid (40 ml) were added and the mixture, which became deep blue, was stirred for 2 h, evaporated to remove carbon disulphide, and filtered to give a blue precipitate (A). Extraction of the filtrate with ether gave unchanged veratrole (3 g). The blue precipitate showed $\nu_{max.}$ (Nujol) at 3300 (phenolic OH) and 1622 cm^{-1} (quinone C=O). It dissolved in chloroform to give a brown solution which, by t.l.c. using chloroform, was shown to contain only 4,4'-diphenoquinone and 4,4'-dihydroxybiphenyl.

Diphenoquinone (50 mg) was heated under reflux with acetic acid (5 ml) and zinc dust (100 mg) for 5 min. The solution was decanted into water (20 ml) and the resulting precipitate was collected, washed with water, and dried to give 4,4'-dihydroxybiphenyl, $\nu_{max.}$ (Nujol) 3430 cm^{-1} (phenolic OH). A solution of 4,4'-dihydroxybiphenyl (20 mg) and 4,4'-dipheno-

quinone (18 mg) in chloroform was allowed to evaporate to dryness. The residual blue quinhydrone was identical (i.r.) with the blue precipitate (A).

(b) In aqueous sulphuric acid

A suspension of 4,4'-diphenoquinone (4 g) and veratrole (5 g) in 70% v/v aqueous sulphuric acid (100 ml) was shaken vigorously for 6 h and kept for 1 week. The mixture was diluted with water (300 ml) and filtered to give a precipitate of crude 4,4'-diphenoquinone (4 g) and a filtrate which on being extracted with ether afforded unchanged veratrole (5 g).

Reaction of 2,3-dichlorobenzoquinone with veratrole

Anhydrous aluminium chloride (3.5 g) was added in small portions to a stirred solution of 2,3-dichlorobenzoquinone (2.5 g) and veratrole (2 g) in carbon disulphide (100 ml).. Stirring was continued for 24 h at room temperature, then ice (50 g) and 1M-sulphuric acid (20 ml) were added. The resulting mixture was stirred for 2 h and filtered to give a dark precipitate (A) (2.2g) and a filtrate. Steam-distillation of the filtrate gave carbon disulphide and unchanged veratrole (1.2 g). The residual involatile solid (0.2 g) was collected and combined with (A), while the aqueous filtrate was extracted with ether to give a mixture (0.7 g) of 2,3-dichlorobenzo-

quinone and 2,3-dichloroquinol.

The precipitate (A) was washed with ethanol (200 ml) and extracted with benzene (250 ml) to give a pale blue-violet solid (B), (230 mg). Evaporation of the benzene gave a dark violet solid which crystallised from chloroform-ethanol to give 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzo-quinone (57) as violet needles (430 mg) m.p. 204-205.5°, mixed m.p. 204-205° with an authentic specimen prepared by the reaction of 2,3-dichlorobenzoquinone with diazotised 3,4-dimethoxyaniline (p.174). A portion (100 mg) of the blue-violet solid (B) was dissolved in benzene-chloroform (1:4) (17 ml) and chromatographed on a column of silica gel. An orange band (C) was eluted using benzene, and a pale violet band (D) using benzene-chloroform (1:4); a blue band (E) remained at the top of the column.

Evaporation of the solvent from the eluted band (C) gave a red solid which crystallised from a small volume of ethanol to give 2,3,6,7-tetrachloro-10,11-dimethoxytri-phenylene-1,4:5,8-diquinone (87) as red micro-crystals (3 mg) m.p. 326°(decomp.) (Found: M, 483.9080. $C_{20}H_8{}^{35}Cl_4O_6$ requires M, 483.9075), $\lambda_{max.}$($CHCl_3$) 321 (log ε 3.99), 418 (3.76), and 488 nm (3.71), $\lambda_{infl.}$($CHCl_3$) 276 (log ε 4.31) and 300 nm (4.13); $\nu_{max.}$(KBr) 1690 and 1678 (both quinone C=O),

1600 (C=C), and 1258 cm^{-1} (ether C-O). Evaporation of the solvent from the eluted band (D) gave a pale violet solid which crystallised from chloroform-ethanol to give 2,3,6,7,10,11-hexamethoxytriphenylene (80 mg) m.p. and mixed m.p. 315-317° (lit.,[31] 317.5-318.5°). The blue band (E) together with the adsorbent at the top of the column was removed, boiled with chloroform, filtered and evaporated to give crude 2,5,6,9,12,13-hexamethoxydibenzo[fg, op]naphthacene-1,10-quinone (19) as a dark blue solid (<1 mg), $\lambda_{max.}(CHCl_3)$ 315, 554, 640 and 690 nm, $\lambda_{infl.}(CHCl_3)$ 275 and 530 nm. [lit.,[31] $\lambda_{max.}(CHCl_3)$ 281, 294, 317, 560, 655, and 715 nm, $\lambda_{infl.}(CHCl_3)$ 273 and 530 nm].

Reaction of chlorobenzoquinone with veratrole

(a) Anhydrous aluminium chloride (3.5 g) was added in small portions to a stirred solution of chlorobenzoquinone (4 g) and veratrole (0.69 g) in carbon disulphide (200 ml). Stirring was continued for 24 h. at room temperature, then ice (50 g) and 1M-sulphuric acid (20 ml) were added. The resulting mixture was stirred for 2 h and filtered to give a dark violet solid (A) and a filtrate which was steam-distilled to remove carbon disulphide and unchanged veratrole (0.25 g). The residual solid was collected and combined with (A), while the aqueous filtrate was extracted with ether

to give a mixture (2 g) of chloroquinol and chlorobenzoquinone.

The combined solids were washed with ethanol (50 ml), extracted with chloroform and filtered. Evaporation of the filtrate gave a red solid which could not be crystallised from toluene, n-hexane or chloroform-ethanol. In each case considerable darkening of the solution occurred, and the solid precipitated on the sides of the vessel. On being subjected to p.l.c. using benzene-ethyl acetate (10:3), the red solid gave one main orange band which afforded a mixture (100 mg) of the three isomeric 2,6-, 3,6-, and 2,7-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinones (88), (89), and (90).

The mixture of isomers was subjected to p.l.c. using benzene-ethyl acetate (10:1) when a broad orange band was obtained. The slower moving portion of this band was removed and crystallised from chloroform-ethanol to give a mixture of 3,6-, and 2,7-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinones as red microcrystals (Found: M, 415.9861. $C_{20}H_{10}{}^{35}Cl_2O_6$ requires M, 415.9854), $\lambda_{max.}$ ($CHCl_3$) 297 (log ε 4.23), 400 (3.87), and 476 nm (3.76), $\lambda_{infl.}$ ($CHCl_3$) 275 (log ε 4.35) and 490 nm (3.73); $\nu_{max.}$ (KBr) 1690, 1680, and 1650 (all quinone C=O), 1618 (C=C), and

1260 cm^{-1} (ether C-O); τ ($CDCl_3$) 5.91 (s, 6H, CH_3O), 2.92 (s, quinone-H at C-2 and C-7), 2.73 (s, quinone-H at C-3 and C-6), and 1.09 (s, 2H, Ar-H at C-9 and C-12). The ratio of the signals at τ 2.92 and τ 2.73 was 6:1.

The remainder of the orange band was again subjected to p.l.c. using benzene. The faster moving portion of the resulting orange band gave a red solid which crystallised from chloroform-ethanol to give 2,6-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone as red microcrystals (5 mg) m.p. 202-205° (decomp.) (Found: M, 415.9853. $C_{20}H_{10}{}^{35}Cl_2O_6$ requires M, 415.9854), $\lambda_{max.}$ ($CHCl_3$) 405 (log ε 3.86) and 480 nm (3.76), $\lambda_{infl.}$ 273 (log ε 4.38) and 295 nm (4.19); τ ($CDCl_3$) 5.92 (s, 6H, CH_3O), 2.94 (s, 1H, quinone-H at C-7), 2.78 (s, 1H, quinone-H at C-3), and 1.09 (s, 2H, Ar-H at C-9 and C-12).

(b) Alternative procedure A solution of veratrole (1.38 g) in carbon disulphide (20 ml) was added slowly to a stirred suspension of chlorobenzoquinone (7.13 g) and anhydrous aluminium chloride (6.8 g) in carbon disulphide (200 ml). Stirring was continued for 48 h, then ice (100 g) and 1M-sulphuric acid (50 ml) were added. The resulting mixture was stirred for 2 h and filtered to give a precipitate and a filtrate (A).

The precipitate was washed with ethanol, extracted with chloroform, and the chloroform extract was filtered through a short column of alumina. Evaporation of the solvent gave a mixture of 3,6- and 2,7-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinones as a red crystalline solid (100 mg), τ ($CDCl_3$) 5.94 (s, 6H, CH_3O), 2.99 (s, quinone-H at C-2 and C-7), 2.77 (s, quinone-H at C-3 and C-6), and 1.17 (s, Ar-H at C-9 and C-12). The ratio of the signals at τ 2.99 and τ 2.77 was 7:1. A portion (90 mg) of this solid was heated under reflux for 45 min. with acetic anhydride (6 ml), zinc dust (200 mg), and triethylamine (0.2 ml). The resulting mixture was poured into hot water, and the aqueous suspension was shaken with chloroform to give an extract which was washed with 10% aqueous sodium carbonate and with water, and dried. Evaporation of the solvent gave a pale yellow solid (110 mg) which crystallised from chloroform-ethanol to give 1,4,5,8-tetra-acetoxy-3,6-dichloro-10,11-dimethoxytriphenylene (93) as needles (80 mg) m.p. 216.5-217.5° (Found: C, 56.9; H, 3.7%; M, 588.0591. $C_{28}H_{22}Cl_2O_{10}$ requires C, 57.05; H, 3.75%. $C_{28}H_{22}{}^{35}Cl_2O_{10}$ requires M, 588.0590), $\lambda_{max.}$ ($CHCl_3$) 284 (log ε 4.85), 364 (3.52), and 381 nm (3.49), $\lambda_{infl.}$ ($CHCl_3$) 277 (log ε 4.77), 307 (4.17), 318 (4.13) and 331 nm (4.05); $\nu_{max.}$ (Nujol) 1760

(acetate C=O) and 1190 cm^{-1} (acetate C-O); τ ($CDCl_3$) 7.69 (s, 6H, CH_3CO_2 at C-4 and C-5), 7.57 (s, 6H, CH_3CO_2 at C-1 and C-8), 5.98 (s, 6H, CH_3O), 2.57 (s, 2H, Ar-H at C-2 and C-7), and 1.67 (s, 2H, Ar-H at C-9 and C-12).

The filtrate (A) was evaporated to remove carbon disulphide, veratrole and chlorobenzoquinone. The residual oily precipitate was collected and extracted with ethanol (100 ml) to give a solid residue and a filtrate (B). The residue, on being subjected to p.l.c. using benzene-ethyl acetate (10:3), gave two coloured bands. The slower moving band afforded a red solid which crystallised from chloroform-ethanol to give 3-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (34 mg) m.p. 200.5-201.5°, mixed m.p. 200-201° with an authentic sample prepared by the reaction of chlorobenzoquinone with diazotised 3,4-dimethoxyaniline (p. 167). The faster moving band gave a mixture of the three isomeric 2,6-, 3,6-, and 2,7-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinones as a red solid. This solid (90 mg) was heated under reflux for 45 min with acetic anhydride (7 ml), zinc dust (200 mg), and triethylamine (0.2 ml). The mixture was poured into water and extracted with chloroform. Evaporation of the chloroform gave a pale yellow solid which by p.l.c. using benzene-chloroform (1:4) afforded two bands which

fluoresced on exposure to u.v. light. The slower moving band gave a solid which crystallised from chloroform-ethanol to give 1,4,5,8-tetra-acetoxy-3,6-dichloro-10,11-dimethoxytriphenylene (30 mg) m.p. and mixed m.p. 216-217°. The faster moving band gave a mixture (66 mg) of the 2,6- and 2,7-dichloro-1,4,5,8-tetra-acetoxy-10,11-dimethoxytriphenylenes which was crystallised from toluene (3 times) and from chloroform-ethanol to give 1,4,5,8-tetra- acetoxy-2,6-dichloro-10,11-dimethoxytriphenylene (94) as needles (20 mg) m.p. 227-229° (Found; M, 588.0591. $C_{28}H_{22}{}^{35}Cl_2O_{10}$ requires M, 588.0590), $\lambda_{max.}(CHCl_3)$ 288 (log ε 4.86) and 381 nm (3.38), $\lambda_{infl.}(CHCl_3)$ 277 (log ε 4.76), 320 (4.14), 335 (4.04), and 360 nm (3.49); $\nu_{max.}$(KCl) 1770 (acetate C=O) and 1180 cm^{-1} (acetate C-O); τ ($CDCl_3$) 7.83 (s, 3H, CH_3CO_2 at C-4 or C-5), 7.62 (s, 3H, CH_3CO_2 at C-5 or C-4), 7.55 (s, 6H, CH_3CO_2 at C-1 and C-8), 5.98 (s, 6H, CH_3O), 2.61 (s, 1H, Ar-H at C-3 or C-7), 2.46 (s, 1H, Ar-H at C-7 or C-3), 1.69 (s, 1H, Ar-H at C-9 or C-12), and 1.57 (s, 1H, Ar-H at C-12 or C-9). A pure sample of 1,4,5,8-tetra-acetoxy-2,7-dichloro-10,11-dimethoxytriphenylene (95) could not be isolated.

The ethanol filtrate (B) was concentrated and the resulting precipitate was collected and subjected to p.l.c.

using benzene-ethyl acetate (10:3) when two bands were obtained, which were orange and red respectively. The orange band gave a mixture of the three isomeric dichlorotriphenylenediquinones. The product from the red band was crystallised from ethanol to give a mixture m.p. 144-147° of 5- and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones. The i.r. spectrum of the mixture was identical with that of an authentic mixture m.p. 144-148° prepared from chlorobenzoquinone and diazotised 3,4-dimethoxyaniline (p. 167).

4,4'-Dichloro-2,5-dimethoxybiphenyl-2',5'-quinone[16]

A solution of sodium dichromate (20 g) in water (75 ml) was added slowly to a stirred solution of 1-chloro-2,5-dimethoxybenzene (12 g) in glacial acetic acid (140 ml), water (24 ml), and concentrated sulphuric acid (16 ml) at 10°. The resulting violet mixture was left at room temperature for 30 min. The precipitate was collected, washed with water, and crystallised from ethanol to give 4,4'-dichloro-2,5-dimethoxybiphenyl-2',5'-quinone as a mixture of violet plates and needles (7.5 g) m.p. 178-179° (lit.,[16] 174-175°), $\nu_{max.}$ (Nujol) 1668 cm^{-1} (quinone C=O); τ ($CDCl_3$) 6.27 (s, 3H, CH_3O), 6.16 (s, 3H, CH_3O), 3.26, 3.06, 3.02 and 2.95 (all s, 1H, Ar-H or quinone-H).

4,4'-Dichlorobiphenyl-2,5:2',5'-diquinone[16]

4,4'-Dichloro-2,5-dimethoxybiphenyl-2',5'-quinone (7 g) was added portionwise, with vigorous stirring, to concentrated nitric acid (10 ml) at room temperature. Water (100 ml) was added and the yellow solid was collected, washed with water, and crystallised from chloroform-ethanol to give 4,4'-dichlorobiphenyl-2,5:2',5'-diquinone (96) as yellow needles (5.5 g) m.p. 199-200.5° (lit.,[16] 194-195° from glacial acetic acid), $\nu_{max.}$ (Nujol) 1665 and 1650 cm^{-1} (both quinone C=O); τ ($CDCl_3$) 3.03 and 2.91 (both s, 2H, quinone-H).

Reaction of 4,4'-dichlorobiphenyl-2,5:2',5'-diquinone with veratrole

A solution of veratrole (0.7 g) in carbon disulphide (50 ml) was added dropwise to a stirred suspension of 4,4'-dichlorobiphenyl-2,5:2',5'-diquinone (2.83 g), and anhydrous aluminium chloride (4 g) in carbon disulphide (100 ml). Stirring was continued for 24 h at room temperature and then ice (30 g) and 1M-sulphuric acid (30 ml) were added. The resulting mixture was stirred for 1.5 h and evaporated to remove carbon disulphide and unchanged veratrole (0.25 g). The residual mixture was filtered and the resulting solid was washed with water and extracted with acetone (75 ml).

Filtration gave a pale yellow solid (A), and evaporation of the acetone filtrate gave another solid (0.58 g) which by t.l.c. was a mixture of 4,4'-dichlorobiphenyl-2,5:2',5'-diquinone and 4,4'-dichloro-2,5:2',5'-tetrahydroxybiphenyl. When this was oxidised with concentrated nitric acid 4,4'-dichlorobiphenyl-2,5:2',5'-diquinone was obtained.

The yellow solid (A) was extracted with chloroform (100 ml) and filtered to give 4,4'-dichlorobiphenyl-2,5:2',5'-diquinone (1 g). The filtrate was concentrated and passed through a column of silica gel using benzene and then benzene-chloroform (1:4). Evaporation of the solvent from the benzene fraction gave 4,4'-dichlorobiphenyl-2,5:2',5'-diquinone, while the benzene-chloroform fraction afforded a solid which crystallised from chloroform-ethanol to give 2,3,6,7,10,11-hexamethoxy-triphenylene (250 mg) m.p. and mixed m.p. 315° (lit.,[31] 317.5-318.5°).

Attempted reaction of benzoquinone with 1,2,3-trimethoxybenzene

A suspension of benzoquinone (18.9 g), 1,2,3,-trimethoxy-benzene (4.2 g), and anhydrous aluminium chloride (16.7 g)in carbon disulphide (150 ml) was stirred at room temperature for 24 h. Ice (150 g) and 1M-sulphuric acid were added and stirring was continued for 2 h. The product was steam-

distilled to remove carbon disulphide, benzoquinone, and 1,2,3-trimethoxybenzene. The residual oily precipitate was collected and the aqueous filtrate was extracted with ether. The ether extract, on evaporation, gave quinol (9 g), but no crystalline material could be obtained from the oily precipitate.

Reaction of benzoquinone with 3',4'-dimethoxyphenylbenzoquinone

A solution of 3',4'-dimethoxyphenylbenzoquinone (0.122 g) in carbon disulphide (100 ml) was added dropwise to a stirred mixture of benzoquinone (0.54 g), anhydrous aluminium chloride (1.0 g), and carbon disulphide (50 ml). Stirring was continued for 24 h at room temperature, then ice (20 g) and 1M-sulphuric acid (20 ml) were added. The resulting mixture was stirred for 1 h and evaporated to remove carbon disulphide and unchanged benzoquinone. The aqueous layer was decanted and the residual red oil was subjected to p.l.c. using benzene. Three bands were obtained which were red, orange, and brown respectively. The red band gave unchanged 3',4'-dimethoxyphenylbenzoquinone (20 mg), while the orange band gave 10,11-dimethoxytriphenylene-1,4:5,8-diquinone (28 mg)(u.v.).

The brown band gave a solid (21 mg) which was dissolved in chloroform and filtered through a short column of alumina.

Evaporation of the chloroform solution afforded a red solid which crystallised from chloroform-ethanol to give a mixture of 2- and 3- (3',4'-dimethoxy-phenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinones (97) and (98) as clusters of red crystals (15 mg) m.p. 210-215° (decomp.) (Found: M, 484.1160. $C_{28}H_{20}O_8$ requires M, 484.1158), $\lambda_{max.}(CHCl_3)$ 298 (log ε 4.33), 383 (3.98), and 470 nm (3.97), $\lambda_{infl.}(CHCl_3)$ 290 (log ε 4.31) and 490 nm (3.91); $\nu_{max.}$(Nujol) 1682, 1660, and 1645 (all quinone C=O), 1600 (C=C), and 1260 cm^{-1} (ether C-O); τ ($CDCl_3$) 6.03 (s, 3H, CH_3O at C-3' or C-4'), 6.00 (s, 3H, CH_3O at C-4' or C-3'), 5.93 (s, 3H, CH_3O at C-10 or C-11), 5.91 (s, 3H, CH_3O at C-11 or C-10), 3.13-2.62 (m, 6H, Ar-H and quinone-H), 1.03 (s, 1H, Ar-H at C-9 or C-12) and 0.95 (s, 1H, Ar-H at C-12 or C-9). This mixture was subjected to p.l.c. using benzene-ethyl acetate (10:3) when only one orange band was obtained. The band was divided into two parts, each was removed separately from the plates and the i.r. spectra of the resulting products were obtained. The spectra of the two products were essentially the same as that of the original mixture apart from slight differences in the relative intensities of the peaks.

Reaction of benzoquinone with 2-(3',4'-dimethoxyphenyl)-1,4-dihydroxybenzene

A solution of 3',4'-dimethoxyphenylbenzoquinone (0.75 g) in ether (400 ml) was shaken with 5% aqueous sodium dithionite (200 ml) until the red colour of the quinone disappeared. The ethereal solution was washed with water, dried and evaporated to give 2-(3',4'-dimethoxyphenyl)-1,4-dihydroxybenzene as a crystalline solid (0.65 g), $\nu_{max.}$ 3460 and 3400 cm^{-1} (phenolic OH).

A suspension of benzoquinone (1.08 g), 2-(3',4'-dimethoxyphenyl)-1,4-dihydroxybenzene (0.246 g), and anhydrous aluminium chloride (1.34 g) in carbon disulphide (200 ml) was stirred at room temperature for 20 h. Ice (20 g) and 1M-sulphuric acid (20 ml) were added, and the resulting mixture was stirred for 1 h and evaporated to remove carbon disulphide and benzoquinone (0.65 g). The residual red precipitate was subjected to p.l.c. using benzene to give a red band and an orange band. The product from the red band crystallised from ethanol to give 3',4'-dimethoxyphenylbenzoquinone (90 mg). The orange band gave a red solid which crystallised from chloroform-ethanol to give 10,11-dimethoxytriphenylene-1,4:5,8-diquinone (u.v.) as red micro-crystals (40 mg).

Reactions of 3',4'-dimethoxyphenylbenzoquinone

a) With aluminium chloride and carbon disulphide

A mixture of 3',4'-dimethoxyphenylbenzoquinone (320 mg), anhydrous aluminium chloride (1 g), and carbon disulphide (200 ml) was stirred at room temperature for 48 h. Ice (50 g) and 1M-sulphuric acid (20 ml) were added and the mixture was stirred for 1 h and evaporated to remove carbon disulphide. The brown residue was collected, shaken with chloroform, and the resulting extract was filtered through a short column of alumina. Evaporation of the eluate afforded a red solid which, on being subjected to p.l.c. using benzene-ethyl acetate (10:3), gave a red band and an orange band. The red band gave unchanged 3',4'-dimethoxyphenylbenzoquinone (20 mg), while the orange band afforded a red solid which crystallised from chloroform-ethanol to give a mixture of 2- and 3-(3',4'-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinones (u.v.) as red micro-crystals (18 mg).

b) With aluminium chloride and benzene

A mixture of 3',4'-dimethoxyphenylbenzoquinone (100 mg), anhydrous aluminium chloride (1 g), and dry benzene (50 ml) was stirred at room temperature for 20 h. Ice (20 g) and 5M-hydrochloric acid (20 ml) were added and the mixture was

evaporated to remove benzene, then shaken with chloroform. Examination of the chloroform extract by t.l.c. showed only one spot which corresponded to unchanged 3',4'-dimethoxyphenylbenzoquinone.

c) With aluminium chloride and nitromethane

Anhydrous aluminium chloride (1 g) was added portionwise, with shaking, to a solution of 3',4'-dimethoxyphenyl-benzoquinone (100 mg) in nitromethane (5 ml) at 0°. The dark mixture was kept for 24 h at room temperature, ice (30 g) and 1M-sulphuric acid (20 ml) were added, the resulting black precipitate was collected and the filtrate was extracted with chloroform. Examination of both the precipitate and the chloroform extract by t.l.c. showed the absence of 3',4'-dimethoxyphenylbenzoquinone, and also of 2- and 3-(3',4'-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinones.

d) With zirconium (IV) chloride and carbon disulphide.

A mixture of 3',4'-dimethoxyphenylbenzoquinone (100 mg), anhydrous zirconium (IV) chloride (1 g), and carbon disulphide (70 ml) was stirred at room temperature for 20 h. Ice (50 g) and 1M-sulphuric acid (10 ml) were added and the mixture was evaporated to remove carbon disulphide. Filtration of the

aqueous residue gave only crude 3',4'-dimethoxyphenylbenzoquinone (85 mg).

e) With boron trifluoride etherate.

3',4'-Dimethoxyphenylbenzoquinone (50 mg) was added with shaking to boron trifluoride-ether complex (10 ml). The dark solution was kept for 3 days at room temperature, ice (20 g) and 1M-sulphuric acid were added, and the mixture was shaken with chloroform. Examination of the chloroform solution by t.l.c. showed the absence of 3',4'-dimethoxyphenylbenzoquinone, and also of 2- and 3-(3',4'-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinones.

f) With tin (IV) chloride and benzene.

A mixture of anhydrous tin (IV) chloride (1 ml) and dry benzene (5 ml) was added dropwise to a stirred solution of 3',4'-dimethoxyphenylbenzoquinone (100 mg) in dry benzene (50 ml) at 0°. The dark solution was stirred at room temperature for 20 h, ice (20 g) and 5M-hydrochloric acid (20 ml) were added, and the mixture was evaporated to remove benzene. The resulting dark red solid was collected and subjected to p.l.c. using benzene-ethyl acetate (10:3). Only one red band was obtained which afforded 3',4'-dimethoxyphenylbenzoquinone (20 mg).

Attempted reaction of benzoquinone with 2,6-di(3',4'-dimethoxyphenyl)benzoquinone

A mixture of finely powdered 2,6-di(3',4'-dimethoxyphenyl)benzoquinone (100 mg), benzoquinone (0.75 g), anhydrous aluminium chloride (1 g), and carbon disulphide (150 ml) was stirred at room temperature for 48 h. Ice (100 g) and 1M-sulphuric acid (20 ml) were added, the mixture was stirred for 1 h, and evaporated to remove carbon disulphide and unchanged benzoquinone. Extraction of the residual solid with chloroform gave a red solid which crystallised from chloroform-ethanol to give unchanged 2,6-di(3',4'-dimethoxyphenyl)benzoquinone (95 mg) m.p. 166-168°.

Arylation of benzoquinone with diazotised 3-methoxyaniline

A cooled solution of sodium nitrite (140 mg) in water (2 ml) was added to a solution of 3-methoxyaniline (246 mg) in 3M-hydrochloric acid (3 ml) at 0-5°. The diazonium solution was added to a vigorously stirred suspension of benzoquinone (250 mg) and sodium acetate (0.7 g) in water (125 ml) at 12°. The mixture was stirred at 12° for 45 min, then at room temperature for 1 h. The yellow product was collected and crystallised from methanol to give 3'-methoxyphenylbenzoquinone as golden yellow prisms (155 mg), m.p.

115-116° (lit.,[37] 112°) (Found: C, 72.7; H, 4.5; MeO, 14.3% Calc. for $C_{13}H_{10}O_3$: C, 72.9; H, 4.7; MeO, 14.5%, $\nu_{max.}$ (Nujol) 1660 and 1647 (both quinone C=O), and 1280 cm^{-1} (ether C-O); τ ($CDCl_3$) 6.16 (s, 3H CH_3O) and 3.50-2.58 (m, 7H, Ar-H and quinone-H).

Attempted reaction of benzoquinone with 3'-methoxyphenyl benzoquinone

A solution of 3'-methoxyphenylbenzoquinone (150 mg) in carbon disulphide (50 ml) was added dropwise to a stirred suspension of benzoquinone (0.8 g) and anhydrous aluminium chloride (1.5 g) in carbon disulphide (50 ml). Stirring was continued for 24 h at room temperature, then ice (30 g) and 1M-sulphuric acid (25 ml) were added. The resulting mixture was stirred for 1 h and evaporated to remove carbon disulphide and benzoquinone. The residual precipitate was collected and extracted with ether. The ether extract was washed with water, dried, and evaporated to give unchanged 3'-methoxyphenylbenzoquinone (145 mg).

Reaction of 2,3-dichlorobenzoquinone with 3',4'-dimethoxyphenylbenzoquinone

A solution of 3',4'-dimethoxyphenylbenzoquinone (244 mg)

in carbon disulphide (100 ml) was added dropwise to a stirred suspension of 2,3-dichlorobenzoquinone (885 mg) and anhydrous aluminium chloride (2.0 g) in carbon disulphide (60 ml) at room temperature. Stirring was continued for 24 h, then ice (70 g) and 1M-sulphuric acid (40 ml) were added. The resulting mixture was stirred for 1 h and evaporated to remove carbon disulphide and unchanged 2,3-dichlorobenzoquinone (350 mg). The residual red-brown precipitate was collected and extraction of the aqueous filtrate with ether gave 2,3-dichloroquinol (380 mg). The red-brown precipitate was subjected to p.l.c. using benzene-ethyl acetate (10:3) to give three bands which were orange, red, and brown respectively. The red band gave crude 3',4'-dimethoxyphenylbenzoquinone (150 mg). The product from the brown band was dissolved in chloroform and filtered through a short column of alumina. Evaporation of the chloroform gave a mixture of 2- and 3-(3',4'-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (u.v.) as a red solid (10 mg).

The product from the orange band, on being subjected to p.l.c. using benzene, separated into two main bands. The faster moving yellow band corresponded to 2,3-dichlorobenzo-quinone. The slower moving orange band gave a solid which

crystallised from chloroform-ethanol to give 2,3-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (86) as red micro-crystals (7 mg) m.p. 286-290° (decomp.) (Found: M, 415.9852. $C_{20}H_{10}{}^{35}Cl_2O_6$ requires M, 415.9854), $\lambda_{max.}$ ($CHCl_3$) 323 (log ε 3.78), 398 (3.84), and 480 nm (3.75), $\lambda_{infl.}$ ($CHCl_3$) 295 nm (log ε 4.15); $\nu_{max.}$ (KBr) 1670 (quinone C=O), 1598 (C=C) and 1263 cm^{-1} (ether C-O).

Reaction of benzoquinone with 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone

A solution of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-benzoquinone (105 mg) in carbon disulphide (100 ml) was added dropwise to a stirred suspension of benzoquinone (540 mg) and anhydrous aluminium chloride (1 g) in carbon disulphide (100 ml). The mixture was stirred for 48 h at room temperature and ice (50 g) and 1M-sulphuric acid (20 ml) were added. The resulting mixture was stirred for 1 h and evaporated to remove carbon disulphide and benzoquinone. The residual solid was collected, washed with water, dried and subjected to p.l.c. using benzene when a red-violet band and an orange band were obtained. The red-violet band gave unchanged 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone (15mg). The product from the orange band crystallised from chloroform-

ethanol to give 2,3-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (u.v.) as a red crystalline solid (53 mg).

Reductive acetylation of 2,3-dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone

2,3-Dichloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (50 mg) was heated under reflux for 1 h with acetic anhydride (7 ml), zinc dust (200 mg), and triethylamine (0.2 ml), and the pale yellow mixture was poured into hot water and stirred vigorously. The aqueous suspension was extracted with chloroform, which was washed with 10% aqueous sodium carbonate and with water, and dried. Evaporation of the solvent gave a pale yellow solid which crystallised from chloroform-ethanol to give 1,4,5,8-tetraacetoxy-2,3-dichloro-10,11-dimethoxytriphenylene (101) as needles (55 mg) m.p. 251-253° (Found M, 588.0586. $C_{28}H_{22}{}^{35}Cl_2O_{10}$ requires M, 588.0590), $\lambda_{max.}$ ($CHCl_3$) 287 (log ε 4.80) and 379 nm (3.35), $\lambda_{infl.}$ ($CHCl_3$) 264 (log ε 4.55), 279 (4.75), 321 (4.10), 332 (4.05), and 358 nm (3.53); $\nu_{max.}$ (KCl) 1774 (acetate C=O), 1210 and 1190 cm^{-1} (both acetate C-O); τ ($CDCl_3$) 7.84 (s, 3H, CH_3CO_2 at C-4 or C-5), 7.60 (s, 6H, CH_3CO_2 at C-1, C-4, C-5 or C-8), 7.50 (s, 3H, CH_3CO_2 at C-1 or C-8), 5.98 (s, 6H, CH_3O), 2.66 (broad s, 2H, Ar-H

at C-6 and C-7), 1.67 (s, 1H, Ar-H at C-9 or C-12) and 1.57 (s, 1H, Ar-H at C-12 or C-9).

Reaction of chlorobenzoquinone with 3',4'-dimethoxyphenylbenzoquinone

A solution of 3',4'-dimethoxyphenylbenzoquinone (244 mg) in carbon disulphide (70 ml) was added dropwise to a stirred solution of chlorobenzoquinone (855 mg) and anhydrous aluminium chloride (2.0 g) in carbon disulphide (70 ml). The mixture was stirred for 24 h at room temperature, ice (60 g) and 1M-sulphuric acid (40 ml) were added and the resulting mixture was stirred for 2 h and filtered. The filtrate was evaporated to remove carbon disulphide and chlorobenzoquinone (400 mg). The aqueous layer was decanted and extracted with ether to give crude chloroquinol (400 mg). The residual red-brown oily solid on being subjected to p.l.c. using benzene-ethyl acetate (10:3) gave orange, red, and orange-brown bands respectively. A chloroform solution of the product from the orange-brown band was passed through a short column of alumina. Evaporation of the chloroform afforded a red solid which crystallised from chloroform-ethanol to give a mixture of 2- and 3-(3',4'-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinones (u.v.) as red micro-

crystals (20 mg). The red band gave unchanged 3',4'-dimethoxyphenylbenzoquinone (88 mg).

The orange band afforded a red solid which crystallised from chloroform-ethanol to give a mixture of 2- and 3-chloro--10,11-dimethoxytriphenylene-1,4:5,8-diquinones (92) and (91) as red micro-crystals (24 mg) (Found: M, 382.0246. $C_{20}H_{11}{}^{35}ClO_6$ requires M, 382.0244), $\lambda_{max.}$ ($CHCl_3$) 396 (log ε 3.78) and 475 nm (3.71), $\lambda_{infl.}$ ($CHCl_3$) 295 (log ε 4.07) and 490 nm (3.68); $\nu_{max.}$ (KCl) 1680 and 1660 (both quinone C=O), 1615 (C=C), and 1260 cm^{-1} (ether C-O); τ ($CDCl_3$) 5.92 (s, 6H, CH_3O), 2.93 (s, quinone-H at C-2), 2.72 (s, quinone-H at C-3), 1.10 (s, 1H, Ar-H at C-9 or C-12), 1.06 (s, 1H, Ar-H at C-12 or C-9) and an AB quartet centred at τ 3.11 and τ 2.95 (J 10Hz, 2H, quinone-H at C-6 and C-7). The integrals for the signals at τ 2.93 and τ 2.72 were in the ratio 3:1, and together correspond to 1H.

Reaction of benzoquinone with 5- and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones

A (1:1) mixture (125 mg) of 5- and 6- chloro-2-(3',4'-dimethoxyphenyl)benzoquinones (p.167) in carbon disulphide (100 ml) was added dropwise to a stirred suspension of benzoquinone (650 mg) and anhydrous aluminium chloride (1.0 g)

in carbon disulphide (70 ml) at room temperature. Stirring was continued for 48 h, ice (50 g) and 1M-sulphuric acid (20 ml) were added, and the resulting mixture was stirred for 1 h and evaporated to remove carbon disulphide and unchanged benzoquinone. The residual oily solid was collected and subjected to p.l.c. using benzene to give two main coloured bands. The faster moving red band afforded unchanged 5- and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones (7 mg). The slower moving orange band afforded a red solid which crystallised from chloroform-ethanol to give a mixture of 2- and 3-chloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinones as red micro-crystals (94 mg), τ ($CDCl_3$) 5.92 (s, 6H, CH_3O), 2.96 (s, 0.5H, quinone-H at C-2), 2.75 (s, quinone-H at C-3 superimposed on $C\underline{H}Cl_3$), 1.09 (s, 1H, Ar-H at C-9 or C-12), 1.05 (s, 1H, Ar-H at C-12 or C-9), and an AB quartet centred at τ 3.14 and τ 2.98 (J 10Hz, 2H, quinone-H at C-6 and C-7).

Reductive acetylation of the mixed 2- and 3-chloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinones

A portion (80 mg) of the mixed 2- and 3-chloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinones from the previous experiment was heated under reflux for 1 h with acetic

anhydride (7 ml), zinc dust (200 mg), and triethylamine (0.2 ml). The mixture was poured into hot water, stirred vigorosuly, and the aqueous suspension was extracted with chloroform which was washed with 10% aqueous sodium carbonate and with water, and dried. Evaporation of the chloroform gave a pale yellow solid which crystallised from chloroform-ethanol to give a mixture of 2- and 3-chloro-1,4,5,8-tetra-acetoxy-10,11-dimethoxytriphenylenes (102) and (103) as clusters of needles (80 mg) m.p. 256-260° (Found: M, 554.0976. $C_{28}H_{23}{}^{35}ClO_{10}$ requires M, 554.0980), $\lambda_{max.}$($CHCl_3$) 282 (log ε 4.86) and 375 nm (3.36), $\lambda_{infl.}$($CHCl_3$) 264 (log ε 4.62), 275 (4.81), 318 (4.13), 330 (4.06) and 356 nm (3.52); $\nu_{max.}$(Nujol) 1760 (acetate C=O) and 1200 cm^{-1} (acetate C-O). It was not possible to separate the mixture by p.l.c. or by crystallisation.

Reaction of benzoquinone with 5-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone

A solution of 5-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (m.p. 150-151°) (100 mg) in carbon disulphide (80 ml) was added dropwise to a stirred suspension of benzoquinone (550 mg) and anhydrous aluminium chloride (1.0 g) in carbon disulphide (100 ml). The mixture was stirred at room

temperature for 48 h. Ice (50 g) and 1M-sulphuric acid (20 ml) were added and the resulting mixture was stirred for 1 h and evaporated to remove carbon disulphide and unchanged benzoquinone. The dark solid was collected and shaken with chloroform (3 x 20 ml). The combined chloroform extracts were washed with water, dried and evaporated to give a dark red solid which was subjected to p.l.c. using benzene-light petroleum (9:1). Two bands were obtained, the faster moving red band giving unchanged 5-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone (10 mg). The slower moving orange band afforded a red solid which was crystallised by slowly concentrating a solution in chloroform-ethanol to give 3-chloro-10,11-dimethoxytriphenylene-1,4:5,8-diquinone as red micro-crystals (75 mg) which slowly darken $>170°$ m.p. 267-270°(decomp.) (Found: M, 382.0246. $C_{20}H_{11}{}^{35}ClO_6$ requires M, 382.0244), $\lambda_{max.}(CHCl_3)$ 396 (log ε 3.91) and 474 nm (3.78), $\lambda_{infl.}(CHCl_3)$ 293 (log ε 4.18) and 494 nm (3.73); $\nu_{max.}$(Nujol) 1685 and 1662 (both quinone C=O), and 1262 cm^{-1} (ether C-O); $\tau(CDCl_3)$ 5.92 (s, 6H, CH_3O), 2.93 (s,1H, quinone-H at C-2), 1.02 (s, 1H, Ar-H at C-9 or C-12), 0.97 (s, 1H, Ar-H at C-12 or C-9), and an AB quartet centred at τ 3.11 and τ 2.95 (J 10Hz, 2H, quinone-H at C-6 and C-7).

A portion (58 mg) of the above triphenylenediquinone was converted to the bisleucoacetate as in the previous experiment. The product crystallised from chloroform-ethanol to give 1,4,5,8-tetra-acetoxy-3-chloro-10,11-dimethoxytriphenylene as needles (40 mg) m.p. 268.5-270.5° (Found: M, 554.0978. $C_{28}H_{23}{}^{35}ClO_{10}$ requires M, 554.0980), $\lambda_{max.}$ ($CHCl_3$) 282 (log ε 4.80) and 375 nm (3.38), $\lambda_{infl.}$ ($CHCl_3$) 265 (log ε 4.58), 275 (4.76), 317 (4.09), 330 (4.03) and 355 nm (3.49); $\nu_{max.}$ (Nujol) 1762 (acetate C=O) and 1198 cm^{-1} (acetate C-O); τ ($CDCl_3$) 7.84 (s, 3H, CH_3CO_2 at C-4 or C-5), 7.62 (s, 3H, CH_3CO_2 at C-5 or C-4), 7.57 (s, 3H, CH_3CO_2 at C-1 or C-8), 7.55 (s, 3H, CH_3CO_2 at C-8 or C-1), 5.98 (s, 6H, CH_3O), 2.59 (s, 1H, Ar-H at C-2), 1.64 (s, 1H, Ar-H at C-9 or C-12), 1.57 (s, 1H, Ar-H at C-12 or C-9), and an AB quartet centred at τ 2.77 and τ 2.62 (J 6Hz, 2H, aromatic protons at C-6 and C-7). A small peak at τ 7.76 is due to 1,4,5,8-tetra-acetoxy-2-chloro-10,11-dimethoxytriphenylene present as impurity, this could not be removed by p.l.c. or by crystallisation.

Reaction of methylbenzoquinone with 3',4'-dimethoxyphenylbenzoquinone

A solution of methylbenzoquinone (3.0 g) in carbon

disulphide (100 ml) was added dropwise to a stirred mixture of 3',4'-dimethoxyphenylbenzoquinone (0.4 g), anhydrous aluminium chloride (3.0 g), and carbon disulphide (100 ml) at 0°. The mixture was stirred at 0° for 2 h and at room temperature for 20 h. Ice (50 g) and 1M-sulphuric acid (30 ml) were added and the resulting mixture was stirred for 1 h, and filtered to give 2-methyl-5-(2',5'-dihydroxy-4'-methylphenyl)benzoquinone (0.2 g), the i.r. spectrum of which was identical with that of the authentic sample prepared by the reaction between methylbenzoquinone and aluminium chloride (p.191).

The filtrate was evaporated to remove carbon disulphide and unchanged methylbenzoquinone. The aqueous solution on being decanted and extracted with ether gave methylquinol (0.2 g). The residual red oil was subjected to p.l.c. using benzene-ethyl acetate (10:3) and gave three bands which were red, golden-yellow, and brown respectively. The red band afforded unchanged 3',4'-dimethoxyphenylbenzoquinone (70 mg). The position of the brown band on the p.l.c. plates corresponded to that of the 2- and 3-(3',4'-dimethoxyphenyl)-10,11-dimethoxytriphenylene-1,4:5,8-diquinones, but as only a small amount of a brown oil was obtained when this band was removed from the plates, no further examination was

carried out. The golden-yellow band gave an orange-red solid which crystallised from chloroform-ethanol to give a mixture of 2- and 3-methyl-10,11-dimethoxytriphenylene-1,4:5,8-diquinones as red micro-crystals (54 mg) m.p. 238-242° (decomp.) (Found: M, 362.0781. $C_{21}H_{14}O_6$ requires M, 362.0790), $\lambda_{max.}$($CHCl_3$) 291 (log ε 4.03), 386 (3.78), and 465 nm (3.64), $\lambda_{max.}$($CHCl_3$) 267 (log ε 4.25), and 490 nm (3.54); $\nu_{max.}$(Nujol) 1680, 1658, and 1638 (all quinone C=O), 1615 (C=C), and 1260 cm^{-1} (ether C-O); τ($CDCl_3$) 7.76 (d, J 2Hz, 3H, CH_3 at C-3), 5.90 (s, 6H, CH_3O), 3.29 (q, J 2Hz, 1H, quinone-H at C-2), 1.02 and 0.98 (both s, 1H, Ar-H at C-9 and C-12), and an AB quartet centred at τ 3.11 and 2.95 (J 10Hz, 2H, quinone-H at C-7 and C-6) due to the 3-methyl isomer (104), and 7.79 (d, J 2H, 3H, CH_3 at C-2), 5.90 (s, 6H, CH_3O), 3.07 (q, J 2Hz, 1H, quinone-H at C-3), 1.02 (s, 2H, Ar-H at C-9 and C-12), and an AB quartet centred at τ 3.11 and τ 2.94 (J 10Hz, 2H, quinone-H at C-7 and C-6) due to the 2-methyl isomer (105). The attempted p.l.c. separation of the mixture using benzene gave a broad golden-yellow band. The lower portion of this band gave 3-methyl-10,11-dimethoxytriphenylene-1,4:5,8-diquinone (6 mg) containing only a trace of the other isomer, τ($CDCl_3$) 7.77 (d, J 2Hz, 3H, CH_3 at C-3), 5.92 (s, 6H, CH_3O), 3.31 (q, J 2Hz, 1H,

quinone-H at C-2), 1.04 and 0.99 (both s, 1H, Ar-H, at C-9 and C-12), and an AB quartet centred at 3.13 and 2.97 (J 10Hz, 2H, quinone-H at C-7 and C-6).

CHAPTER 4

Cyclisation of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone

(a) With aluminium chloride

A suspension of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (75 mg) and anhydrous aluminium chloride (0.5 g) in carbon disulphide (100 ml) was stirred at room temperature for 3 days. Ice (30 g) and 1M-sulphuric acid were added and the mixture was stirred for 1 h. After evaporation of the carbon disulphide, the residual aqueous mixture was shaken with chloroform. The chloroform extract was washed with water, dried, and shaken with iron (III) chloride (200 mg). The solution was washed with 2M-hydrochloric acid, and with water, and dried. Evaporation of the chloroform gave a red-brown solid which was subjected to p.l.c. using benzene-ethyl acetate (4:1). A red band (A), a broad violet band (B), and a pale yellow band (C) which remained at the origin, were obtained.

Band (A) gave unchanged 2,3-di(3',4'-dimethoxyphenyl)-

benzoquinone (18 mg). Band (B) gave a solid which cystallised from chloroform-ethanol to give 6,7,10,11-tetramethoxytriphenylene-1,4-quinone (114) as deep violet needles (24 mg) m.p. 289-291°. (Found: M, 378.1091. $C_{22}H_{18}O_6$ requires M, 378.1103), $\lambda_{max.}(CHCl_3)$ 271 (log ε 4.77), 326 (3.62), 346 (3.40) and 498 (3.76), $\lambda_{infl.}(CHCl_3)$ 298 (log ε 4.23), 304 (4.15), and 312 (3.92); $\nu_{max.}$(Nujol) 1645 (quinone C=O), 1618 (C=C), and 1262 cm^{-1} (ether C-O); τ ($CDCl_3$) 5.92 (s, 6H, CH_3O), 5.89 (s, 6H, CH_3O), 3.18 (s, 2H, quinone-H), 2.42 (s, 2H at C-8 and C-9), and 1.01 (s, 2H, Ar-H at C-5 and C-12). The product from band (C) crystallised from chloroform-ethanol to give fine yellow needles (4 mg) m.p. >350°, $\lambda_{max.}(CHCl_3)$ 281 ($A^{1\%}_{1cm}$ 1066), 293 (1033), and 376 (247.9), $\lambda_{infl.}(CHCl_3)$ 422 ($A^{1\%}_{1cm}$ 132.2); $\nu_{max.}$(Nujol) 1688 and 1662 (both quinone C=O), 1618 (C=C), and 1260 cm^{-1} (ether C-O). No definite structure could be assigned to this product and the lack of material prevented further investigation.

(b) With aluminium chloride and 2,3-dichloro-5,6-dicyano-benzoquinone (D.D.Q.)

A suspension of 2,3-di(3',4'-dimethoxyphenyl)benzo-quinone (50 mg), D.D.Q. (100 mg), and anhydrous aluminium chloride (0.5 g) in carbon disulphide (100 ml) was stirred

at room temperature for 3 days. Ice (30 g) and 1M-sulphuric acid (10 ml) were added and the mixture was stirred for 1 h. The carbon disulphide was evaporated, and the residual aqueous mixture was extracted with chloroform. The extract was washed with water, dried, and evaporated to give a dark red solid which on being subjected to p.l.c. using benzene-ethyl acetate (4:1) gave one broad violet band. This afforded a solid which crystallised from chloroform-ethanol to give 6,7,10,11-tetramethoxytriphenylene-1,4-quinone as deep violet needles (25 mg) m.p. 289-291°.

(c) With D.D.Q. in benzene

A solution of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (30 mg) and D.D.Q. (60 mg) in benzene (25 ml) was boiled under reflux for 5 h. Evaporation of the benzene afforded a red solid which on being subjected to p.l.c. using benzene-ethyl acetate (4:1) gave one red band from which unchanged 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (27 mg) was obtained.

(d) With aqueous sulphuric acid

A suspension of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (100 mg) in 70% v/v aqueous sulphuric acid (15 ml) was shaken vigorously for 2 h and kept for 3 days at room temperature. The resulting mixture was diluted with water (60 ml) and shaken with chloroform. The extract was washed

with water, dried, and shaken with iron (III) chloride (250 mg), washed with 2M-hydrochloric acid and with water. Evaporation of the dried chloroform solution gave a brown solid which was separated by p.l.c. using benzene-ethyl acetate (4:1) into three components, a red band (A), a broad, pale violet band (B), and a yellow band which remained at the origin.

Band (A) gave unchanged 2,3-di(3',4'-dimethoxyphenyl)-benzoquinone (21 mg). The product from band (B) crystallised from chloroform-ethanol to give 6,7,10,11-tetramethoxytriphenylene-1,4-quinone (u.v.) as deep violet needles (3 mg). After the removal of bands (A) and (B), further development using benzene-chloroform (1:9) gave a pale yellow band (C) which moved slowly away from the origin. Band (C) afforded a pale yellow solid which crystallised from chloroform-ethanol to give an unknown product as fine yellow needles (12 mg) m.p. $> 350°$. The i.r. absorption was identical with that of the yellow product from experiment (a) above.

(e) With chloranil and aqueous sulphuric acid

A suspension of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (30 mg) and chloroanil (60 mg) in 70% v/v aqueous sulphuric acid (10 ml) was shaken vigorously for 2 h, and kept for 3 days. Water (75 ml) was added and the mixture

was shaken with chloroform. The chloroform extract was washed successively with water, 1M-sodium hydroxide, and water, dried and evaporated. The residual brown solid on being subjected to p.l.c. using benzene-chloroform (1:9) gave a slow moving yellow band. This afforded a solid which crystallised from chloroform-ethanol to give an unknown product as yellow needles (3 mg) m.p. > 350°. The i.r. and u.v. spectra were identical with those of the yellow product from experiment (a), apart from differences in the relative intensities of the peaks.

Arylation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-benzoquinone with diazotised 3,4-dimethoxyaniline

A cooled solution of sodium nitrite (140 mg) in water (1 ml) was added to a solution of 3,4-dimethoxyaniline (304 mg) in 3M-hydrochloric acid (3 ml) at 0-4°. The resulting solution was added, together with a solution of sodium acetate (0.7 g) in water (2 ml) to a vigorously stirred solution of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzo-quinone (306 mg) in acetone (250 ml) at 10°, and the mixture was stirred for 3 h at room temperature. Water was added and the resulting precipitate was collected and crystallised from chloroform-ethanol to give unchanged 5,6-dichloro-2-

(3',4'-dimethoxyphenyl)benzoquinone (180 mg). The filtrate was concentrated (to ca. 120 ml), shaken with chloroform and the chloroform extract was washed with water, dried, and evaporated. The resulting solid on being subjected to p.l.c. using benzene-ethyl acetate (10:1) gave two violet bands. The faster moving band afforded unchanged 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone (30 mg). The slower moving band gave crude 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)benzoquinone (50 mg) as a dark violet solid. This could not be purified by p.l.c. or by crystallisation but on being sublimed at 120°/0.1 Torr gave 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)benzoquinone (11%) m.p. 85-90°. (Found: M, 448.0484. $C_{22}H_{18}{}^{35}Cl_2O_6$ requires M, 448.0481), $\lambda_{max.}$(EtOH) 253 (log ε 4.29), 325 (3.58), and 466 (broad) nm (3.31), $\lambda_{infl.}$(EtOH) 272 nm (log ε 4.20); $\nu_{max.}$(Nujol) 1670 (quinone C=O), 1602 (C=C), and 1250 cm^{-1} (ether C-O); τ ($CDCl_3$) 6.37 and 6.14 (both s, 6H, CH_3O), 3.47 (d, J 2Hz, 2H, Ar-H at C-2'), and an AB quartet centred at τ 3.32 and τ 3.23 (J 8Hz, 4H, Ar-H at C-6' and C-5' respectively). The signal centred at τ 3.32 is also coupled (J 2Hz) to the signal at τ 3.47.

Cyclisation of 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)-benzoquinone

A suspension of chloranil (100 mg) and 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)benzoquinone (40 mg) in 70% v/v aqueous sulphuric acid (40 ml) was shaken for 24 h, diluted with water (100 ml) and shaken with chloroform. The extract was washed with water, dried, and evaporated to give a violet solid which, on being subjected to p.l.c. using benzene-ethyl acetate (10:1) gave a yellow band and a broad violet band. The position of the yellow band corresponded to that of chloranil and this band was not further examined. The violet band afforded a solid which crystallised from chloroform-ethanol to give 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (116) as fine, violet needles (35 mg) m.p. 310-313°. (Found: M, 446.0338. $C_{22}H_{16}{}^{35}Cl_2O_6$ requires M, 446.0325), $\lambda_{max.}(CHCl_3)$ 276 (log ε 4.84), 350 (3.61), and 532 nm (3.80), $\lambda_{infl.}(CHCl_3)$ 300 (log ε 4.39), 317 (4.06), and 329 nm (3.84); $\nu_{max.}$(Nujol) 1658 (quinone C=O), 1620 (C=C), and 1265 cm^{-1} (ether C-O).

Reductive acetylation of 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone

2,3-Dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (27 mg) was heated under reflux for 1 h with acetic anhydride (10 ml), zinc dust (200 mg), and triethylamine (0.2 ml). The mixture was poured into hot water (50 ml) and shaken with chloroform. The extract was washed with 10% aqueous sodium carbonate and with water. Evaporation of the chloroform gave a solid which crystallised from chloroform-ethanol to give 1,4-diacetoxy-2,3-dichloro-6,7,10,11-tetramethoxytriphenylene (106) as needles (28 mg), m.p. 231.5 - 233° (Found: M, 532.0663; M', 534.0642. $C_{26}H_{22}{}^{35}Cl_2O_8$ requires M, 532.0692; $C_{26}H_{22}{}^{35}Cl{}^{37}ClO_8$ requires M, 534.0662), $\lambda_{max.}$ ($CHCl_3$) 287 (log ε 4.93), 361 (3.53), and 379nm(3.48), $\lambda_{infl.}$ ($CHCl_3$) 258 (log ε 4.42), 269 (4.60), 277 (4.73), 305 (4.53) and 340 nm (3.66); $\nu_{max.}$ (Nujol) 1765 and 1755 (both acetate C=O), and 1160 cm^{-1} (acetate C-O); τ ($CDCl_3$) 7.53 (s, 6H, CH_3CO_2), 5.96 and 5.92 (both s, 6H, CH_3O) 2.30 (s, 2H, Ar-H at C-8 and C-9), and 1.54 (s, 2H, Ar-H at C-5 and C-12).

Reaction of 2,3-dichlorobenzoquinone with 3,3',4,4'-tetramethoxybiphenyl

(a) In aqueous sulphuric acid

A suspension of 2,3-dichlorobenzoquinone (0.5 g) and finely powdered 3,3',4,4'-tetramethoxybiphenyl (130 mg) in 70% v/v aqueous sulphuric acid (15 ml) was shaken vigorously for 3 h and kept at room temperature for 4 days. The mixture was shaken with water (100 ml) and filtered to give a blue solid and a filtrate (A). The blue solid was washed with water, and extracted with chloroform. The insoluble blue residue (90 mg) was crude 2,5,6,9,12,13-hexamethoxydibenzo[fg,op]naphthacene-1,8-quinone[32] (22). Evaporation of the dried chloroform solution gave a pale blue solid (200 mg). On being subjected to t.l.c. using benzene-ethyl acetate (3:2) this gave three spots corresponding to 2,3-dichlorobenzoquinone, 2,3-dichloroquinol, and 2,5,6,9,12,13-hexamethoxydibenzo[fg,op]naphthacene-1,8-quinone. The filtrate (A) on being extracted with ether gave a mixture (350 mg) of 2,3-dichlorobenzoquinone and 2,3-dichloroquinol.

(b) In the presence of aluminium chloride

A suspension of 2,3-dichlorobenzoquinone (0.7 g), 3,3',4,4'-tetramethoxybiphenyl (274 mg), and anhydrous aluminium chloride (540 mg) in carbon disulphide (100 ml)

was stirred at room temperature for 24 h. Ice (10 g) and 1M-sulphuric acid (5 ml) were added and the mixture was stirred for 2 h. The carbon disulphide was evaporated and the yellow solid (850 mg) was collected and dried. Examination by t.l.c. and by i.r. showed this to be a mixture of unchanged 2,3-dichlorobenzoquinone and 3,3',4,4'-tetramethoxybiphenyl.

Arylation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone with diazotised 3-methoxyaniline

A cooled solution of sodium nitrite (140 mg) in water (2 ml) was added to a solution of 3-methoxyaniline (246 mg) in 3M-hydrochloric acid (3 ml) at 0-4°. The resulting solution was added together with a solution of sodium acetate (0.7 g) in water (2 ml) to a vigorously stirred solution of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone (100 mg) in acetone (150 ml) at 12°. The mixture was stirred at room temperature for 3 h, water (100 ml) was added, and the resulting mixture was evaporated to remove the acetone. Extraction with chloroform gave a dark red solid which on being subjected to p.l.c. using benzene gave two violet bands. The faster moving band afforded unchanged 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone (65 mg). The

slower moving band gave 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-3-(3'-methoxyphenyl)benzoquinone (117) as a violet solid (14 mg) which could not be crystallised from chloroform-ethanol and did not give a distinct m.p.; examination by t.l.c. using benzene-ethyl acetate (10:1), and benzene-light petroleum (9:1) showed it to be homogeneous; (Found: M, 418.0374. $C_{21}H_{16}{}^{35}Cl_2O_5$ requires M, 418.0376), $\lambda_{max.}(CHCl_3)$ 264 (log ε 4.27), 332 (3.66), and 517 (broad) nm (3.30), $\lambda_{infl.}$ ($CHCl_3$) 275 nm (4.22); $\nu_{max.}$ (Nujol) 1673 (quinone C=O), 1602 (C=C), and 1257 cm^{-1} (ether C-O); τ ($CDCl_3$) 6.42, 6.34, and 6.15 (all s, 3H, CH_3O), and 3.57-2.67 (m, 7H, Ar-H).

Cyclisation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-3-(3'-methoxyphenyl)benzoquinone

A suspension of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-3-(3'-methoxyphenyl)benzoquinone (12 mg) and chloranil (25mg) in 70% v/v aqueous sulphuric acid (20 ml) was shaken vigorously for 2 h and kept overnight. The mixture was diluted with water (100 ml), and shaken for 1 h. Extraction with chloroform gave a violet solid which on being subjected to p.l.c. using benzene-ethyl acetate (5:1) gave two bands which were yellow and violet respectively. The yellow band corresponded to chloranil and was not further examined. The

violet band afforded a solid which crystallised from chloroform-ethanol to give 2,3-dichloro-6,7,11-trimethoxytriphenylene-1,4-quinone (118) as fine violet needles (8 mg) m.p. 270-272°. (Found: M, 416.0221. $C_{21}H_{14}{}^{35}Cl_2O_5$ requires M, 416.0219), $\lambda_{max.}(CHCl_3)$. 273 (log ε 4.81) and 536 nm (3.61), $\lambda_{infl.}(CHCl_3)$ 268 (log ε 4.75), 292 (4.38), 305 (4.24), 322 (3.90), and 354 nm (3.44); $\nu_{max.}$(Nujol) 1660 (quinone C=O), 1616 (C=C), and 1250 cm^{-1} (ether C-O); τ ($CDCl_3$) 6.02, 5.95, and 5.89 (all s, 3H, CH_3O), 2.69 (d d, $J_{10,12}$ 3Hz, $J_{9,10}$ 9Hz, 1H, Ar-H at C-10), 2.36 (s, 1H, Ar-H at C-8), 1.76 (d, $J_{9,10}$ 9Hz, 1H, Ar-H at C-9), 1.40 (s, 1H, Ar-H at C-5), and 1.33 (d, $J_{10,12}$ 3Hz, Ar-H at C-12).

Arylation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-benzoquinone with diazotised aniline

A cooled solution of sodium nitrite (280 mg) in water (2 ml) was added to a solution of aniline (372 mg) in 3M-hydrochloric acid (5 ml) at 0-4°. The resulting solution was added together with a solution of sodium acetate (1.4 g) in water (5 ml) to a vigorously stirred solution of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone (100 mg) in acetone (150 ml) at 8°. The mixture was stirred at room temperature for 3 h, water (100 ml) was added, and the

resulting mixture was evaporated to remove the acetone. Extraction with chloroform gave a red solid which on being subjected to p.l.c. using benzene gave a red-violet band. This afforded 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-3-phenylbenzoquinone (119) as a deep violet solid (30 mg). (Found: M, 388.0267. $C_{20}H_{14}{}^{35}Cl_2O_4$ requires M, 388.0269), $\lambda_{max.}(CHCl_3)$ 262 (log ε 4.28), 331 (3.73), and 522 nm (3.25), $\lambda_{infl.}(CHCl_3)$ 257 (log ε 4.26), and 287 nm (3.95); $\nu_{max.}$ (Nujol) 1668 (quinone C=O) 1602 (C=C) and 1253 cm^{-1} (ether C-O); τ($CDCl_3$) 6.44 and 6.15 (both s, 3H, CH_3O), 3.55 (broad s, 1H, Ar-H at C-2'), 3.26 (broad s, 2H, Ar-H at C-5' and C-6'), and 3.00-2.63 (m, 5H, Ph-H).

Cyclisation of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-3-phenylbenzoquinone

A suspension of 5,6-dichloro-2-(3',4'-dimethoxyphenyl)-3-phenylbenzoquinone (20 mg) and chloroanil (40 mg) in 70% v/v aqueous sulphuric acid (20 ml) was shaken vigorously for 4 h, kept overnight, diluted with water (60 ml), and shaken for 1 h. Extraction with chloroform gave a pale-red solid which on being subjected to p.l.c. using benzene gave a yellow band which corresponded to chloranil, a red band (A) and a colourless band (B) which fluoresced in u.v. light.

Band (A) afforded a red solid which crystallised from chloroform-ethanol to give 2,3-dichloro-6,7-dimethoxytriphenylene-1,4-quinone (120) as fine red needles (2 mg) m.p. 247.5-249.5° (Found: M, 386.0101. $C_{20}H_{12}{}^{35}Cl_2O_4$ requires M, 386.0113), $\lambda_{max.}$ ($CHCl_3$) 268 (log ε 4.75) and 514 nm (3.62), $\lambda_{infl.}$ ($CHCl_3$) 250 (log ε 4.46), 264 (4.72), 291 (4.29), 309 (4.06), 320 (3.92), and 354 nm (3.32); $\nu_{max.}$ (Nujol) 1662 (quinone C=O), 1612 (C=C), 1272 and 1255 cm^{-1} (both ether C-O). Band (B) afforded a solid which crystallised from chloroform-ethanol to give 1,2-dichloro-3-hydroxy-6,7-dimethoxy-4-phenyldibenzofuran (122) as needles (10 mg) m.p. 173.5-174.5° (Found: M, 388.0271. $C_{20}H_{14}{}^{35}Cl_2O_4$ requires M, 388.0269), $\lambda_{max.}$ (EtOH) 250 (log ε 4.23) and 319 nm (4.35), $\lambda_{infl.}$ 221 (log ε 4.46), and 262 nm (4.14); $\nu_{max.}$ (Nujol) 3530 (sharp, phenolic OH) and 1215 cm^{-1} (ether C-O); τ ($CDCl_3$) 6.44 and 6.08 (both s, 3H, CH_3O), 4.54 (s, 1H, OH, exchangeable), 3.64 (s, 1H, Ar-H at C-5), 2.90 (s, 1H, Ar-H at C-8), and 2.66-2.46 (m, 5H, Ph-H). Concentration of the mother liquor gave crude 1,2-dichloro-3-hydroxy-6,7-dimethoxy-4-phenyldibenzofuran as a crystalline solid (5 mg).

Reaction of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone with concentrated hydrochloric acid

A vigorously stirred mixture of 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (50 mg) and concentrated hydrochloric acid (25 ml) was boiled under reflux for 1.5 h, cooled, and poured into water (100 ml). The mixture was shaken with chloroform and the extract was washed with water and dried. The chloroform solution was shaken with anhydrous iron (III) chloride (200 mg), washed with 2M-hydrochloric acid and with water, and dried. Evaporation gave a dark red solid which on being subjected to p.l.c. using benzene-ethyl acetate (9:1) gave a red band and a broad violet band.

The slower moving band yielded a solid which crystallised from chloroform-ethanol to give a mixture of 2,3-dichloro- (3.5%), 2-chloro- (86.5%), and unsubstituted- (10%)-6,7,10,11-tetramethoxytriphenylene-1,4-quinones as violet rhombohedra (20 mg), m.p. 285-290° [Found: m/e 446.0330 (4%), 412.0717 (100%), and 378 (12%). Calc. for $C_{22}H_{16}{}^{35}Cl_2O_6$: M, 446.0324; calc. for $C_{22}H_{17}{}^{35}ClO_6$: M, 412.0714; calc. for $C_{22}H_{18}O_6$: M, 378], $\lambda_{max.}$($CHCl_3$) 274 (log ε 4.80), 357 (3.63), and 517 nm (3.81), $\lambda_{infl.}$($CHCl_3$) 299 (log ε 4.35), 316 (3.93), and 327 nm (3.74); $\nu_{max.}$(Nujol) 1657 (quinone C=O), 1618 (C=C), and 1260 cm^{-1} (ether C-O); τ ($CDCl_3$) 6.02, (s, 3H, CH_3O), 6.00 (s, 9H, CH_3O), 3.22 (s, 1H, quinone-H), 2.82

(s, 2H, Ar-H at C-8 and C-9), 1.42 and 1.36 (both s, 1H, Ar-H at C-5 and C-12).

The faster moving band afforded a red product which crystallised from chloroform-ethanol to give a mixture of 2,3,5-trichloro- (125) (4.5%), 2,5-dichloro- (124) (46.75%), 3,5-dichloro- (123) (46.75%), and 5-chloro- (126) (2%),-6,7,10,11-tetramethoxytriphenylene-1,4-quinones as red needles (10 mg) m.p. 254-258°. [Found: m/e 479.9939 (1%), 446.0320 (15%), 445 (5%), 412 (25%), 411 (100%), 377 (2%). Calc. for $C_{22}H_{15}{}^{35}Cl_3O_6$: M, 479.9934, M-^{35}Cl, 445; calc. for $C_{22}H_{16}{}^{35}Cl_2O_6$: M', 446.0324, M'-^{35}Cl, 411; calc. for $C_{22}H_{17}{}^{35}ClO_6$: M", 412, M"-^{35}Cl, 377], $\lambda_{max.}$ ($CHCl_3$) 276 (log ε 4.76) and 485 nm (3.79), $\lambda_{infl.}$ ($CHCl_3$) 301 (log ε 4.40), 319 (4.08), 330 (3.90), and 362 nm (3.35); $\nu_{max.}$ (Nujol) 1665 and 1645 (both quinone C=O), 1610 (C=C), 1282 and 1265 cm^{-1} (both ether C-O); τ ($CDCl_3$) 6.00 and 5.90 (both s, 3H, CH_3O), 5.88 (s, 6H, CH_3O), 3.02 and 2.83 (both s, 0.5H, quinone-H), 2.38 (broad s, 2H, Ar-H at C-8 and C-9) and 0.98 (s, 1H, Ar-H at C-12). Neither of the above mixtures could be separated into its components by p.l.c. or by crystallisation.

When 2,3-di(3',4'-dimethoxyphenyl)benzoquinone (130 mg) and concentrated hydrochloric acid (75 ml) was boiled under

reflux for a longer period (2.5 h), the same mixtures of products (19 mg and 28 mg respectively) were obtained.

Reductive acetylation of the mixture of 5-chlorotriphenylene-1,4-quinones

A portion (25 mg) of the red product from the previous experiment was heated under reflux for 1 h with acetic anhydride (10 ml), zinc dust (200 mg) and triethylamine (0.2 ml). The mixture was poured into hot water with vigorous stirring, and shaken with chloroform to give an extract which was washed with 10% aqueous sodium carbonate and with water, dried, and evaporated. The residue on being subjected to p.l.c. using benzene-ethyl acetate (10:1) gave two slightly overlapping bands which fluoresced on exposure to u.v. light.

The product from the faster moving band crystallised from chloroform-ethanol to give a mixture (A) of 2,3,5-trichloro- (128) (7%), 3,5-dichloro- (107) (83%), and 5-chloro- (129) (0.7%)-1,4-diacetoxy-6,7,10,11-tetramethoxytriphenylenes and of 2,3-dichloro- (134) (1.0%), 2- or 3-chloro- (136) or (131) (7%), and unsubstituted- (135) (1.0%)-1-acetoxy-4,5-epoxy-6,7,10,11-tetramethoxytriphenylenes as fine needles (8 mg) m.p. 230-234°. [Found: m/e 566.0317 (7%), 532.0678

(81%), 498 (0.7%), 488 (1%), 454 (7%), 420 (1%). Calc. for $C_{26}H_{21}{}^{35}Cl_3O_8$: $\underline{M}_1$, 566.0301; calc. for $C_{26}H_{22}{}^{35}Cl_2O_8$: $\underline{M}_2$, 532.0692; calc. for $C_{26}H_{23}{}^{35}ClO_8$: $\underline{M}_3$, 498; calc. for $C_{24}H_{18}{}^{35}Cl_2O_7$: $\underline{M}_4$, 488; calc. for $C_{24}H_{19}{}^{35}ClO_7$: $\underline{M}_5$, 454; calc. for $C_{24}H_{20}O_7$: $\underline{M}_6$, 420], $\nu_{max.}$(Nujol) 1762 (acetate C=O) and 1170 cm^{-1} (acetate C-O); τ ($CDCl_3$) 7.77 and 7.49 (both s, 3H, CH_3CO_2), 6.06, 5.94, 5.92, and 5.90 (each s, 3H, CH_3O), 2.44 (s, 1H, Ar-H at C-2), 2.40, and 2.34 (both s, 1H, Ar-H at C-8 and C-9), and 1.58 (s, 1H, Ar-H at C-12).

The product from the slower moving band crystallised from chloroform-ethanol to give a mixture (B) of 2,3,5-trichloro- (0.3%), 2,5-dichloro- (90%), and 5-chloro- (1.5%)- 1,4-diacetoxy-6,7,10,11-tetramethoxytriphenylenes and of 2- or 3-chloro- (7%), and unsubstituted- (0.5%)-1-acetoxy-4,5-epoxy-6,7,10,11-tetramethoxytriphenylenes as needles (4 mg) m.p. 190-194° [Found: m/e 566 (0.2%), 532.0693 (62%), 498 (1%), 454 (5%), 420 (0.4%). Calc. for $C_{26}H_{22}{}^{35}Cl_2O_8$: $\underline{M}$, 532.0692], $\lambda_{max.}$($CHCl_3$) 290 (log ε 4.91), and 377 nm (3.33), $\lambda_{infl.}$($CHCl_3$) 265 (log ε 4.52), 281 (4.80), 318 (4.28), 333 (4.03), and 357 nm (3.47); $\nu_{max.}$(Nujol) 1762 (acetate C=O) and 1178 cm^{-1} (acetate C-O); τ ($CDCl_3$) 7.78 and 7.50 (both s, 3H, CH_3CO_2), 6.04, 5.94, 5.91, and 5.89 (each s, 3H, CH_3O), 2.62 (s, 1H, Ar-H at C-3), 2.40 and 2.34 (both s, 1H, Ar-H

at C-8 and C-9), and 1.58 (s, 1H, Ar-H at C-12).

A portion (7 mg) of the mixture (A) on being subjected to further p.l.c. using benzene-ethyl acetate (10:1), separated into two bands. The faster moving band gave a mixture (C) which was similar to the mixture (A) (see p. 125). The product from the slower moving band crystallised from chloroform-ethanol to give a mixture (D) of 2,3-dichloro- (8%), 2- or 3-chloro- (86%), and unsubstituted- (5.5%)-1-acetoxy-4,5-epoxy-6,7,10,11-tetramethoxytriphenylenes as needles (1 mg) m.p. 253-255° [Found: m/e 488.0426 (3%), 454.0821 (32%), 420.1189 (2%), 378.1095 (9%). Calc. for $C_{24}H_{18}{}^{35}Cl_2O_7$: $\underline{M}_4$, 488.0429; calc. for $C_{24}H_{19}{}^{35}ClO_7$: $\underline{M}_5$, 454.0822; calc. for $C_{24}H_{20}O_7$: $\underline{M}_6$, 420.1209, $\underline{M}_6$-CH_2CO, 378.1103], $\lambda_{max.}$ ($CHCl_3$) 289 (log ε 4.82), 333 (3.98), 360 (3.52), and 379 nm (3.59), $\lambda_{infl.}$ ($CHCl_3$) 257 (log ε 4.38), 283 (4.78), 308 (4.22), and 318 nm (4.19); $\nu_{max.}$ (Nujol) 1760 (acetate C=O), 1268 (ether C-O) and 1190 cm^{-1} (acetate C-O).

Reaction of 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)-benzoquinone with concentrated hydrochloric acid

A vigorously stirred mixture of 5,6-dichloro-2,3-di(3',4'-dimethoxyphenyl)benzoquinone (25 mg) and concentrated hydrochloric acid (25 ml) was boiled under reflux for 3 h, cooled,

and poured into water (100 ml). The mixture was shaken with chloroform and the extract was washed with water and dried. The chloroform solution was shaken with anhydrous iron (III) chloride,(250 mg), washed with 2M-hydrochloric acid and with water, and dried. Evaporation gave a violet solid which on being subjected to p.l.c. using benzene-ethyl acetate (9:1) gave a narrow, red band and a broad violet band. The red band afforded a solid which crystallised from chloroform-ethanol to give 2,3,5-trichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (125) as clusters of red needles (0.5 mg) m.p. 263-267° (Found: M, 479.9942. $C_{22}H_{15}{}^{35}Cl_3O_6$ requires M, 479.9934), $\lambda_{max.}$($CHCl_3$) 278 (logε 4.54) and 490 nm (3.54), $\lambda_{infl.}$($CHCl_3$) 305 (logε 4.13), 320 (3.93), 335 (3.81), and 354 nm (3.51). The violet band yielded a solid which crystallised from chloroform-ethanol to give 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone as violet needles (8 mg).

Attempted chlorination of 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone

(a) Using concentrated hydrochloric acid

2,3-Dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (45 mg) was boiled under reflux for 3 h with

concentrated hydrochloric acid (50 ml), cooled, poured into water (200 ml), and shaken with chloroform. The chloroform extract was washed with water, dried, and shaken with iron (III) chloride (250 mg). The mixture was washed with 2M-hydrochloric acid, and with water, dried, and evaporated to give a violet solid, which showed only one spot on t.l.c. using benzene-ethyl acetate (9:1). This crystallised from chloroform-ethanol to give unchanged 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone as a mixture of violet needles and rhombohedra (44 mg) m.p. and mixed m.p. 310-313°.

(b) Using hydrogen chloride

Dry hydrogen chloride was passed into a cold solution of 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (20 mg) in chloroform (25 ml) for 2 h, and then into the boiling solution for 2 h. No change in the colour of the solution occurred. The chloroform solution was washed with water, dried and evaporated to give a violet solid which was homogeneous by t.l.c. using benzene-ethyl acetate (9:1), and which crystallised from chloroform-ethanol to give unchanged 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (17 mg).

Attempted chlorination of 6,7, 10,11-tetramethoxytriphenylene-1,4-quinone

A mixture of 6,7,10,11-tetramethoxytriphenylene-1,4-quinone (23 mg) and concentrated hydrochloric acid (30 ml) was boiled under reflux for 3 h, cooled and poured into water (200 ml). The chloroform extract was treated with iron (III) chloride as in the previous experiment (a). Evaporation of the chloroform gave a violet solid which was homogeneous by t.l.c. using benzene-ethyl acetate (9:1), and which crystallised from chloroform-ethanol to give unchanged 6,7,10,11-tetramethoxytriphenylene-1,4-quinone (13 mg).

CHAPTER 5

Reaction of veratrole with chlorobenzoquinone in aqueous sulphuric acid

A suspension of finely powdered chlorobenzoquinone (2 g) and veratrole (1.5 g) in 70% v/v aqueous sulphuric acid (30 ml) was shaken vigorously for 6 h, and kept in a stoppered flask for 1 week at room temperature. The mixture was diluted with water (250 ml), kept for 3 days and the dark blue precipitate (A) was collected (2.5 g). Extraction of the filtrate with ether gave crude chloroquinol (1 g).

A portion (0.15 g) of the blue solid (A) was dissolved in chloroform, shaken with iron (III) chloride (0.5 g), washed with 2M-hydrochloric acid and with water, and dried. Evaporation of the chloroform afforded a dark red oily solid which when subjected to p.l.c. using benzene-ethyl acetate (20:1) gave four red-violet bands (B), (C), (D), and (E). Band (B) furnished a red solid which crystallised from chloroform-ethanol to give 5-chloro-2-(3',4'-dimethoxyphenyl)-benzoquinone as violet needles (5 mg). The product from band (C) crystallised from chloroform-ethanol to give 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone as violet needles (10 mg) m.p. 153-155° (authentic m.p. 157.5-158.5°; p.169). Band (D) afforded a red solid which crystallised from chloroform-ethanol to give 3-chloro-2-(3',4'-dimethoxyphenyl)benzo-quinone as clusters of red needles (5 mg) m.p. 196-199° (authentic m.p. 200.5-201.5°; p.167). Band (E) gave a red solid (12 mg) which showed the i.r. spectrum of a mixture of 3-chloro-2,5- and 3-chloro-2,6-di(3',4'-dimethoxyphenyl)-benzoquinones.

Another portion (0.5 g) of the blue solid (A) was extracted with acetone (20 ml). The insoluble blue residue which showed $\lambda_{max.}(CHCl_3)$ at 277, 316 and 560 nm, was not further examined because of the lack of material. The

acetone solution was evaporated and the resulting solid was chromatographed on silica gel using a) benzene which eluted unreacted veratrole (ca. 100 mg), b) benzene-chloroform (5:1) which eluted a mixture (by t.l.c.) of 3-, 5-, and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones (25 mg), and c) benzene-chloroform (1:1) which eluted a pale violet solid (170 mg). A solution of the pale violet solid in chloroform was shaken with 1M-sodium hydroxide. The aqueous layer was acidified with 1M-hydrochloric acid, and extraction with chloroform gave a solid (65 mg) which after repeated crystallisation from chloroform-ethanol gave 3-chloro-2-hydroxy-6,7,10,11-tetramethoxytriphenylene (143) as needles (10 mg) m.p. 285-289° (Found: M, 398.0922. $C_{22}H_{19}{}^{35}ClO_5$ requires M, 398.0921), $\lambda_{max.}$($CHCl_3$) 269 (log ε 4.74), 278 (4.88), 308 (4.25), 347 (3.34), and 364 nm (3.01), $\lambda_{infl.}$($CHCl_3$) 262 (log ε 4.56), 315 (4.21), 321 (4.13), and 331 nm (3.79); $\nu_{max.}$(Nujol) 3430 (sharp, phenolic OH), 1620 (C=C), and 1260 cm^{-1} (ether C-O); τ [$(CD_3)_2SO/CDCl_3$] 5.91 (s, 12H, CH_3O), 2.37, 2.23, 2.01, and 1.66 (each s, 1H, Ar-H) 2.27 (s, 2H, Ar-H) and 0.28 (broad, s, 1H, OH, exchangeable).

Reaction of veratrole with a mixture of 5- and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones in aqueous sulphuric acid

A suspension of veratrole (150 mg) and a (1:1) mixture of 5- and 6-chloro-2-(3',4'-dimethoxyphenyl)benzoquinones (280 mg) in 70% v/v aqueous sulphuric acid (60 ml) was shaken vigorously for 3 h and kept for 3 days at room temperature. The mixture was diluted with water (250 ml), kept for 4 days and the resulting grey precipitate (300 mg) was collected. A solution of this (150 mg) in chloroform (100 ml) was shaken with iron (III) chloride (0.5 g) and the mixture was washed with 2M-hydrochloric acid and with water, and shaken with 2M-sodium hydroxide. The alkaline extract (A) was separated, and the chloroform extract was washed with water, dried and evaporated. The resulting red solid, on being subjected to p.l.c. using benzene-ethyl acetate (9:1), gave two red-violet bands (B) and (C), a pale violet band (D), and a dark blue band (E) which remained at the origin.

Band (B) afforded a deep red solid (20 mg) which showed the i.r. absorption of 6-chloro-2-(3',4'-dimethoxyphenyl) benzoquinone containing a small amount of 5-chloro-2-(3',4'-dimethoxyphenyl)benzoquinone. Band (C) also gave a red solid (8 mg), this showed the i.r. absorption of a mixture of

3-chloro-2,5- and 3-chloro-2,6-di(3',4'-dimethoxyphenyl) benzoquinones. The solid from band (D) was dissolved in chloroform and the solution was washed with 1M-sodium hydroxide, and then with alkaline aqueous sodium dithionite. The latter aqueous layer was acidified and shaken with chloroform, and the chloroform layer was treated with anhydrous iron (III) chloride, washed with 2M-hydrochloric acid and with water, dried and evaporated. The resulting solid, on being subjected to p.l.c. using benzene-ethyl acetate (4:1), gave a broad violet band. The product from this band crystallised from chloroform-ethanol to give 2-chloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone (69) as long violet rhombohedra (2 mg) m.p. 302-305° (Found: M, 412.0714. $C_{22}H_{17}{}^{35}ClO_6$ requires M, 412.0714), $\lambda_{max.}(CHCl_3)$ 274 (logε 4.85), 351 (3.57), and 517 nm (3.80), $\lambda_{infl.}(CHCl_3)$ 300 (logε 4.40), 316 (3.95), and 328 nm (3.72); $\nu_{max.}$(Nujol) 1650 (quinone C=O), 1620 (C=C), and 1260 cm^{-1}(ether C-O). Band (E) afforded a blue solid (ca. 1 mg) which showed $\lambda_{max.}$ ($CHCl_3$) at 278, 318, and 560 nm, but this was not further examined because of the lack of material.

After the alkaline extract (A) had been acidified, extraction with chloroform gave a solid which crystallised from chloroform-ethanol to give crude 3-chloro-2-hydroxy-

6,7,10,11-tetramethoxytriphenylene (40 mg), τ [$(CD_3)_2SO$] 5.97 (s, 12H, CH_3O), 2.23, 1.95, and 1.37 (each s, 1H, Ar-H), 2.10 (broad s, 3H, Ar-H), and -0.29 (s, 1H, OH, exchangeable). Small signals due to impurities appeared at τ [$(CD_3)_2SO$] 6.05, 2.76, 1.12 and -0.07. The impurities could not be removed by p.l.c. on silica gel or by repeated crystallisation.

Acetylation of crude 3-chloro-2-hydroxy-6,7,10,11-tetramethoxytriphenylene

Crude 3-chloro-2-hydroxy-6,7,10,11-tetramethoxytriphenylene (45 mg) from the previous experiment, was heated under reflux for 45 min with acetic anhydride (15 ml), and concentrated sulphuric acid (0.2 ml). The mixture was poured into hot water (100 ml), stirred vigorously, and shaken with chloroform. The chloroform extract was washed with 10% aqueous sodium carbonate and with water, dried, and evaporated to give a solid which on being subjected to p.l.c. using benzene-ethyl acetate (5:1), gave three bands which fluoresced on exposure to u.v. light. The main, slowest moving band afforded a solid which crystallised from chloroform-ethanol to give 2-acetoxy-3-chloro-6,7,10,11-tetramethoxytriphenylene (145) as needles (32 mg) m.p. 256.5-258° (Found: M, 440.1026. $C_{24}H_{21}{}^{35}ClO_6$ requires M,

440.1026), $\lambda_{max.}(CHCl_3)$ 269 (log ε 4.75), 278 (4.91), 305 (4.32), 346 (3.40) and 364 nm (2.98), $\lambda_{infl.}(CHCl_3)$ 260 (log ε 4.56), 313 (4.25), 319 (4.16), and 329 nm (3.77); $\nu_{max.}$(Nujol) 1758 (acetate C=O), 1622 (C=C), 1262 and 1200 cm^{-1} (ether and acetate C-O); $\tau(CDCl_3)$ 7.54 (s, 3H, CH_3CO_2), 6.08 and 6.06 (both s, 3H, CH_3O), 5.97 (s, 6H, CH_3O), 2.94 (s, 2H, Ar-H), 2.80, 2.70, 2.34 and 1.98 (each s, 1H, Ar-H).

The middle band gave a solid which crystallised from chloroform-ethanol to give 2-acetoxy-4-chloro-6,7,10,11-tetramethoxytriphenylene (146) as a mixture of needles and micro-crystals (4 mg) m.p. 159-163° (Found: M, 440.1013. $C_{24}H_{21}{}^{35}ClO_6$ requires M, 440.1026), $\lambda_{max.}(CHCl_3)$ 281 (log ε 4.95), 304 (4.44), 350 (3.59), and 369 nm (3.38), $\lambda_{infl.}$ ($CHCl_3$) 264 (log ε 4.64), 273 (4.81), 314 (4.33), and 334 nm (3.78); $\nu_{max.}$(Nujol) 1750 (acetate C=O), 1618 (C=C), 1260, 1207 and 1195 cm^{-1} (ether and acetate C-O); $\tau(CDCl_3)$ 7.59 (s, 3H, CH_3CO_2),5.91 and 5.88 (both s, 3H, CH_3O), 5.85 (s, 6H, CH_3O), 2.22, 1.86 and 0.89 (Ar-H, signals too weak to permit integration). The fastest moving band gave only a small amount of material (<2 mg) which was not further examined.

Hydrolysis of 2-acetoxy-3-chloro-6,7,10,11-tetramethoxytriphenylene

A mixture of potassium hydroxide (6 g), water (20 ml), ethanol (10 ml), and 2-acetoxy-3-chloro-6,7,10,11-tetramethoxytriphenylene (25 mg) was boiled under reflux for 1 h. The ethanol was evaporated and the alkaline solution was acidified with 2M-hydrochloric acid and extracted with chloroform. The extract was washed successively with water, 10% aqueous sodium carbonate, and water, dried and evaporated. The residue was a pale yellow solid which on being subjected to p.l.c. using benzene-acetone (9:1) gave a band which fluoresced in u.v. light. This band afforded a solid which crystallised from chloroform-ethanol to give 3-chloro-2-hydroxy-6,7,10,11-tetramethoxytriphenylene as needles (7 mg) m.p. 294-295° (Found: M, 398.0925. $C_{22}H_{19}{}^{35}ClO_5$ requires M, 398.0921), $\lambda_{max.}(CHCl_3)$ 269 (log ε 4.84), 278 (4.96), 308 (4.36), 346 (3.50), and 365 nm (3.07), $\lambda_{infl.}(CHCl_3)$ 262 (log ε 4.66), 315 (4.32), 321 (4.24), and 331 nm (3.91); $\nu_{max.}$(Nujol) 3430 (sharp, phenolic OH), 1620 (C=C), and 1260 cm^{-1} (ether C-O); τ ($CDCl_3$) 5.97 (s, 12H, CH_3O), 2.19, 1.91, and 1.32 (each s, 1H, Ar-H), and 2.04 (broad, s, 3H, Ar-H).

Reaction of veratrole with 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone in aqueous sulphuric acid

A mixture of veratrole (80 mg), 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone (50 mg), and 70% v/v aqueous sulphuric acid (20 ml) was shaken vigorously for 1 h, kept for 3 days at room temperature, diluted with water (60 ml), kept for 1 day, and shaken with chloroform. The chloroform extract was washed with water, dried, shaken with anhydrous iron (III) chloride (250 mg), washed with 2M-hydrochloric acid and with water, dried and evaporated. The resulting violet solid on being subjected to p.l.c. using benzene-ethyl acetate (4:1) gave a red-violet band (A) and a broad violet band (B). Band (A) afforded a red solid which crystallised from chloroform-ethanol to give unchanged 5,6-dichloro-2-(3',4'-dimethoxyphenyl)benzoquinone as violet needles (30 mg) m.p. and mixed m.p. 205-206°.

The solid from band (B) was subjected to p.l.c. using benzene-acetone (7:1). This gave a colourless band which fluoresced on exposure to u.v. light and which afforded crude 2,3,6,7,10,11-hexamethoxytriphenylene (3 mg), and a violet band. The latter afforded a solid which was dissolved in chloroform (30 ml) and shaken with 1M-sodium

hydroxide. The chloroform extract yielded a solid which crystallised from chloroform-ethanol to give 2,3-dichloro-6,7,10,11-tetramethoxytriphenylene-1,4-quinone as violet needles (4 mg). The alkaline extract was acidified, and on being extracted with chloroform gave a solid which crystallised from chloroform-ethanol to give 3,4-dichloro-2-hydroxy-6,7,10,11-tetramethoxytriphenylene (147) as needles (5 mg) m.p. 264-265.5°. (Found: M, 432.0548. $C_{22}H_{18}{}^{35}Cl_2O_5$ requires M, 432.0532), $\lambda_{max.}$($CHCl_3$) 282 (log ε 4.92), 308 (4.38), and 374 nm (3.09), $\lambda_{infl.}$($CHCl_3$) 273 (log ε 4.74), 314 (4.37), and 356 nm (3.33), $\lambda_{max.}$(EtOH) 249 (log ε 4.32), 280 (4.87), 308 (4.30), 352 (3.33) and 371 nm (3.11), $\lambda_{infl.}$ (EtOH) 264 (log ε 4.53), 273 (4.74), and 315 nm (4.26); $\nu_{max.}$ (Nujol) 3430 (sharp, phenolic OH) 1622 (C=C), and 1260 cm^{-1} (ether C-O); τ [$(CD)_3SO$] 6.03 and 5.97 (both s, 3H, CH_3O), 5.92 (s, 6H, CH_3O), 2.18, 1.84, and 1.20 (each s, 1H, Ar-H), and 2.02 (s, 2H, Ar-H).

Reaction of veratrole with 3',4'-dimethoxyphenylbenzoquinone in aqueous sulphuric acid

A mixture of veratrole (200 mg), 3',4'-dimethoxyphenylbenzoquinone (244 mg), and 70% v/v aqueous sulphuric acid (30 ml) was shaken vigorously for 5 h and kept for 6 days at

room temperature. Water (200 ml) was added and the mixture was shaken for 1 h and extracted with chloroform. Evaporation of the extract gave a dark tarry solid from which crystalline material could not be obtained.

Attempted reaction of veratrole with 4,4'-dichloro-2,5-dimethoxybiphenyl-2',5'-quinone in aqueous sulphuric acid.

A mixture of veratrole (0.5 g), 4,4'-dichloro-2,5-dimethoxybiphenyl-2',5'-quinone (1.0 g), and 70% v/v aqueous sulphuric acid (60 ml) was shaken for 4 h and kept for 6 days at room temperature. Water (300 ml) was added and the mixture was kept overnight. The resulting precipitate was unchanged 4,4'-dichloro-2,5-dimethoxybiphenyl-2',5'-quinone (0.95 g).

CHAPTER 6

Attempted reaction between 1,4-naphthaquinone and veratrole

A solution of veratrole (6.9 g) in carbon disulphide (50 ml) was added dropwise to a stirred suspension of 1,4-naphthaquinone (15.8 g) and anhydrous aluminium chloride (16.75 g) in carbon disulphide (250 ml) and the mixture was stirred for 27 h at room temperature. Ice (120 g) and 5M-hydrochloric acid (100 ml) were added and the mixture was stirred for 2 h and filtered to give a solid residue and a filtrate (A). Extraction of the solid residue with acetone removed unchanged naphthaquinone (3.5 g), and left a blue-grey solid (3.2 g), a portion (0.5 g) of which was extracted with boiling chloroform. The extract was filtered through a column of silica gel which was washed with chloroform. A yellow-green band was eluted and evaporation of the eluate afforded a solid which crystallised from chloroform-ethanol to give 2,2'-binaphthyl-1,4:1',4'-diquinone (152) as yellow needles m.p. 270° (decomp.), mixed m.p. 270° (decomp.) with an authentic specimen prepared from 1,4-naphthaquinone in the presence of quinoline and acetic acid.[90] The pale yellow band which remained at the top of the column was removed and boiled with a large volume of ethanol which was filtered

and evaporated. The residue sublimed at 490°/2×10^{-5} torr to give 6,7:12,13:18,19:24,1-tetraepoxytetra(2,3-naphtho)cyclo-octatetraene (31) as pale yellow crystals. The i.r. absorption of this was identical with that of an authentic sample supplied by Professor H.G.H. Erdtman.[40]

The filtrate (A) was steam-distilled to remove carbon disulphide and veratrole (6 g). The residual flocculent violet solid (2 g) was collected and the aqueous filtrate was decanted from oily material and extracted with ether. Evaporation of the ether gave 1,4-dihydroxynaphthalene (1 g) the i.r. absorption of which was identical with that of an authentic sample prepared by the reduction of 1,4-naphthaquinone with sodium dithionite.

The violet solid was impure 8-hydroxydinaptho[1,2-b:2',1'-d] furan-5,6-quinone (155). It was insoluble in acetone, ethanol, and toluene, sparingly soluble in chloroform, and nitrobenzene, and soluble in dimethylsulphoxide, and in N,N-dimethylformamide; crystallisation from nitrobenzene did not give a pure product. A portion (230 mg) of the violet solid was added to acetic anhydride (35 ml) and concentrated sulphuric acid (0.2 ml), and the mixture was shaken vigorously, warmed on a water bath at 40° for 30 min, and poured into water (100 ml).

The red precipitate (230 mg) was collected and air-dried and a portion (80 mg) was subjected to p.l.c. using benzene-ethyl acetate (5:2). The resulting red band afforded a solid which crystallised from benzene to give 8-acetoxydinaphtho[1,2-b:2',1'-d]furan-5,6-quinone (156) as clusters of red rhombohedra (10 mg) m.p. 261.5-263° (Found: M, 356.0686. $C_{22}H_{12}O_5$ requires M, 356.0685), $\lambda_{max.}$ (EtOH) 265 (log ε 4.70), 275 (4.75), 336 (3.70), and 470 nm (3.40), $\lambda_{infl.}$ (EtOH) 253 (log ε 4.60), 290 (4.28), 299 (4.23), and 322 nm (3.84), $\lambda_{max.}$ ($CHCl_3$) 266 (log ε 4.68), 276 (4.73), 336 (3.75), and 474 nm (3.46), $\lambda_{infl.}$ ($CHCl_3$) 255 (log ε 4.61), 261 (4.66), 290 (4.30), 298 (4.27), 320 (3.90), and 378 nm (3.23); $\nu_{max.}$ (KBr) 1765 (acetate C=O), 1698, 1665, and 1650 (quinone C=O), and 1200 cm^{-1} (C-O).

Another portion (0.4 g) of the violet solid was boiled under reflux for 1 h with acetic anhydride (25 ml), zinc dust (1 g) and triethylamine (0.2 ml). The mixture was poured into water, shaken with chloroform, and the extract was washed with 10% aqueous sodium carbonate and with water, dried and evaporated. The resulting solid crystallised from chloroform-ethanol to give 5,6,8-triacetoxydinaphtho[1,2-b:2',1'-d]furan (157) as needles (100 mg) m.p. 270-271° (Found: C, 70.4; H, 3.8; AcO, 36.5%; M, 442. $C_{26}H_{18}O_7$ requires

C, 70.6; H, 4.1; 3AcO, 40.05%; M, 442), $\lambda_{max.}$(EtOH) 259 (log ε 4.88), 266 (4.84), 277 (4.78), 315 (4.09), 329 (4.21), and 341 nm (3.99), $\lambda_{infl.}$(EtOH) 250 (log ε 4.62), 294 (4.18), 302 (4.09), and 349 nm (3.25), $\lambda_{max.}$ ($CHCl_3$) 262 (log ε 4.83), 271 (4.80), 281 (4.76), 317 (4.12), 331 (4.27), and 343 nm (4.05), $\lambda_{infl.}$($CHCl_3$) 299 (log ε 4.20), 304 (4.13), and 353 nm (3.30); $\nu_{max.}$(Nujol) 1765 (acetate C=O) and 1205 cm^{-1}(C-O); τ ($CDCl_3$) 7.52 (s, 6H, CH_3CO_2), 7.46 (s, 3H, CH_3CO_2), 2.60-2.20 (m, 5H, Ar-H at C-2, C-3, C-7, C-10 and C-11), 2.20-2.00 (m, 2H, Ar-H at C-4 and C-9), and 1.60-1.40 (m, 2H, Ar-H at C-1 and C-12).

Reaction of 1,4-naphthaquinone with aluminium chloride in carbon disulphide

A mixture of 1,4-naphthaquinone (15.8 g), anhydrous aluminium chloride (16.75 g) and carbon disulphide (250 ml) was stirred at room temperature for 24 h. Ice (120 g) and 5M-hydrochloric acid (100 ml) were added and the mixture was stirred for 2 h and filtered. The solid residue was extracted with acetone to remove unchanged naphthaquinone (5 g), and the remaining blue-grey solid (3.5 g) showed the i.r. absorption of a mixture of 2,2'-binaphthyl-1,4:1',4'-diquinone and 6,7:12,13:18,19:24,1-tetraepoxytetra(2,3-

naphtho)cyclo-octatetraene.

The filtrate was steam-distilled to remove carbon disulphide and naphthaquinone, and the residual violet solid (1 g) was collected. A portion (450 mg) of this was added to acetic anhydride (100 ml) and concentrated sulphuric acid (0.2 ml). The mixture was shaken for 15 min, warmed to 50°, shaken for 30 min, and poured into water (250 ml) The resulting red solid (250 mg) was collected, washed with acetone and subjected to p.l.c. using benzene-ethyl acetate (5:2). A red band was obtained which afforded a solid which crystallised from chloroform-ethanol to give 8-acetoxydinaphtho[1,2-b: 2',1'-d]furan-5,6-quinone as red rhombohedra (100 mg), m.p. 260-262°, mixed m.p. 259-261° with an authentic specimen from the previous experiment.

Another portion (60 mg) of the violet solid was subjected to p.l.c. using benzene-N,N-dimethylformamide (6:1). The violet band obtained afforded a red solid which crystallised from chloroform-ethanol containing a little N,N-dimethylformamide to give 8-hydroxydinaphtho[1,2-b: 2',1'-d] furan-5,6-quinone (155) as dark red needles (13 mg), m.p. > 350°, (Found: M, 314.0571. $C_{20}H_{10}O_4$ requires M, 314.0579), $\lambda_{max.}$(EtOH) 279 (log ε 4.77), 332 (3.90), 348 (3.90), and 526 nm (3.49), $\lambda_{infl.}$(EtOH) 218 (log ε 4.64), 260 (4.63),

273 (4.74), 300 (4.16), and 314 nm (3.98); $\nu_{max.}$ (Nujol) 3350 (phenolic OH), 1690, 1655, and 1642 cm^{-1} (quinone C=O).

1,4-Diacetoxynaphthalene

1,4-Naphthaquinone (1.0 g) was boiled under reflux for 1 h with acetic anhydride (50 ml), zinc dust (1.0 g) and triethylamine (0.2 ml). The solution was poured into water and stirred vigorously. The resulting precipitate was collected and crystallised from ethanol to give 1,4-diacetoxynaphthalene as plates (0.6 g) m.p. 130-131° (lit.,[132] m.p. 128-130°), τ ($CDCl_3$) 7.61 (s, 6H, CH_3CO_2), 2.80 (s, 2H, Ar-H at C-2 and C-3), 2.58-2.42 (m, 2H, Ar-H at C-6 and C-7), and 2.24-2.08 (m, 2H, Ar-H at C-5 and C-8).

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