

The Reactions of Some *ortho*-Naphthoquinones with 2,3-Dimethylbutadiene †

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The reactions of dimethylbutadiene with 1,2-naphthoquinones are shown to involve either addition to the 3,4-double bond [substituents 3-chloro-, 4-cyano-, 3-methoxycarbonyl, 3-nitro-, and 3-methoxy- (partially)] or to the 2-carbonyl group [substituents 4-chloro-, 4-bromo-, 3,4-dichloro-, 3-methoxy- (partially)]. The adduct from 3-chloro-1,2-naphthoquinone is shown to eliminate hydrogen chloride to yield a phenanthrene-9,10-diol, which then undergoes acid-catalysed addition of dimethylbutadiene to yield a hydroxyphenanthrenone.

THE reaction between a 1,2-naphthoquinone and a conjugated diene was first reported in 1934 by Fieser and Seligman,¹ who showed that 3,7-dimethyl-1,2-naphthoquinone and 2,3-dimethylbutadiene yielded the adduct (1a). Also the 4-substituted 1,2-naphthoquinones (2a—c) have been shown to yield^{1,2} the adducts (3a—c), respectively. The adduct from the 4-cyano-methyl quinone is reported^{2b} to exist in the enol form

(4). However, the primary adduct (3d) from the 4-chloro-quinone was not isolated;^{3a} only the degradation product, 2,3-dimethylphenanthrene-9,10-quinone, was obtained, in low yield. Fieser and Dunn³ reported that 3-chloro- and 3-bromo-1,2-naphthoquinone yielded similar products, (1b) and (1c), which reacted with a further molecule of the diene with loss of hydrogen halide to give a compound having the novel structure

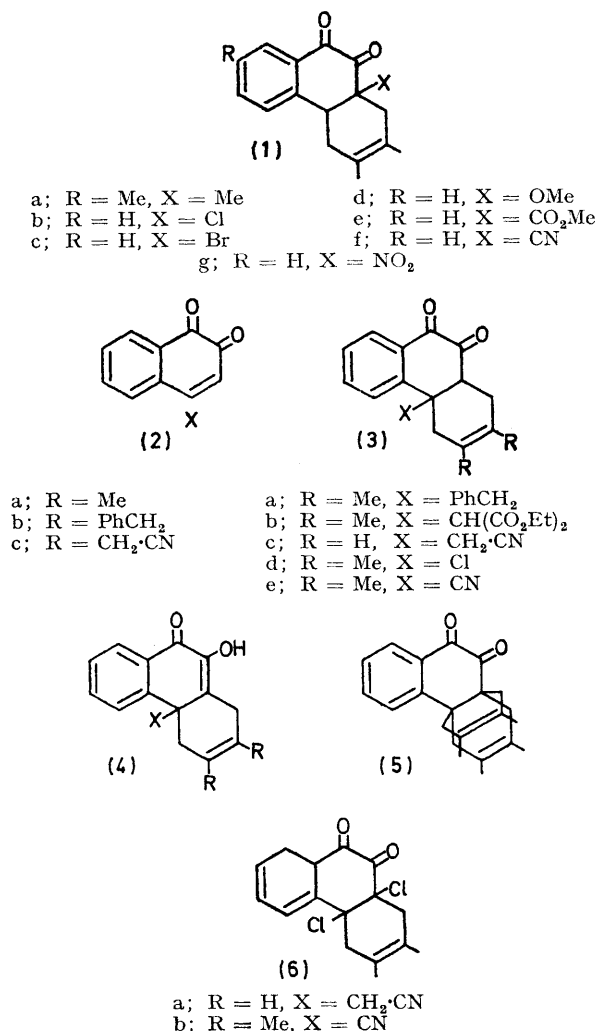
† Preliminary communications, M. F. Ansell and R. A. Murray, *Chem. Comm.*, 1968, 1583; 1969, 1111.

¹ L. F. Fieser and A. M. Seligman, *J. Amer. Chem. Soc.*, 1934, **56**, 2690.

² (a) M. Gates and W. F. Newhall, *J. Amer. Chem. Soc.*, 1948, **70**, 2261; (b) M. Gates, *ibid.*, 1950, **72**, 228.

³ L. F. Fieser and J. T. Dunn, *J. Amer. Chem. Soc.*, 1937, **59**, (a) 1016; (b) 1021.

(5). 3,4-Dichloro-1,2-naphthoquinone was also reported^{3a} to give a stable adduct (6) with 2,3-dimethylbutadiene, and its reactivity may be contrasted with the



failure to obtain an adduct from either 1,2-naphthoquinone or its 4-methyl derivative.⁴ However 1,2-naphthoquinone is reported⁵ to react as a dienophile towards (–)-pimaric acid. More recently, 3-bromonaphthoquinone has been shown to react with 1-vinylnaphthalene to give, after loss of hydrogen bromide and subsequent oxidation, picene-5,6-quinone (Scheme 1).⁶ The unsubstituted naphthoquinone yielded only tar.

The success⁷ obtained in the addition of dimethylbutadiene to *o*-benzoquinones prompted us to reinvestigate the reaction of 1,2-naphthoquinone, and the novel behaviour of the tetrahalogeno-*o*-benzoquinones⁸ led us to reinvestigate the reactions of 1,2-naphthoquinones halogenated in the quinonoid ring, particularly the formation of the 'further reaction product' (5).

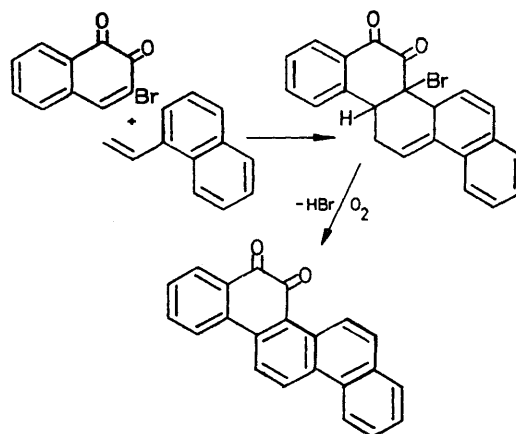
When 1,2-naphthoquinone prepared by iron(III)

⁴ L. F. Fieser and C. K. Bradsher, *J. Amer. Chem. Soc.*, 1939, **61**, 417.

⁵ B. A. Arbuzov, *J. Gen. Chem. (U.S.S.R.)*, 1942, **12**, 343.

⁶ W. Davies and B. C. Ennis, *J. Chem. Soc.*, 1959, 915.

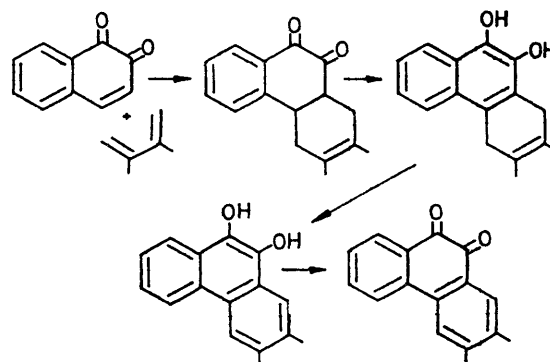
chloride oxidation of 1-amino-2-naphthol hydrochloride was used, no addition product with dimethylbutadiene could be isolated, since extensive decomposition of the quinone occurred, yielding intractable tars. When, however, the quinone was first purified by reduction and subsequent reoxidation with *o*-chloranil, no decomposition took place. The product isolated in 69% yield was 2,3-dimethylphenanthrene-9,10-quinone. This must



SCHEME 1

have arisen by initial addition of dimethylbutadiene to the 3,4-bond of 1,2-naphthoquinone to give 2,3-dimethyl-1,4,4a,10a-tetrahydrophenanthrene-9,10-quinone, which then underwent rearrangement to 1,4-dihydro-2,3-dimethylphenanthrene-9,10-diol. Under the conditions of the reaction, this dihydrophenanthrene eliminated hydrogen by a symmetry-allowed process and the resulting 2,3-dimethylphenanthrene-9,10-diol was oxidised by air to the observed product.

The concerted loss of hydrogen from the dihydrophenanthrene-9,10-diol is analogous to the thermal dehydrogenation of the 5,8-dihydronaphthalenes obtained from addition of dimethylbutadiene to *o*-benzoquinones (Scheme 2).



SCHEME 2

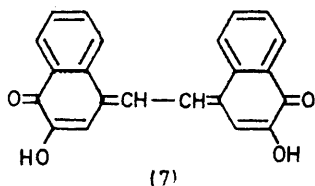
Fieser and Bradsher⁴ reported that 4-methyl-1,2-naphthoquinone decomposed extensively when treated

⁷ M. F. Ansell, A. J. Bignold, A. F. Gosden, V. J. Leslie, and R. A. Murray, *J. Chem. Soc. (C)*, 1971, 1414.

⁸ M. F. Ansell and V. J. Leslie, preceding paper.

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with dimethylbutadiene. Since purified samples of 1,2-naphthoquinone can be induced to react with dimethylbutadiene, it was thought that similar results might be obtained with 4-methyl-1,2-naphthoquinone, if carefully purified. However several attempts yielded only decomposition products. The work of Bradley and Watkinson^{9a} and of Bradley and Sanders^{9b} suggests a possible reason for this instability. They have shown that on heating, 4-methyl-1,2-naphthoquinone yields a red-violet decomposition product, from which a stilbenequinone (7) may be isolated. The decomposition

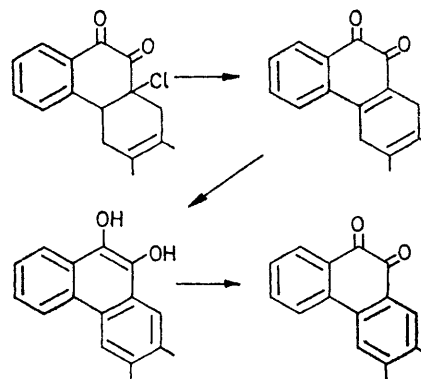


product from treatment of this quinone with dimethylbutadiene was violet in colour, and may have contained the stilbenequinone. A further point of interest is that both 4,6,7-trimethyl- and 3,4,6,7-tetramethyl-1,2-naphthoquinones are much less stable to heat and when in solution, than 1,2-naphthoquinones which do not have a 4-methyl group. Their decomposition may be analogous to that of 4-methyl-1,2-naphthoquinone.

The conditions employed for the reaction of 3-chloro-1,2-naphthoquinone with dimethylbutadiene were milder than those of Fieser and Dunn;³ this may account for the higher yield of adduct obtained (84 rather than 70%). The previous structural assignment (1b) was confirmed by consideration of the i.r. and n.m.r. spectra. The i.r. spectrum indicated the presence of an unconjugated and a conjugated carbonyl group and of a conjugated carbon-carbon double bond, and the n.m.r. spectrum was in accord with formulation of the compound as an adduct in which the diene had undergone addition to the 3,4-bond. The adduct was thermally unstable, but could be stored unchanged at -40° . When a solution in deuteriochloroform was heated at 100° in a sealed tube, 2,3-dimethylphenanthrene-9,10-diol was formed; this was identified from its n.m.r. spectrum (at 100°). The diol precipitated as a colourless solid on cooling the solution. Additional evidence as to the mode of decomposition was provided by the isolation of 2,3-dimethylphenanthrene-9,10-quinone (89%) when a solution in chloroform was heated in air. These observations can be rationalised as follows: the adduct on heating eliminates hydrogen chloride to give a 1,4-dihydrophenanthrene-9,10-quinone, which undergoes ready intra- or inter-molecular oxidation-reduction to a phenanthrene-9,10-diol. This diol is then oxidised by air to the quinone¹⁰ (Scheme 3).

It is possible that the hydrogen chloride is eliminated from the 1- and 10a-positions, rather than the 4a- and

10a-positions (Scheme 3), yielding a 4,4a-dihydrophenanthrene-9,10-quinone. However, since the product so formed is not a naphthoquinone, as in the alternative mechanism, the corresponding transition state would probably have a higher energy than that arising from 4a-10a-elimination, so this process is probably less



SCHEME 3

favoured. Neither the direction nor the mechanism of the elimination reaction is certain, but unless the initial adduct isomerises to the *trans*-isomer, an *anti*-elimination is not possible. This is evident from molecular models of the *cis*- and *trans*-isomers. In the *cis*-isomer the dihedral angles between the 10a-chloro-substituent and the three protons at positions 1 and 4a are *ca.* 55° , which is only compatible with a *syn*-elimination. In the *trans*-isomer the dihedral angle between the 10a-chlorine atom and the equatorial (relative to the non-oxygenated ring) 1-proton is also *ca.* 55° , but the dihedral angles between the chlorine atom and the axial 1-proton and between the chlorine atom and the 4a-proton are 180° , *i.e.* a coplanar *anti*-elimination is possible. It is not possible to assign either *cis*- or *trans*-stereochemistry to the adduct on the basis of the observed coupling constants between the 4a-proton and the two 4-protons. In the *cis*- and in the *trans*-isomer, the dihedral angles are *ca.* 35° and 155° , which by application of the Karplus curve¹¹ would lead to coupling constants of *ca.* 6 and 12 Hz, as observed.

The Diels-Alder adduct (1b) reacted with a second mol. of dimethylbutadiene³ within 36 hr. at 70° . The mixture initially became red after 5.5 hr., and had become yellow again after 36 hr. The product, which had the same m.p. as that obtained by Fieser and Dunn,³ could not have the structure assigned by them; its i.r. and n.m.r. spectra were in accord with a compound possessing a hydrogen-bonded hydroxy-group, a conjugated carbonyl group, six aromatic protons, two aromatic methyl groups, three vinylic methyl groups, and a methylene group. On the basis of this evidence, it was formulated as the hydroxyphenanthrenone (9a).

Since under the conditions used the initial adduct

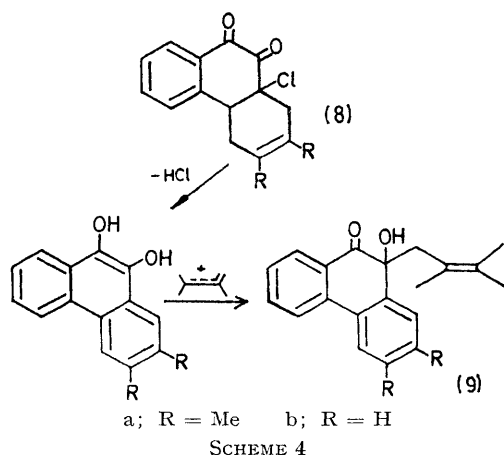
⁹ (a) W. Bradley and L. J. Wilkinson, *J. Chem. Soc.*, 1956, 319; (b) W. Bradley and J. D. Sanders, *ibid.*, 1962, 480.

¹⁰ Elsevier Encyclopedia of Organic Compounds, vol. 13, Elsevier, New York—Amsterdam, 1946, p. 848.

¹¹ M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.

would eliminate hydrogen chloride to give a phenanthrene-9,10-diol, the formation of the hydroxyphenanthrenone possibly involved addition of dimethylbutadiene to the diol. To test this hypothesis, a solution of phenanthrene-9,10-diol in chloroform and dimethylbutadiene was heated under reflux, but no reaction occurred. However, when the mixture was saturated with hydrogen chloride, a quantitative yield of the corresponding hydroxyphenanthrenone (9b) was obtained after 12 hr. at room temperature.

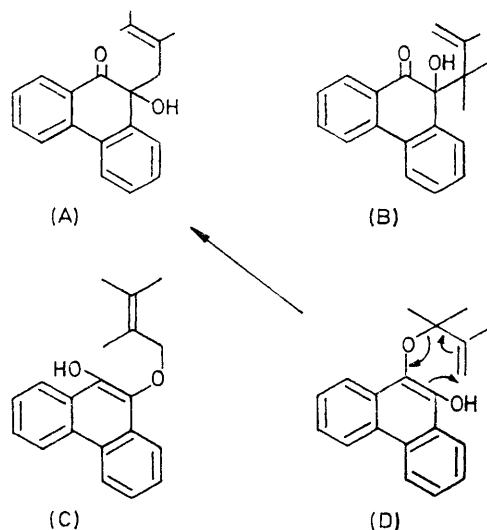
The n.m.r. spectrum of this compound was essentially identical to that of the 3,4-dimethyl analogue (9a), with the exception of the replacement of the absorptions due to the aromatic methyl groups by those due to the aromatic protons, and since compound (9b) has been independently synthesised¹² by the photochemical addition of tetramethylethylene to phenanthraquinone, this observation provides confirmation of the structure of the product isolated from the 3-chloro-1,2-naphthoquinone-dimethylbutadiene adduct. The reaction of 2,3-dimethylphenanthrene-9,10-diol with dimethylbutadiene in the presence of hydrogen chloride similarly gives a hydroxyphenanthrenone identical with that isolated from the 3-chloro-1,2-naphthoquinone adduct. Since attack at either end of the 9,10-bond is possible (the dissymmetry arising from the 2- and 3-methyl groups is far removed from the reaction centre) it is probable that a mixture of two isomers is formed. These would be expected to possess essentially identical spectra and so could not be distinguished. The sequence of reactions leading to the formation of the hydroxyphenanthrenone is rationalised in Scheme 4. The Diels-Alder adduct



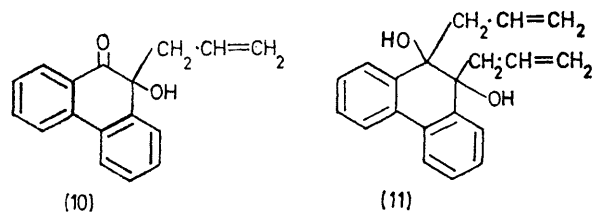
initially eliminates hydrogen chloride, which rapidly protonates dimethylbutadiene to give an allylic carbonium ion. This can then add to the phenanthrenediol, either at the 9,10-bond (C-alkylation) or to one of the hydroxy-groups (O-alkylation). Since the carbonium ion is allylic, it will be mesomeric and so could undergo these additions at the primary or the tertiary centre, leading to four possible products. However the n.m.r.

¹² S. Farid and K. Scholz, *Chem. Comm.*, 1968, 412, and personal communication.

spectrum of the crude product from phenanthrene-9,10-diol and dimethylbutadiene shows only absorptions due to the isolated product. The specificity of the reaction may be explained by postulating (see Scheme 5) that C-alkylation is faster than O-alkylation, favouring (A) rather than (C), but that steric hindrance to attack of the double bond by a tertiary centre favours formation of (D) rather than (B). However (D) is still subject to steric compression and since it is a phenolic allyl ether it could undergo Claisen rearrangement to the more stable (A). Thus both O- and C-alkylation would lead to the same product.



In order to obtain an authentic sample of the hydroxyphenanthrenone, the Grignard reaction between phenanthrenequinone and 2,3,3-trimethylallylmagnesium bromide was attempted. However this Grignard reagent was found to be so reactive towards the parent bromide that even when a cyclic Grignard reactor¹³ was used only dodecadienes were obtained. An analogous reaction with allylmagnesium bromide was, however, successful, and both mono- and di-addition products [(10) and (11)] were isolated.

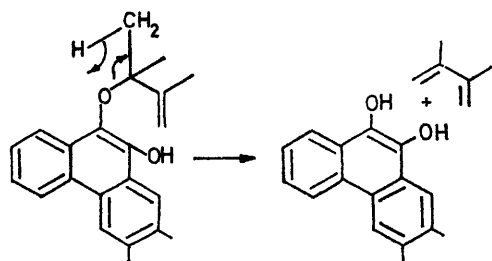


The trimethylallylhydroxyphenanthrenones readily eliminate dimethylbutadiene on pyrolysis. The dimethylbutadiene was readily identified by trapping with tetracyanoethylene to give the known Diels-Alder adduct. The elimination was also evident from the mass spectrum of the adduct (9a). No molecular ion was

¹³ G. M. Whiteside, J. E. Norlander, and J. D. Roberts, *Discuss. Faraday Soc.*, 1962, **34**, 185.

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observed, the base peak of the spectrum (m/e 238) corresponding to loss of dimethylbutadiene. A peak observed at m/e 41 is characteristic of symmetrical cleavage of dimethylbutadiene facilitated by the two adjacent tertiary centres. A prominent peak at m/e 83 was attributed to total loss of the trimethylallyl side chain from the parent compound. The ready elimination of dimethylbutadiene on pyrolysis to yield 2,3-dimethylphenanthrene-9,10-diol must involve rearrangement of the initial species, since an effective transfer of a proton from the 3'-methyl group to the carbonyl group must be made. This can be rationalised (Scheme 6) by postulating a retro-Claisen rearrangement of the allyl- α -dienone (a Claisen rearrangement intermediate) to an allyl ether, which then undergoes a four-centre rearrangement to give the observed products. A one-step rearrangement to the products is unlikely, since it would involve an eight-membered cyclic transition state. Such rearrangements have been discussed by Mathieu and Valls.¹⁴



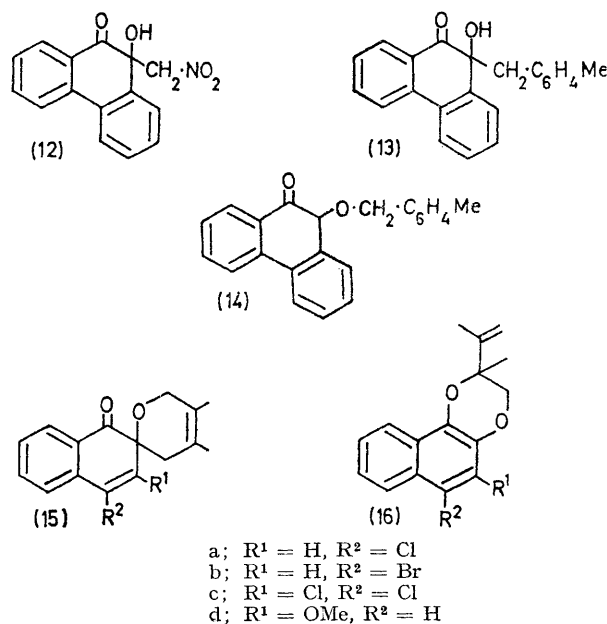
SCHEME 6

Hydroxyphenanthrenones have been previously reported, but have never before been prepared from phenanthrene-9,10-diol. Treatment of phenanthrenequinone with nitromethane gives¹⁵ an 'adduct' (12) which decomposes thermally to phenanthrenequinone. Grignard reagents react with phenanthrenequinone to give hydroxyphenanthrenones (see before and ref. 16a).

The third main route to the hydroxyphenanthrenones is by photochemical addition involving phenanthrenequinone and is exemplified by the addition of tetramethylethylene to phenanthrenequinone cited earlier¹² and by the work of Rubin and his co-workers. Rubin and Zwitkowitz^{15a} have shown that photochemical addition of *p*-xylene to phenanthrenequinone gives the *p*-methylbenzylhydroxyphenanthrenone (13). Interrupted additions permit isolation of the isomeric ether (14) which^{15b} can be converted photochemically into the hydroxyphenanthrenone (13). The rearrangement of the ether is of interest in view of trimethylallyl etherhydroxyphenanthrenone rearrangements postulated.

The addition product of the 4-chloro-1,2-naphthoquinone with dimethylbutadiene was not isolated by Fieser and Dunn² but was converted directly into 2,3-dimethylphenanthrene-9,10-quinone. No formation of a hydroxyphenanthrenone such as (9a) was reported.

Such a reaction would be expected, since their adduct lost hydrogen chloride in an analogous manner to the 3-chloro-1,2-naphthoquinone adduct. We repeated the reaction under milder conditions and isolated an adduct in 67% yield. On the basis of spectral evidence it was



shown to be a spirodihydropyran (15a) arising from addition of the diene to one of the carbonyl groups of the quinone.

Such additions have been extensively studied⁸ and it is known that they are characteristic of tetrahalogenated *o*-benzoquinones and certain acyclic dienes. Such spirodihydropyrans can be regarded as Claisen rearrangement intermediates and can undergo retro-Claisen rearrangement to benzodioxans. Thus the observation of rearrangement of the adduct from 4-chloro-1,2-naphthoquinone to a naphthodioxan (16a) is additional evidence for the structure of the former compound. The naphthodioxan (16a) was not isolated but the rearrangement was followed by observation of the carbonyl region of the i.r. spectrum of the rearrangement mixture. The absorption at 1690 cm^{-1} was replaced by less intense absorptions at 1625 and 1650 cm^{-1} . By analogy with the rearrangement of the spirodihydropyran from 3,4-dichloro-1,2-naphthoquinone (see later), this is consistent with the formation of a naphthodioxan.

Since the non-photochemical cycloaddition of a diene to a carbonyl group is dependent on the carbonyl group being electron deficient,⁸ we consider that addition to the 2-carbonyl group is the more probable course of the reaction, as it is only to this group that the electron-withdrawing effect of the chlorine atom is relayed by conjugation. Structure (15a) is supported by the observation that the signal of the naphthalene 3-proton

¹⁴ J. Mathieu and J. Valls, *Bull. Soc. chim. France*, 1957, 1509.

¹⁵ A. I. Yakubovich, *J. prakt. Chem.*, 1935, **37**, 142.

¹⁶ M. R. Rubin and P. Zwitkowitz, (a) *J. Org. Chem.*, 1964, **29**, 2360; (b) *Tetrahedron Letters*, 1965, 2453.

in the n.m.r. spectrum of the adduct (τ 3.72) is at a higher field than that (τ 3.21) of the 3-proton in the parent quinone.¹⁷ This would not occur if the 3-proton in the adduct was still deshielded by the 2-carbonyl group.

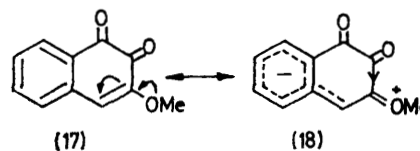
The n.m.r. spectrum of the crude reaction mixture from 4-chloro-1,2-naphthoquinone and dimethylbutadiene, showed no significant peaks other than those of the spirodihydropyran, and in the region where the 1- and 4-protons of the adduct (3d) might be expected to appear as a multiplet (τ 6.5—8.2) only the absorption due to the 3'-CH₂ of the spirodihydropyran (a singlet at τ 7.60) was observed. The isolation of the 2,3-dimethylphenanthrenequinone by Fieser and Dunn^{3a} in this reaction is thus puzzling. A possible explanation is that their sample of 4-chloro-1,2-naphthoquinone was contaminated with *ca.* 15—20% of some other quinone (possibly 1,2-naphthoquinone or the 3-chloro-isomer), which could give rise to this product.

4-Bromo-1,2-naphthoquinone, when treated like the 4-chloro-analogue, gave an 89% yield of adduct in 72 hr. The adduct was a spirodihydropyran, whose n.m.r. and i.r. spectra were almost identical with those of the chloro-analogue. Preliminary investigations indicated that it similarly underwent retro-Claisen rearrangement to a naphthodioxan.

Fieser and Dunn^{3a} reported that the two halogen atoms of 3,4-dichloro-1,2-naphthoquinone seemed to hinder the addition of dimethylbutadiene, but that the adduct isolated was much more stable than that from the 3-chloro-analogue. However, in the light of the work of Ansell and Leslie,⁸ addition to the tetrasubstituted 3,4-double bond of the quinone seemed unlikely, and as no structural evidence was provided by Fieser and Dunn the reaction was repeated under milder conditions than those of the original work. On the basis of its n.m.r. and i.r. spectra, the adduct was shown to be the spirodihydropyran (15c), which underwent retro-Claisen rearrangement in refluxing xylene to yield the corresponding naphthodioxan (16c). For the reason already discussed we consider that the diene added to the 2-carbonyl group.

Examples of the non-photochemical addition of a conjugated diene to the carbonyl group of a quinone discussed so far (this paper and the preceding paper) have involved halogenated quinones. 3-Methoxy-1,2-naphthoquinone reacts in the presence of excess of 2,3-dimethylbutadiene to give a mixture (separable by t.l.c.) of the spirodihydropyran (15d) and the tetrahydrophenanthraquinone (1d) in the ratio 1:3. This reaction is remarkable since a methoxy-substituent is expected to reduce the dienophilic reactivity of the 3,4-double bond, and indeed the formation of adducts containing angular methoxy-groups is rare; 4,5-dimethoxy-*o*-benzoquinone and 4-methoxy-1,2-naphthoquinone are inert towards dimethylbutadiene. Formation of the spirodihydropyran is consistent with the

view that an electron-withdrawing group is necessary. Formulae (17) and (18) show how the methoxy-group can act in this manner.



In compounds derived from 1,2-naphthoquinones in which there is a carbonyl group at C-1 but no halogen at C-4, the n.m.r. signal of the naphthalene 8-proton is distinct from those of the other aromatic protons, and occurs between τ 2.33 and 1.85 owing to the deshielding effect of the 1-carbonyl group. An ether oxygen at the *peri*-position would not be expected to have a comparable deshielding effect. The observation that the signal of the 8-proton is at τ 2.05 in 3-methoxy-1,2-naphthoquinone and at τ 2.18 in the adduct (15d), together with the observation that the 4-proton signal appears at lower field (τ 3.58) in the spectrum of the parent quinone than in that of the adduct (15d) (τ 4.37) supports the conclusion that the diene has added to the 2-carbonyl group as shown.

In contrast to the 3-methoxy-quinone, 4-methoxy-1,2-naphthoquinone is unreactive towards 2,3-dimethylbutadiene. In this case the electron-donating methoxy-group enhances the electron density in both the 3,4-double bond and the 2-carbonyl group, thereby preventing addition at either unsaturated centre. This lack of reactivity is also shown by 4-acetamido-1,2-naphthoquinone, which was unchanged in the presence of a 20 molar excess of diene after 21 days at 70°.

Diels-Alder reactions of 1,2-naphthoquinones containing electron-withdrawing groups (other than halogen) directly attached to the quinone ring have not previously been reported. 3-Methoxycarbonyl-1,2-naphthoquinone reacted with dimethylbutadiene to give the adduct (1e), arising from addition to the 3,4-double bond. Similarly 4-cyano-1,2-naphthoquinone reacted readily to yield the adduct (3e). This compound (identified spectroscopically) melted at 138—141°, resolidified, and remelted at 152—153°. Recrystallisation of the adduct from ethanol gave the enol (4b), m.p. 155—156°. Thus the resolidification of the melted adduct (3e) is attributable to thermally induced enolisation. This is to be expected, since enolisation of adducts from 4-cyano- and 4-methoxycarbonyl-*o*-benzoquinone with dimethylbutadiene has been observed,⁷ and similar enolisations have been reported^{2b} with the analogous adducts from 4-cyanomethyl-1,2-naphthoquinones and butadiene. The difference in behaviour between 4-chloro- and 4-cyano-1,2-naphthoquinone is attributed to the linear nature of the cyano-group, which thus offers less steric hindrance to 3,4-double bond addition.

3-Nitro-1,2-naphthoquinone reacted with dimethylbutadiene comparatively rapidly (1 hr.) and a yellow adduct (1g) was isolated, which melted at 130—132°.

¹⁷ R. W. A. Oliver, R. M. Rashman, and A. W. Sommerville, *Tetrahedron Letters*, 1968, 4067.

resolidified, and remelted at 230°. Spectroscopic data indicated that addition of dimethylbutadiene to the 3,4-double bond of the quinone had occurred. The resolidification of the melted adduct suggested an elimination of nitrous acid to yield 2,3-dimethylphenanthrene-9,10-quinone, by analogy with the behaviour of the 3-chloro-1,2-naphthoquinone adduct. Confirmation was provided by carrying out the decomposition in refluxing mesitylene at 165° (the adduct was stable in refluxing xylene); evidence for the evolution of nitrous acid was provided by the formation of its decomposition products, nitrogen dioxide and water.

EXPERIMENTAL

All the reactions involving dimethylbutadiene were carried out in the dark. All n.m.r. spectra were determined for solutions in deuteriochloroform (unless otherwise specified); integrations of spectra of pure compounds gave satisfactory results.

Petroleum refers to light petroleum b.p. 40–60°. T.l.c. was performed with Merk Silica Gel HF₂₅₄ activated at 110° for 4 hr.

Reaction of 2,3-Dimethylbutadiene with 1,2-Naphthoquinone.—A suspension of pure 1,2-naphthoquinone (see later) (1.85 g.) in chloroform (10 ml.) and the diene (10 ml.) was heated under reflux for 24 hr. The red solution was cooled to 0° and the precipitated solid was filtered off, washed with ether (10 ml.), and dried to yield 2,3-dimethylphenanthrene-9,10-quinone (1.9 g., 69%) as orange red needles, m.p. 240–243° (from glacial acetic acid) (lit.³ 237–238°); ν_{\max} , 1760 (conj. C=O) and 1600 cm⁻¹ (conj. C=C); τ 1.8–2.6 (m, 5-, 6-, 7-, and 8-H), 2.15 (s, 1-H), 2.33 (s, 4-H), and 7.7 (s) and 7.62 (s) (2- and 3-Me).

Treatment of 4-Methyl-1,2-naphthoquinone with Dimethylbutadiene.—A solution of 4-methyl-1,2-naphthoquinone⁴ (2.5 g.) in chloroform (10 ml.) and dimethylbutadiene (10 ml.) was kept in the dark for 2 days. A fine violet precipitate separated out; the mother liquor was almost colourless. The precipitate was filtered off, washed with ether, and dried. It was insoluble in all common solvents.

Reaction of 3-Chloro-1,2-naphthoquinone with Dimethylbutadiene.—3-Chloro-1,2-naphthoquinone¹⁷ (1.0 g.) was suspended in a mixture of chloroform (5 ml.) and dimethylbutadiene (10 ml.), and the suspension was stirred for 48 hr.; the quinone had then dissolved and the colour of the solution had faded to orange. Evaporation *in vacuo* left a dark red oil which was chromatographed on a silica gel column with 1:1 ether–petroleum (b.p. 40–60°) as eluant. The yellow eluate was evaporated to give a yellow oil, which crystallised from ether and petroleum (b.p. 40–60°) to give yellow needles. Recrystallisation (ether and petroleum) gave 10a-chloro-1,4-dihydro-2,3-dimethylphenanthrene-9,10-quinone (1b) (1.2 g., 84%) as yellow needles, m.p. 82–83° (decomp. with effervescence); ν_{\max} , 1745 (C=O), 1690 (conj. C=O), and 1610 (conj. C=C) cm⁻¹; τ 2.00 (pair of d, *J* 7.5 and 2 Hz, 8-H), 2.3–2.9 (m, 5-, 6-, and 7-H), 6.32 (pair of d, *J* 12 and 6 Hz, 4a-H), 6.6–8.2 (m, 1- and 4-H₂), 8.3 (s, 2-Me), and 8.47 (s, 3-Me) (lit.³ m.p. 87–88°).

Reaction of 10a-Chloro-1,4-dihydro-2,3-dimethylphenanthrene-9,10-quinone with Dimethylbutadiene.—A solution of the quinone (1b) (0.85 g.) in chloroform (3 ml.) and di-

methylbutadiene (10 ml.) was heated under reflux. The solution began to darken after 4 hr. and within 5.5 hours was red in colour. Within 36 hr. it had become yellow again. The solvent was evaporated off to leave a pale yellow solid (1.0 g.). Recrystallisation from ethanol gave 10-(2,3-dimethylbut-2-enyl)-10-hydroxy-2,3- (or 6,7-)dimethylphenanthren-9(10H)-one (9a) (or a mixture of both compounds) (0.85 g., 86%) as pale yellow tablets, m.p. 130–135° (lit.³ m.p. 130–135°) (Found: C, 82.2; H, 7.8. Calc. for C₂₂H₂₄O₂: C, 82.45; H, 7.55%); ν_{\max} , 3490 sharp (H-bonded OH), 1680 (conj. C=O), and 1610 (conj. C=C) cm⁻¹; τ 2.1–2.8 (m, 1-, 4-, 5-, 6-, 7-, and 8-H), 6.02 (s, exchangeable, OH), 2.75 and 2.34 (ABq, *J* 14 Hz, 1'-CH₂), 7.63 (s) and 7.7 (s) (2- and 3-Me), 8.5 (s, 3'-Me₂), and 8.72 (s, 2'-Me); *m/e* (220°; direct insertion) 238 [100%, *M* – 82 (C₈H₁₀)], 237 [89%, *M* – 83 (C₈H₁₁) and (*M* – 82 – H, *m** 236)], 223 [13%, (*M* – 82) – Me, *m** 209], 209 (25%, 237 – CO, *m** 184), 195 (10%, 223 – CO, *m** 171), 165 (28%), 83 (36%, C₈H₁₁), 55 (34%), and 41 (33%, C₃H₅).

Thermal Decomposition of the Phenanthrenequinone (1b).—(a) A solution of the quinone (1b) (100 mg.) in deuteriochloroform (1 ml.) contained in a sealed n.m.r. tube was heated at 100° for 30 min. After this time, the n.m.r. signals due to the starting material had disappeared and had been replaced by signals attributable to 2,3-dimethylphenanthrene-9,10-diol; τ 1.3–3.0 (m, 1-, 4-, 5-, 6-, 7-, and 8-H), 5.5br (s, 9- and 10-OH), and 7.7br (s, 2- and 3-Me). The cool solution deposited a colourless solid.

(b) A solution of the quinone (1b) (100 mg.) in chloroform (10 ml.) was heated under reflux; the reaction was followed by observation of the carbonyl region of the i.r. spectrum of the solution. After 8 hr. the solution began to darken, but within 24 hr. it had again become yellow; the absorption at 1735 cm⁻¹ had disappeared. Evaporation left an orange-brown solid, which was suspended in ether (5 ml.), filtered off, and dried to yield 2,3-dimethylphenanthrene-9,10-quinone (77 mg., 89%), m.p. and mixed m.p. 236–237° (lit.³ 237–238°).

Thermal Decomposition of 10-(2,3-dimethylbut-2-enyl)-10-hydroxy-2,3-dimethylphenanthren-9(10H)-one.—The phenanthrenone (9a) (0.5 g.) was heated at 150° for 5 min. in a stream of nitrogen, which was then bubbled into a solution of tetracyanoethylene (0.25 g.) in tetrahydrofuran (10 ml.). The tetrahydrofuran was evaporated off under reduced pressure to give a pale brown solid which yielded 1,2-dimethyl-4,4,5,5-tetracyanocyclohexene (0.24 g., 67%) as colourless plates, m.p. and mixed m.p. 140–143° (from ethanol) (lit.¹⁸ 136–137°).

The residue from the pyrolysis on digestion with ether afforded 2,3-dimethylphenanthrene-9,10-quinone (0.3 g., 82%), m.p. and mixed m.p. 237–238°.

Reaction of 2,3-Dimethylphenanthrene-9,10-diol and Dimethylbutadiene.—A solution of the diol (200 mg.; prepared by reduction of 2,3-dimethylphenanthrenequinone with sodium dithionite) in hydrogen chloride-saturated chloroform (5 ml.) and dimethylbutadiene (5 ml.) was heated under reflux for 1 hr. The yellow solution was evaporated to yield an orange solid, which was chromatographed on a Florisil column with ether as eluant. The eluate was evaporated to give a colourless crystalline solid (240 mg.). Recrystallisation from petroleum (b.p. 80–100°) afforded the phenanthrenone (9a) (185 mg., 69%)

¹⁸ W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1958, **80**, 2783.

as pale yellow crystals, m.p. 128–132° (decomp.), identical with the material obtained directly from the quinone (1b).

Reaction of Phenanthrene-9,10-diol and Dimethylbutadiene.

—A suspension of phenanthrene-9,10-diol (1.8 g.; prepared from phenanthrenequinone by reduction with sodium dithionite) in hydrogen chloride-saturated chloroform (5 ml.) and dimethylbutadiene (5 ml.) was left for 12 hr. The resulting yellow solution was evaporated (vacuum) to yield 10-(2,3-dimethylbut-2-enyl)-10-hydroxyphenanthrene-9(10H)-one (9b) (2.5 g., 100%) as a pale brown solid which yielded colourless needles [from petroleum (b.p. 80–100°)], m.p. 91–94° (lit.¹² 88–91°) (Found: C, 81.9; H, 7.2. Calc. for $C_{20}H_{20}O_2$: C, 82.2; H, 6.9%); ν_{\max} 3490 sharp (H-bonded OH), 1680 (conj. C=O), and 1602 (conj. C=C) cm^{-1} ; τ 1.9–2.85 (m, 8H, aromatic), 5.9 (s, exchangeable, OH), 2.77 and 2.37 (ABq, J 14 Hz, 1'-CH₂), 8.53 (s, 3'-Me₂), and 8.80 (s, 2'-Me).

Addition of Allylmagnesium Bromide to Phenanthrene-9,10-quinone.—A solution of allyl bromide (2.9 g.) in dry ether (50 ml.) was added to a stirred suspension of magnesium turnings (1.5 g.) in dry ether (10 ml.) at such a rate as to maintain reflux after the reaction had commenced. When the addition was complete, the resulting solution was refluxed for 0.5 hour, filtered through a glass wool plug into a dropping funnel, and added dropwise during 1 hr. to a stirred, refluxing solution of phenanthrenequinone (5 g.) in dry benzene (200 ml.). The dark green solution was cooled, poured into ice cold 2N-sulphuric acid (50 ml.), and shaken with benzene (50 ml.); the mixture was filtered. The organic layer was separated, washed with water (50 ml.), dried (MgSO₄), concentrated to (50 ml.), and refiltered to remove unchanged phenanthrenequinone (3.75 g.). The filtrate was reduced to ca. 5 ml. and chromatographed on a Florisil column with benzene as eluent. The pale yellow eluate was evaporated to give a yellow oil, which by t.l.c. [petroleum (b.p. 40–60°)-ether (1:1)] yielded (R_F ca. 0.8) 10-allyl-10-hydroxyphenanthrene-9(10H)-one (10) (650 mg., 37% based on unrecovered phenanthraquinone) as a pale yellow oil (Found: C, 81.4; H, 5.6. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%); ν_{\max} 3490 sharp (H-bonded OH), 1690 (conj. C=O), 1603 (conj. C=C), and 935 and 985 (—CHR=CH₂) cm^{-1} ; τ 2.0–2.9 (m, 8H, aromatic), 3.9–5.4 (m, 3'-CH₂ and 2'-CH), 5.93 (s, exchangeable, OH), 7.52 (d, J 7 Hz, 1'-CH₂); and (R_F ca. 0.6) 9,10-diallyl-9,10-dihydrophenanthrene-9,10-diol (11) (350 mg., 20%) [colourless needles from petroleum (b.p. 60–80°)], m.p. 73–75° [(Found: C, 81.9; H, 6.9. $C_{20}H_{20}O_2$ requires C, 82.2; H, 6.9%); ν_{\max} 3560 (OH), 1640 (C=C), and 935 and 980 cm^{-1} (—CHR=CH₂); τ 2.2–2.9 (m, 8H, aromatic), 4.0–5.3 (m, 2 × CH₂CH₂), 7.77 and 7.33 (d of ABq, J 14 and 8 Hz, 2 × CH₂), and 7.42 (s, exchangeable, 2 × OH)].

Reaction of 4-Chloro-1,2-naphthoquinone with Dimethylbutadiene.—A solution of 4-chloro-1,2-naphthoquinone¹⁷ (0.5 g.) in chloroform (5 ml.) and dimethylbutadiene (5 ml.) was heated under reflux for 12 hr., then was evaporated to give a red oil, a portion (50 mg.) of which was retained for determination of its n.m.r. spectrum. The remainder was chromatographed on a column of Florisil (3 × 15 cm.) [1:1 petroleum (b.p. 40–60°)-ether]. The yellow eluate was evaporated to give a yellow oil which crystallised when triturated with petroleum. Recrystallisation from petroleum (b.p. 60–80°) yielded 4-chloro-3',6'-dihydro-4',5'-dimethylspiro[naphthalene-2,2'-pyran]-1(2H)-one (15a) (0.48 g., 67%) as pale yellow prisms, m.p. 87–88° (Found:

C, 69.6; H, 5.5; Cl, 12.8. $C_{16}H_{15}ClO_2$ requires C, 69.9; H, 5.5; Cl, 12.6%); ν_{\max} 1690 (conj. C=O) 1610 (conj. C=C), and 1100 cm^{-1} (C—O stretch of pyran); τ 2.0–2.8 (m, 5-, 6-, 7-, and 8-H), 3.72 (s, 3-H), 5.11 and 5.80 (ABq, J 16 Hz, 6'-H₂), 7.60br (s, 3'-CH₂), and 8.37 (5'- and 4'-Me). The n.m.r. spectrum of the crude product showed no significant additional absorption.

Reaction of 4-Bromo-1,2-naphthoquinone with Dimethylbutadiene.—A solution of 4-bromo-1,2-naphthoquinone¹⁷ (150 mg.) in chloroform (2 ml.) and dimethylbutadiene (2 ml.) was heated under reflux for 72 hr. It was then evaporated to dryness to give a brown oil, which was chromatographed on a column of Florisil (1 × 15 cm.) [1:1 petroleum (b.p. 40–60°)-ether]. The yellow eluate was evaporated to give a pale yellow oil which crystallised when triturated with petroleum. Recrystallisation from petroleum (b.p. 60–80°) gave 4-bromo-3',6'-dihydro-4',5'-dimethylspiro[naphthalene-2,2'-pyran]-1(2H)-one (15b) (180 mg., 89%) as pale yellow needles, m.p. 192–195° (Found: C, 60.5; H, 4.9; Br, 24.8. $C_{16}H_{15}BrO_2$ requires C, 60.2; H, 4.7; Br, 25.0%); ν_{\max} 1690 (conj. C=O), 1605 (conj. C=C), and 1100 cm^{-1} (C—O stretch of pyran); τ 2.1–2.8 (m, 5-, 6-, 7-, and 8-H), 3.48 (s, 3-H), 5.1 and 5.8 (ABq, J 16 Hz, 6'-CH₂), 7.60br (s, 3'-CH₂), and 8.38br (s, 5'- and 4'-Me).

Reaction of 3,4-Dichloro-1,2-naphthoquinone with Dimethylbutadiene.—A solution of 3,4-dichloro-1,2-naphthoquinone¹⁹ (3.3 g.) in chloroform (10 ml.) and dimethylbutadiene (10 ml.) was heated under reflux for 72 hr. in the dark. (T.l.c. indicated one major component in the mixture, a yellow compound with R_F ca. 0.8.) Evaporation left a dark oil which crystallised and was chromatographed on a column of Florisil (3 × 20 cm.) [9:1 benzene-petroleum (b.p. 60–80°)]. Evaporation of the yellow eluate gave a pale yellow solid which on recrystallisation from petroleum (b.p. 40–60°) gave 3,4-dichloro-3',6'-dihydro-4',5'-dimethylspiro[naphthalene-2,2'-pyran]-1(2H)-one (15c) (3.6 g., 80%) as pale yellow needles, m.p. 126–128° (Found: C, 62.0; H, 4.4; Cl, 22.7. $C_{16}H_{14}Cl_2O_2$ requires C, 62.15; H, 4.6; Cl, 23.0%); ν_{\max} 1700 (conj. C=O) and 1590 cm^{-1} (conj. C=C), τ 2.0–2.8 (m, 5-, 6-, 7-, and 8-H), 5.11 and 5.80 (ABq, J 16 Hz, 6'-H₂), 7.60br (s, 3'-H₂), and 8.37br (s, 5'- and 4'-Me) (for product of this reaction lit.³ m.p. 130.5–131.5°).

A solution of the spiro-compound (15c) (0.5 g.) in xylene (15 ml.) was boiled under reflux. After 10 hr. it no longer absorbed at 1700 cm^{-1} (C=O region). The solvent was removed and the residue was chromatographed on alumina (Brockmann grade I) (1:1 ether-petroleum). The colourless eluate, which exhibited a blue fluorescence under u.v. light, was collected and evaporated. The residual colourless oil crystallised from petroleum (b.p. 80–100°) to give 5,6-dichloro-2,3-dihydro-2-isopropenyl-2-methylnaphtho-[1,2,b]-p-dioxan (16c) (340 mg., 68%) as colourless prisms, m.p. 107–109° (Found: C, 62.0; H, 4.6; Cl, 22.9. $C_{16}H_{14}Cl_2O_2$ requires C, 62.15; H, 4.6; Cl, 22.9%); ν_{\max} 1590 and 1503 (aromatic C=C) and 905 cm^{-1} (RCH=CH₂); τ 1.8–2.1 and 2.4–2.85 (m, 7-, 8-, 9-, and 10-H), 4.9br (s) and 5.05br (s) (=CH₂), 5.59 and 5.96 (ABq, J 11.5 Hz, 3-H₂), 8.14 (pair of d, J 3 and 1 Hz, vinyl Me), and 8.48 (s, 2-Me).

Reaction of 3-Methoxy-1,2-naphthoquinone with Dimethyl-

¹⁹ N. Latif, I. Fathy, and N. Mishriky, *J. Org. Chem.*, 1959, 24, 1883.

butadiene.—A solution of 3-methoxy-1,2-naphthoquinone ²⁰ (0.25 g.) in chloroform (10 ml.) and dimethylbutadiene (5 ml.) was heated under reflux for 36 hr. in the dark. Analytical t.l.c. indicated that the yellow solution contained two components of R_F ca. 0.7 and 0.8. Evaporation left a yellow oil. A portion (50 mg.) was retained for measurement of its n.m.r. spectrum, and the remainder was chromatographed (thin-layer) on silica gel [1:1 ether–petroleum (b.p. 40–60°)].

The yellow band R_F ca. 0.7 was eluted with ether and gave 3',6'-dihydro-3-methoxy-4',5'-dimethylspiro[naphthalene-2,2'-pyran]-1(2H)-one (15d) (70 mg., 19.5%) as a yellow oil (Found: C, 75.4; H, 6.8. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.7%; ν_{\max} 1690 (conj. C=O) and 1640 (conj. C=C) cm^{-1} ; τ 2.18 (d, 8-H), 2.4–3.1 (m, 5-, 6-, and 7-H), 4.37 (s, 4-H), 5.37 and 5.86 (ABq, J 17 Hz, 3'-H₂), and 8.36br (s, 5'- and 4'-Me). The yellow band R_F ca. 0.8 was eluted with ether and gave 1,4,4a,10a-tetrahydro-10a-methoxy-2,3-dimethylphenanthrene-9,10-quinone (1d) (270 mg., 75%) as a yellow oil (Found: C, 75.7; H, 6.6. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.7%; ν_{\max} 1740 (C=O), 1690 (conj. C=O), and 1600 cm^{-1} (conj. C=C); τ 1.90 (pair of d, J 8 and 2 Hz, 8-H), 2.2–2.8 (m, 5-, 6-, and 7-H), 6.5 (pair of d, J 12 and 6 Hz, 4a-H), 6.84 (s, 10a-OMe), 6.9–8.2 (m, 1- and 4-H₂), and 8.21br (s) and 8.39 (s) (2- and 3-Me). The n.m.r. spectrum of the crude product showed only peaks due to these two compounds. Comparison of the intensities of the absorptions of the methoxy-protons in the two compounds showed that the spiropyran and phenanthrene-quinone derivatives were present in the ratio 1:3, respectively.

Reaction of 3-Methoxycarbonyl-1,2-naphthoquinone with Dimethylbutadiene.—A solution of 3-methoxycarbonyl-1,2-naphthoquinone (see later) (300 mg.) in chloroform (5 ml.) and dimethylbutadiene (5 ml.) was left for 12 hr. in the dark. It was then evaporated under reduced pressure to give a dark oil, which was chromatographed on a column of silica gel (3.0 × 15 cm.) [1:1 ether–petroleum (b.p. 40–60°)]. The yellow eluate was evaporated to give a yellow oil, which crystallised on trituration with petroleum. Recrystallisation from petroleum (b.p. 80–100°) gave 1,4,4a,10a-tetrahydro-10a-methoxycarbonyl-2,3-dimethylphenanthrene-9,10-quinone (1e) (350 mg., 84%) as yellow prisms, m.p. 132–135° (Found: C, 72.6; H, 6.2. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.1%; ν_{\max} 1760 (C=O), 1735 (ester C=O), 1685 (conj. C=O), and 1600 (conj. C=C) cm^{-1} ; τ 1.85 (pair of d, J 8 and 1.5 Hz, 8-H), 2.25–2.75 (m, 5-, 6-, and 7-H), 6.28 (pair of d, J 12 and 6 Hz, 4a-H), 6.48 (s, CO₂Me), 6.8–8.2 (m, 1- and 4-H₂), 8.25br (s, 2-Me), and 8.42 (s, 3-Me).

Reaction of 4-Cyano-1,2-naphthoquinone with Dimethylbutadiene.—A suspension of 4-cyano-1,2-naphthoquinone ²¹ (1.0 g.) in chloroform (5 ml.) and dimethylbutadiene (5 ml.) was stirred for 24 hr. in the dark. The yellow solution was evaporated under reduced pressure to give a yellow solid. Recrystallisation from ethanol gave 4a-cyano-1,4,4a,10a-tetrahydro-2,3-dimethylphenanthrene-9,10-quinone (3e) (1.2 g., 83%) as pale yellow needles, m.p. 138–141° (resolidified and remelted at 152–153°); ν_{\max} 2235 (C≡N), 1745 (C=O), 1700 (conj. C=O), and 1600 cm^{-1} (conj. C=C); τ 1.7–2.6

(m, 5-, 6-, 7-, and 8-H), 5.55–5.85 (m, 10a-H), 6.2–8.0 (m, 1- and 4-H₂), and 8.18br (s) and 8.37br (s) (2- and 3-Me). Subsequent recrystallisation from ethanol gave 4a-cyano-1,4,10,10a-tetrahydro-10-hydroxy-2,3-dimethylphenanthrene-9(4aH)-one (4b) as pale yellow needles, m.p. 155–156° [from petroleum (b.p. 80–100°)] (Found: C, 76.7; H, 5.7; N, 5.2. $C_{17}H_{15}NO_2$ requires C, 77.0; H, 5.7; N, 5.3%; ν_{\max} 3400 sharp (OH), 2280 (C≡N), and 1650 cm^{-1} (conj. C=O); τ 1.73br (d, J 8 Hz, 8-H), 2.0–2.6 (m, 1- and 4-H₂), and 8.17br (s) and 8.27br (s) (2- and 3-Me).

Reaction of 3-Nitro-1,2-naphthoquinone with Dimethylbutadiene.—A suspension of 3-nitro-1,2-naphthoquinone ^{22a} (1.0 g.) in chloroform (5 ml.) and dimethylbutadiene (5 ml.) was stirred for 1 hr. in the dark. The mixture initially became warm and the solid slowly dissolved, yielding a yellow solution. Evaporation *in vacuo* left a yellow solid, which was recrystallised from petroleum (b.p. 80–100°) to give 1,4,4a,10a-tetrahydro-2,3-dimethyl-10a-nitrophenanthrene-9,10-quinone (1g) (1.2 g., 85%) as yellow needles, m.p. 130–132° (resolidified and remelted at 230°) (Found: C, 67.6; H, 5.65; N, 4.6. $C_{16}H_{15}NO_4$ requires C, 67.35; H, 5.3; N, 4.9%; ν_{\max} 1750 (C=O), 1690 (conj. C=O), 1600 (conj. C=C), and 1550 cm^{-1} (NO₂); τ 1.85 (pair of d, J 7.5 and 2 Hz, 8-H), 2.1–2.9 (m, 5-, 6-, and 7-H), 5.93 (pair of d, J 12 and 6 Hz, 4a-H), 6.5–8.2 (m, 1- and 4-H₂), 8.22br (s, 2-Me), and 8.39br (s, 3-Me).

A solution of the nitro-adduct (1 g.) (0.5 g.) in mesitylene (10 ml.) was heated under reflux for 30 min. Evolution of nitrogen dioxide was observed and droplets of water condensed in the condenser. The solution was evaporated to give a dark brown solid which was recrystallised from glacial acetic acid to yield 2,3-dimethylphenanthrene-9,10-quinone (0.32 g., 73%) as dark orange plates, m.p. and mixed m.p. 238–240°.

Purification of 1,2-Naphthoquinone.—The crude quinone ^{22b} (6.3 g.) was suspended in water (50 ml.) and sodium dithionite (20 g.) was added. The mixture was shaken with ether (25 ml.) until the quinone had been reduced and the resulting naphthalene-1,2-diol had gone into the ether. The aqueous layer was further extracted with ether (2 × 25 ml.) and the dried combined extracts were evaporated to yield naphthalene-1,2-diol (4.5 g.) as a purple solid. This was dissolved in ether (5 ml.) and a solution of *o*-chloranil ²³ (9 g.) in ether (90 ml.) was added. The precipitated solid was filtered off and dried to yield pure 1,2-naphthoquinone (3.7 g., 46%) as an orange brown solid, m.p. 146–148° (decomp.) (lit., ^{22b} 145–147°).

3-Methoxycarbonyl-1,2-naphthoquinone.—A solution of *o*-chloranil ²³ (1.15 g.) in ether (10 ml.) was added to a solution of 3-methoxycarbonylnaphthalene-1,2-diol ²⁴ (1 g.) in ether (20 ml.). The resultant suspension was cooled to 0° and the orange-coloured precipitate was filtered off, washed with ether (5 ml.), and air-dried to yield 3-methoxycarbonyl-1,2-naphthoquinone (0.65 g., 66%) as orange needles, m.p. 141–142° (lit., ²⁴ 139–140°).

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