556. *The Diels–Alder Reaction of* p-*Benzoquinones.*

By M. F. Ansell, B. W. Nash, and D. A. Wilson.

The Diels–Alder reactions of a number of mono-, di-, tri-, and tetra-substituted *p*-benzoquinones are reported, mostly with 2,3-dimethylbutadiene. It is shown that three factors determine which ethene linkage of a quinone is preferentially attacked by a diene. These are the electronic nature of the quinone substituents, and two distinct steric considerations, one a consequence of the quinone substituents alone, and the other of the quinone and diene substituents together. Also reported is the hydrolysis of only one of the two angular cyano-groups of compounds (XXXIV) when chromatographed on alkaline alumina. A list of *K*-band ultraviolet maxima for substituted cyclic enedione systems is given.

It has been suggested [1,2] that the electronic nature of the substituents of a substituted *p*-benzoquinone determines which of the ethylene linkages is preferentially attacked by a diene in the Diels–Alder reaction, and [1] that there is steric opposition to the formation of adducts containing angular substituents. For the acetoxy-diene (I) it was shown [1-4] that addition of a diene takes place preferentially at the more electron-deficient ethene linkage of a quinone, and previously recorded [5] Diels–Alder reactions of *p*-benzoquinones are consistent with this suggestion. However, the reactions of quinones bearing electron-withdrawing substituents have been studied almost entirely with the diene (I), and we now report the Diels–Alder reactions of a variety of *p*-benzoquinones with 2,3-dimethylbutadiene and, in some cases, buta-1,3-diene itself.

Two structurally isomeric monoadducts may be formed in the Diels–Alder reaction between a symmetrical diene and an unsymmetrically substituted *p*-benzoquinone. Thus, 2,3-dimethylbutadiene, with the quinone (II) may yield the adduct (IIIb) and/or the adduct (IVb). The structure of a particular adduct may be determined in several ways. Thus, only adducts such as (IIIb) can be aromatised to the quinol (Vb) which in turn may be oxidised to the quinone (VIb). The aromatisation is effected, in this work, either by hydrochloric acid in acetic acid or by chromatography of the adduct (IIIb) on alkaline

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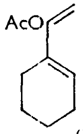
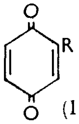
[1] Ansell, Culling, Nash, Wilson, and Lown, *Proc. Chem. Soc.*, 1960, 405.
[2] Ansell and Culling, *J.*, 1961, 2908.
[3] Ansell, Nash, and Wilson, preceding paper.
[4] Ansell and Knights, *J.*, 1961, 2903.
[5] For a review, see Butz and Rytina, *Org. Reactions*, 1949, **5**, 136.

alumina; occasionally the aromatic adduct (Vb) is obtained directly from the reaction mixture. Nuclear magnetic resonance spectroscopy may be used to distinguish between structures (III) and (IV) by determining the number of vinyl protons in the molecule. Often of value in structural determination is the ultraviolet absorption of an adduct,



(I)



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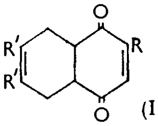

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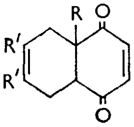

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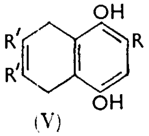

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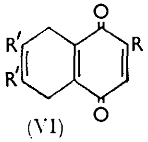

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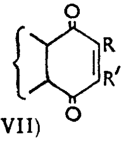

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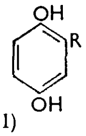

(VIII)

[a : R' = H;
b: R' = Me]

for the position of the *K*-band maximum of a substituted enedione system (VII) depends on the groups R and R'. Table 1 lists the values for this maximum now available (ε *ca.* 10,000 for the compounds prepared in the present work).

The ultraviolet spectrum of an adduct is not always decisive between alternative structures [for example, if R = CO_2Me in (III) and (IV)]. It is to be noted that replacement of hydrogen by methoxycarbonyl or acetyl groups on the chromophore does not shift the maximum at all. The ultraviolet absorption of quinols (V) closely resembles that of the quinols (VIII). If R = CO_2Me, CN, or COMe, the spectrum of quinols (V) and (VIII) consists of a very strong peak at *ca.* 215 mμ (ε *ca.* 20,000) and strong peaks at *ca.* 245 (ε *ca.* 10,000) and *ca.* 345 mμ (ε *ca.* 8000). When R in (V) and (VIII) is a group that cannot conjugate with the aromatic ring, the spectrum consists of a strong peak at *ca.* 215 (ε *ca.* 15,000), a weaker peak (often appearing only as a shoulder) at *ca.* 225 (ε *ca.* 6000), and a peak at *ca.* 290 mμ (ε *ca.* 6000). These characteristics are also observed with the more substituted quinols.

TABLE 1.

Ultraviolet maxima for substituted cyclic enedione systems (VII) (EtOH soln.).

R	R'	*K*-band max. (mμ)	R	R'	*K*-band max. (mμ)	R	R'	*K*-band max. (mμ)
H	H	220—228 *	NMePh	H	252 †	COMe	Me	243 †
F	H	236	OH	H	*ca.* 256 *	CO_2Me	Me	242—246
AcO	H	*ca.* 240	MeO	H	270—278	Me	Me	254 †
Me	H	240—245 *	CO_2Me	H	225 ‡	MeO	MeO	298 †
Cl	H	250—255	NO_2	Me	228 †			

* Knights, Ph.D. Thesis, London, 1960, p. 104. † Recorded for one compound only. ‡ Beyler and Sarett, *J. Amer. Chem. Soc.*, 1952, **74**, 1397.

The infrared spectra of these adducts are rarely of diagnostic value, but the great variations in intensity of the CN stretching frequency absorption found between quinols, quinones, and adducts with cyano-substituents is discussed elsewhere.[6]

RESULTS

In the results now given, yields are quoted. No attempts were made to find optimum conditions, and the yields obtained depend greatly on the reactivity and stability of the quinones used, and on the relative ease of separating mixed products.

Monosubstituted Quinones.—Addition of 2,3-dimethylbutadiene or buta-1,3-diene to the unsubstituted ethene linkage of a monosubstituted *p*-benzoquinone will afford

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[6] Ansell, Nash, and Wilson, following paper.

the general adduct (III); the alternative mode of addition is indicated by reference to structure (IV). These results are listed in Table 2.

TABLE 2.

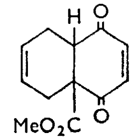
Products of reaction of benzoquinones (II) with butadiene and 2,3-dimethylbutadiene [yields (%) in parentheses].

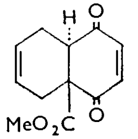
No.	R	(CH:CH$_2$) (R′ = H)		(CMe:CH$_2$)$_2$ (R′ = Me)		No.	R	(CH:CH$_2$) (R′ = H)		(CMe:CH$_2$)$_2$ (R′ = Me)	
1	Me	III *	(65)	III †	(61)	6	CO$_2$Me	III + IV	(6 + 65)	IV	(95)
2	MeO	—		III	(30)	7	CN	IV	(84)	IV	(85)
3	Cl	III	(70)	III ‡	(42)	8	COMe	IV	(86)	IV	(86)
4	F	III	(55)	III	(50)	9	CF$_3$	III + IV? §	(15 + ?)	IV	(64)
5	NMePh	—		III	(47)						

* Fieser, Tishler, and Wendler, *J. Amer. Chem. Soc.*, 1940, **62**, 2861. † Bergman and Bergman, *J. Org. Chem.*, 1938, **3**, 125. ‡ Fr. P. 667,296 reports this reaction but does not characterise the product; Butz and Rytina [5] give the correct structure, but do not cite any evidence. § See text.

The reactions between butadiene and the quinones (II; R = MeO) and (II; R = NMePh) were not attempted, but products of the general structure (IIIa) may be predicted (see Discussion). The reaction between butadiene and methoxycarbonyl-1,4-benzoquinone (II; R = CO$_2$Me) afforded an oil, which on chromatography on alkaline alumina yielded the aromatised adduct (Va; R = CO$_2$Me) (as a solid) and a mixture of the epimeric adducts (IX) and (X) (as a semi-solid). The latter was shown to be a 1 : 1·4 mixture of the two epimers by nuclear magnetic resonance spectroscopy. A small amount of one of the epimers was obtained as a pure solid, and this solid (CO$_2$Me, τ 6·37 p.p.m.) was probably the *trans*-epimer (X), since the other epimer (CO$_2$Me, τ 6·23 p.p.m.) resembled, in this spectrum, the adduct between this quinone and 2,3-dimethylbutadiene (CO$_2$Me, τ 6·27 p.p.m.) which is considered to have the *cis*-structure. This shift to higher fields of the methoxycarbonyl protons on epimerisation from a *cis*- to a *trans*-adduct is discussed elsewhere.[7]

(IX)





(X)

The reaction between trifluoromethylbenzoquinone (II; R = CF$_3$) and butadiene in acetic acid is reported [8] to give, after oxidation, the quinone (VIa; R = CF$_3$). In ethanol, the same reaction, after chromatography, gave the quinol (Va; R = CF$_3$) in low yield; the alternative adduct may have been formed but the oils obtained from the chromatography were not examined; in the light of the other results reported here, it is probable that a mixture of adducts did in fact result. With 2,3-dimethylbutadiene this quinone (II; R = CF$_3$) gave the adduct (IVb; R = CF$_3$) in fair yield, despite the obvious decomposition of the quinone that accompanied addition. The instability of this quinone (it decomposes in about 14 hr.) accounts for the relatively poor yields of adducts obtained from it.

Disubstituted Quinones.—Table 3 lists the reactions between disubstituted *p*-benzoquinones and the two dienes that were studied. Addition to the disubstituted linkage of 2,3-dicyanobenzoquinone (XI; R = CN) has been demonstrated with the acetoxy-diene (I),[1,3] and with 1,2-dimethylenecyclobutane,[9] and the isolation of some of the alternative adduct (XII) when butadiene was used was unexpected. Also, during the separation of the products of the latter reaction by chromatography on alkaline alumina, partial hydrolysis of the adduct (XIII; R = H) was observed, and this apparently general

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[7] Ansell, Lown, Turner, and Wilson, *J.*, 1963, 3036.

[8] Helin, Sveinbjornsson, and VanderWerf, *J. Amer. Chem. Soc.*, 1951, **73**, 1189.

[9] Hartzler and Benson, *J. Org. Chem.*, 1961, **26**, 3507.

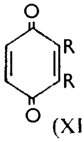
TABLE 3.

Products of reaction between disubstituted *p*-benzoquinones and butadiene or 2,3-dimethylbutadiene [yields (%) in parentheses].

No.		$(CH{:}CH_2)_2$ Angular groups		$(CMe{:}CH_2)_2$ Angular groups	
10	2,3-$(CN)_2$	CN, CN + H, H	(62 + 16)	CN, CN	(96)
11	2,3-$(CO_2Me)_2$	H, H	(70)	H, H + CO_2Me, CO_2Me	(25 + 25)
12	2-Me, 3-NO_2	—		H, H	(35)
13	2-CN, 3-Me	—		H, H	(80)
14	2-Cl, 6-Me	Cl, H	(40)	Cl, H	(55)
15	2-OAc, 5-Me	Me, H *	(30)	AcO, H	(36)
16	2,5-$(MeO)_2$	—		Bis-adduct †	(5)

* Butz and Butz, *J. Org. Chem.*, 1942, **7**, 199. † Isolated as (XXI).

result is discussed below. 2,3-Dimethoxycarbonylbenzoquinone (XI; R = CO_2Me) gave a mixture of adducts with the acetoxy-diene (I) (XIVd and XVd; 3 : 2),[1,3] as it did with 2,3-dimethylbutadiene (XIVb and XVb); 1 : 1), with isoprene (XIVc and XVc; *ca.* 1 : 2), and with 1-vinylcyclohexene (XIVe and XVe; 2 : 1). With butadiene, however, it gave only the adduct (XVa).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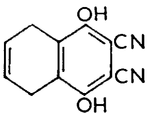
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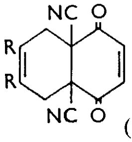
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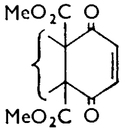
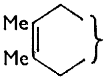

(XIV)


(a)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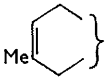
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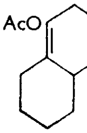
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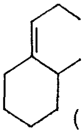
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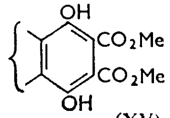
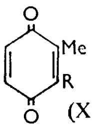

(XV)

Addition of 2,3-dimethylbutadiene occurred at the unsubstituted ethene linkage of the quinones (XVI; R = NO_2 and CN), and a similar result may be expected with buta-1,3-diene (see Discussion). With the chloro-quinone (XVII), the adducts (XVIII; R = Me or H) readily lost hydrogen chloride, to give the known quinones (VIa and VIb; R = Me) either on desiccation (XVIII; R = H) or on chromatography on alumina (XVIII; R = Me). Addition of butadiene to the quinone (XIX) is reported[10] to give products bearing angular methyl groups, while addition of 2,3-dimethylbutadiene gives[10] a product (XX) bearing an angular acetoxy-group. The latter result has been confirmed; the adduct (XX), on treatment with alumina, lost acetic acid to give the quinone (VIb; R = Me). The loss of acetic acid from (XX) and hydrogen chloride from (XVIII) is probably preceded by epimerisation of the primary *cis*- to the *trans*-adduct.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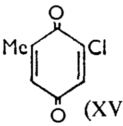
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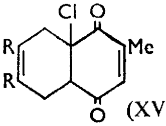
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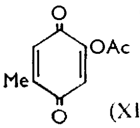
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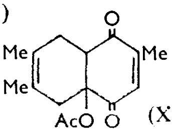
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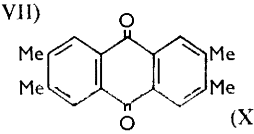
(XXI)

Reaction between 2,3-dimethylbutadiene and 2,5-dimethoxy-1,4-benzoquinone at 180° gave 2,3,6,7-tetramethylanthraquinone (XXI), together with some 2,5-dimethoxy-

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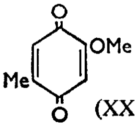
[10] Butz and Butz, *J. Org. Chem.*, 1942, **7**, 199.

quinol. This is the result of diaddition of diene, loss of methanol from the adduct, and dehydrogenation, the order of these steps, particularly in relation to the addition of the second molecule of diene, being in doubt.[11] Butadiene has been shown to add to the methyl-substituted linkages of the quinones (XXII) [12] and (XXIII) [13] and to the unsubstituted linkage of the quinone (XXIV) [14] (the last result is deduced from the ultraviolet absorption of the adduct [14]).



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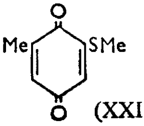
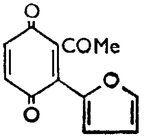


(XXIII)



(XXIV)

Trisubstituted Quinones.—Table 4 gives the results obtained with these quinones. Chromatography of the adducts from the two dicyano-quinones (XXV; R = Me or Cl) resulted in partial hydrolysis to monoamides (discussed below) whereas the adducts from the quinones (XXVI and XXVII; R = CN) were unchanged on chromatography. Adducts from the quinones (XXVI and XXVII; R = CO_2Me) were isolated only in low yields. This may have been due to formation of a mixture of adducts, but chromatography on alumina was used in the isolation procedure, so that primary adducts which had only one angular group probably gave mixtures of epimers [cf. (IX) and (X)]. The adduct from the quinone (XXVI; R = COMe) was difficult to purify, but the crude adduct (XXXVIk) was obtained in a 56% yield. The reaction between 2,3-dimethylbutadiene and 2,5-dimethyl-3-nitrobenzoquinone [6] (XXVI; R = NO_2) gave no isolable adduct. (Also, oxidation of nitroquinol [15] with silver oxide in the presence of the same diene afforded no adduct.) It would be expected that any adduct from these nitroquinones would have an angular nitro-group, and the ready elimination of angular nitro-groups as nitrous acid has been reported.[16] Adducts of the type (III; R = NO_2) are stable (see reaction 12, Table 3). Reaction between the quinone (XXVIII) and 2,3-dimethylbutadiene, at 200°, afforded 2,3,6,7-tetramethylanthraquinone (XXI) (80%) and the quinol (XXIX) (90%) (both yields based on the assumption made in footnote † to Table 4), diaddition having taken place (cf. reaction 16, Table 3) together with dehydrogenation (by starting quinone, as was probably the case in reaction 16) and elimination of acetyl and methoxy-groups. The reaction between the quinone (XXX) and dimethylbutadiene, at 200°, gave a mixture of a normal adduct (XXXI; R = Me), formed by addition to the disubstituted ethene linkage, and 2,3,6,7-tetramethylnaphthaquinone, again showing the facility with which an angular methoxy-group is lost under these

TABLE 4.

Products of reaction of trisubstituted benzoquinones with 2,3-dimethylbutadiene [yields (%) in parentheses].

No.	Benzoquinone	Angular groups		No.	Benzoquinone	Angular groups	
17	5-Cl, 2,3-$(CN)_2$	CN, CN	(88)	23	3-CO_2Me, 2,5-Me_2	Me, H	(34)
18	2,3-$(CN)_2$, 5-Me	CN, CN	(87)	24	2-COMe, 2,5-Me_2	Me, H	(14) *
19	2,3-$(CO_2Me)_2$, 5-Me	CO_2Me, CO_2Me	(76)	25	3-COMe, 2,5-$(MeO)_2$	Diadduct (XXI)	(80) †
20	2-CN, 3,5-Me_2	Me, CN	(45)	26	5-MeO, 2,3-Me_2	Me, Me + MeO, H	(20 + 13)
21	3-CN, 2,5-Me_2	Me, CN	(66)	27	5-MeO, 2-CO_2Me, 3-Me	Me, CO_2Me	(81)
22	2-CO_2Me, 3,5-Me_2	Me, H	(23)				

* 56% crude yield, 14% yield of pure adduct. † Based on the assumption that two molecules of quinone gave one of diadduct [isolated as (XXI)] and one molecule of the quinol (see Experimental).

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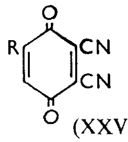
[11] Wilson, Ph.D. Thesis, London, 1962, p. 106.
[12] Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.
[13] Skaletzky, *Diss. Abs.*, 1960, **20**, 360.
[14] Eugster and Bosshard, *Chimia*, 1961, **15**, 530.
[15] Astle and Stephenson, *J. Amer. Chem. Soc.*, 1943, **65**, 2399.
[16] Hurd and Juel, *J. Amer. Chem. Soc.*, 1955, **77**, 601.

conditions. The quinone (XXXII) gave an adduct (XXXI; R = CO_2Me) bearing two angular substituents, and the acetoxy-diene (I) is known [2] to add to the same ethene linkage.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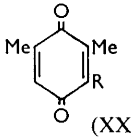
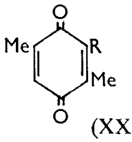
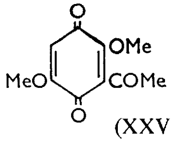
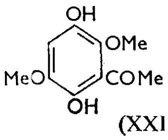
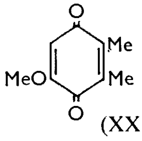
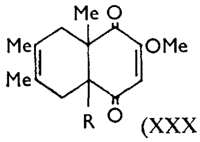

(XXVI)

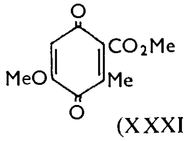

(XXVII)


(XXVIII)


(XXIX)


(XXX)


(XXXI)


(XXXII)

Tetrasubstituted Quinones.—The three examples of this class of quinone that were used are given in Table 5. It is reported [5] that duroquinone does not react with hexatriene at 100°, but affords duroquinol when the reaction is attempted at 150° or 200°. The product from reaction 30 is probably the first example of the isolation of a Diels–Alder adduct having angular methoxy-groups.

TABLE 5.

Products of reaction of tetrasubstituted benzoquinones with 2,3-dimethylbutadiene [yields (%) in parentheses].

No.	Benzoquinone	Adducts	
28	2,6-$(CO_2Me)_2$, 3,5-Me_2	Monoadduct	(90)
29	Me_4	Monoadduct	(87)
30	$(MeO)_4$	Monoadduct	(95)

DISCUSSION

The major premise of Ansell and his co-workers,[1,2] that an electron-attracting group will activate the ethene linkage of a quinone to which it is attached, while an electron-donating group will deactivate it towards Diels–Alder addition of a diene, is seen to hold true. Thus, with respect to the ethene linkage of benzoquinone, a quinone double bond to which CN, COMe, CO_2Me, or CF_3 (Table 2) is attached is seen to be activated as a dienophil; MeO, Cl, F, etc. (Table 2) are seen to deactivate the double bonds to which they are attached, these being effects of conjugation and hyperconjugation rather than induction.

The suggestion of steric opposition to the formation of adducts with angular groups is amply borne out. A group in an angular position will be more compressed than it would be in a non-angular position or in the parent quinone.[17] The opposition is clearly greater when two such groups are involved, and the reactions of the dimethoxycarbonyl-quinone (XI; R = CO_2Me) compared with those of methoxycarbonylbenzoquinone (II; R = CO_2Me) clearly show this. The quinones (XVI; R = NO_2 and CN) (reactions 12 and 13) might be expected, on electronic grounds, to add the diene to the more substituted ethylene linkage, but this would lead to a product having two angular substituents. Addition to the more substituted linkages of quinones (XXVI and XXVII; R = CN) shows that the deactivating effect of a single methyl group is sufficient to force addition on to the more substituted linkages. However, with quinones (XXVI and XXVII; R = CO_2Me) (the adducts isolated are assumed to be the major products) addition takes place preferentially on the more electronically deactivated ethene linkages, illustrating the greater activating effect of the cyano-group than of the methoxycarbonyl group (an effect both steric and electronic in origin). Comparison between these reactions and that of the quinone (XXXII) shows the greater deactivating effect of the methoxy-group than

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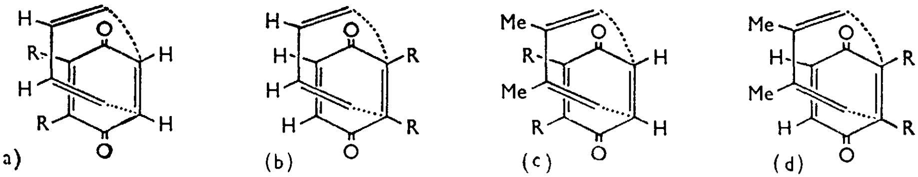
[17] Martin and Hill, *Chem. Rev.*, 1961, 540.

of the methyl group [cf. also reactions of (XXII)]. Similar comparisons among the results given above lead to the following order of activating effect of groups on the Diels–Alder reactivity of a quinone double-bond: CN > COMe > CO_2Me > CF_3 > H > F? > Cl > Me, OAc > NMePh, MeO, SMe. The position of fluorine in the series is not certain, and the position of any group in the series depends on its electronic character and its size.

The quinones used in the reactions 6, 10, 11, and possibly 9, give more of the angularly substituted products with the dimethylbutadiene than with butadiene. With the latter diene, products having non-angular groups are formed from 2,3-dicyanobenzoquinone (reaction 10) and methoxycarbonylbenzoquinone (reaction 6), whereas dimethylbutadiene gives only angularly substituted products in very high yields. This tendency is explicable if all these reactions proceed through *endo*-transition states, and this is in agreement with previous experimental evidence.[17] The *endo*-transition states for reaction between a 2,3-disubstituted quinine and the two dienes, leading to the alternative products, are shown (XXXIIIa, b, c, and d). The steric opposition to the formation of adducts with angular substituents (from XXXIIIb and d) will be essentially the same for both dienes, but the non-bonded repulsions between substituents on the 2,3-positions of the diene and the substituents of the non-reacting ethene linkage of the quinone will be greater in (XXXIIIc) than in (XXXIIIa, b, and d), thus favouring the formation of angularly substituted adducts derived from 2,3-dimethylbutadiene relative to butadiene and the same quinone. In the cases where such product ratios have been observed, this is the case. In the example of 2,3-dimethoxycarbonylbenzoquinone (XI; R = CO_2Me), 2,3-dimethylbutadiene, isoprene, 1-vinylcyclohexene, and 1-1′-acetoxyvinylcyclohexene[3] all give mixtures of adducts, whereas butadiene gives only the non-angularly substituted product (XVa).

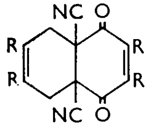


(XXXIII)

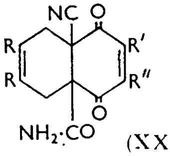
Thus, in any Diels–Alder reaction between a diene and a *p*-benzoquinone, to decide to which ethene linkage of the quinone the diene will add, three factors must be considered: (*a*) the electronic nature of the quinone substituents so that the more electron-deficient ethene linkage may be decided; (*b*) the number and size of the substituents that would be expected, on electronic grounds, to be angular in the products; (*c*) the size of the substituents on the 2,3-positions of the diene, and the non-bonded interactions with the quinone substituents in the possible transition states.

The formation of adducts from duroquinone and the even less reactive tetramethoxybenzoquinone (reactions 29 and 30) suggests that even the most deactivated quinones will undergo a Diels–Alder reaction provided that the reactants are stable at the temperatures required.

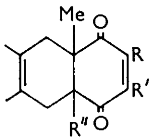
During the work just described, several adducts with two angular cyano-groups were prepared (from reactions 10, 17, and 18) and these adducts are partially hydrolysed on chromatography. A solution of the adduct (XXXIV) in benzene was put on to a column of alkaline alumina, elution with benzene–ethanol affording a monoamide (XXXV) in good yield. The structures of these high-melting amides (XXXVa, b, c or e, d or f) are based on analyses and spectroscopic evidence. Their infrared spectra (paraffin mulls) showed a number of peaks attributable to free and bonded NH, CN absorption [in the cases where the CN absorption of (XXXIV) appeared as two peaks, only a single peak was observed with (XXXV)], and usually three CO peaks, while their ultraviolet spectra showed that the original chromophores were retained. Nuclear magnetic resonance measurements on two of the amides (XXXVa and b) both showed a fairly broad peak



(XXXIV)



(XXXV)

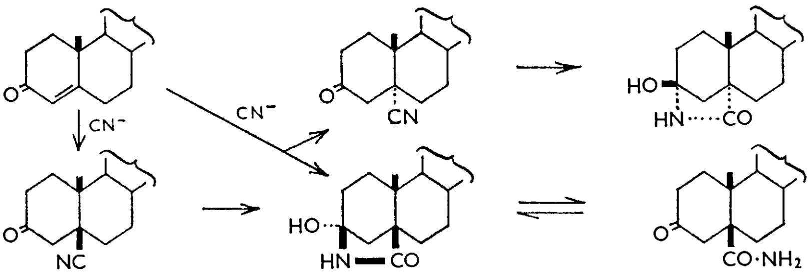


(XXXVI)

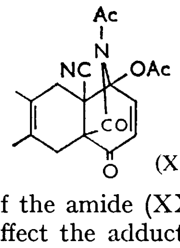
a: R = H, R' = R'' = H
b: R = Me, R' = R'' = H
c: R = Me, R' = Cl, R'' = H
d: R = Me, R' = Me, R'' = H
e: R = Me, R' = H, R'' = Cl
f: R = Me, R' = H, R'' = Me

g: R = Me, R' = H, R'' = CN
h: R = H, R' = Me, R'' = CN
i: R = Me, R' = CO_2Me, R'' = H
j: R = CO_2Me, R' = Me, R'' = H
k: R = Me, R' = COMe, R'' = H
l: R = MeO, R' = H, R'' = CO_2Me

equivalent to two protons which could be assigned to CO·NH_2 protons, as well as the other features of the molecules. It might be expected that the two adducts (XXXIVc and d) should each give two isomeric amides (XXXVc and e) and (XXXVd and f), but only one was found in each case, although it was not determined which of the two possibilities each was. It is also to be noted that the monocyano-adducts (XXXVIg and h) could be chromatographed unchanged. Of bearing on these results is work by Nagata *et al.*,[18] summarised in the formulae below, on the addition of hydrogen cyanide to cholest-4-enone: of the two epimeric 5-cyano-compounds, the β-epimer (where the cyano-group is axial to one ring and equatorial to the other) was hydrolysed by alkali faster than the α-epimer (where the cyano-group is axial to both rings); also, the 5β-cyanide was partly converted into the (5→3) β-lactam by alkaline alumina.



In the two adducts (XXXVIg and h), the methyl group is bulkier than the cyano-group and thus might be expected to lie equatorial to the cyclohexene ring. This, together with Nagata's work, suggests that it is a cyano-group equatorial to the cyclohexene ring that is hydrolysed in the adducts (XXXIV). An equatorial cyano-group will be more prone to nucleophilic attack than will an axial group, for in the latter the carbon atom of the group (the site of attack) will be largely shielded by the rest of the molecule.[18] After initial attack on the equatorial cyano-group of (XXXIV), the resulting carbamoyl group will ensure that the remaining cyano-group keeps its axial position where it is not attacked under the mild conditions used in which the nucleophil will presumably be bound to the alumina surface. However, the participation of a carbonyl group γ to the cyano-group cannot be ruled out. The amides (XXXV) were too insoluble for their infrared spectra to be measured in non-hydrogen-bonding solvents, and so the presence of lactam form in those solvents could not be shown (cf. ref. 18). However, treatment of the amide (XXXVb) with acetic anhydride and acetic acid [a reagent that did not affect the adduct (XXXIVb)] gave a diacetyl derivative which is tentatively given the



(XXXVII)

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[18] Nagata, Hirai, Itazaki, and Takeda, *J. Org. Chem.*, **1961**, **26**, 2413.

structure (XXXVII) on spectroscopic evidence, being, it may be supposed, derived by diacetylation of the lactam form of (XXXVb).

EXPERIMENTAL

Ultraviolet spectra are recorded for ethanol (95%) solutions. Nuclear magnetic resonance spectra were determined for chloroform, deuterochloroform, or carbon tetrachloride solutions unless otherwise stated, and peak intensities were all correct for the number of protons assigned. The 6,7-Me_2 and 6,7-H_2 τ-values are not usually quoted for each compound, but the former came within the range 8·46—8·25 p.p.m. and the latter at 4·30—4·10 p.p.m. τ-Values for ring CH_2 groups and bridgehead protons are not quoted. Infrared spectra of solids were recorded as Nujol mulls, and of liquids as liquid films. All reactions with buta-1,3-diene were done in glass pressure-bottles. The alkaline alumina used was " Type H " (100—200 mesh) from Peter Spence. Diels–Alder reactions were effected at room temperature unless otherwise stated.

5,8-*Dihydro*-6,7-*dimethyl*-1,4-*naphthaquinone* (VIb; R = H).—5,8-Dihydro-6,7-dimethyl-1,4-naphthaquinol [19] (500 mg.) was oxidised with silver oxide [20] to give, after chromatography of the product on alumina, the *quinone* (260 mg., 53%), m. p. 129—131° (decomp.) [from ethanol–light petroleum (b. p. 60—80°)], $\lambda_{max.}$ 256, 262infl., 355 mμ (ε 17,500, 16,000, and 2700), 6·03sh, 6·07 (C=O), 6·27 μ (C=C) (Found: C, 76·7; H, 6·0. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%). Fieser *et al.*[21] obtained what was probably this quinone by oxidising the same quinol with chromium trioxide, but did not recognise it as such.

5,8-Dihydro-1,4-naphthaquinone [22] had $\lambda_{max.}$ 248, 357 mμ (ε 14,500 and 890); 5,8-dihydro-2-methyl-1,4-naphthaquinone [23] had $\lambda_{max.}$ 253, 355 mμ (ε 16,000 and 256); 5,8-dihydro-2,6,7-trimethyl-1,4-naphthaquinone [24] had $\lambda_{max.}$ 260, 352 mμ (ε 20,500 and 2300).

4a,5,8,8a-*Tetrahydro*-2-*methoxy*-6,7-*dimethyl*-1,4-*naphthaquinone* (IIIb; R = MeO).—A solution of methoxybenzoquinone [25] (3·3 g.) and 2,3-dimethylbutadiene [26] (3 g.) in methanol (150 ml.) was left for 3 days in the dark. The filtered solution was reduced to *ca.* 15 ml., then addition of light petroleum (b. p. 60—80°) gave the *methoxy-adduct* (1·5 g., 30%), m. p. 140—141·5° [from light petroleum (b. p. 80—100°)], $\lambda_{max.}$ 270 mμ (ε 6500), 5·90 (C=O), 6·07 (C=O or C=C), 6·27 μ (C=C), τ 6·23 (2-MeO), 4·11 p.p.m. (3-H) (Found: C, 71·1; H, 7·35. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

This adduct (1 g.) was dissolved in hot glacial acetic acid (2 ml.), and concentrated hydrochloric acid (2 drops) was added. (This is the general procedure used for aromatisations.) Crystallisation of the precipitated solid from aqueous ethanol gave 5,8-*dihydro*-2-*methoxy*-6,7-*dimethyl*-1,4-*naphthaquinol* (Vb; R = MeO) (900 mg., 90%), m. p. 209—211°, $\lambda_{max.}$ 227infl., 293 mμ (ε 7350 and 4500), 3.01 (OH), 6·15, 6·26 μ (C=C) (Found: C, 71·2; H, 7·5. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

This quinol (500 mg.) was oxidised by hydrated ferric chloride (2 g.) in ethanol (20 ml.) at 70° to give 5,8-*dihydro*-2-*methoxy*-6,7-*dimethyl*-1,4-*naphthaquinone* (VIb; R = MeO) (300 mg., 60%), m. p. 151—153° (from ethanol), $\lambda_{max.}$ 274, 358 mμ (ε 13,000 and 920), 6·01, 6·05 (C=O), 6·13, 6·23 μ (C=C) (no secondary methyl absorption was observed in the nuclear magnetic resonance spectrum, thereby excluding the 5,6-dihydro-isomer) (Found: C, 71·8; H, 5·9. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5%) (cf. ultraviolet absorption quoted in the first experiment).

2-*Chloro*-4a,5,8,8a-*tetrahydro*-1,4-*naphthaquinone* (IIIa; R = Cl).—An excess of butadiene was added to a solution of chlorobenzoquinone (3·5 g.) in benzene (50 ml.) and the solution was left for 3 days, then heated at 70° for 21 hr. Removal of the solvent gave a residue (4·96 g.) which was twice crystallised from ethanol–light petroleum (b. p. 60—80°), to afford the *chloro-adduct* (3·3 g., 70%), m. p. 89—91°, $\lambda_{max.}$ 254 mμ (ε 10,000), 5·88, 6·00 (C=O), 6·06sh, 6·34 μ (C=C) (Found: C, 61·1; H, 4·3. $C_{10}H_9ClO_2$ requires C, 61·2; H, 4·6%).

This adduct (1 g.) was aromatised in the usual way to 2-*chloro*-5,8-*dihydro*-1,4-*naphthaquinol*

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[19] Lora-Tamayo and Leon, *J.*, 1948, 1499.

[20] For method see ref. 6.

[21] Fieser, Campbell, and Fry, *J. Amer. Chem. Soc.*, 1939, **61**, 2206.

[22] Diels and Alder, *Ber.*, 1929, **62**, 2337.

[23] Nudenberg, Gaddis, and Butz, *J. Org. Chem.*, 1943, **8**, 500.

[24] Bergman and Bergman, *J. Org. Chem.*, 1938, **3**, 125.

[25] Ioffe and Sukhina, *Zhur. obshchei Khim.*, 1953, **23**, 295.

[26] Allen and Bell, *Org. Synth.*, 1955, Coll. Vol. III, p. 312.

(Va; R = Cl) (800 mg., 80%), m. p. 147·5—149° (from aqueous ethanol), $\lambda_{max.}$ 226infl., 296 mμ (ε 5750 and 3750), 3·02 (OH), 6·21 μ (C=C) (Found: C, 61·9; H, 4·9. $C_{10}H_9ClO_2$ requires C, 61·2; H, 4·6%). Gaertner [27] prepared this quinol in solution, but did not isolate it.

2-*Chloro*-4a,5,8,8a-*tetrahydro*-6,7-*dimethyl*-1,4-*naphthaquinone* (IIIb; R = Cl).—A solution of chlorobenzoquinone (7·5 g.) and 2,3-dimethylbutadiene (5 g.) in benzene (30 ml.) was left for 20 hr., then evaporated to dryness. The residue was washed with light petroleum (b. p. 40—60°), leaving a solid (5·0 g., 42%), m. p. 107—115°, which crystallised from ethanol–light petroleum (b. p. 80—100°) to give the *chloro-adduct*, m. p. 120—121°, $\lambda_{max.}$ 253 mμ (ε 11,000), 5·90sh, 6·02 (C=O), 6·35 μ (C=C), τ 3·07 p.p.m. (3-H) (Found: C, 64·2; H, 6·0; Cl, 15·9. $C_{12}H_{13}ClO_2$ requires C, 64·15; H, 5·6; Cl, 15·8%). This product is recorded in a patent [28] but was not characterised.

This adduct (1 g.) was aromatised in the usual way, affording 2-*chloro*-5,8-*dihydro*-6,7-*dimethyl*-1,4-*naphthaquinol* (Vb; R = Cl) (900 mg., 90%), m. p. 162—165° (decomp.), raised only slowly to m. p. 175—177° (from aqueous acetic acid), $\lambda_{max.}$ 295 mμ (ε 4000), 3·05 (OH), 6·28 μ (C=C) (Found: C, 64·5; H, 6·0; Cl, 15·4. $C_{12}H_{13}ClO_2$ requires C, 64·15; H, 5·8; Cl, 15·8%). Gaertner [27] prepared this quinol in solution but did not isolate it.

2-*Fluoro*-4a,5,8,8a-*tetrahydro*-1,4-*naphthaquinone* (IIIa; R = F).—An excess of butadiene was added to a solution of fluoro-1,4-benzoquinone [29] (1·1 g.) in benzene (50 ml.) and after 67 hr. the solvent was removed at <35°/18 mm. The residue crystallised from ethanol–light petroleum (b. p. 60—80°) to afford the *fluoro-adduct* (860 mg., 55%), m. p. 65—67°, $\lambda_{max.}$ 236 mμ (ε 10,000), 5·85, 5·96 (C=O), 6·10 μ (C=C), τ 3·58 p.p.m. (3-H doublet, $J_{H,F}$ = 11·4 c./sec.) (Found: C, 66·7; H, 5·0. $C_{10}H_9FO_2$ requires C, 66·7; H, 5·0%).

This adduct (65 mg.) was aromatised in the usual way; crystallisation of the product from aqueous acetic acid gave the light-sensitive 2-*fluoro*-5,8-*dihydro*-1,4-*naphthaquinol monohydrate* (53 mg., 75%), m. p. 153—155°, $\lambda_{max.}$ 219infl., 242infl., 287 mμ (ε 6700, 1600, and 3000), 2·80—3·20 (OH), 6·03, 6·11 μ (C=C) (Found: C, 61·0; H, 5·6. $C_{10}H_{11}FO_3$ requires C, 60·7; H, 5·6%). The same fluoro-adduct (50 mg.), in benzene solution, was passed down a column of alkaline alumina; the eluate contained the fluoro-quinol (27 mg.) (from the ultraviolet spectrum). No anhydrous quinol was prepared.

2-*Fluoro*-4a,5,8,8a-*tetrahydro*-6,7-*dimethyl*-1,4-*naphthaquinone* (IIIb; R = F).—A solution of fluorobenzoquinone (1·2 g.) and 2,3-dimethylbutadiene (1·02 g.) in benzene (40 ml.) was left in the dark for 21·5 hr. Removal of the solvent left a solid (1·5 g.), m. p. 70—100°, containing some unchanged quinone and from which was obtained, by crystallisation from ethanol–light petroleum (b. p. 80—100°), the *fluoro-adduct* (*ca.* 50%), m. p. 125—126°, $\lambda_{max.}$ 236 mμ (ε 10,000), 5·87, 5·96 (C=O), 6·11 μ (C=C), τ 3·70 p.p.m. (3-H doublet, $J_{H,F}$ = 10 c./sec.) (Found: C, 69·0; H, 6·3. $C_{12}H_{13}FO_2$ requires C, 69·3; H, 6·25%).

This fluoro-adduct (*ca.* 15 mg.) was aromatised in the usual way, to give a solid, m. p. 176—178° (from aqueous acetic acid), $\lambda_{max.}$ 217infl., 286 mμ (ε 7900 and 2790), 3·16br (OH), 6·14, 6·21 μ (C=C). No analysis was obtained for this solid which was 2-fluoro-5,8-dihydro-6,7-dimethyl-1,4-naphthaquinol (Vb; R = F) or its monohydrate (ultraviolet maxima are calculated for the pure quinol).

4a,5,8,8a-*Tetrahydro*-6,7-*dimethyl*-2-N-*methylanilino*-1,4-*naphthaquinone* (IIIb; R = NMePh).—A solution of *N*-methylanilino-1,4-benzoquinone (2 g.) and 2,3-dimethylbutadiene (1·08 g.) in methanol (110 ml.) was heated under reflux for 21 hr. The cooled solution was filtered; the residue (1·5 g.), m. p. 126—136°, crystallised from ethanol–light petroleum (b. p. 80—100°) to give the *adduct* (1·3 g., 47%), m. p. 139—140·5° (golden-yellow needles), $\lambda_{max.}$ 252, 342 mμ (doublet) (ε 10,500 and 13,000), 5·90 (C=O), 6·14, 6·43, 6·74 μ (C=C), τ 6·75 (*N*-Me), 4·27 (3-H), 2·7 p.p.m. (envelope of C_6H_5 protons) (Found: C, 76·9; H, 7·0; N, 4·6. $C_{19}H_{21}NO_2$ requires C, 77·3; H, 7·2; N, 4·7%).

N-Methylanilino-1,4-benzoquinone, prepared as described by Suida and Suida,[30] had m. p. 139—140° (lit.,[30] 125—130°). Anilinobenzoquinone was also prepared and had m. p. 139—140° in agreement with Barakat *et al.*[31] (m. p. 139°) but not with Suida and Suida [30] (m. p. 119—120°). The addition of methylaniline to toluquinone afforded a mixture of two isomeric

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[27] Gaertner, *J. Amer. Chem. Soc.*, 1954, **76**, 6150.
[28] Fr. P. 667,296.
[29] Hodgson and Nicholson, *J.*, 1941, 645.
[30] Suida and Suida, *Annalen*, 1918, **416**, 113.
[31] Barakat, Shebab, and El-Sadr, *J.*, 1958, 901.

quinones, m. p. 143—145° and m. p. 91—93° (in the ratio 7 : 1). These were (from analysis) two of the three possible adducts. Suida *et al.*[30] report only one product from this reaction, m. p. 110—112°, and consider it to be the 2,5-compound.

Reaction between Methoxycarbonylbenzoquinone and Buta-1,3-*diene*.—The quinone[32] (6 g.) and an excess of the diene were heated together in benzene (50 ml.) at 70° for 6 hr. After removal of the solvent the residual oil was chromatographed on alumina in benzene. The first fractions afforded an oil, from which, after several days, crystallised one of the epimers of *methyl* 1,4,4a,5,8,8a-*hexahydro*-1,4-*dioxonaphthalene*-4a-*carboxylate* [probably (X), see text] (173 mg.), m. p. 73—75° [from ethanol–light petroleum (b. p. 60—80°)], $\lambda_{max.}$ 228 mμ (ε 9500), 5·79 (ester), 5·94 (enedione C=O), 6·23 μ (conj. C=C), τ 6·37 (4a-CO_2Me), 4·30, 4·27 (6,7-H_2), 3·29, 3·13 p.p.m. (2,3-H_2) (Found: C, 65·1; H, 5·4. $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·5%). The crude oil was sublimed at 110—120°(bath)/1·5 mm.; the sublimate partly solidified and was a mixture of the epimeric adducts (IX) and (X). This semi-solid had $\lambda_{max.}$ 226 mμ (ε 9500) 5·75sh, 5·79 (ester), 5·93 (enedione), 6·23 μ (conj. C=C) (Found: C, 65·9; H, 5·6%). The epimer not isolated as a solid [probably (IX)] had τ 6·23 (4a-CO_2Me), 4·28 (6,7-H_2), 3·22 p.p.m. (2,3-H_2). The two epimers were present in the ratio 1·4 : 1, the one isolated as a solid predominating. The original oil contained *ca.* 80% of the pure epimers (from ultraviolet spectra), representing a yield of *ca.* 65%.

The later chromatography fractions afforded 5,8-*dihydro*-2-*methoxycarbonyl*-1,4-*naphthaquinol* (Va; R = CO_2Me) (470 mg., 6%), m. p. 185—187° (from ethanol), $\lambda_{max.}$ 217, 262, 343 mμ (ε 21,500, 7700, and 6600), 2·94, 3·04 (OH), 6·10 (C=O), 6·20, 6·32, 6·66 μ (C=C), τ 6·11 (2-CO_2Me), 4·12 (6,7-H_2), 2·92 p.p.m. (3-H) (Found: C, 65·2; H, 5·5. $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·5%).

Methyl 1,4,4a,5,8,8a-*hexahydro*-6,7-*dimethyl*-1,4-*dioxonaphthalene*-4a-*carboxylate* (IVb; R = CO_2Me).—A solution of methoxycarbonylbenzoquinone (1·3 g.) and 2,3-dimethylbutadiene (1·5 g.) in benzene (70 ml.) was left for 18 hr. in the dark. Removal of the solvent left a solid (1·9 g., 95%), m. p. 107—112°, which crystallised from ethanol–light petroleum (b. p. 80—100°) to give the *methoxycarbonyl adduct*, m. p. 112·5—114°, $\lambda_{max.}$ 224 mμ (ε 9700), 5·78 (ester), 6·00 (enedione C=O), 6·25 μ (conj. C=C), τ 6·27 (4a-CO_2Me), 3·32 p.p.m. (2,3-H_2) (Found: C, 67·6; H, 6·5. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5%).

4a-*Cyano*-4a,5,8,8a-*tetrahydro*-1,3-*naphthaquinone* (IVa; R = CN).—A solution of cyanobenzoquinone[6] (300 mg.) and an excess of butadiene in benzene (25 ml.) was kept at 80° for 1 hr. Removal of the solvent left a solid (350 mg., 84%), m. p. 118—123°, which crystallised from ethanol–light petroleum (b. p. 80—100°) to give the *cyano-adduct*, m. p. 125—127°, $\lambda_{max.}$ 228 mμ (ε 9400), 4·45 (CN, fairly weak), 5·86, 5·94 (C=O), 6·24 μ (conj. C=C), τ 3·17 p.p.m. (2,3-H_2) (Found: C, 70·7; H, 4·6; N, 7·85. $C_{11}H_9NO_2$ requires C, 70·6; H, 4·85; N, 7·5%).

4a-*Cyano*-4a,5,8,8a-*tetrahydro*-6,7-*dimethyl*-1,4-*naphthaquinone* (IVb; R = CN).—Reaction between cyanobenzoquinone (300 mg.) and 2,3-dimethylbutadiene (300 mg.) in benzene (25 ml.) for 19 hr. gave, on removal of the solvent, the *cyano-adduct* (400 mg., 85%), m. p. 102—107°, raised to m. p. 107—109° [from ethanol–light petroleum (b. p. 80—100°)], $\lambda_{max.}$ 229 mμ (ε 9950), 4·45 (CN, fairly weak), 5·93 (C=O), 6·22 μ (C=C), τ 3·00 p.p.m. (2,3-H_2) (Found: C, 72·7; H, 6.6; N, 6·4. $C_{13}H_{13}NO_2$ requires C, 72·5; H, 6·1; N, 6·5%).

4a-*Acetyl*-4a,5,8,8a-*tetrahydro*-1,4-*naphthaquinone* (IVa; R = COMe).—Reaction of acetylbenzoquinone (1 g.) and an excess of butadiene in benzene (30 ml.) for 16 hr. gave, on removal of the solvent, the *acetyl adduct* (1·165 g., 86%), m. p. 85—87° [from ethanol–light petroleum (b. p. 60—80°)], $\lambda_{max.}$ 228 mμ (ε 10,000), 5·79 (Ac), 5·90sh (enedione C=O), 6·24 μ (conj. C=C), τ 7·83 (4a-COMe), 3·34 p.p.m. (2,3-H_2) (Found: C, 71·0; H, 6·2. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%).

(The product from the silver oxide oxidation[20] of 2,5-dihydroxyacetophenone was sublimed to give the acetylbenzoquinone, m. p. 65—68°. Kloetzel *et al.*[33] give m. p. 65·5—66·5°. Vorozhtsov *et al.*[34] give m. p. 55·5—57·5°.)

4a-*Acetyl*-4a,5,8,8a-*tetrahydro*-6,7-*dimethyl*-1,4-*naphthaquinone* (IVb; R = COMe).—Acetylbenzoquinone (800 mg.) and 2,3-dimethylbutadiene (600 mg.) in benzene (50 ml.) were left for 18 hr. Then removal of the solvent gave a solid (1·1 g., 86%), m. p. 73—81°, which

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[32] Cason, *Org. Reactions*, 1948, **4**, 354.

[33] Kloetzel, Dayton, and Abadir, *J. Org. Chem.*, 1955, **20**, 38.

[34] Vorozhtsov and Mamaev, *Sbornik Statei obshch. Khim., Akad. Nauk S.S.S.R.*, 1953, **1**, 533. *Chem. Abs.*, 1953, **49**, 925.

crystallised from ethanol–light petroleum (b. p. 60—80°) to give the *acetyl adduct*, m. p. 79—81°, $\lambda_{\text{max.}}$ 228 mμ (ε 10,000), 5·85sh (Ac), 6·00 (enedione C=O broad), 6·24 μ (conj. C=C), τ 7·93 (4a-COMe), 3·35 p.p.m. (2,3-H_2) (Found: C, 72·45; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

Reaction between Trifluoromethylbenzoquinone and Buta-1,3-*diene*.—The quinone[8] (600 mg.) and an excess of butadiene in ethanol (100 ml.) were heated at 60—65° for 16 hr. Removal of the solvent left an oil which was chromatographed on alumina in benzene. The first fractions gave gums which were not investigated, but the later fractions afforded 5,8-*dihydro*-2-*trifluoromethyl*-1,4-*naphthaquinol* (Va; R = CF_3) (*ca.* 100 mg., *ca.* 15%), m. p. 137—138·5° [from light petroleum (b. p. 80—100°)], $\lambda_{\text{max.}}$ 218infl., 230infl., 290 mμ (ε 9100, 6200, and 4100), 3·03 (OH), 6·17 μ (C=C) (Found: C, 57·0; H, 3·8. $C_{11}H_9F_3O_2$ requires C, 57·4; H, 3·9%).

4a,5,8,8a-*Tetrahydro*-6,7-*dimethyl*-4a-*trifluoromethyl*-1,4-*naphthaquinone* (IVb; R = CF_3).—A solution of trifluoromethylbenzoquinone (800 mg.) and 2,3-dimethylbutadiene (720 mg.) in ethanol (60 ml.) was heated under reflux for 15 hr. The solvent was removed and the residue dissolved in light petroleum (b. p. 60—80°) (10 ml.). The solution was cooled to −70° and the precipitate (420 mg., 64%), m. p. 70—76°, was crystallised from ethanol–light petroleum (b. p. 60—80°), giving the *trifluoromethyl adduct*, m. p. 78—80°, $\lambda_{\text{max.}}$ 229 mμ (ε 10,500), 5·91 (C=O), 6·23 μ (conj. C=C), τ 3·35 p.p.m. (2,3-H_2) (Found: C, 60·7; H, 5·0. $C_{13}H_{13}F_3O_2$ requires C, 60·5; H, 5·0%).

Reaction between 2,3-*Dicyanobenzoquinone and Buta*-1,3-*diene*.—The quinone[35] (2 g.) and an excess of butadiene were maintained at 55° for 80 min. in benzene–ether (100 ml.; 1 : 1); removal of the solvent left a solid, m. p. 130—∼280°. Crystallisation from benzene gave a solid (1·95 g.), m. p. 145—153°, which crystallised from ethanol to give, as the first crop, 4a,8a-*dicyano*-4a,5,8,8a-*tetrahydro*-1,4-*naphthaquinone* (XIII; R = H) (1·35 g., 50%), m. p. 165—168°, $\lambda_{\text{max.}}$ 226 mμ (ε 8500), 4·44sh, 4·46 (CN, fairly weak), 5·81, 5·89 (C=O), 6·23 μ (conj. C=C), τ 2·95 p.p.m. (2,3-H_2) (Found: C, 68·2; H, 4·1; N, 12·7. $C_{12}H_8N_2O_2$ requires C, 67·9; H, 3·8; N, 13·2%).

The ethanolic mother-liquors then afforded 2,3-*dicyano*-5,8-*dihydro*-1,4-*naphthaquinol* (XII) (425 mg., 16%), m. p. 285° (charring with previous darkening), $\lambda_{\text{max.}}$ 218, 263infl., 343, 388 mμ (ε 28,500, 3100, 7100, and 1500), 3·03 (OH), 4·44vs (CN), 6·28 μ (C=C) (Found: C, 67·6; H, 3·6; N, 12·95. $C_{12}H_8N_2O_2$ requires C, 67·9; H, 3·8; N, 13·2%).

The combined mother-liquors from all the above crystallisations were chromatographed on alumina, affording an amide (see next experiment) (328 mg., 12%), m. p. 238° (decomp.), which was derived from the adduct (XIII; R = H), which was thus formed in *ca.* 62% yield.

8a-*Cyano*-1,4,4a,5,8,8a-*hexahydro*-1,4-*dioxonaphthalene*-4a-*carboxamide* (XXXVa).—The above dicyano-adduct (XXXIVa = XIII, R = H) (450 mg.), in benzene, was chromatographed on alkaline alumina, elution with benzene–ethanol (450 ml., 9 : 1) affording the *cyano-amide* (290 mg., 60%), m. p. 238° (decomp.), $\lambda_{\text{max.}}$ 224 mμ (ε 9400), 2·88, 2·99 (free NH), 3·04, 3·13 (bonded NH), 4·44 (CN, fairly weak), 5·86, 5·95 (C=O), broad), 6·23 (conj. C=C), 7·01 μ ($CO{\cdot}NH_2$), τ (in acetone) 6·87 (4a-$CO{\cdot}NH_2$, broad), 4·73 (6,7-H_2), 3·72, 3·69 p.p.m. (2,3-H_2) (Found: C, 63·0; H, 4·2; N, 12·0. $C_{12}H_{10}N_2O_3$ requires C, 62·6; H, 4·35; N, 12·15%).

4a,8a-*Dicyano*-4a,5,8,8a-*tetrahydro*-6,7-*dimethyl*-1,4-*naphthaquinone* (XIII; R = Me).—2,3-Dimethylbutadiene (3·7 g.) and 2,3-dicyanobenzoquinone (3·7 g.) were left in benzene–ethanol (220 ml., 9 : 1) for 17 hr. Removal of the solvent, and washing the residue with light petroleum (b. p. 40—60°), left a solid (5·4 g., 96%), m. p. 150—157°, which crystallised from ethanol–light petroleum (b. p. 80—100°) to give the *dicyano-adduct*, m. p. 157—158°, $\lambda_{\text{max.}}$ 229 mμ (ε 7400), 4·48 (CN, fairly weak), 5·92 (C=O), 6·28 μ (conj. C=C), τ-3·08 p.p.m. (2,3-H_2) (Found: C, 69·7; H, 4·8; N, 12·0. $C_{14}H_{12}N_2O_2$ requires C, 70·0; H, 5·0; N, 11·7%).

8a-*Cyano*-1,4,4a,5,8,8a-*hexahydro*-6,7-*dimethyl*-1,4-*dioxonaphthalene*-4a-*carboxamide* (XXXVb).—The above dicyano-adduct (XXXIVb = XIII; R = Me) (600 mg.) was chromatographed on alumina, as above, to afford the *cyano-amide* (545 mg., 85%), m. p. 238—239° (decomp.) (from benzene–acetone), $\lambda_{\text{max.}}$ 225 mμ (ε 9950), 2·91 (free NH), 3·03, 3·15 (bonded NH), 4·45 (CN, fairly weak), 5·86, 5·96 (C=O) broad), 6·21, 6·26 (C=C), 7·05 μ ($CO{\cdot}NH_2$), τ (in acetone) 3·68, 3·63 (2,3-H_2), 3·37br p.p.m. (4a-$CO{\cdot}NH_2$) (Found: C, 65·7; H, 5·4%; *M*, 296. $C_{14}H_{14}N_2O_3$ requires C, 65·2; H, 5·4%; *M*, 258).

The amide (700 mg.) was heated in acetic anhydride (10 ml.) containing concentrated sulphuric acid (2 drops) at 90° for 20 hr. [This treatment did not affect the parent adduct (XIII; R = Me).] The dark solution was poured into water and extracted with ether. The washed (bicarbonate) extracts afforded a *substance* (500 mg., *ca.* 70%), m. p. 170—171° (from ethanol), $\lambda_{max.}$ 231, 246 mμ ($E^{1\%}_{1\,cm.}$ 66·4 and 75·3), 5·69, 5·77, 5·88 μ (C=O) (no OH, NH, CN, or C=C absorption), τ 8·37, 8·25 (two vinyl Me), 7·72, 7·45 (two COMe), 7·45, 7·12, 6·78 (two aliphatic CH_2), 4·04, 2·33 p.p.m. (two vinyl H, AB quartet, J_{AB} = 10 c./sec.) (Found: C, 63·6; H, 5·4; N, 8·2. $C_{18}H_{18}N_2O_5$ requires C, 63·2; H, 5·3; N, 8·4%). The structure (XXXVII) is suggested for this substance, which evolved ammonia with hot alkali.

5,8-Dihydro-2,3-dimethoxycarbonyl-1,4-naphthaquinol (XVa).—2,3-Dimethoxycarbonyl-1,4-benzoquinone [6] (1·45 g.) was allowed to react with an excess of butadiene in methanol (30 ml.) at 90° for 4 days. The volume was reduced (to 10 ml.), then the cooled solution deposited the *dimethoxycarbonyl-quinol* (920 mg., 51%), m. p. 142—143° [from ethanol–light petroleum (b. p. 60—80°)], $\lambda_{max.}$ 268, 345 mμ (ε 6000 and 6900), 3·09 (OH), 5·96, 6·00sh (C=O), 6·25, 6·34 μ (C=C), τ 6·71 (5,8-H_4), 6·15 [2,3-$(CO_2Me)_2$], 4·13 p.p.m. (6,7-H_2) (Found: C, 60·4; H, 5·15. $C_{14}H_{14}O_6$ requires C, 60·4; H, 5·1%). Chromatography of the mother-liquors of the reaction afforded more of the quinol (10%) as a solid, and gums which were demonstrated to contain the quinol (total 70—75%) by absorption spectra.

Reaction between 2,3-*Dimethoxycarbonylbenzoquinone and Isoprene*.—The quinone (1 g.) and the diene (400 mg.) were maintained at 60° for 22 hr. in methanol (50 ml.), then the solvent was removed. The residue was chromatographed on alumina, in benzene, to give gums from the first fractions and a solid from the later ones. The solid was 5,8-*dihydro*-2,3-*dimethoxycarbonyl*-6-*methyl*-1,4-*naphthaquinol* (XVc) (450 mg., 45%), m. p. 141—143° (from ethanol), $\lambda_{max.}$ 266, 344 mμ (ε 4800 and 7000), 2·95 (OH), 5·88, 6·00sh (C=O), 6·22, 6·29 μ (C=C) (Found: C, 61·6; H, 5·5. $C_{15}H_{16}O_6$ requires C, 61·6; H, 5·5%).

The gums had $\lambda_{max.}$ 237, 267infl., 308infl. mμ (ε 11,000, 2900, and 1400 for *M* 292), 5·76, 5·89 (C=O), 6·23 μ (C=C) and only a very little OH absorption; the whole spectrum closely resembled that of the adduct (XIVb) (next experiment) and the gums were, predominantly, dimethyl 1,4,4a,5,8,8a-hexahydro-6-methyl-1,4-dioxonaphthalene-4a,8a-dicarboxylate (XIVc).

Reaction between 2,3-*Dimethoxycarbonylbenzoquinone and* 2,3-*Dimethylbutadiene*.—The quinone (1 g.) and the diene (720 mg.) were heated under reflux in methanol (50 ml.) for 2 hr. and then left for a further 3 hr. The solvent was removed and the residue was chromatographed on alumina, in benzene; the first fractions afforded *dimethyl* 1,4,4a,5,8,8a-*hexahydro*-6,7-*dimethyl*-1,4-*dioxonaphthalene*-4a,8a-*dicarboxylate* (XIVb) (330 mg., 25%), m. p. 132—135° (from ether), $\lambda_{max.}$ 229 mμ (ε 7400), 5·75sh, 5·79 (ester), 5·86sh, 5·91 (enedione C=O), 6·21 μ (conj. C=C), τ 6·29 [4a,8a-$(CO_2Me)_2$], 3·27 p.p.m. (2,3-H_2) (Found: C, 63·0; H, 6·1. $C_{16}H_{18}O_6$ requires C, 62·7; H, 5·9%).

The later chromatography fractions afforded 5,8-*dihydro*-2,3-*dimethoxycarbonyl*-6,7-*dimethyl*-1,4-*naphthaquinol* (XVb) (345 mg., 25%), m. p. 189—190° [from ethanol–light petroleum (b. p. 80—100°)], $\lambda_{max.}$ 254infl., 342 mμ (ε 4800 and 7500), 3·10 (OH), 5·90, 6·00 (C=O), 6·25 μ (C=C), τ 6·14 [2,3-$(CO_2Me)_2$], 2·74 p.p.m. [1,4-$(OH)_2$] (Found: C, 62·8; H, 5·95. $C_{16}H_{18}O_6$ requires C, 62·7; H, 5·9%).

Reaction between 2,3-*Dimethoxycarbonylbenzoquinone and* 1-*Vinylcyclohexene* (with Mr. J. E. Lakeman).—The quinone (1 g.) and the diene (600 mg.) were heated under reflux in methanol (50 ml.) for 3 hr. and then left for 18 hr. Removal of the solvent and chromatography of the residue gave, from the first fractions, *dimethyl* $\Delta^{2,8a(9)}$-*decahydro*-1,4-*dioxophenanthrene*-4a,10a-*dicarboxylate* (XIVe) (560 mg., 38%), m. p. 157—159° (from ether), $\lambda_{max.}$ 226 mμ (ε 7300), 5·76, 5·81 (ester), 5·92 (enedione C=O), 6·21 μ (conj. C=C), τ 6·31, 6·21 [4a,10a-$(CO_2Me)_2$], 4·71 (9-H), 3·36, 3·14 p.p.m. (2,3-H_2) (Found: C, 65·15; H, 6·0. $C_{18}H_{20}O_6$ requires C, 65·05; H, 6·05%).

The later chromatography fractions afforded *dimethyl* 4b,5,6,7,8,10-*hexahydro*-1,4-*dihydroxyphenanthrene*-2,3-*dicarboxylate* (XVe) (250 mg., 17%), m. p. 166—169° (from ether), $\lambda_{max.}$ 219, 269, 343 mμ (ε 21,500, 5500, and 8100), 2·93 (OH), 5·90sh, 5·96 (ester), 6·26 μ (C=C), τ 6·10 [2,3-$(CO_2Me)_2$], 4·43 p.p.m. (9-H) (Found: C, 64·6; H, 5·9. $C_{18}H_{20}O_6$ requires C, 65·05; H, 6·05%).

4a,5,8,8a-*Tetrahydro*-2,6,7-*trimethyl*-3-*nitro*-1,4-*naphthaquinone*.—2-Methyl-3-nitrobenzoquinone [6] (1·1 g.) and 2,3-dimethylbutadiene (720 mg.) were heated under reflux in methanol (50 ml.) for 17 hr. After removal of the solvent, the semi-solid residue was taken up in hot light petroleum (b. p. 60—80°); cooling afforded, in two crops, a solid (480 mg.), m. p. 90—102°, which was crystallised from light petroleum (b. p. 80—100°) to give the *nitro-adduct* (*ca.* 35%), m. p. 110—112°, $\lambda_{max.}$ 228 mμ (ε 9500), 5·89, 5·92 (C=O), 6·12 (C=C), 6·50 μ

(NO_2) (no vinyl protons) (Found: C, 62·3; H, 6·45; N, 5·15. $C_{13}H_{15}NO_4$ requires C, 62·6; H, 6·1; N, 5·6%). The mother-liquors did not yield any more solid on chromatography.

The nitro-adduct (32 mg.) was aromatised in the usual way, to afford 5,8-*dihydro*-2,6,7-*trimethyl*-3-*nitro*-1,4-*naphthaquinol* (16 mg., 50%), m. p. 183—184° (deep red crystals from aqueous acetic acid), $\lambda_{max.}$ 222infl., 264, 286infl. mμ (ε 12,500, 5500, and 4500), 2·94 (OH), 6·27 (C=C), 6·53 μ (C=C or NO_2) (Found: C, 62·5; H, 5·8. $C_{13}H_{15}NO_4$ requires C, 62·6; H, 6·1%).

2-*Cyano*-5,8-*dihydro*-3,6,7-*trimethyl*-1,4-*naphthaquinol*.—A solution of 2-cyano-3-methylbenzoquinone [6] (400 mg.) and 2,3-dimethylbutadiene (350 mg.) in benzene (15 ml.) was heated under reflux for 2 hr. Removal of the solvent left a solid (500 mg., 80%), m. p. 220—230° (decomp.), which crystallised from ethanol (mother-liquors purple-brown, indicative of a light-sensitive dihydronaphthaquinol), to give the *cyano-quinol*, m. p. 248—250° (decomp.), $\lambda_{max.}$ 215 (doublet), 252, 322 mμ (ε 20,000, 3000, and 2500), 3·00 (OH), 4·48s (CN), 6·18 μ (C=C) (Found: C, 73·15; H, 6·4; N, 6·3. $C_{14}H_{15}NO_2$ requires C, 73·4; H, 6·55; N, 6·1%).

Reaction between 2-*Chloro*-6-*methylbenzoquinone and Buta*-1,3-*diene*.—The quinone [35] (2 g.) and an excess of butadiene were allowed to react in benzene (30 ml.) for 11 days, then at 70° for 15 hr. Removal of the solvent left a semi-solid which evolved hydrogen chloride. Desiccation of this residue at 0·1 mm. in the dark, and crystallisation of the product from ethanol, gave light-sensitive 5,8-dihydro-2-methyl-1,4-naphthaquinone (VIa; R = Me) (1·2 g., 55%), m. p. 84—87°, identical with an authentic specimen,[23] m. p. 86—87°.

Reaction between 2-*Chloro*-6-*methylbenzoquinone and* 2-3-*Dimethylbutadiene*.—The quinone (3 g.) and the diene (2·1 g.) in ethanol (70 ml.) were left for 64 hr. Removal of the solvent gave an inhomogeneous solid (primary adduct and unchanged quinone) that was chromatographed on alumina, in benzene. The red-brown eluate afforded a dark yellow solid (1·5 g.) which crystallised from ethanol–light petroleum (b. p. 60—80°) to give the light-sensitive 5,8-dihydro-2,6,7-trimethyl-1,4-naphthaquinone (VIb; R = Me) (1·4 g., 40%), m. p. 133—135°, identical with an authentic specimen,[24] m. p. 130—134° (placed in the bath at 115°; if the m. p. was taken slowly, the sample darkened at *ca.* 125° and melted from 150—185°, probably owing to thermal aromatisation to the naphthaquinol).

Reaction between 2-*Acetoxy*-5-*methylbenzoquinone and* 2,3-*Dimethylbutadiene*.—A solution of the quinone [36] (2·5 g.) and the diene (2·1 g.) in methanol (30 ml.) was heated under reflux for 17 hr. Removal of the solvent left an orange gum which was chromatographed on alumina, in benzene. The yellow eluate afforded 5,8-dihydro-2,6,7-trimethyl-1,4-naphthaquinone (VIb; R = Me) (*ca.* 30%) (see above). The mother-liquors [ethanol–light petroleum (b. p. 80—100°)] from which the quinone had crystallised then afforded 4a-acetoxy-4a,5,8,8a-tetrahydro-2,6,7-trimethyl-1,4-naphthaquinone (XX) (150 mg., 6%), m. p. 119—121° (lit.,[10] 116—117°), $\lambda_{max.}$ 240 mμ (ε 13,000) (lit.,[10] 236 mμ), τ 7·95 (4a-COMe), 7·84 (2-Me, doublet), 3·37 p.p.m. (3-H, quartet). Incomplete elimination of acetic acid from (XX) had taken place on the column; the primary adduct (XX) was formed in *ca.* 36% yield.

Reaction between 2,5-*Dimethoxybenzoquinone and* 2,3-*Dimethylbutadiene*.—The quinone [37] (5 g.), the diene (3·6 g.), and benzene (10 ml.) were heated together at 180° for 20 hr. The cooled mixture was filtered, and the residue was extracted with hot benzene (3 × 20 ml.) which, on cooling, deposited 2,5-dimethoxyquinol (627 mg., 12·5%), m. p. 169—171°, identical with an authentic specimen,[38] m. p. 164—166°. The residue left after benzene-extraction gave the starting quinone (22%). The filtrate from the reaction mixture was chromatographed on alumina; the yellow eluate afforded 2,3,6,7-tetramethylanthraquinone (XXI) (412 mg., 5%), m. p. 325—329° (softening *ca.* 290°), identical (infrared spectra) with an authentic specimen.[39]

2-*Chloro*-4a,8a-*dicyano*-4a,5,8,8a-*tetrahydro*-6,7-*dimethyl*-1,4-*naphthaquinone* (XXXIVc).—2,3-Dimethylbutadiene (820 mg.) was added to a suspension of 2-chloro-5,6-dicyanobenzoquinone [6] (1·92 g.) in methanol (50 ml.). After 10 min. the bulk of the solvent was distilled off. The cooled solution deposited the *chloro-dicyano-adduct* (2·4 g., 88%), m. p. 113—114° (from aqueous methanol), $\lambda_{max.}$ 250 mμ (ε 7950), 4·44, 4·47 (CN, fairly weak), 5·78, 5·86 (C=O), 6·30 μ

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[35] Kehrmann, Mussmann, and Facchinetti, *Ber.*, 1915, **48**, 2021.

[36] Thiele and Winter, *Annalen*, 1900, **311**, 349.

[37] Rodgers, U.S.P. 2,743,286.

[38] Ramage and Stead, *J.*, 1953, 1393.

[39] Barnett, Goodway, and Watson, *Chem. Ber.*, 1933, **66**, 1887, record m. p. 326°, but Morgan and Coulson, *J.*, 1931, 2323, give m. p. 338° (sublimation) (corr.). The method of Barnett *et al.* was used to prepare the authentic quinone, since that of Morgan *et al.* could not be repeated.

(conj. C=C), τ 2·84 p.p.m. (3-H) (Found: C, 60·75; H, 3·9; Cl, 13·0; N, 10·2. $C_{14}H_{11}ClN_2O_2$ requires C, 61·2; H, 4·05; Cl, 12·9; N, 10·2%).

2(or 3)-*Chloro*-8a-*cyano*-1,4,4a,5,8,8a-*hexahydro*-6,7-*dimethyl*-1,4-*dioxonaphthalene*-4a-*carboxmide* (XXXVc or e).—The above adduct (XXXIVc) (3 g.) was chromatographed on alumina in 9 : 1 benzene–ethanol, yielding the *monoamide* (2·5 g., 78%), m. p. 220—220·5° (decomp.) (from benzene), $\lambda_{max.}$ 253 mμ (ε 7950), 2·81, 2·99 (free NH), 3·22 (bonded NH), 4·45w (CN), 5·80, 5·90, 6·03 (C=O), 6·20 μ (conj. C=C) (Found: C, 57·2; H, 4·2; Cl, 12·25; N, 9·45. $C_{14}H_{13}ClN_2O_3$ requires C, 57·45; H, 4·5; Cl, 12·1; N, 9·55%)

4a,8a-*Dicyano*-4a,5,8,8a-*tetrahydro*-2,6,7-*trimethyl*-1,4-*naphthaquinone* (XXXIVd).—2,3-Dimethylbutadiene (820 mg.) was added to a suspension of 2,3-dicyano-5-methylbenzoquinone [36] (1·72 g.) in methanol (10 ml.). An exothermic reaction ensued, and the quinone dissolved. The cooled solution deposited the *dicyano-adduct* (2·1 g., 87%), m. p. 110—111° (from methanol), $\lambda_{max.}$ 249 mμ (ε 5900), 4·57 (CN, fairly weak), 5·90 (C=O), 6·19 μ (conj. C=C), τ 7·88 (2-Me, doublet), 3·22 p.p.m. (3-H, quartet) (Found: C, 71·15; H, 5·55; N, 11·0. $C_{15}H_{14}N_2O_2$ requires C, 70·85; H, 5·55; N, 11·0%).

8a-*Cyano*-1,4,4a,5,8,8a-*hexahydro*-2(or 3),6,7-*trimethyl*-1,4-*dioxonaphthalene*-4a-*carboxamide* (XXXVd or f).—The adduct (XXXIVd) (500 mg.) was chromatographed on alumina in 9 : 1 benzene–ethanol, affording the *monoamide* (460 mg., 86%), m. p. 220—222° (decomp.) (from benzene–acetone), $\lambda_{max.}$ 244 mμ (ε 11,500), 2·90, 3·01 (free NH), 3·12 (bonded NH), 4·47w (CN), 5·86sh, 5·93, 6·00 (C=O), 6·19 μ (conj. C=C) (Found: C, 66·35; H, 6·05; N, 10·5. $C_{15}H_{16}N_2O_3$ requires C, 66·15; H, 5·9; N, 10·3%).

Dimethyl 1,4,4a,5,8,8a-*Hexahydro*-2,6,7-*trimethyl*-1,4-*dioxonaphthalene*-4a,8a-*dicarboxylate.*—2,3-Dimethoxycarbonyl-5-methylbenzoquinone [6] (2·38 g.) and 2,3-dimethylbutadiene (820 mg.) in methanol (15 ml.) were heated under reflux for 6 hr. Removal of the solvent, and crystallisation of the residue from methanol, afforded the *adduct* (2·43 g., 76%), m. p. 81—83°, $\lambda_{max.}$ 246 mμ (ε 10,000), 5·75sh, 5·78 (ester), 5·89, 5·97 (enedione C=O), 6·13 μ (conj. C=O), τ 7·96 (2-Me, doublet $J_{H,Me} = 1\cdot5$ c./sec.), 6·25, 6·22 [4a,8a-$(CO_2Me)_2$], 3·46 p.p.m. (3-H, quartet) (Found: C, 63·75; H, 6·25. $C_{17}H_{20}O_6$ requires C, 63·75; H, 6·3%).

4a-*Cyano*-4a,5,8,8a-*tetrahydro*-2,6,7,8a-*tetramethyl*-1,4-*naphthaquinone* (XXXVIg).—2-*Cyano*-3,5-*dimethylbenzoquinone* [6] (4·83 g.) and 2,3-dimethylbutadiene (2·87 g.) were allowed to react in methanol (30 ml.) for 4 days, then the solvent was removed and the residue was chromatographed on alumina. The eluate afforded the *cyano-adduct* (3·3 g., 45%), m. p. 112—113·5° (from methanol), $\lambda_{max.}$ 245 mμ (ε 10,500), 4·45 (CN, fairly weak), 5·91, 6·04 (C=O), 6·18 μ (conj. C=C), τ 8·58 (8a-Me), 7·97 (2-Me), 3·47 p.p.m. (3-H) (Found: C, 73·95; H, 7·0; N, 5·95. $C_{15}H_{17}NO_2$ requires C, 74·05; H, 7·05; N, 5·75%). A similar yield of the adduct was obtained by direct crystallisation of the crude product from methanol.

8a-*Cyano*-4a,5,8,8a-*tetrahydro*-2,4a,6,7-*tetramethyl*-1,4-*naphthaquinone* (XXXVIh).—3-Cyano-2,5-dimethylbenzoquinone [6] (1·61 g.) and 2,3-dimethylbutadiene (820 mg.) were allowed to react in methanol (15 ml.) for 3 days. The bulk of the solvent was distilled off, then the residual solution, on cooling, afforded crystals of the *cyano-adduct* (1·6 g., 66%), m. p. 157—158° (from benzene), $\lambda_{max.}$ 246 mμ (ε 12,500), 4·47 (CN, fairly weak), 5·97 (C=O), 6·18 μ (conj. C=C), τ 8·56 (4a-Me), 7·90 (2-Me), 3·43 p.p.m. (3-H) (Found: C, 74·15; H, 7·25; N, 5·85. $C_{15}H_{17}NO_2$ requires C, 74·05; H, 7·05; N, 5·75%). This adduct was chromatographed without change on alumina in benzene–ethanol. The quinone used in this experiment is more stable than that used in the previous one, resulting in the different yields from these comparable reactions.

Methyl 1,4,4a,5,8,8a-*hexahydro*-3,4a,6,7-*tetramethyl*-1,4-*dioxo*-2-*naphthoate* (XXXVIi).—A solution of 2-methoxycarbonyl-3,5-dimethylbenzoquinone [6] (9·7 g.) and 2,3-dimethylbutadiene (4·9 g.) in methanol (50 ml.) was heated under reflux for 12 hr. The oil remaining after removal of the solvent was chromatographed on alumina in 1 : 1 benzene–light petroleum (b. p. 60—80°). The eluate afforded oils which partly solidified. The solids were washed with a little methanol and then crystallised from methanol, to afford the *methoxycarbonyl adduct* (3·2 g., 23%), m. p. 124—124·5°, $\lambda_{max.}$ 242 mμ (ε 8700), 5·76 (ester), 5·97, 6·03sh (enedione C=O), 6·17 μ (conj. C=C), τ 9·13 (4a-Me), 8·16 (3-Me), 6·18 p.p.m. (3-CO_2Me)(no vinyl protons) (Found: C, 69·8; H, 7·65. $C_{16}H_{20}O_4$ requires C, 69·55; H, 7·3%).

Methyl 1,4,4a,5,8,8a-*hexahydro*-3,6,7,8a-*tetramethyl*-1,4-*dioxo*-2-*naphthoate* (XXXVIj).—A solution of 3-methoxycarbonyl-2,5-dimethylbenzoquinone [6] (5·8 g.) and 2,3-dimethylbutadiene (3·3 g.) in methanol (25 ml.) was heated under reflux for 12 hr., and the solution was treated as in the previous experiment, to afford the *methoxycarbonyl adduct* (2·8 g., 34%), m. p. 125—126° (from methanol), $\lambda_{max.}$ 243 mμ (ϵ 8900), 5·78 (ester), 5·92, 6·00 (enedione C=O), 6·16 μ (conj. C=C), τ 8·88 (4a-Me), 8·02 (2-Me), 6·10 p.p.m. (3-Me) (no vinyl protons) (Found: C, 69·6; H, 7·3. $C_{16}H_{20}O_4$ requires C, 69·55; H, 7·3%).

2-*Acetyl*-4a,5,8,8a-*tetrahydro*-3,4a,6,7-*tetramethyl*-1,4-*naphthaquinone* (XXXVIk).—A solution of 2-acetyl-3,5-dimethylbenzoquinone [6] (6·24 g.) and 2,3-dimethylbutadiene (3·28 g.) in methanol (10 ml.) was heated under reflux for 12 hr. Removal of the solvent gave an oil which partly solidified at 0° in a week. Filtration afforded a solid (5·2 g., 56%), m. p. 49—63°, which was crystallised many times from methanol; this gave the *acetyl adduct* (1·3 g., 14%), m. p. 83—85°, $\lambda_{max.}$ 243 mμ (ϵ 10,500), 5·85 (Ac), 5·92, 5·99 (enedione C=O), 6·11 μ (conj. C=C), τ 8·68 (4a-Me), 8·06 (3-Me), 7·63 p.p.m. (2-COMe) (no vinyl protons) (Found: C, 73·6; H, 7·55. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·75%).

Reaction between 3-*Acetyl*-2,5-*dimethoxybenzoquinone and* 2,3-*Dimethylbutadiene*.—A mixture of the quinone [6] (2 g.), the diene (5·8 g.), and a few crystals of quinol was heated at 200° for 15 hr. in a sealed tube. The cooled mixture was filtered, the residue was boiled with methanol (30 ml.) for 5 min., and the hot mixture was filtered. The residue was 2,3,6,7-tetramethylanthraquinone (XXI) (1·0 g., 80% based on half the starting quinone), m. p. 340—341° (sublimation) (purified by sublimation at 280°), $\lambda_{max.}$ 268 mμ (ϵ 30,000), identical with an authentic specimen.[39]

The methanolic filtrate was evaporated to dryness and the residue was crystallised from water containing sulphur dioxide, to give 2,5-dihydroxy-3,6-dimethoxyacetophenone (XXIX) (900 mg., 90% based on half the starting quinone), m. p. 172—174°, undepressed in admixture with an authentic specimen,[38] m. p. 174—176°.

Reaction between 5-*Methoxy*-2,3-*dimethylbenzoquinone and* 2,3-*Dimethylbutadiene*.—The quinone [6] (3 g.), the diene (7·2 g.), and a crystal of quinol were heated at 200° for 10 hr. in a sealed tube. The cooled mixture was extracted with acetone (5 ml.). The bulk of the acetone was removed and light petroleum (b. p. $<40°$) (10 ml.) was added. A slight flocculent precipitate was filtered off. The filtrate then deposited pale yellow crystals. The mother-liquors were decanted; colourless crystals were then deposited. The pale yellow crystals were 2,3,6,7-tetramethylnaphthaquinone (500 mg., 13%), m. p. 172—173° (from methanol) (undepressed in admixture with an authentic specimen,[40] m. p. 170—171°), $\lambda_{max.}$ 260, 279, 338 mμ (ϵ 42,000, 32,500, and 11,500) (Found: C, 78·2; H, 6·45. Calc. for $C_{14}H_{14}O_2$: C, 78·5; H, 6·6%).

The colourless crystals were 1,4,4a,5,8,8a-*hexahydro*-2-*methoxy*-4a,6,7,8a-*tetramethyl*-1,4-*naphthaquinone* (XXXI; R = Me) (900 mg., 20%), m. p. 119—120°, $\lambda_{max.}$ 270 mμ (ϵ 9300), 5·89, 6·05 (C=O), 6·24 μ (conj C=C), τ 8·85, 8·81 (4a,8a-Me$_2$), 6·23 (2-MeO), 4·23 p.p.m. (3-H) (Found: C, 72·4; H, 8·0. $C_{15}H_{20}O_3$ requires C, 72·55; H, 8·1%). When the reaction was attempted in boiling methanol for 6 days, only unchanged quinone was isolated.

Methyl 1,4,4a,5,8,8a-*hexahydro*-2-*methoxy*-6,7,8a-*trimethyl*-1,4-*dioxonaphthalene*-4a-*carboxylate* (XXXI; R = CO_2Me).—A solution of 5-methoxy-2-methoxycarbonyl-3-methylbenzoquinone [2] (1·05 g.) and 2,3-dimethylbutadiene (1 g.) in methanol (10 ml.) was heated under reflux for 3 days. Removal of the solvent and crystallisation of the residue from methanol gave the *adduct* (1·18 g., 81%), m. p. 142—143°, $\lambda_{max.}$ 273 mμ (ϵ 9300), 5·83 (ester), 6·02 (enedione C=O), 6·27 μ (conj. C=C), τ 8·65 (8a-Me), 6·36 (4a-CO_2Me), 6·10 (2-MeO), 4·17 p.p.m. (3-H) (Found: C, 65·45; H, 6·65. $C_{16}H_{20}O_5$ requires C, 65·75; H, 6·9%).

Dimethyl 1,4,4a,5,8,8a-*Hexahydro*-3,4a,6,7-*tetramethyl*-1,4-*dioxonaphthalene*-2,8a-*dicarboxylate*.—A solution of 2,6-dimethoxycarbonyl-3,5-dimethylbenzoquinone [6] (5·04 g.) and 2,3-dimethylbutadiene (1·64 g.) in methanol (50 ml.) was heated under reflux for 12 hr. The bulk of the solvent was removed and the cooled solution gave the *adduct* (6·0 g., 90%), m. p. 99—105°, raised to m. p. 108—110° by crystallisation from methanol, $\lambda_{max.}$ 243 mμ (ϵ 2200), 5·77sh, 5·80 (ester), 5·93, 6·05 (enedione C=O), 6·12 μ (conj. C=C) (Found: C, 64·45; H, 6·45. $C_{18}H_{22}O_6$ requires C, 64·65; H, 6·65%).

4a,5,8,8a-*Tetrahydro*-2,3,4a,6,7,8a-*hexamethyl*-1,4-*naphthaquinone*.—A mixture of duroquinone [41] (3 g.), 2,3-dimethylbutadiene (3·6 g.), and a crystal of quinol was heated at 180° for 12 hr. in a sealed tube. The cooled mixture was filtered and the residue was crystallised from methanol, to give the *adduct* (3·9 g., 87%), m. p. 115—117°, $\lambda_{max.}$ 254 mμ (ϵ 11,500), 5·99

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[40] Fieser and Ardao, *J. Amer. Chem. Soc.*, 1956, **78**, 774.

[41] Smith, *Org. Synth.*, Coll. Vol. II, p. 254.

(C=O), 6·16 μ (conj. C=C) (Found: C, 77·9; H, 9·0. $C_{16}H_{22}O_2$ requires C, 78·0; H, 9·0%). When this reaction was attempted at 100° for 50 hr., duroquinone was recovered.

4a,5,8,8a-*Tetrahydro*-2,3,4a,8a-*tetramethoxy*-6,7-*dimethyl*-1,4-*naphthaquinone*.—A mixture of tetramethoxybenzoquinone[42] (1 g.), 2,3-dimethylbutadiene (4·3 g.), and a few crystals of quinol were heated at 200° for 15 hr. in a sealed tube. The volatile material was removed and the residue was washed with light petroleum (b. p. $<40°$), giving the *adduct* (1·3 g., 95·5%), m. p. 84—92°, raised to m. p. 92—93° (from methanol), $\lambda_{max.}$ 298 mμ (ε 7950), 5·89, 5·94 (C=O), 6·28 μ (conj. C=C) (Found: C, 62·15; H, 7·1. $C_{16}H_{22}O_6$ requires C, 61·9; H, 7·15%).

Added in proof. The major product from the addition of *N*-methylaniline to toluquinone is 2-*methyl*-5-N-*methylanilinobenzoquinone*, m. p. 143—145° [shining purple plates from ethanol–light petroleum (b. p. 60—80°)] (Found: C, 74·3; H, 6·0; N, 6·7. $C_{14}H_{13}NO_2$ requires C, 74·0; H, 5·8; N, 6·2%), τ 7·78 (2-Me doublet, $J \approx 1·7$ c/sec.), 6·72 (*N*-Me), 4·19 (6-H), 3·66 (3-H, quartet, $J \approx 1·5$) 2·78 p.p.m. (envelope of C_6H_5 protons). The minor product is 2-*methyl*-6-N-*methylanilinobenzoquinone*, m. p. 90—92° [deep-purple needles from ethanol–light petroleum (b. p. 60—80°)] (Found: C, 73·7; H, 5·8; N, 6·4%), τ 8·05 (2-Me, doublet, $J \approx 1·7$ c/sec.), 6·68 (*N*-Me), 4·16 (5-H, doublet, $J \approx 3$ c/sec.), 3·52 (3-H, 6 line complex), 2·80 p.p.m. (envelope of C_6H_5 protons). In the spectrum of the latter compound long-range coupling occurs between 3-H and 5-H; this is also found in the spectrum of 2-chloro-6-methylbenzoquinone, τ 7·87 (6-Me, doublet, $J \approx 1·5$ c/sec.), 3·31 (5-H, multiplet), 3·03 p.p.m. (H-3, doublet, $J \approx 2·5$ c/sec.).

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[42] Robinson and Vasey, *J.*, 1941, 660.