Diels–Alder Reaction of Unsymmetrical Dienes with Unsymmetrical *p*-Benzoquinones

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A number of Diels–Alder reactions between 1-phenyl-, 1-*p*-methoxyphenyl-, and 1-*p*-nitrophenyl-2,3-dimethylbutadiene and methoxycarbonyl-, 2,6-dimethyl-, 2,5-dimethyl-, 2-methoxy-6-methyl-, 5-methoxy-2-methoxycarbonyl-3-methyl-, and 2-cyano-3,5-dimethyl-*p*-benzoquinone are reported. The structures of the major products are established and their formation is interpreted on the basis of a transition state having some diradical character.

A DIELS–ALDER reaction between an unsymmetrical *p*-benzoquinone [*e.g.* (1)] and an unsymmetrical diene (2) can, in principle, give rise to four structurally distinct adducts (Scheme 1). Although the factors controlling the ' side of addition ' [to give (3) or (4) or alternatively (5) or (6)] have been established,[1] the factors controlling the relative orientation of the substituents have not been extensively investigated.[2] Such factors may be electronic and/or steric and changing the nature of the substituent R in the diene (2) may alter both factors simultaneously. In order to avoid this complication, we studied the *trans*-1-aryl-2,3-dimethyl-buta-1,3-dienes (2a—c), in which the electronic nature of the 1-substituent was varied while its steric effect was kept essentially constant. The presence of the methyl groups at positions 2 and 3 of the diene facilitated the interpretation of the n.m.r. spectra of the adducts. The unsymmetrical quinones studied were chosen so that in each case addition occurred at a substituted ethylene linkage.

The effect of varying the electronic nature of the substituent in the diene was first examined in the reactions of methoxycarbonyl-*p*-benzoquinone (1). The effect of changing the substituent on the reacting ethylene linkage of the quinone was revealed from the reactions of the dienes (2) with 2,6-dimethyl-*p*-benzoquinone (7). The effect on the course of the reaction when both quinone substituents (Me and CO_2Me) were on the ethylene linkage at which addition took place, was determined by use of 5-methoxy-2-methoxycarbonyl-3-methyl-*p*-benzoquinone (12). Similarly the reactions of 2-cyano-3,5-dimethyl-*p*-benzoquinone (19) showed the result of replacing the methoxycarbonyl group by the cyano-group. The influence of substituents on the non-reacting ethylene linkage was studied by use of 2,5-dimethyl-*p*-benzoquinone and 2-methoxy-6-methyl-*p*-benzoquinone. The adducts from the latter quinone were also of importance in the determination of the structures of the adducts from the quinone (12).

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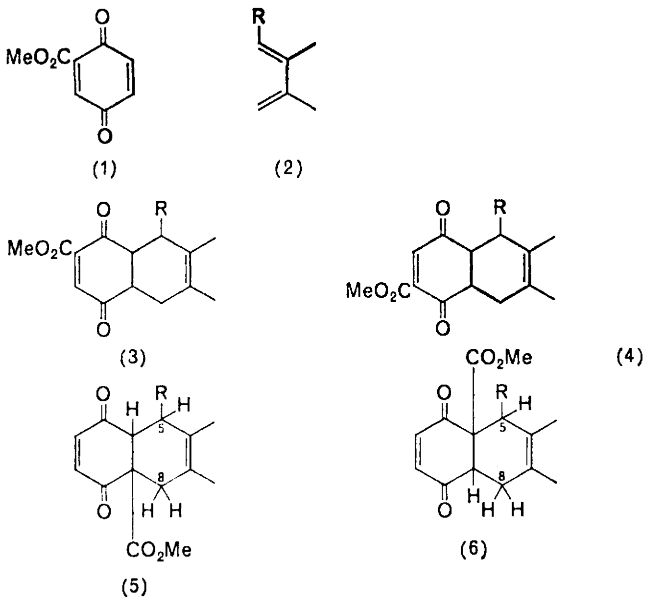
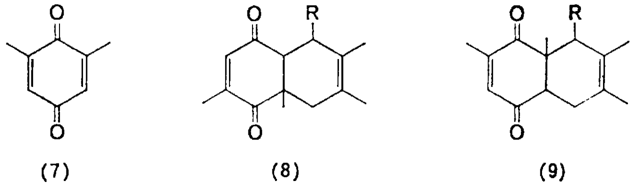
[1] M. F. Ansell, B. W. Nash, and D. A. Wilson, *J. Chem. Soc.*, 1963, 3012.

[2] Reviews on Diels–Alder reaction: (*a*) J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16; 1966, **5**, 211: (*b*) R. Huisgen, R. Grashey, and J. Sauer in ' The Chemistry of the Alkenes,' ed. S. Patai, Interscience, New York, 1964: Yu. A. Titov, *Russ. Chem. Rev.*, 1962, **31**, 267; A. S. Onishchenko ' Diene Synthesis,' Israel Programme for Scientific Translation, Jerusalem, 1964.



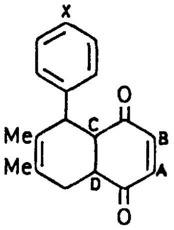
SCHEME 1

Results.—At room temperature the reactive methoxycarbonyl-quinone (1) added readily to each of the dienes (2a—c), the reactivity of the dienes being in the expected sequence (2a) > (2b) > (2c). In each case a pure major adduct was isolated in high yield (see Table). The n.m.r. spectrum of each showed the presence of two vinyl protons, thus excluding structures of types (3) and (4). It was possible to distinguish between the structures (5) and (6) by a consideration of the expected n.m.r. characteristics of the four protons specifically indicated. The remaining protons were accounted for (see Table). In the spectrum for structure (6), the 5-proton would appear as a singlet, and the signals due to both the 8-protons would be split owing to mutual coupling (unless their chemical shifts were identical) and by coupling to the 8a-proton (depending on the dihedral angles between these protons). In the spectrum for structure (5) the 4a-H, 5-H system would give rise either to a pair of



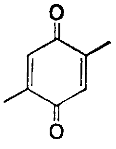
a; R = p-MeO·C$_6$H$_4$ b; R = Ph c; R = p-NO$_2$·C$_6$H$_4$

Yields and n.m.r. data (τ values) for Diels–Alder adducts



Adduct	Yield (%)	X	A	B	C	6,7-Me$_2$	Aryl protons	X = OMe	5-H	8-H$_a$	8-H$_a$	D
A = B = D = H	76	H	3·92 ^{a}	4·12 ^{a}	6·20	8·22 8·47	3 ^{g}		5·80	6·90 ^{b}	8·0 ^{c}	6·35 ^{d}
C = CO$_2$Me	75	OMe	3·83 ^{a}	4·30 ^{a}	6·21	8·24 8·48	3·31	6·28	5·84	6·90 ^{b}	7·98 ^{c}	6·32 ^{d}
	77	NO$_2$	3·77 ^{a}	3·98 ^{a}	6·36	8·19 8·48	1·9, 2·65 2·9, 3·02		5·68	6·87 ^{b}	8·0 ^{c}	6·22 ^{d}
A = D = H	85	H	4·08 ^{e}	8·50 ^{e}	8·50	8·18 8·50	3 ^{g}		6·83	6·82 ^{b}	7·91 ^{c}	7·32 ^{d}
B = C = Me	65	OMe	3·99 ^{e}	8·48 ^{e}	8·50	8·2 8·5	3·32	6·28	6·89	6·80 ^{b}	7·95 ^{c}	7·31 ^{d}
	67	NO$_2$	4·04 ^{e}	8·60 ^{e}	8·44	8·16 8·53	1·9, 2·04 2·92, 3·07		6·74	6·81 ^{b}	7·88 ^{c}	7·20 ^{d}
A = H, B = OMe	59	H	4·97	6·78	8·49	8·14 8·49	3 ^{g}		6·70	6·54 ^{d}	7·69 ^{d}	6·39
C = Me, D = CO$_2$Me	67	OMe	4·88	6·72	8·51	8·15 8·51	3·3	6·27	6·72	6·55 ^{d}	7·70 ^{d}	6·38
	53	NO$_2$	4·93	6·75	8·46	8·11	1.94, 2·01 2·92, 3·07		6·62	6·50 ^{d}	7·68 ^{d}	6·35
A = D = H	64	H	4·82	6·74	8·46	8·18 8·46	3 ^{g}		6·78	6·78 ^{b}	7·95 ^{c}	7·35 ^{d}
B = OMe, C = Me	80	OMe	4·7	6·70	8·48	8·19 8·48	3·30	6·28	6·85	6·82 ^{b}	7·90 ^{c}	7·35 ^{d}
A = D = Me B = H, C = CN	56	H	8·53 ^{e}	4·10 ^{e}		8·14 8·47	3·0		6·06	6·75 ^{f}	7·93 ^{f}	8·60
A = C = Me B = D = H	68	H	8·54 ^{e}	4·16 ^{e}	8·53	8·17 8·53	3 ^{g}		6·87	6·81 ^{b}	7·90 ^{b}	7·36 ^{d}

[a] d, |J| 10 Hz. [b] d, |J| 18 Hz. [c] dd, |J| 8 and 18 Hz. [d] d, |J| 18 Hz. [e] Appears as d, |J| 1·5 Hz. [f] d, |J| 20 Hz. [g] Complex



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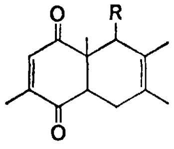

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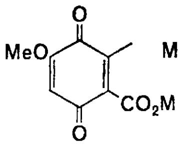

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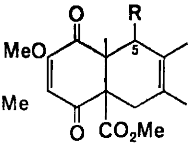

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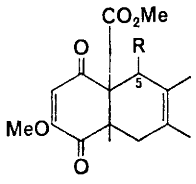

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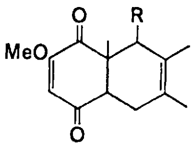

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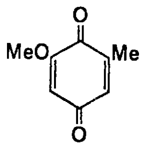

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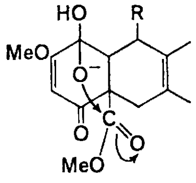

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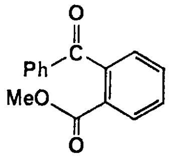

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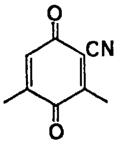
a; R = *p*-MeO·C_6H_4 b; R = Ph c; R = *p*-NO_2·C_6H_4



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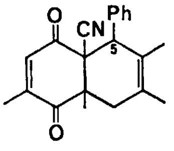

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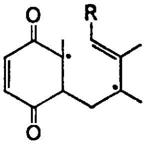

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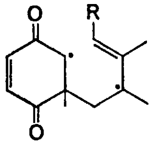

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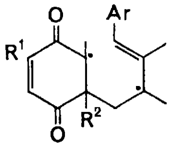

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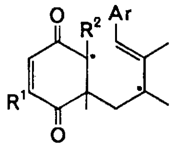

(24)

a; R^1 = MeO, R^2 = CO_2Me b; R^1 = Me, R^2 = CN

doublets or to a two-proton singlet, if the protons had the same chemical shift, or to two singlets, if they had different chemical shifts, and the dihedral angle between them was 90°. Similarly the 8-H_2 system would give rise either to an AB quartet or to a two-proton singlet. Only structure (6) can give rise to a spectrum containing a lone one-proton singlet.

The n.m.r. spectrum of each of the adducts isolated contained a lone one-proton singlet (due to the 5-proton) and therefore the major adducts from the reactions between the quinone (1) and the dienes (2a—c) had the structures (6a—c), respectively. Also in each spectrum the signals due to the 8-H_2, 8a-H system could be interpreted as an AMX system; $J_{8,8a}$ 0 and 8 Hz; $J_{8,8}$ 18 Hz, leading to two doublets and a quartet.

The major adducts isolated from the reactions between the three dienes (2a—c) and 2,6-dimethylbenzoquinone (7) could have either structures (8) or structures (9). It was possible to assign structures (9a—c), respectively, to these adducts on the basis of their n.m.r. spectra. Each exhibited a lone one-proton singlet (5-proton) and an AMX system (8-H_2, 8a-H). The latter system was similar to that observed for the adducts of structure (6), the protons having slightly different chemical shifts, but the same coupling constants.

2,5-Dimethyl-*p*-benzoquinone (10) and the diene (2b) also lead to an adduct (11) with an angular 4a-methyl group.

The Diels–Alder reactions between the dienes (2a—c) and the quinone (12) proceeded slowly; long reaction times (90 hr.) were necessary to obtain good yields. In each reaction a pure adduct was isolated (>50% yield) by crystallisation, and the presence of more of the adduct in the mother liquors was inferred by t.l.c. examination. The n.m.r. spectrum of each adduct showed the presence of one vinyl proton; therefore addition of the diene had occurred at the disubstituted ethylene linkage of the quinone, but the spectra did not unequivocally differentiate between the structures (13) and (14). However, the chemical shifts of the 5-protons (τ 6·62—6·7) favour structures (13) (4a-methyl) rather than structures (14) (4a-methoxycarbonyl), since in the adducts (9), which have a 4a-methyl group, the chemical shift of the 5-proton is in the range τ 6·74—6·83, whereas in adducts (6), in which the 4a-substituent is methoxycarbonyl, the 5-protons resonate between τ 5·68 and τ 5·80. That this inference was correct was shown by hydrolysis and decarboxylation of the adducts (13a and b) to compounds (15a and b). The structures of the latter compounds were established spectroscopically (see Table) and by their syntheses from the appropriate dienes and 2-methoxy-6-methyl-*p*-benzoquinone (16). The adducts (13a and b) were hydrolysed by treatment with cold dilute alkali. This ready hydrolysis of the ester of a tertiary acid may be due to the initial attack by hydroxide ion on the carbonyl group at C-1 [see (17)]. A similar mechanism has been proposed[3] for the hydrolysis of methyl *o*-benzoylbenzoate (18), in which the ester group and the carbonyl group are in the same relative positions.

The addition of 2-cyano-3,5-dimethyl-*p*-benzoquinonone (19) to the diene (2b) gave an adduct (isolated in 63% yield) whose n.m.r. spectrum showed that the addition had occurred at the disubstituted ethylene linkage of the quinone. The 5-proton signal appeared as a singlet at τ 6·06, which is not in the region (τ 6·62—6·89) expected for a 5-proton adjacent to a 4a-methyl group

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[3] K. Bowden and G. R. Taylor, *Chem. Comm.*, 1967, 1112.

but is close to the value expected (τ 5·68—5·80) for a 5-proton adjacent to a 4a-ester group. We therefore consider that the adduct has the structure (20). Attempts to remove the angular cyano-group by hydrolysis were unsuccessful.

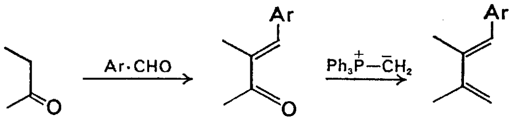
Discussion.—The results show that in the addition of a 1-substituted diene to a *p*-benzoquinone leading to the formation of a major product containing one angular substituent, the relative orientation of the quinone and diene substituents in the product is not affected by the electronic nature of the substituent on the diene or on the quinone. The angular substituent and the diene substituent are *ortho* to each other with respect to the new ring formed in the reaction. This is consistent with previous results [2] and parallels the results obtained [2,4] with acyclic dienophiles. The results may be rationalised on the basis of the suggestion by Georgian [5] that 'the gross structural character of the adduct will be determined by an association of the addends in the transition state (of possibly a spin-paired nature) generating greatest electron delocalisation.' Although the Diels–Alder reaction is essentially a one-step pericyclic reaction, and although both new σ bonds begin to form at the same time, they will not both be equally pronounced in the transition state. If the bond formation is faster at one centre than at the other the transition state will have some diradical or zwitterion character. Since the structures of the product isomers are essentially independent of the electronic nature of the substituents, the transition state must have diradical rather than zwitterion character.[2a] On this basis the transition state involving a contribution from the structure (21), in which electron delocalisation embraces a tertiary centre on the quinonoid ring, would be preferred to that to which structure (22), involving delocalisation over a secondary centre on the quinonoid ring, contributes.

In the reaction of the trisubstituted quinone (12) the structure of the product was again independent of the nature of the substituent on the diene and was the '*ortho*-methyl' isomer (13). On the basis of the preceding discussion this is unexpected, as it implies that the transition state involving the contributing structure (23a) is more stable than that involving structure (24a). This requires a radical centre to be more stabilised by the hyperconjugative effect of a methyl group than by delocalisation on to a carbonyl oxygen. However, in the quinone (12) the methyl and methoxycarboxyl groups are *cis* to each other and steric hindrance between these groups might be expected to cause rotation of the ester group about the single bond linking it to the ring, so that the ester carbonyl group is displaced from the plane of the quinone ring, and no longer fully conjugated. The lower frequency (1745 cm.$^{-1}$) of the i.r. absorption of the ester carbonyl group in the quinone (12) compared with that (1752 cm.$^{-1}$) of the ester carbonyl group in the methoxycarbonylquinone (1) is consistent with partial steric inhibition of conjugation in structure (12). For the reactions of quinone (12) a similar steric effect would be expected in the transition state, and if this reduced the conjugative stabilisation due to the ester group in structure (24a) to less than the hyperconjugative stabilisation due to the methyl group in structure (23a), the latter would be preferred and the reaction would lead to the observed product (13). Steric inhibition of conjugation has been previously invoked to rationalise [6] the variation in dissociation constant among the *o*-alkylbenzoic acids, and to explain [7] the increased rate of esterification by diazodiphenylmethane of *o*-methylbenzoic acid as compared with benzoic acid.

In the reaction between the cyano-quinone (19) and the diene (2b), owing to the linear nature of the cyano-group, steric inhibition of conjugation, analogous to that just described, cannot occur, and thus the transition state to which structure (24b) contributes is favoured over that involving (23b); hence the adduct (20) is obtained.

The observation that 2,5-dimethyl-, 2,6-dimethyl-, and 2-methoxy-6-methyl-*p*-benzoquinone all react with the aryl-substituted dienes to yield products in which the angular methyl group and the aryl group are *ortho*, indicates that the substituents on the non-reacting ethylene linkage of the quinone do not have any effect on the structural specificity of these reactions.

Preparation of Precursors.—Of the dienes (2a—c) referred to, only the preparation of (2b) has been previously reported [8] (without experimental details): the synthesis involved treatment of methyl α-methylcinnamate with excess of methylmagnesium iodide followed by dehydration of the resulting tertiary alcohol. This method was used for the preparation of the 1-phenyl- and 1-*p*-methoxyphenyl-dienes but could not be utilised for the 1-*p*-nitrophenyl-diene. The route illustrated in Scheme 2 was used to synthesise all three dienes. The structures of the intermediate butenones (25) were established by n.m.r. spectroscopy; they are considered to have *trans*-structures, since the final dienes readily underwent the Diels–Alder reaction. Although good yields were obtained of the gas-chromatographically homogeneous dienes (2b) and (2c) the nitro-diene (2a) was only obtained in 2% yield. The interference of nitro-groups in the Wittig reaction has been previously recorded,[9] although Wittig reported [10] that *p*-nitro-



SCHEME 2

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[4] M. F. Ansell and A. H. Clements, following paper.

[5] V. Georgian and J. Lepe, *J. Org. Chem.*, 1964, **9**, 40.

[6] J. F. L. Dippy, S. R. C. Hughes, and J. W. Laxton, *J. Chem. Soc.*, 1954, 1470.

[7] N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1962, 1824.

[8] E. P. Kohler, *Amer. Chem. J.*, 1906, **36**, 538.

[9] S. Trippett, *Quart. Rev.*, 1963, **17**, 406.

[10] G. Wittig and U. Schollkopf, *Chem. Ber.*, 1954, **87**, 1318.

benzophenone reacted satisfactorily with methylenetriphenylphosphine. 1-*p*-Nitrophenylbutadiene is formed[11] by the addition of *p*-nitrobenzenediazonium chloride to buta-1,3-diene (overall addition of $O_2N{\cdot}C_4H_4Cl$) followed by dehydrohalogenation of the chloro-intermediate. By a similar procedure we have prepared 2,3-dimethyl-1-*p*-nitrophenylbuta-1,3-diene (2a) from 2,3-dimethylbutadiene in low yield.

EXPERIMENTAL

G.l.c. analyses were carried out on a Pye Argon chromatograph: column A, 30% silicone oil on brickdust; column B 10% Apiezon on brickdust; column C, 10% Reoplex on Celite.

N.m.r. spectra were determined for solutions in deuteriochloroform with a Varian A60 spectrometer.

p-*Substituted* 2,3-*Dimethyl*-1-*phenylbuta*-1,3-*dienes*.—(a) *By Wittig reaction*. An ethereal solution (34 ml.) of *n*-butyllithium (0·5 mol.) was added to a stirred suspension of methyltriphenylphosphonium bromide (17·4 g.); after 2·5 hr. a solution of the appropriate 3-methyl-4-(*p*-substituted phenyl)but-3-en-2-one (0·05 mol) in benzene (100 ml.) was added during 30 min. The stirred mixture was heated under reflux for 4 hr., then left to cool overnight, poured into water (*ca*. 400 ml.), and extracted with ether. The dried ($MgSO_4$) extract was distilled.

By this method 3-methyl-4-phenylbut-3-en-2-one[12] [τ 7·94 (d, |*J*| 1·5 Hz, 3-Me), 7·54 (2-Me), 2·65 (4-Ph), and 2·50 (' d ', |*J*| 1·5, 4-H)] gave 2,3-dimethyl-1-phenylbuta-1,3-diene (63%), b.p. 73—81°/0·5 mm., $\lambda_{\text{max.}}$ 213 (ε 9300) and 267 nm. (ε 15,000), which showed only one peak on g.l.c. (columns A and B) (lit.,[8] b.p. 165°/35 mm.); 4-*p*-methoxyphenyl-3-methylbut-3-en-2-one[13] [τ 7·95 (d |*J*| 1·5 Hz, 3-Me), 7·57 (s, 2-Me), 6·17 (s, *p*-OMe), and 2·54—3·16 (m, 4-Ph)] gave 1-p-*methoxyphenyl*-2,3-*dimethylbuta*-1,3-*diene* (47%), b.p. 100—104°/0·5 mm. (Found: C, 82·9; H, 8·4. $C_{13}H_{16}O$ requires C, 82·9; H, 8·6%), $\lambda_{\text{max.}}$ 219 (ε 13,000) and 280 nm. (ε 25,400): 3-methyl-4-*p*-nitrophenylbut-3-en-2-one[14] [τ 7·90 (d |*J*| 1·5 Hz, 3-Me) 7·45 (s, 2-Me), and 2·35 (' d ' |*J*| 1·5 Hz, 4-H)] gave 2,3-*dimethyl*-1-*p*-*nitrophenylbuta*-1,3-*diene* (2%), m.p. 59—60° (yellow needles from methanol) $\lambda_{\text{max.}}$ 234 (ε 12,300) and 329 nm. (ε 12,800) (Found: C, 70·8; H, 6·5; N, 7·0. $C_{12}H_{13}NO_2$ requires C, 70·9; H, 6·45; N, 6·9%).

(b) *By Grignard reaction*. A solution of the *p*-substituted methyl α-methylcinnamate (0·25 mol.) in ether (100 ml.) was added slowly to a stirred solution of methylmagnesium iodide (0·5 mol.) in ether (100 ml.). The mixture was boiled for 2 hr., cooled, and poured on ice, and sulphuric acid was added (temperature kept below 5° by addition of ice) until two clear phases were obtained. The ethereal layer was separated and the aqueous layer extracted with ether (2 × 150 ml.). The combined extracts were washed with 10% aqueous sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. Quinol (0·5 g.) was added to the residue, which was rapidly distilled (b.p. 108—112°/20 mm.) under nitrogen. The distillate, containing some water, was extracted with ether. The dried ($MgSO_4$) extract was evaporated and the residue was distilled (under nitrogen from quinol). In this way methyl α-methylcinnamate[15] gave 2,3-dimethyl-1-phenylbuta-1,3-diene (50%), b.p. 74—80°/0·7 mm., which g.l.c. (column A at 150°) showed was 93% pure. *Methyl* p-*methoxy*-α-*methylcinnamate* [prepared by Fischer esterification of the corresponding acid,[16] m.p. 42—43° (from aqueous ethanol) (Found: C, 69·6; H, 6·85. $C_{12}H_{14}O_3$ requires C, 69·8; H, 6·85%)] similarly gave 1-*p*-methoxyphenyl-2,3-dimethylbuta-1,3-diene (47%), b.p. 100—104°/0·5 mm., gas chromatographically homogeneous (columns A and C at 150°).

(c) *By radical addition to* 2,3-*dimethylbutadiene*. A stirred mixture of *p*-nitroaniline (69 g.), concentrated hydrochloric acid (120 ml.), and water (50 ml.) was heated at 100° for 15 min. and then cooled rapidly to 0° to precipitate the hydrochloride in finely divided form. Sodium nitrite (35 g.) in water (100 ml.) was added dropwise during 1 hr., the temperature being maintained between −5 and +5°. After being stirred for a further 20 min. the cold solution was filtered and added during 90 min. to a vigorously stirred mixture of acetone (500 ml.), sodium acetate trihydrate (40 g.), copper(II) chloride (15 g.), and 2,3-dimethylbutadiene (100 ml.) maintained between −3 and +2°. Stirring (without cooling) was continued for 16 hr., then ether (500 ml.) was added. The ether layer was removed, washed with water (4 × 500 ml.), dried ($MgSO_4$), and evaporated. Charcoal (2·5 g.) was added to a solution of the residue in petroleum (b.p. 60—80°; 250 ml.) and benzene (250 ml.). The mixture was refluxed for 2 hr., filtered, and evaporated under (reduced pressure). To a stirred solution of this crude material in methanol (200 ml.) was added slowly a solution of potassium hydroxide (56 g.) in methanol (300 ml.); the resulting mixture was boiled for 15 min., cooled, poured into water (600 ml.), and extracted with ether. The extract was washed with water (2 × 500 ml.), dried ($MgSO_4$), and evaporated to leave a black oil (*ca*. 60 g.). This oil (in 15 g. portions), dissolved in ether (50 ml.), was passed through a column of alumina (30 × 2·5 cm.) and eluted with ether (200 ml.). Evaporation of the eluant left a yellow oil, which was dissolved in ether (25 ml.), chromatographed on a column of alumina (30 × 2·5 cm.), and eluted with petroleum (b.p. <40°; 250 ml.). Evaporation of the eluant left a yellow semi-solid which gave 2,3-dimethyl 1-*p*-nitrophenylbuta-1,3-diene (total yield 4·3 g.), m.p. 60—61° (from methanol) identical with the material prepared by the Wittig reaction.

Reactions of Methoxycarbonyl-p-*benzoquinone*.[17]—(a) *With* 2,3-*dimethyl*-1-*phenylbuta*-1,3-*diene*. A solution of the diene (5·0 g.) and the quinone (5·0 g.) in benzene (40 ml.) was left overnight. Evaporation then gave a semi-solid which yielded pale yellow crystals of 4a,5,8,8a-*tetrahydro*-4a-*methoxycarbonyl*-6,7-*dimethyl*-5-*phenyl*-1,4-*naphthoquinone* (7·4 g., 76%), m.p. 115—125° (from ethanol), raised to 120—125° on further recrystallisation from methanol and carbon tetrachloride (Found: C, 74·0; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·0; H, 6·2), $\nu_{\text{max.}}$ 1750 (ester C=O), and 1690 and 1675 cm.$^{-1}$ (conj. C=O), $\lambda_{\text{max.}}$ 227 nm. (ε 19,000). This material decomposed on thin-layer plates of alumina, silica gel kieselguhr, or Microcel C.

(b) *With* 1-p-*methoxyphenyl*-2,3-*dimethylbuta*-1,3-*diene*. The diene (6·1 g.) was added to a solution of the quinone (5 g.) in methanol (15 ml.). The solution became red, the

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methanol boiled spontaneously, and a solid was precipitated. When the mixture had cooled to room temperature the light yellow precipitate (8·7 g.) was filtered off; it yielded 4a,5,8,8a-*tetrahydro*-4a-*methoxycarbonyl*-5-p-*methoxyphenyl*-6,7-*dimethyl*-1,4-*naphthoquinone* (8·0 g., 75%), m.p. 140—145° (from methanol) (Found: C, 71·7; H, 6·3. $C_{21}H_{22}O_5$ requires C, 71·2; H, 6·3%), $\nu_{max.}$ 1735 (ester C=O), 1690 and 1680 (conj. C=O), and 1610 cm.$^{-1}$ (conj. C=C), $\lambda_{max.}$ 228 (ε 24,000) and 268 nm. (ε 3500). This adduct was unchanged after chromatography on alumina or Microcel C.

The filtrate from the foregoing recrystallisation deposited an isomeric adduct (110 mg.), m.p. 198—199° (from methanol) (Found: C, 71·5; H, 6·2. $C_{21}H_{22}O_5$ requires C, 71·2; H, 6·3%), $\nu_{max.}$ 1735 (ester C=O), 1695 and 1685 (conj. C=O), and 1610 cm.$^{-1}$ (conj. C=C), $\lambda_{max.}$ 227 (ε 21,000) and 275 nm. (ε 6600). Similar results were obtained when the reaction was carried out in benzene solution.

(c) *With* 2,3-*dimethyl*-1-p-*nitrophenylbuta*-1,3-*diene*. A solution of the quinone (0·33 g.) in benzene (2 ml.) was added to a solution of the diene (0·51 g.) in benzene (3 ml.) and the mixture was left overnight. The deposited crystals (0·65 g.; m.p. 196—207°) were filtered off and the mother liquors were concentrated to *ca.* 3 ml. to give a further crop (0·04 g.) of crystals. Recrystallisation of the combined material from benzene gave 4a,5,8,8a-*tetrahydro*-4a-*methoxycarbonyl*-6,7-*dimethyl*-5-p-*nitrophenyl*-1,4-*naphthoquinone* (0·56 g., 77%) as pale yellow chunky crystals, m.p. 226—227° (Found: C, 65·2; H, 5·25; N, 4·0. $C_{20}H_{19}NO_6$ requires C, 65·05; H, 5·2; N, 3·8%), $\nu_{max.}$ 1735 (ester C=O), 1690 and 1685 (conj. C=O), and 1520 and 1350 cm.$^{-1}$ (NO_2), $\lambda_{max.}$ 216 (ε 15,000) and 268 nm. (ε 9400).

Reactions of 2,6-*Dimethyl*-p-*benzoquinone*.[18]—(a) *With* 2,3-*dimethyl*-1-*phenylbuta*-1,3-*diene*. A solution of the diene (1·2 g.), a few crystals of quinol, and the quinone (0·9 g.) in methanol (3 ml.) was boiled for 4 hr. The cooled mixture deposited pale yellow crystals which were filtered off, washed with methanol, and dried to give 4a,5,8,8a-*tetrahydro*-3,4a,6,7-*tetramethyl*-5-*phenyl*-1,4-*napthoquinone* (1·65 g., 85%), m.p. 146—148° (from methanol) (Found: C, 81·65; H, 7·55. $C_{20}H_{22}O_2$ requires C, 81·7; H, 7·5%), $\nu_{max.}$ 1675 (conj. C=O) and 1635 cm.$^{-1}$ (conj. C=C), $\lambda_{max.}$ 242 nm. (ε 8000).

(b) *With* 1-p-*methoxyphenyl*-2,3-*dimethylbuta*-1,3-*diene*. A solution of the diene (0·65 g.), a few crystals of quinol, and the quinone (0·45 g.) in benzene (2·5 ml.) was boiled for 4 hr., and then evaporated. The residual yellow oil was dissolved in hot petroleum (b.p. 60—80°). The cool solution deposited 4a,5,8,8a-*tetrahydro*-5-p-*methoxyphenyl*-3,4a,6,7-*tetramethyl*-1,4-*naphthoquinone* (0·7 g., 65%) as hexagonal plates, m.p. 106—107° (from petroleum) (Found: C, 77·8; H, 7·5. $C_{21}H_{24}O_3$ requires C, 77·8; H, 7·4%), $\nu_{max.}$ 1670 (conj. C=O) and 1620 cm.$^{-1}$ (conj. C=C), $\lambda_{max.}$ 230 nm. (ε 3200).

(c) *With* 2,3-*dimethyl*-1-p-*nitrophenylbuta*-1,3-*diene*. A solution of the diene (0·5 g.) and the quinone (0·33 g.) in benzene (2 ml.) was boiled for 5 hr. and then evaporated. The residual solid gave 4a,5,8,8a-*tetrahydro*-3,4a,6,7-*tetramethyl*-5-p-*nitrophenyl*-1,4-*naphthoquinone* (0·55 g., 67%), m.p. 185—186° (from methanol) (Found: C, 71·0; H, 6·3; N, 4·2. $C_{20}H_{21}NO_4$ requires C, 70·8; H, 6·2; N, 4·1%), $\nu_{max.}$ 1670 (conj. C=O), 1625 (conj. C=C), and 1530 and 1355 cm.$^{-1}$ (NO_2), $\lambda_{max.}$ 244 (ε 14,000) and 275 nm. (ε 12,400).

Reactions of 5-*Methoxy*-2-*methoxycarbonyl*-3-*methyl*-p-*benzoquinone*.[19]—(a) *With* 2,3-*dimethyl*-1-*phenylbuta*-1,3-*diene*. A solution of the diene (4·5 g.) and the quinone (5 g.) in benzene (25 ml.) was heated under reflux for 90 hr. and then evaporated. The residual yellow oil was extracted with hot methanol; the extract was filtered and then left to cool. Off-white crystals deposited were filtered off, washed with methanol, and dried to give 4a,5,8,8a-*tetrahydro*-3-*methoxy*-8a-*methoxycarbonyl*-4a,6,7-*trimethyl*-5-*phenyl*-1,4-*naphthoquinone* (5·2 g., 59%), m.p. 130—132° (from methanol) (Found: C, 72·7; H, 6·6. $C_{22}H_{24}O_5$ requires C, 71·7; H, 6·6%), $\nu_{max.}$ 1730 (ester C=O), and 1705 and 1670 cm.$^{-1}$ (conj. C=O), $\lambda_{max.}$ 272 nm. (ε 6400).

Evaporation of the filtrate from the first crystallisation left an oil which on t.l.c. examination showed the presence of the starting quinone and three other components, one of which had the same R_F value as the isolated adduct.

Sodium hydroxide solution (10%; 20 ml.) was added to a solution of the foregoing adduct (0·5 g.) in methanol (30 ml.). The wine-red solution was left for 2 min. and then made acid (Congo Red) with 5N-hydrochloric acid. The resulting pale yellow solution was immediately diluted with water (50 ml.) and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated to yield an oil which partially solidified and was recrystallised twice from methanol to yield 4a,5,8,8a-tetrahydro-3-methoxy-4a,6,7-trimethyl-5-phenyl-1,4-naphthoquinone (0·170 g., 41%), m.p. and mixed m.p. 140—142°, identical with the material prepared from 2-methoxy-6-methyl-*p*-benzoquinone (see later).

(b) *With* 1-p-*methoxyphenyl*-2,3-*dimethylbuta*-1,3-*diene*. A solution of the diene (1 g.) and the quinone (1 g.) in benzene (2·5 ml.) was boiled for 90 hr. and then evaporated. The residual oil, which solidified when triturated with a little methanol, was crystallised from methanol to give 4a,5,8,8a-*tetrahydro*-3-*methoxy*-8a-*methoxycarbonyl*-5-p-*methoxyphenyl*-4a,6,7-*trimethyl*-1,4-*naphthoquinone* (0·65 g., 67%), m.p. 134—142°. Examination of this material on t.l.c. showed the presence of only one component, whereas the filtrate from the recrystallisation contained two components (other than starting material) one of which had the same R_F value as the isolated adduct. A sample of the adduct twice recrystallised from methanol had m.p. 142—145° (Found: C, 70·0; H, 6·4. $C_{24}H_{26}O_6$ requires C, 70·2; H, 6·4%), $\nu_{max.}$ 1735 (ester C=O), and 1705 and 1655 cm.$^{-1}$ (conj. C=O), $\lambda_{max.}$ 228 (ε 17,000) and 276 nm. (ε 8900).

Hydrolysis of this adduct (0·5 g.) as for the preceding adduct gave 4a,5,8,8a-*tetrahydro*-3-methoxy-5-*p*-methoxyphenyl-4a,6,7-trimethyl-1,4-naphthoquinone (0·160 g., 38%), m.p. and mixed m.p. 108—109° (from methanol), identical with the compound prepared from 2-methoxy-6-methyl-*p*-benzoquinone (see later).

(c) *With* 2,3-*dimethyl*-1-p-*nitrophenylbuta*-1,3-*diene*. A solution of the diene (0·4 g.) and the quinone (0·4 g.) in benzene (2·5 ml.) was boiled for 90 hr. and then evaporated. The residual oil was dissolved in hot benzene–petroleum (b.p. 60—80°) (2 : 1) and the cool solution deposited yellow crystals which gave 4a,5,8,8a-*tetrahydro*-3-*methoxy*-4a-*methoxycarbonyl*-4a,6,7-*trimethyl*-5-p-*nitrophenyl*-1,4-*naphthoquinone* (0·42 g., 53%), m.p. 189—190° [from benzene–petroleum (b.p. 60—80°) (1 : 2)] (Found: C, 63·7; H, 5·6; N, 3·2. $C_{22}H_{22}NO_7$ requires C, 63·9; H, 5·35; N, 3·4%), $\nu_{max.}$ 1710 (ester C=O), and 1695 and 1660 cm.$^{-1}$ (conj. C=O), $\lambda_{max.}$ 285 nm. (ε 14,000).

Reactions of 2-*Methoxy*-6-*methyl*-p-*benzoquinone*.[20]—(a)

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With 2,3-*dimethyl*-1-*phenylbuta*-1,3-*diene*. A solution of the diene (0·6 g.) and the quinone (0·5 g.) in benzene (10 ml.) was boiled for 8 hr., then evaporated, and the residual oil was dissolved in the minimum amount of hot methanol. The cold solution deposited 4a,5,8,8a-*tetrahydro*-3-*methoxy*-4a,6,7-*trimethyl*-5-*phenyl*-1,4-*naphthoquinone* (0·65 g., 64%), m.p. 142—143° (not raised on recrystallisation) (Found: C, 77·4; H, 7·1. $C_{20}H_{22}O_3$ requires C, 77·4; H, 7·1%), $\nu_{max.}$ 1660 and 1685 cm.$^{-1}$ (conj. C=O), $\lambda_{max.}$ 265 nm. (ε 7100).

(b) *With* 1-p-*methoxyphenyl*-2,3-*dimethylbuta*-1,3-*diene*. A solution of the diene (0·7 g.) and the quinone (0·5 g.) in benzene (10 ml.) was boiled for 13 hr. Evaporation left a semi-solid which was crystallised from methanol and then petroleum (b.p. 60—80°) to give 4a,5,8,8a-*tetrahydro*-3-*methoxy*-5-p-*methoxyphenyl*-4a,6,7-*trimethyl*-1,4-*naphthoquinone* (0·9 g., 80%), m.p. 109—109·5° (Found: C, 74·0; H, 7·2. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·1%), $\nu_{max.}$ 1695 and 1660 cm.$^{-1}$ (conj. C=O), $\lambda_{max.}$ 228 (ε 24,000) and 273 nm. (ε 9000).

Reaction of 2-*Cyano*-3,5-*dimethylbenzoquinone* [21] *with* 2,3-*Dimethyl*-1-*phenylbuta*-1,3-*diene*.—A solution of the quinone (2 g.) and the diene (2 g.) in benzene (30 ml.) was left overnight, then boiled for 5 hr. and evaporated. The residual semi-solid gave 4a-*cyano*-4a,5,8,8a-*tetrahydro*-2,6,7,8a-*tetramethyl*-5-*phenyl*-1,4-*naphthoquinone* (2·2 g., 56%) as prisms, m.p. 165—167° (from methanol) (Found: C, 79·1; H, 6·8; N, 4·5. $C_{21}H_{21}NO_2$ requires C, 79·0; H, 6·6; N, 4·4%), $\nu_{max.}$ 1675 (conj. C=O) and 2250vw cm.$^{-1}$ (CN), $\lambda_{max.}$ 211 (ε 10,000), 243 (8860), and 282 nm. (1100). Examination of this adduct by t.l.c. showed only one component: the filtrate from the initial crystallisation contained two compounds (other than starting material) one of which had the same R_F value as the adduct.

The action of alkali on the adduct gave no identifiable product.

Reaction of 2,3-*Dimethyl*-1-*phenylbuta*-1,3-*diene with* 2,5-*Dimethyl*-p-*benzoquinone*.[22]—A solution of the diene (5·8 g.) and the quinone (5 g.) in methanol (15 ml.) was boiled for 15 hr. The cool solution deposited crystals which were filtered off, washed with methanol, and dried to give 4a,5,8,8a-*tetrahydro*-2,4a,6,7-*tetramethyl*-5-*phenyl*-1,4-*naphthoquinone* (7·3 g., 68%), m.p. 142—143° (from methanol) (Found: C, 81·2; H, 7·4. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%), $\nu_{max.}$ 1670 and 1685 (conj. C=C), and 1635 cm.$^{-1}$ (conj. C=C), $\lambda_{max.}$ 242 nm. (ε 8200).

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