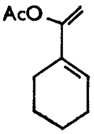
558. *Reduced Cyclic Compounds. Part XIII.* The Reaction of* 1-1′-*Acetoxyvinylcyclohexene with* p-*Benzoquinones containing a Methoxycarbonyl Group.*†

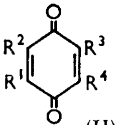
By M. F. Ansell and G. C. Culling.

The Diels–Alder reactions of 1-1′-acetoxyvinylcyclohexene with methoxycarbonyl- and 2,5-dimethoxycarbonyl-benzoquinone and 6-methoxycarbonyl- and 6-methoxy-3-methoxycarbonyl-tolu-1,4-quinone are reported. In each case the product contained an angular methoxycarbonyl group. Some comments are made on the Diels–Alder reactions of substituted *p*-benzoquinones. An attempted preparation of the 2,5-dimethoxycarbonylquinone is described.

An unsymmetrically substituted *p*-benzoquinone may undergo the Diels–Alder reaction, preferentially or exclusively, at either of the double bonds, the nature of the substituents being the determining factor. For the addition of buta-1,3-diene to such quinones Orchin and Butz[1] formulated the following hypothesis: " Butadiene reacts faster with carbon atoms attached to hydrogen than to others (steric effect) and of these as an anionoid reagent it reacts fastest with the most cationoid carbon in the quinone (electrostatic effect)." As these authors point out, this hypothesis satisfactorily explains the addition of butadiene to the methoxycarbonyl-ethene linkage of the quinone (IIa), but does not explain the addition at the methyl-ethene linkage of the quinone (IIb) unless it is assumed that the steric effect of a methoxy-group is greater than that of a methyl group. However, we considered that the order of dienophilic activity observed with these quinones, namely, methoxycarbonyl-ethene > methyl-ethene > methoxy-ethene is explicable if the dienophilic activity of the ethene linkage depends on whether its electron-density is greater or less than that of the ethene linkage in benzoquinone. Thus the lower the electron-density the greater the reactivity of the ethene linkage. The Diels–Alder reactions of monosubstituted benzoquinones in which the substituent is electron-donating, have been shown to occur at the unsubstituted ethene linkage, in accord with the views of Orchin and Butz and of ourselves. However, if the substituent is an electron-attracting group such as confers dienophilic properties on an olefin, we consider that, in contrast to the first part of Orchin and Butz's hypothesis, the reaction should occur at the substituted ethene linkage. The Diels–Alder reactions of such quinones have never been investigated.



(I)



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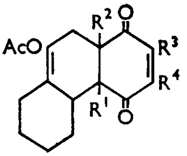

(III)

a: $R^1 = CO_2Me$, $R^2 = R^3 = H$, $R^4 = Me$.
b: $R^1 = H$, $R^2 = Me$, $R^3 = OMe$, $R^4 = H$.
c: $R^1 = CO_2Me$, $R^2 = R^3 = R^4 = H$.
d: $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$, $R^4 = H$.
e: $R^1 = Me$, $R^2 = CO_2Me$, $R^3 = H$, $R^4 = OMe$.

f: $R^1 = CO_2Me$, $R^2 = R^3 = H$, $R^4 = Me$.
g: $R^1 = CO_2Me$, $R^2 = R^3 = Me$, $R^4 = H$.
h: $R^1 = CO_2Me$, $R^2 = H$, $R^3 = CO_2Me$, $R^4 = H$.
i: $R^1 = R^2 = R^3 = R^4 = H$.

We now report, as a continuation of another investigation,[2] the Diels–Alder reaction of 1-1′-acetoxyvinylcyclohexene (I) with methoxycarbonylbenzoquinone (IIc), 6-methoxy-3-methoxycarbonyl-1,4-toluquinone (IId), and 6-methoxycarbonyl-1,4-toluquinone (IIf), to

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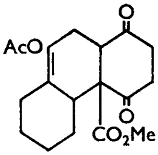
* Part XII, preceding paper. † For a preliminary communication see ref. 3.

[1] Orchin and Butz, *J. Org. Chem.*, 1943, **8**, 509.

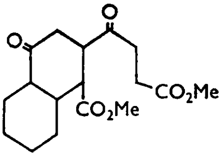
[2] (*a*) Ansell and Brooks, *J.*, 1956, 4518; (*b*) Ansell and Knights, preceding paper.

form the adducts (IIIc), (IIId or e), and (IIIf) respectively, each containing an angular ester group. The adducts (IIIc) and (IIId or e) constitute the first two examples of addition of a diene to the more substituted ethene linkage of a benzoquinone. These results are not explicable on the hypothesis of Orchin and Butz (should this be applicable to dienes in general), but are consistent with our view that addition of the diene occurs at the more electron-deficient ethene-linkage of the quinone provided that there is no steric opposition to such a reaction. In these two examples the activation of the ethene linkage by the methoxycarbonyl group overcomes any steric factors operating against addition of the diene to the more substituted ethene linkage. That steric factors do operate in such reactions has been shown[3] by addition of the acetoxy-diene (I) to the monosubstituted ethene linkage of the quinone (IIg).

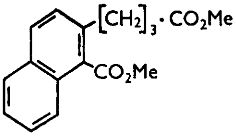
Adding methoxycarbonylbenzoquinone (IIc) to 1-1′-acetoxyvinylcyclohexene (I) caused a spontaneous exothermic reaction which formed 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-12-methoxycarbonyl-1,4-dioxophenanthrene (IIIc) in a 97% yield. That addition had occurred at the methoxycarbonyl-ethene linkage was suggested by the ultraviolet spectrum of the adduct which showed an absorption maximum at 225 mμ, identical with that of the adduct (IIIi) from *p*-benzoquinone, and was confirmed when the product was not aromatised under conditions which aromatise the simple adduct (IIIi); further, the nuclear magnetic resonance spectrum indicated the presence of two vinyl-hydrogen atoms (τ 3·215, 3·179) as well as an enol acetate (τ 7·859) and a methoxycarbonyl group (τ 6·180). Supporting evidence was reduction of the adduct by potassium borohydride to a mixture of isomeric triols which on dehydration and dehydrogenation by palladium afforded phenanthrene. If the methoxycarbonyl group had been non-angular the product could have been 2- or 3-methoxycarbonylphenanthrene. It was expected from a consideration of the polarities of the diene and dienophil, the structure of the adduct from the acetoxy-diene (I) and 6-methoxycarbonyltoluquinone (IIf) (see below), and from the structure[4] of the adduct from the same diene and methyl acrylate, that the methoxycarbonyl group would be attached to $C_{(12)}$ and not $C_{(11)}$. This was confirmed by the following degradation. The benzoquinone adduct (IIIc) was reduced with zinc and acetic acid to its dihydro-derivative (IV) (a β-keto-ester) which was treated with sodium methoxide in anhydrous methanol. The product contained both neutral and acidic material, the latter arising by alkyl–oxygen fission under these conditions.[5] The product at this stage was expected to be the compound (V) (or the derived acid) and was subjected to Clemmensen reduction followed by esterification and dehydrogenation. It was hoped to isolate the diester (VI). However,



(IV)



(V)



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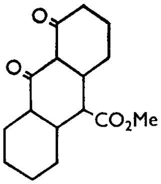

(VII)

the product was anthracene, produced by cyclisation of the keto-ester (V) to the perhydroanthracene derivative (VII), which by the subsequent procedure yielded anthracene. This unexpected result confirms our view that the ester group is attached at $C_{(12)}$ in the original adduct. The intermediate (V) could arise if the ester group was attached at position 3, but the previous evidence is against this. An adduct containing the ester group either at position 11 or 2 could not give anthracene by a rational sequence of reactions.

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[3] Ansell, Culling, Nash, Wilson, and Lown, *Proc. Chem. Soc.*, 1960, 405.

[4] Winternitz and Balmossiere, *Tetrahedron*, 1958, **2**, 100.

[5] Cf. Bunnett, Robinson, and Pennington, *J. Amer. Chem. Soc.*, 1950, **72**, 2378.

6-Methoxycarbonyltoluquinone (IIf) reacted readily with the acetoxy-diene (I) to yield 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-12-methoxycarbonyl-3-methyl-1,4-dioxophenanthrene (IIIf). The ultraviolet absorption spectrum of the latter had a maximum at 243 mμ, indicating (cf. ref. 2) the presence of a methyl-substituted ene-dione system. The adduct (IIIf) was reduced with potassium borohydride to a mixture of triols, and then dehydrogenated by palladium or selenium to 3-methylphenanthrene, thus confirming its structure.

It is known[2b] that 5- and 6-methoxytoluquinone react with the acetoxy-diene (I) at the methyl-ethene linkage. This we consider (see above) to be due to the deactivating effect of the methoxy-group. We therefore considered that 6-methoxy-3-methoxycarbonyltoluquinone (IId) would undergo the Diels–Alder reaction at the more substituted ethene linkage. The quinone (IId) was prepared by oxidation of the known[6] parent quinol, and unlike the previous methoxycarbonylquinones is stable. It (IId) reacted slowly with acetoxy-diene, only a 39% yield of adduct (IIId or e) being obtained after 60 hr. at 100°. That addition had occurred at the disubstituted ethene linkage was shown by the adduct's having a maximum at 278 mμ in its ultraviolet absorption spectrum, indicative[2b] of a methoxy-substituted ene-dione system, and from its nuclear magnetic resonance spectrum, which showed the presence of one vinyl-hydrogen atom (τ 4·101) besides the angular methyl group (τ 8·833), the enol-acetate group (τ 7·817), the methoxy-group (τ 6·3505), and the methoxycarbonyl group (τ 6·173). Decision between the possible structures (IIId) and (IIIe) is under investigation, but structure (IIIe) is considered the more probable. This is the second example of the addition of a diene to the more substituted side of a substituted *p*-benzoquinone.

At one stage in our studies we wished to ascertain the ultraviolet absorption maximum associated with the methoxycarbonyl-enedione system. Such a system would be found in the monoadduct from the acetoxy-diene (I) and a quinone such as 2,5-dimethoxycarbonylbenzoquinone (IIh). Dimethyl 2,5-dihydroxyterephthalate was prepared by dehydrogenation of dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate with bromine; the ethyl ester has been similarly prepared.[7] This quinol, like the diethyl ester, was bright yellow (many aromatic *o*-hydroxy-carbonyl compounds are coloured[8]) and exhibited a blue fluorescence in benzene solution. Its structure was confirmed by conversion into the known[9] diacetate (colourless). An attempted oxidation of this quinol with oxides of nitrogen[10] yielded dimethyl 2,5-dihydroxy-3,6-dinitroterephthalate, even at 0° in the presence of anhydrous potassium carbonate with the oxides of nitrogen dried over potassium carbonate. The structure of this product was proved by its infrared spectrum and its analysis and that of its diacetate. Oxidation of dimethyl 2,5-dihydroxyterephthalate with silver oxide gave a mixture of the unchanged quinol and the red quinhydrone, the latter being obtained even when a large excess of freshly prepared oxide was used for a long time. The infrared spectra of the quinhydrone and 2,3-dimethoxycarbonylbenzoquinone[11] both have two peaks (5·79 and 6·01 μ) in the carbonyl region. A weak peak at 3·0 μ (OH) in the spectrum of the quinhydrone is not surprising as the weak and broad absorption in this region of the parent quinol would be further broadened by the effect of hydrogen-bonding[12] and weakened by the dilution effect of the quinone portion of the quinhydrone. The assignment of the quinhydrone structure was confirmed by estimation[13] of its quinone content, and by the fact that solutions of the red quinhydrone, in ether or benzene, were yellow, as could be explained by its dissociation in solution. However, when the material was warmed with methanol it was reduced to the yellow

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[6] Aghoramurithy and Seshadri, *Proc. Indian Acad. Sci.*, 1952, 327.
[7] Herrmann, *Annalen*, 1882, **211**, 327.
[8] Smith and Thomson, *J.*, 1960, 346.
[9] Bernatek and Thorensen, *Acta Chem. Scand.*, 1955, **9**, 743.
[10] Cf. Brook, *J.*, 1952, 5040.
[11] Ansell and Wilson, unpublished observation.
[12] Fox and Martin, *Proc. Roy. Soc.*, 1937, **162**, *A*, 419.
[13] Hickinbottom, "Reactions of Organic Compounds," Longman, Green & Co., Ltd., London, 1957, p. 288.

quinol. Further, the quinhydrone reacted with the acetoxy-diene (I) to yield dimethyl 2,5-dihydroxyterephthalate together with an adduct. The latter was also obtained when dimethyl 2,5-dihydroxyterephthalate was oxidised by silver oxide in the presence of the diene. The analysis of the adduct indicated that it was a bis-adduct, from two molecules of the diene and one of the quinone, and, in agreement, its ultraviolet spectrum showed no ene-dione absorption in the region 200—350 mμ.

EXPERIMENTAL

Ultraviolet absorption spectra are recorded for ethanol solutions.

9-*Acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-12-*methoxycarbonyl*-1,4-*dioxophenanthrene* (IIIc).—Methoxycarbonylbenzoquinone [14] (IIc) (2·6 g., 0·016 mole) was added to 1-1′-acetoxyvinylcyclohexene [2a] (I) (3·0 g., 0·018 mole) containing a crystal of quinol. An exothermic reaction ensued and the mixture was cooled. Dry benzene (10 ml.) was added and the mixture left overnight. The solvent was removed under reduced pressure, and the residue triturated with light petroleum (b. p. 60—80°), to yield 9-*acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-12-*methoxycarbonyl*-1,4-*dioxophenanthrene* (IIIc) (5·0 g., 97%), orange, m. p. 100—115°. Crystallisation from methanol gave the pure compound, m. p. 128·5—130°, $\lambda_{\text{max.}}$ 225 mμ (log ε 4·02), 5·71 (enol-acetate), 5·80 (ester), 5·90 and 5·95 μ (αβ-unsaturated C=O) (Found: C, 64·8; H, 6·2. $C_{18}H_{20}O_6$ requires C, 65·0; H, 6·0%). When the adduct was treated as in the following experiment, 90% of it was recovered.

Aromatisation of 9-*Acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-1,4-*dioxophenanthrene* (IIIi).—48% Hydrobromic acid (1 drop) was added to a solution of the dioxo-phenanthrene [2a] (0·5 g.) in glacial acetic acid (3 ml.) at 90°. After 10 min. a precipitate was formed which, after 1 hr., was filtered off and washed with acetic acid to yield 10-acetoxy-1,2,3,4,9,12-hexahydro-5,8-dihydroxyphenanthrene (0·4 g.), m. p. 185—195° (decomp.). Recrystallisation from acetic acid gave the pure compound, m. p. 226—230° (decomp.) (lit.,[2b] 228—231°).

9-*Acetoxy*-$\Delta^{9(14)}$-*dodecahydro*-12-*methoxycarbonyl*-1,4-*dioxophenanthrene* (IV).—Zinc powder (60 g.) was added to 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-1,4-dioxophenanthrene (IIIc) (30 g.) in acetic acid (400 ml.), and the mixture was stirred and heated on a steam-bath for 16 hr., then cooled and filtered. Trituration, with dry methanol (100 ml.), of the residue obtained on evaporation of the filtrate under reduced pressure gave 9-*acetoxy*-$\Delta^{9(14)}$-*dodecahydro*-12-*methoxycarbonyl*-1,4-*dioxophenanthrene* (IV) (28 g., 93%), m. p. 179—183°. The analytical sample (from methanol) had m. p. 185—186° (Found: C, 64·7; H, 6·7. $C_{18}H_{22}O_6$ requires C, 64·8; H, 6·6%). The double-bond peak (6·22 μ) in the infrared spectrum of the starting material was absent from the spectrum of the reduced material.

Degradation of the Dihydro-derivative (IV) *to Anthracene*.—The dihydro-derivative (IV) (20 g.) was dissolved in oxygen-free sodium methoxide (from sodium, 2·4 g.) in methanol (120 ml.) at 5°, left at room temperature for 14 hr., and then boiled under reflux (nitrogen) for 15 min. The cool, brown mixture was poured on ice and 4N-sulphuric acid and extracted with ether. The product was separated into acidic and non-acidic material in the usual way. The non-acidic material (7 g.) was discarded. A mixture of acidic material (10 g.), amalgamated zinc wool (40 g.), water (30 ml.), concentrated hydrochloric (70 ml.), toluene (40 ml.), and glacial acetic acid (1 ml.) was heated under reflux for 40 hr., three further portions (20 ml.) of hydrochloric acid being added at 10-hr. intervals. The toluene layer was then separated and evaporated to a yellow semisolid residue (9·0 g.), the infrared spectrum of which showed absorption (5·8 and 5·9 μ) in the carbonyl region. This material (7 g.) was treated with diazomethane, and the product heated with 10% palladium–charcoal (1·4 g.) in a stream of carbon dioxide at 280° for 1·5 hr. and then at 330° (b. p.) for 4 hr. The organic material was distilled at 1 mm. from the catalyst, chromatographed in 2 : 1 light petroleum (b. p. 40—60°)–ether, and crystallised from methanol, to yield anthracene (0·2 g.), m. p. 215° (with sublimation) (Found: C, 94·6; H, 5·9%; *M*, 160·5. Calc. for $C_{14}H_{10}$: C, 94·4; H, 5·6%; *M*, 178). The m. p.s of the derived picrate (red needles, m. p. 145°) and the 1,3,5-trinitrobenzene complex (orange needles, m. p. 167—170°) were not depressed on admixture with authentic specimens.

Degradation of the Adduct (IIIc) *to Phenanthrene*.—A slurry of potassium borohydride (5 g.) in dry tetrahydrofuran (100 ml.) was added to a solution of the adduct (6·0 g.) in tetrahydrofuran and the mixture was stirred for 2 hr. Potassium borohydride (2 g.) and potassium

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[14] Brunner, *Monatsh.*, 1913, **34**, 913.

hydroxide (0·4 g.) in water (75 ml.) were added and stirring was continued overnight. The tetrahydrofuran layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with saturated brine and evaporated, to yield a yellow oil (5 g.) (mixture of triol esters). This material was heated with 10% palladium–charcoal (0·8 g.) in a slow stream of nitrogen at 210° for 1·5 hr. and then at 330—340° for 4 hr. The organic material (1 g.) that distilled at 300°/1 mm. from the catalyst was chromatographed in 2 : 1 light petroleum (b. p. 40—60°)–ether on alumina. The eluant, with picric acid, yielded phenanthrene picrate, m. p. 140—146° undepressed on admixture with an authentic specimen of m. p. 143—146°.

9-*Acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-12-*methoxycarbonyl*-3-*methyl*-1,4-*dioxophenanthrene* (IIIf).—The acetoxy-diene (I) (2·0 g.) was added to a solution of 6-methoxycarbonyltoluquinone [15] (IIf) (1·8 g.) in benzene (20 ml.); the solution became warm and was left overnight, and the solvent then removed under reduced pressure. Trituration of the residue with ether at 0° yielded 9-*acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-12-*methoxycarbonyl*-3-*methyl*-1,4-*dioxophenanthrene* (IIIf) (2·2 g., 63%), m. p. 114—118°. A pure sample had m. p. to 116·5—118° and $\lambda_{max.}$ 243, 350—360 mμ (log ε 4·037, 1·978) (Found: C, 66·0; H, 6·6. $C_{19}H_{22}O_6$ requires C, 65·8; H, 6·4%).

9-*Acetoxy*-$\Delta^{9(14)}$-*dodecahydro*-12-*methoxycarbonyl*-3-*methyl*-1,4-*dioxophenanthrene*.—(*a*) A solution of 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-12-methoxycarbonyl-3-methyl-1,4-dioxophenanthrene (IIIf) (3 g.) in absolute methanol (150 ml.) was hydrogenated at 50 lb./sq. in. in the presence of Adams catalyst (0·5 g.). The catalyst was filtered off, and the filtrate concentrated to 10 ml.; it then deposited crystals of 9-*acetoxy*-$\Delta^{9(14)}$-*dodecahydro*-12-*methoxycarbonyl*-3-*methyl*-1,4-*dioxophenanthrene* (2·1 g., 70%), m. p. 143—147°. An analytical sample (from methanol) had m. p. 147—149° (Found: C, 65·7; H, 7·2. $C_{19}H_{24}O_6$ requires C, 65·5; H, 6·9%).

(*b*) Zinc powder (1 g.) was added to a stirred solution of the adduct (IIIf) (1 g.) in acetic acid (50 ml.). After 30 min. the insoluble material was filtered off and the residue obtained on removal of the acetic acid under reduced pressure was extracted with boiling light petroleum (b. p. 100—120°; 2 × 20 ml.). Evaporation of the extracts gave the crude dihydro-derivative (0·5 g.), m. p. 132—137°. Recrystallisation from methanol gave pure material, m. p. 145—148° identical with that prepared as in (*a*). The ultraviolet absorption spectrum of this compound showed no maximum in the range 200—350 mμ.

Degradation of the Adduct (IIIf).—The adduct (6·0 g.) was reduced with potassium borohydride, as described for the reduction of the adduct (IIIc), to a mixture of triol esters (6 g.) which was dehydrated 220—235° for 75 min. in a stream of nitrogen with powdered fused potassium hydrogen sulphate (9 g.). After addition of water the product was extracted with ether. The residue (3·8 g.) obtained on evaporation of the dried (K_2CO_3) extract was heated with selenium (10 g.) at 350° ±10° for 24 hr. The organic material was extracted with toluene, and the resulting solution boiled with sodium. After cooling and filtering, the solvent was removed and the residue chromatographed in light petroleum on alumina. Treatment of the eluted material (620 mg.) with picric acid yielded 3-methylphenanthrene picrate, m. p. 138—140°, from which was isolated 3-methylphenanthrene, m. p. 58—60° undepressed in admixture with an authentic sample [2a] of m. p. 61·5—62·5°. Similar results were obtained when the dehydrogenation was carried out with palladium–charcoal

6-*Methoxy*-3-*methoxycarbonyltoluquinone* (IId).—4-Methoxycarbonyl-5-methylcyclohexane-1,3-dione [16] was treated with bromine (as described [17] for the ethyl ester), to yield *methyl* 3,5-*dibromo-orsellinate* (90%; m. p. 103—110°) which, when crystallised from dry methanol, had m. p. 107·5—109° (Found: C, 32·0; H, 2·3; Br, 46·3. $C_9H_8Br_2O_4$ requires C, 31·8; H, 2·4; Br, 47·0%). Stenhouse [18] obtained this compound by brominating methyl orsellinate but did not record its m. p. It was reduced, as for the ethyl ester,[17] except that palladium–charcoal and not palladium on polyvinyl alcohol was the catalyst. The resulting methyl orsellinate, m. p. 143—146° (lit.,[19] 140°), was methylated (to yield methyl everninate, 66%), and then oxidised (as described for the ethyl ester [6]) to methyl 4-methoxy-6-methylgentisate (34%), m. p. 154—156° (lit.,[6] 153—154°).

Silver oxide (15 g.) was added portion-wise to a shaken, boiling solution of methyl

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

[16] Sonn, *Ber.*, 1929, **63**, 3014.

[17] Anker and Cook, *J.*, 1945, 311.

[18] Stenhouse, *Annalen*, 1863, **125**, 355.

[19] Herzig, Wenzel, and Kurzweil, *Monatsh.*, 1903, **24**, 898.

4-methoxy-6-methylgentisate (5 g.) in dry benzene (50 ml.) containing freshly dried potassium carbonate (5 g.), at such a rate that boiling was maintained. The solution was cooled to 50—60° for 15 min. and the insoluble material was filtered off and washed with hot dry benzene (30 ml.). Evaporation at $<40°$ of the dried (K_2CO_3) combined filtrates gave the light yellow 6-*methoxy*-3-*methoxycarbonyltoluquinone* (IId) (5 g., 100%), m. p. 76—82°, $\lambda_{max.}$ 267 mμ (log ε 4·12) (Found: C, 57·3; H, 5·1. $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8%). Recrystallisation from dry carbon disulphide did not improve the m. p. and sublimation caused decomposition.

Diels–Alder Reaction of 1-1′-*Acetoxyvinylcyclohexene* (I) *and* 6-*Methoxy*-3-*methoxycarbonyltoluquinone* (II*d*) (with B. W. Nash).—The quinone (3·0 g.), the diene (3·0 g.), and a crystal of quinol were heated at 100° under nitrogen for 60 hr. The resultant dark brown oil, when triturated with ether, yielded a solid which was filtered off and washed with ether, to yield an *adduct* (IIId or e) (2·1 g., 39%), m. p. 180—184°. An analytical sample (from dioxan or aqueous dioxan) had m. p. 181—183°, $\lambda_{max.}$ 278 mμ (log ε 3·81) (Found: C, 63·7; H, 6·6. $C_{20}H_{24}O_7$ requires C, 63·8; H, 6·4%). This material appeared to be polymorphic. When heated slowly the crystals became opaque at 75—95° but melting did not occur until 180°. When heated rapidly from room temperature it melted at ~120°, and when immersed in a bath at 160° it melted instantly.

Methanolysis of the Adduct (IIId) *or* (IIIe).—A solution of the adduct (20 g.) in dry methanol (600 ml.) containing " AnalaR " sulphuric acid (7 ml.) was heated under reflux for 30 min., then concentrated to 100 ml. under reduced pressure and cooled. The crystalline product (13·2 g., 74%), when washed with methanol and dried, had m. p. 160—180°. The pure Δ^2-*dodecahydro*-2(or 3)-*methoxy*-12(or 11)-*methoxycarbonyl*-11(or 12)-*methyl*-1,4,9-*trioxophenanthrene* (recrystallised from methanol) had m. p. 200—202° (Found: C, 64·7; H, 6·6; MeO, 18·6. $C_{18}H_{22}O_6$ requires C, 64·8; H, 6·4; MeO, 18·9%).

Dimethyl 2,5-*Dihydroxyterephthalate*.—A cold (0°) solution of bromine (4·26 ml.) in chloroform (100 ml.) was added to dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate [20] (9·4 g.) in chloroform (100 ml.) also at 0°. The solution was kept at room temperature for 2 hr., then at 40° for 2 hr., washed with 10% sodium thiosulphate solution, then with water, and dried (K_2CO_3). Evaporation at reduced pressure left *dimethyl* 2,5-*dihydroxyterephthalate* (8 g., 85%), m. p. 170—175°. The pure compound (a yellow fluorescent solid from benzene) had m. p. 177—179° (Found: C, 53·2; H, 4·4. $C_{10}H_{20}O_6$ requires C, 53·1; H, 4·4%), $\lambda_{max.}$ 3·1w (OH) and 5·98s μ (C=O). Its diacetate had m. p. 168·5—171° (lit.,[9] 166—168°).

Dimethyl 2,5-*Dihydroxy*-3,6-*dinitroterephthalate*.—An excess of a solution of oxides of nitrogen [10] in carbon tetrachloride was added to a stirred suspension of dimethyl 2,5-dihydroxyterephthalate (1·0 g.) in the same solvent. Stirring was continued for 30 min. and then the light yellow product was filtered off, washed with a little carbon tetrachloride, and dried, to yield the *dinitro-ester* (0·7 g.), m. p. 153° (decomp.). The pure compound formed light yellow plates (from benzene or methanol), m. p. 245° (decomp.) (Found: C, 38·4; H, 2·4; N, 8·7. $C_{10}H_8N_2O_{10}$ requires C, 38·0; H, 2·5; N, 8·9%), $\lambda_{max.}$ 3·22 (OH) 5·95 (ester C=O), and 6·45 and 7·50 μ (NO_2). The derived *diacetate*, recrystallised from methanol, had m. p. 183·5—186·5° (Found: C, 42·0; H, 3·1. $C_{14}H_{12}N_2O_{12}$ requires C, 42·0; H, 3·0%). Oxidation in the presence of potassium carbonate with dried oxides of nitrogen gave a nitrogenous product.

Quinhydrone of 2,6-*Dimethoxycarbonylbenzoquinone*.—To a stirred solution of dimethyl 2,5-dihydroxyterephthalate (13 g.) in dry benzene (750 ml.) containing anhydrous magnesium sulphate (26 g.) at 55° silver oxide (39 g.) was added. The temperature was kept at 55° for 3 hr., and the insoluble material then filtered off and washed with dry benzene. Evaporation of the combined filtrates yielded a mixture (10 g.) of a red and a yellow solid. This mixture was extracted with boiling ether (4 × 100 ml.), and the extracts were cooled to 0° for 16 hr.; mainly dimethyl 2,5-dihydroxyterephthalate (1·2 g.) was deposited. Evaporation of the extracts gave mainly red crystals (1·9 g.; m. p. 120—170°) which when purified by fractional crystallisation from ether and benzene or by sublimation gave the essentially pure, red *quinhydrone*, m. p. 140—142° (Found: C, 53·4; H, 4·2. $C_{20}H_{18}O_{12}$ requires C, 53·4; H, 4·0%), $\lambda_{max.}$ 3·0vw (OH), 5·79s, and 6·01s μ (C=O). The quinone content of this material was estimated [13] as 45%.

Diels–Alder Reaction of 2,5-*Dimethoxycarbonylbenzoquinone*.—(*a*) Dimethyl 2,5-dihydroxyterephthalate (1 g.) was dissolved in dry benzene (50 ml.) together with 1-1′-acetoxyvinylcyclohexene (1 g.). Freshly dried magnesium sulphate (2 g.) and silver oxide (3 g.) were added

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[20] Prepared by method described by Hauser and Boyd, *Org. Reactions*, 1942, **1**, p. 283, for ethyl ester.

and the mixture was stirred at 45—50° for 3 hr. The resultant mixture was filtered and the filtrate evaporated, to yield a yellow solid from which the excess of diene was extracted with boiling light petroleum (b. p. 100—120°; 25 ml.). The resultant solid crystallised from methanol and acetic acid, to yield the ***bis-adduct*** as white needles (0·15 g.), m. p. 228—230°. This material resolidified to cubes which melted at 274—276° (Found: C, 65·2; H, 6·4%; *M*, 390. $C_{30}H_{36}O_{10}$ requires C, 64·8; H, 6·5%; *M*, 556).

(*b*) A solution of the quinhydrone of 2,5-dimethoxycarbonylbenzoquinone (1·9 g.) in dry benzene (25 ml.) was stirred at 55° while 1-1′-acetoxyvinylcyclohexene (1·3 g.) in benzene (50 ml.) was added dropwise during 2 hr. After a further 2 hr. at 55° the solvent was removed and the residue extracted with boiling light petroleum (b. p. 100—120°; 25 ml.) [to remove dimethyl 2,5-dihydroxyterephthalate (0·3 g.)]. The residue (1·2 g.) recrystallised from methanol and acetic acid to yield the above bis-adduct, m. p. 228—230°.

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