555. *Reduced Cyclic Compounds. Part XIV.*[1] *Diels–Alder Reactions of* 1-1'-*Acetoxyvinylcyclohexene with* p-*Benzoquinones Containing Electron-withdrawing Groups.*

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

The Diels–Alder reactions of 1-1'-acetoxyvinylcyclohexene with 2,3-dicyano-, 2,3-dimethoxycarbonyl-, 2-methoxycarbonyl-3,5-dimethyl-, and 2,6-dimethoxycarbonyl-3,5-dimethyl benzoquinone are reported, and structures are assigned to the main products of each reaction.

The Diels–Alder reaction of 1-1'-acetoxyvinylcyclohexene (I) with an unsymmetrically substituted *p*-benzoquinone could give four structurally isomeric adducts. We have previously[1,2] suggested factors that determine to which ethene linkage of a quinone a diene will preferentially add, and these have been found[3] to account for the reactions of a wide range of quinones. When it is known to which side of a quinone addition takes place, the factors that determine which of the two remaining structural isomers is preferentially formed are less readily deduced.[4] We now report further Diels–Alder reactions of this diene which support our solution to the first problem, although giving little further information about the second.

2,3-Dicyanobenzoquinone[5] (II; R = CN) and the diene (I) readily reacted to give the adduct (III; R = CN) in good yield. That addition had taken place to the substituted ethene linkage of the quinone was shown by the nuclear magnetic resonance spectrum of the adduct (two vinyl protons), a result consistent with its ultraviolet absorption[6] ($\lambda_{max.}$ 227 mμ). We have already pointed out[2] that this result is contrary to the hypothesis put forward by Orchin and Butz[7] to predict the products of such reactions, and a similar result has since been recorded by Hartzler and Benson,[8] who obtained a product with angular cyano-groups from the reaction between this quinone and 1,2-dimethylenecyclobutane. Although this quinone is a very reactive dienophil, it is also a strong oxidising agent[9] and its reaction with diene (I) in methanol was accompanied by the formation of some 3,6-dihydroxyphthalonitrile.[10] The methanol was presumably oxidised, for Ansell and Culling[1] record that the quinhydrone of 2,5-dimethoxycarbonyl-1,4-benzoquinone and its quinol is reduced to the quinol by methanol.

The reaction between 2,3-dimethoxycarbonylbenzoquinone[5] (II; R = CO_2Me) and the diene (I) is rather slow, but in boiling cumene the adducts (III; R = CO_2Me) (30%) and (IV) (20%) were formed. These products were separated by chromatography on silica gel; the primary adduct with non-angular methoxycarbonyl groups aromatised either during the reaction or on the column [this enedione–quinol rearrangement is usually effected by acidic or basic catalysts, but it can also be done thermally;[11] the diene (I)–benzoquinone adduct[12] (III; R = H) is aromatised during chromatography on silica gel in benzene]. Although the methoxycarbonyl-substituted ethene linkage of the quinone is electronically more reactive than the unsubstituted one[2] there is some steric opposition to the formation of an adduct with bulky angular groups. This is also illustrated in the following results, and is more fully discussed elsewhere.[3] A very small

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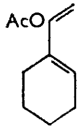
[1] Part XIII, Ansell and Culling, *J.*, 1961, 2908.
[2] Ansell, Culling, Nash, Wilson, and Lown, *Proc. Chem. Soc.*, 1960, 405.
[3] Ansell, Nash, and Wilson, following paper.
[4] Ansell and Knights, *J.*, 1961, 2903.
[5] Ansell, Nash, and Wilson, *J.*, 1963, 3028.
[6] Ref. 3, Table 1.
[7] Orchin and Butz, *J. Org. Chem.*, 1943, **8**, 509.
[8] Hartzler and Benson, *J. Org. Chem.*, 1961, **26**, 3507.
[9] Braude, Brook, and Linstead, *J.*, 1954, 3569.
[10] Thiele and Meisenheimer, *Ber.*, 1900, **33**, 675.
[11] Lora-Tamayo and Leon, *J.*, 1948, 1499.
[12] Ansell and Brooks, *J.*, 1956, 4518.

amount of what was probably the 9-ketone (m. p. 145°) derived from (IV) was also formed in this reaction in cumene. The same reaction, in cold benzene solution, gave a little of the quinone (V), which was reduced to the quinol (IV) with sulphur dioxide. In boiling methanol solution, this Diels–Alder reaction gave a very small amount of the compound formed by the action of methanol and acid on the adduct (IV) [*i.e.*, probably the quinol ketal (VI)] and an amount (25%) of another compound, m. p. 189—190°, whose structure is unknown but which could be the compound (VII) (or its tautomer) formed by ring-opening of the adduct (III; R = CO_2Me) (cleavage of 4,4a-bond) and subsequent closure (at C-10) (cf. degradation below and ref. 1).



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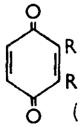

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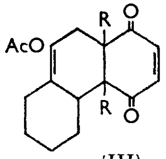

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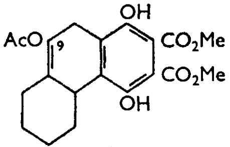

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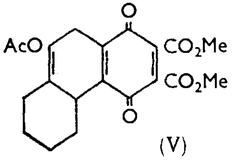

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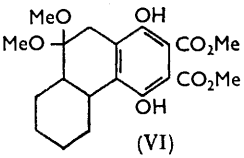

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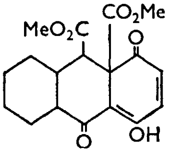
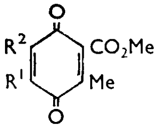


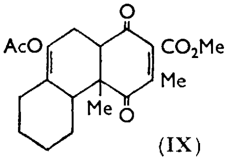
(VII)

The reaction between the diene (I) and 2-methoxycarbonyl-3,5-dimethylbenzoquinone[5] (VIII; R^1 = Me, R^2 = H) gave two adducts, the major one (IX) (56%) formed by addition to the monosubstituted ethene linkage of the quinone, and the minor one (X; R^1 = Me, R^2 = H) (11%) formed by addition to the electronically more reactive but sterically less favoured disubstituted linkage. The structure of adduct (IX) followed from its spectroscopic properties, and its degradation to 3-methylphenanthrene. On treatment with zinc and acetic acid, it gave the monounsaturated acetate (XI); this was reduced by potassium borohydride and hydrolysed to give a mixture of triol acids which was dehydrated with potassium hydrogen sulphate and then dehydrogenated with selenium to give 3-methylphenanthrene. The minor adduct (X; R^1 = Me, R^2 = H) similarly gave a reduced derivative (XII; R^2 = Me, R^2 = H) with zinc and acetic acid, but treatment of this compound successively with potassium borohydride, potassium hydrogen sulphate, and selenium gave 2-methylanthracene. It is considered that this degradation sequence involved cleavage of the 4,4a-bond and that the resultant compound recyclised at C-10 (phenanthrene numbering). A somewhat analogous degradation has been reported by Ansell and Culling.[1] The formation of an anthracene derivative by this sequence shows that the methoxycarbonyl group was at position 4a and not at 10a. This methylanthracene could result if the methoxycarbonyl group were at position 3, but the presence of a vinyl proton in the nuclear magnetic resonance spectrum of the adduct (X; R^1 = Me, R^2 = H) excludes this.

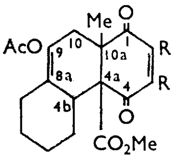
2,6-Dimethoxycarbonyl-3,5-dimethylbenzoquinone[5] (VIII; R^1 = Me, R^2 = CO_2Me) and the acetoxy-diene (I) gave the adduct (X; R^1 = Me, R^2 = CO_2Me) (43%), which was obtained as rosettes, m. p. 119—121°, or as needles, m. p. 104—107°. The ultraviolet absorption of this adduct ($\lambda_{max.}$ 244 mμ) showed that a methoxycarbonyl substituent has little effect on the position of the *K*-band maxima of enedione systems.[6] Clearly, the only problem in assigning a structure to the adduct was whether the angular methoxycarbonyl group was at position 4a or 10a. Treatment of the adduct with zinc and acetic acid did not give the expected dihydro-derivative, but gave a substance in low yield (30%) that retained the chromophore but in a modified form ($\lambda_{max.}$ 260 mμ). The adduct (X; R^1 = Me, R^2 = CO_2Me), with methanolic hydrogen chloride at room temperature gave the triketone (XIII) ($\lambda_{max.}$ 246 mμ), the enedione double bond of which was unreactive towards zinc and acetic acid, osmium tetroxide, and ozonised oxygen at $-70°$ and 0°. The original adduct, or the triketone (XIII), in boiling methanolic hydrogen chloride, gave a compound the spectroscopic properties of which suggested that it had the structure (XIV) (cf. VII). The triketone (XIII) was degraded by hydrogenation over Raney nickel; reduction of the product with potassium borohydride, with addition of alkali to hydrolyse the non-angular methoxycarbonyl group, followed by dehydration with potassium hydrogen sulphate and dehydrogenation with selenium, gave 1,2-dimethylphenanthrene (identified as its picrate and 1,3,5-trinitrobenzene complex). Thus, during the degradation sequence the angular methyl group migrated from C-10a to C-1. It is known that angular methyl groups can migrate in both dehydration[13] and dehydrogenation[14] reactions.



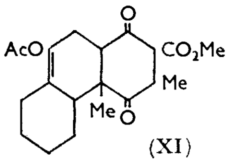
(VIII)



(IX)



(X)



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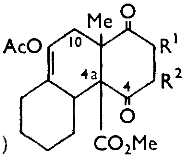

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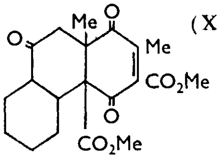

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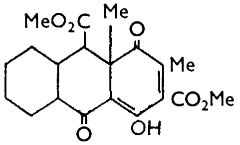

(XIV)

It was shown earlier[1] that the adduct of 2-methoxy-5-methoxycarbonyl-6-methylbenzoquinone (VIII; R^1 = MeO, R^2 = H) and the diene (I) had a non-angular methoxy-group. In the light of the above results it seems that the more likely structure for the adduct is (X; R^1 = MeO, R^2 = H), with the methoxycarbonyl group at position 4a. It was previously reported that the action of hot methanolic sulphuric acid on the methoxy-adduct gave a compound, m. p. 200—202°, considered to be the triketone formed by hydrolysis of the enol acetate group. The adduct, on treatment with hot methanolic hydrogen chloride, gave three compounds, all of which gave analyses for the triketone and had strong absorption in the region 268—280 mμ, suggesting[6] that a methoxy-substituted enedione or enone system remained. The product formed in greatest amount also had a hydroxyl peak in the infrared region, but degradation to phenanthrene indicated that it was not a compound analogous to (VII) or (XIV).

The results herein presented and those previously reported,[2,4] suggest that when the acetoxy-diene (I) adds to a methyl-substituted ethylene linkage of a benzoquinone, the adduct with the 4a-methyl group will result. This is contrary to the result expected from a consideration of the polarity of the diene[4] (C-2 of the diene will be slightly positively charged). When the diene adds to an ethylene linkage bearing a methoxy-carbonyl group (with or without a methyl group as well), that methoxycarbonyl group is found at position 4a in the adduct, a result in keeping with polarity considerations. Addition of methyl acrylate to the diene (I)[15] gives an adduct with the acetoxy- and the methoxycarbonyl group similarly related. Whilst this affords a means of obtaining compounds with angular methyl groups in positions related to those in which they are found in steroids, its usefulness is offset by the difficulty of hydrolysing an angular alkoxycarbonyl group[16] without effecting skeletal changes.

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[13] Cohen, Cook, and Hewett, *J.*, **1935**, 445.
[14] Fieser and Fieser, " Steroids," Reinhold Publ. Corp., New York, 1959, p. 83.
[15] Winternitz and Balmossière, *Tetrahedron*, 1958, **2**, 100.
[16] Fieser and Holmes, *J. Amer. Chem. Soc.*, 1936, **58**, 2319.

EXPERIMENTAL

Ultraviolet absorption spectra are recorded for ethanol (95%) solutions. Nuclear magnetic resonance spectra were recorded for deuterochloroform or carbon tetrachloride solutions, unless otherwise stated.

9-Acetoxy-4a,10a-dicyano-$\Delta^{2,8a(9)}$*-decahydrophenanthrene-1,4-dione* (III; R = CN).—2,3-Dicyanobenzoquinone[5] (9·8 g.) was added in portions to a cooled and stirred solution of 1-1'-acetoxyvinylcyclohexene[12] (12 g.) in methanol (80 ml.); the quinone dissolved and a solid came out of solution. The solid (11·6 g., 58%), m. p. 183—186°, was filtered off and crystallised from ethyl acetate to give the *dicyano-adduct*, m. p. 189—191°, $\lambda_{max.}$ 227 mμ (ε 7300); 4·48 (CN, fairly weak), 5·70 (enol OAc), 5·82, 5·90 (enedione C=O), 6·25 μ (conj. C=C), τ 2·97 (two vinyl protons), 2·71 p.p.m. (two vinyl protons, acetone solution) [the parent quinone had τ 2·77 p.p.m. (acetone solution)] (Found: C, 66·8; H, 5·0; N, 8·9. $C_{18}H_{16}N_2O_4$ requires C, 66·7; H, 5·0; N, 8·6%). The filtrate from the reaction mixture, on dilution with chloroform and light petroleum (b. p. 60—80°), gave 3,6-dihydroxyphthalonitrile (1·6 g., 16%), m. p. 225—230° (charring) [lit.,[10] 230° (charring)].

Diels–Alder Reaction of 1-1'-Acetoxyvinylcyclohexene and 2,3-Dimethoxycarbonylbenzoquinone.—A solution of the quinone[5] (1·6 g.) and the diene (1·2 g.) in cumene (50 ml.) was heated under reflux (150°) for 11 hr. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (8 × 3 cm.), elution being effected with benzene and benzene–ether (4 : 1). The first fractions gave unchanged diene and an oil, but the next fraction gave a solid which was crystallised from ether to give *dimethyl 9-acetoxy-4b,5,6,7,8,10-hexahydro-1,4-dihydroxyphenanthrene-2,3-dicarboxylate* (IV) (550 mg., 20%), m. p. 163—165°, (Found: C, 61·1; H, 5·7; active H, 0·7. $C_{20}H_{22}O_8$ requires C, 61·5; H, 5·7; active H, 0·5%), $\lambda_{max.}$ 216br, 264, 340 mμ (ε 20,000, 5000, and 6200) 2·91 (OH), 5·73 (enol OAc), 5·83, 5·96 (ester), 6·25 μ (C=C), τ 7·81 (OAc), 6·14 (two ester Me), 0·805, 0·63 p.p.m. (two OH protons). The position of the OH protons was temperature-invariant (in deuterochloroform solution), but disappeared for triethylamine solution where the ester peak split into a doublet, suggesting strong intramolecular hydrogen bonding in the former solvent but preferential hydrogen bonding to the solvent molecules in the amine solution.

A further chromatography fraction afforded a second adduct which crystallised from light petroleum (b. p. 60—80°) to give *dimethyl 9-acetoxy-*$\Delta^{2,8a(9)}$*-decahydro-1,4-dioxophenanthrene-4a,10a-dicarboxylate* (III; R = CO_2Me) (850 mg., 30%), m. p. 114—115·5°, $\lambda_{max.}$ 232 mμ (ε 7050), 5·72sh (enol OAc), 5·78, 5·81sh (ester), 5·94 (enedione C=O), 6·26 μ (conj. C=C): τ 7·85 (OAc), 6·31, 6·16 (ester Me), 3·34, 3·12 p.p.m. (AB quartet of vinyl protons, *J* = 10 c./sec.) (Found: C, 61·3; H, 5·4. $C_{20}H_{22}O_8$ requires C, 61·5; H, 5·7%).

From a similar reaction solution, in cold benzene (7·5 days), was isolated, by chromatography and crystallisation from ether–light petroleum (b. p. <40°), *dimethyl 9-acetoxy-1,4,4b,5,6,7,8,10-octahydro-1,4-dioxophenanthrene-2,3-dicarboxylate* (V) (8%), m. p. 142·5—144·5°, $\lambda_{max.}$ 5·72—5·79 (enol acetate and ester), 6·03sh, 6·06 (quinone C=O), 6·14sh μ (C=C) (Found: C, 61·6; H, 5·5%; *M*, 361. $C_{20}H_{20}O_8$ requires C, 61·9; H, 5·2%; *M*, 388). This quinone (100 mg.) was reduced by sulphur dioxide in water–ethanol (40 ml., 1 : 3) to the quinol (IV) (50%), m. p. and mixed m. p. 164—165° (correct infrared spectrum).

A similar reaction, in boiling methanol for 5 days, gave, after chromatography on silica gel, a small amount (<1%) of the compound formed by the action of methanol–acid on the adduct (IV), and a *substance* (VII?) (25%), m. p. 189—190° [from ethyl acetate–light petroleum (b. p. 60—80°)], $\lambda_{max.}$ 253 mμ (ε 3600, calc. for *M*, 348), 2·87 (OH), 5·77, 5·82, 5·92 μ (C=O), τ 6·51 6·44 (ester Me), 3·96, 3·76, 3·215, 3·02 p.p.m. (AB quartet of vinyl protons, *J* = 11 c./sec.) (Found: C, 62·0; H, 5·65%; *M*, 346. $C_{18}H_{20}O_7$ requires C, 62·1; H, 5·8%; *M*, 348).

Action of Methanolic Acid on Adduct (IV).—The diester-quinol (IV) (100 mg.) was heated under reflux in dry methanol (10 ml.) containing concentrated sulphuric acid (2 drops) for 60 min. Dilution with water (20 ml.), extraction with ether (3 × 10 ml.), and removal of the solvent gave a solid (85 mg.) which crystallised from benzene–light petroleum (b. p. 80—100°) to give a substance [probably *dimethyl 4b,5,6,7,8,8a,9,10-octahydro-1,4-dihydroxy-9,9-dimethoxyphenanthrene-2,3-dicarboxylate* (IV)], m. p. 162—164°, $\lambda_{max.}$ 2·92 (OH), 5·85, 5·98 (C=O), 6·18, 6·27, 6·42 μ (C=C) (Found: C, 61·4; H, 6·7. $C_{20}H_{26}O_8$ requires C, 60·9; H, 6·6%).

Diels–Alder Reaction of 1-1′-*Acetoxyvinylcyclohexene and* 2-*Methoxycarbonyl*-3,5-*dimethylbenzoquinone*.—A solution of the diene (6·64 g.) and the quinone[5] (6·3 g.) in dry methanol (20 ml.) was heated under reflux for 12 hr. (a little quinol was added to the solution). The cooled solution deposited crystals (5·1 g.), m. p. 130—151°, from which, by repeated crystallisation from methanol, was obtained *methyl* 9-*acetoxy*-$\Delta^{2,8a(9)}$-*decahydro*-3,4a-*dimethyl*-1,4-*dioxophenanthrene*-2-*carboxylate* (IX) (3·0 g., 26%), m. p. 154—155°, $\lambda_{max.}$ 245 mμ (ε 7950), 5·72sh (enol OAc), 5·78 (ester), 5·85sh, 5·98 (enedione C=O), 6·13 μ (conj. C=C), τ 8·53 (angular Me), 8·05 (vinyl Me), 7·86 (OAc), 6·14 p.p.m. (ester Me) (Found: C, 66·55; H, 6·65. $C_{20}H_{24}O_6$ requires C, 66·65; H, 6·7%). Crystallisation (from methanol) of the residue from the combined mother-liquors from above, and hand-sorting of the resulting crystals, yielded a further quantity (3·5 g., total 56%) of the above adduct, and *methyl* 9-*acetoxy*-$\Delta^{2,8a(9)}$-*decahydro*-2,10a-*dimethyl*-1,4-*dioxophenanthrene*-4a-*carboxylate* (X; R^1 = Me, R^2 = H) (1·25 g., 11%), m. p. 123—124°, $\lambda_{max.}$ 244 mμ (ε 8700) 5·72sh (enol OAc), 5·79 (ester), 5·98sh, 5·94 (enedione C=O), 6·19 μ (conj. C=C), τ 8·52 (angular Me), 8·03 (vinyl Me), 7·93 (OAc), 6·32 (ester Me), 3·43 p.p.m. (vinyl proton) (Found: C, 66·6; H, 6·8. $C_{20}H_{24}O_6$ requires C, 66·65; H, 6·7%).

Methyl 9-*Acetoxy*-$\Delta^{8a(9)}$-*dodecahydro*-3,4a-*dimethyl*-1,4-*dioxophenanthrene*-2-*carboxylate* (XI).—The adduct (IX) (10 g.) and zinc powder (50 g.) were added to acetic acid (300 ml.), and the mixture was stirred for 60 hr., then filtered and taken to dryness. The residue crystallised from methanol to yield the *dodecahydro-derivative* (XI) (7·2 g., 72%), m. p. 151—153°, $\lambda_{max.}$ 5·73 (enol OAc), 5·77 (ester), 5·87, 5·88sh μ (C=O) [the double-bond (6·13 μ) and enedione (245 mμ) absorptions of the precursor were absent] (Found: C, 66·35; H, 7·2. $C_{20}H_{26}O_6$ requires C, 66·3; H, 7·25%).

Degradation of the Dodecahydro-derivative (XI) *to* 3-*Methylphenanthrene*.—Potassium borohydride (7 g.) was added to a solution of the dodecahydro-derivative (IX) (58·3 g.) in dry methanol–tetrahydrofuran (1 l.; 3 : 2), and the mixture was left for 20 hr. 10% Aqueous potassium hydroxide (200 ml.) and potassium borohydride (10 g.) were then added, and after 2 hr. the mixture was heated on the water-bath for 2 hr. and then concentrated at reduced pressure to a small volume. 30% Aqueous potassium hydroxide (100 ml.) was then added, and heating was continued for 6 hr. The mixture was acidified with 4N-sulphuric acid and extracted with ether–tetrahydrofuran (1 : 1). Evaporation of the dried ($MgSO_4$) solution gave a semi-solid (53·8 g.) (triol acids) (which did not react with 2,4-dinitrophenylhydrazine). This material was heated with potassium hydrogen sulphate (100 g.) at 260° for 30 min. in a stream of nitrogen. Water was added to the cooled mixture which was then extracted with ether. The dried ($MgSO_4$) extracts afforded a dark oil (43·3 g.) which was heated with selenium (10 g.) at 300° ± 10° for 5 hr. More selenium (20 g.) was added, and the heating was continued (360° ± 10°) for 20 hr. The material which distilled below 360°(bath)/8 mm. was treated with picric acid, affording 3-methylphenanthrene picrate (1 g.), m. p. 134—136° (from ethanol), undepressed in admixture with an authentic specimen,[12] m. p. 136—137°. The picrate, in benzene, was chromatographed on alumina, and the eluant, with 1,3,5-trinitrobenzene, gave the 3-*methylphenanthrene*–1,3,5-*trinitrobenzene complex*, m. p. 163—164°, undepressed on admixture with a specimen prepared from authentic 3-methylphenanthrene (Found: C, 61·9; H, 3·7; N, 10·2. $C_{21}H_{15}N_3O_6$ requires C, 62·2; H, 3·75; N, 10·35%).

Methyl 9-*Acetoxy*-$\Delta^{8a(a)}$-*dodecahydro*-1,10a-*dimethyl*-1,4-*dioxophenanthrene*-4a-*carboxylate* (XII; R^1 = Me, R^2 = H).—The adduct (X; R^1 = Me, R^2 = H) (1 g.) and zinc powder (5 g.) were added to acetic acid (170 ml.), and the mixture was stirred for 24 hr. and then filtered. The residue obtained on evaporation of the solvent crystallised from methanol to afford the *dodecahydro-derivative* (690 mg., 69%), m. p. 142—143°, $\lambda_{max.}$ 5·73 (enol OAc), 5·81sh (ester), 5·83, 5·90sh (C=O) [the double-bond (6·16 μ) and enedione (244 mμ) absorptions of the precursor were absent] (Found: C, 66·3; H, 7·35. $C_{20}H_{26}O_6$ requires C, 66·3; H, 7·25%).

Degradation of the Dodecahydro-derivative (XII; R^1 = Me, R^2 = H) *to* 2-*Methylanthracene*.—The dodecahydro-derivative was reduced in a manner similar to that used for the compound (XI). The sequence was: compound (28 g.) in methanol–tetrahydrofuran (600 ml.; 2 : 1) with potassium borohydride (4 g.) for 10 hr.; addition of 10% aqueous potassium hydroxide (100 ml.) and borohydride (5 g.), and the mixture left overnight; addition of borohydride (5 g.) and heating on the water-bath for 30 min., the volume of the mixture being reduced. Acidification with 4N-sulphuric acid and extraction with ether–tetrahydrofuran (1 : 1) afforded a semi-solid (triol acids) which was dehydrated and dehydrogenated, as above. The material (1·1 g.) that distilled from the dehydrogenation mixture above 360°(bath)/2 mm. partly solidified and, with picric acid, gave a crude picrate, m. p. 95—100°. Crystallisation from ethanol, however, gave 2-methylanthracene, m. p. and mixed m. p. 206—207°. Fischer[17] records m. p. 207° for the hydrocarbon and reports that its picrate is very unstable.

Dimethyl 9-*Acetoxy*-$\Delta^{2,8a(9)}$-*decahydro*-2,10a-*dimethyl*-1,4-*dioxophenanthrene*-3,4a-*dicarboxylate* (X; R^1 = Me, R^2 = CO_2Me).—A solution of 1-1′-acetoxyvinylcyclohexene (6·7 g.) and 2,6-dimethoxycarbonyl-3,5-dimethylbenzoquinone[5] (10 g.) in dry methanol (25 ml.) was heated under reflux for 15 hr. (a little quinol was added). The cooled solution deposited crystals (8·3 g.), m. p. 116—120°, which crystallised from methanol to give the *adduct* (7·0 g., 38%), m. p. 119—121° (rosettes), $\lambda_{max.}$ 244 mμ (ε 8700), 5·72sh (enol OAc), 5·74, 5·76sh (ester), 5·89, 5·94sh (enedione C=O), 6·13 μ (conj. C=C) (Found: C, 63·15; H, 6·3. $C_{22}H_{26}O_8$ requires C, 63·15; H, 6·25%). More of the adduct was recovered from the mother-liquors (total 43%). The adduct had two crystalline forms, rosettes, m. p. 119—121°, and needles, m. p. 104—107°, but some of the former were always formed when the latter recrystallised from methanol.

Attempted Reduction of Adduct (X; R^1 = Me, R^2 = CO_2Me).—The adduct (1 g.) and zinc powder (3 g.) in acetic acid (30 ml.) were stirred together for 2 hr. and the mixture was then filtered. The filtrate, on evaporation, afforded a solid (650 mg.), m. p. 128—132°, which crystallised from light petroleum (b. p. 100—120°) to give a *substance* (300 mg., 30%), m. p. 144—147°, $\lambda_{max.}$ 260 mμ (ε 5900), 5·70 (enol OAc), 5·74, 5·79 (ester?), 5·83, 6·08 (C=O), 6·20 μ (C=C) (Found: C, 62·4; H, 6·7. $C_{22}H_{28}O_8$ requires C, 62·85; H, 6·7%). This substance was clearly not the desired derivative (XII; R^1 = Me, R^2 = CO_2Me).

Dimethyl Δ^2-*Dodecahydro*-2,10a-*dimethyl*-1,4,9-*trioxophenanthrene*-3,4a-*dicarboxylate* (XIII).—The adduct (X; R^1 = Me, R^2 = CO_2Me) (10 g.) was dissolved in dry methanol (250 ml.), and dry hydrogen chloride was bubbled into the solution for 30 sec. The solution was left for 1 hr. and then evaporated at <40°/15 mm. to dryness. The residue crystallised from methanol to yield the *trioxo-compound* (XIII) (7·9 g., 88%), m. p. 137·5—138°, $\lambda_{max.}$ 246 mμ (ε 7950), 5·73sh, 5·74 (ester), 5·82, 5·90sh, 5·91 (C=O), 6·10 μ (C=C) (Found: C, 63·6; H, 6·35. $C_{20}H_{24}O_7$ requires C, 63·8; H, 6·45%).

When this triketone, or the parent adduct, was treated with boiling methanolic hydrogen chloride, a *substance*, m. p. 183—185°, was formed in variable yield; it had $\lambda_{max.}$ 260 mμ (ε 6600), 2·86 (OH), 5·71, 5·80sh (ester), 5·83, 5·99 (C=O), 6·14 μ (C=C), τ 8·71 (Me), 7·90 (vinyl Me), 6·26, 6·17 p.p.m. (two ester Me) (no vinyl proton signal) (Found: C, 64·0; H, 6·45. $C_{20}H_{24}O_7$ requires C, 63·8; H, 6·45%). This compound was possibly compound (XIV).

Degradation of Triketone (XIII) *to* 1,2-*Dimethylphenanthrene*.—The triketone (XIII) (23·5 g.) in ethanol (500 ml.) was hydrogenated at 85 lb./sq. in. over Raney nickel for 6 hr. Potassium borohydride (16 g.) was added to the resultant solution which was then left for 4 hr. More borohydride (11 g.) was added and the mixture was heated under reflux for 15 hr. Potassium hydroxide (200 g.) in water (200 ml.), and potassium borohydride (11 g.), were added, and the mixture was heated for a further 24 hr., after which the solvent was removed. The residue was acidified with 4N-sulphuric acid and extracted with ether–tetrahydrofuran (1 : 1). The dried ($MgSO_4$) extracts afforded a semi-solid which was dehydrated and dehydrogenated as in the degradation of the derivative (XI). The material that distilled from the dehydrogenation mixture above 360°(bath)/1 mm. afforded the 1,2-*dimethylphenanthrene*–1,3,5-*trinitrobenzene complex*, m. p. 176—178° (orange needles from ethanol), $\lambda_{max.}$ 219, 253 mμ (consistent with a phenanthrene rather than an anthracene complex) (Found: C, 63·6; H, 4·15; N, 9·9. $C_{22}H_{17}N_3O_6$ requires C, 63·0; H, 4·1; N, 10·0%). The complex was dissolved in the minimum volume of benzene, and was put on to a column of alumina; the eluant [light petroleum (b. p. 40—60°)] afforded a picrate, m. p. 153—154°, undepressed in admixture with an authentic specimen of 1,2-dimethylphenanthrene picrate (lit.,[18,19] 153—154°).

Methanolysis of Methyl 9-*Acetoxy*-$\Delta^{2,8a(9)}$-*decahydro*-2(or 3)-*methoxy*-10a(or 4a)-*methyl*-1,4-*dioxophenanthrene*-4a(or 10a)-*carboxylate*.—The adduct[1] (5 g.) was dissolved in dry methanol (70 ml.), and dry hydrogen chloride was bubbled into the solution for 30 sec. The solution was heated under reflux for 30 min. and then evaporated to dryness. The residue (3·5 g.), m. p. 159—190°, was fractionally crystallised from methanol to give three substances: *A* (800 mg., 18%), m. p. 172—173°, $\lambda_{max.}$ 272 mμ (ε 10,000), 5·73 (ester), 5·87, 6·08 (C=O), 6·21 μ (C=C) (Found: C, 64·45; H, 6·65. Calc. for $C_{18}H_{22}O_6$: C, 64·65; H, 6·65%); *B* (1·6 g., 36%),

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[17] Fischer, *J. prakt. Chem.*, 1909, **79**, 555.

[18] Haworth, Mavin, and Sheldrick, *J.*, 1934, 454.

[19] Turner, *J. Amer. Chem. Soc.*, 1957, **79**, 2271.

m. p. 196—198°, $\lambda_{max.}$ 269 mμ (ε 4700); 3·03br (OH), 5·79 (ester), 5·90, 6·03 (C=O), 6·12 μ (C=C) (Found: C, 64·5; H, 6·65%); *C* (600 mg., 14%), m. p. 208—209°, $\lambda_{max.}$ 212, 279 mμ (ε 4100 and 8500), 5·78 (ester), 5·84, 6·00 (C=O), 6·17 μ (C=C) (Found: C, 64·85; H, 6·65%).

The major product *B* (7·3 g.) was treated with potassium borohydride, potassium hydrogen sulphate, and then selenium in the manner used for the degradation of the hydro-derivative (XII). The dehydrogenation mixture was extracted with hot ethanol, and the extracts afforded, on removal of the solvent and evaporative distillation of the residue, an oil which afforded the phenanthrene–1,3,5-trinitrobenzene complex, m. p. 162—165°, undepressed in admixture with an authentic specimen but depressed in admixture with the anthracene–1,3,5-trinitrobenzene complex. The anthracene and the phenanthrene complex both have m. p. 164°.

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QUEEN MARY COLLEGE (UNIVERSITY OF LONDON),
MILE END ROAD, LONDON, E.1.

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