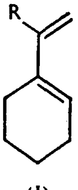
869. *Reduced Cyclic Compounds. Part II.* The Synthesis of 1-1'-Acetoxyvinyl*cyclo*hexene and its Reactions with Some Dienophils.*†

By M. F. Ansell and G. T. Brooks.

The preparation of 1-1'-acetoxyvinyl*cyclo*hexene and its conversion into 4-acetoxy-Δ^4-octahydronaphthalene-1 : 2-dicarboxylic anhydride, and the phenanthrene derivatives (VIII; R = OAc) and (XI), and related compounds are described.

The use of the Diels–Alder reaction in the synthesis of reduced cyclic systems related to the steroids has been extensively studied,[1] and it has been shown [2] that by the use of an alkoxybutadiene, *e.g.*, 3-methoxybuta-1 : 3-diene, it is possible to prepare cyclic compounds containing a potential carbonyl group. Robinson and Acheson,[3] and Newman and McPherson,[4] have pointed out that by the use of a suitable oxygenated diene the Diels–Alder reaction might be used as a route to 11-keto-steroids. A suitable model compound for such an investigation is a 1'-acyloxy- (I; R = R·CO·O) or 1'-alkoxy-derivative (I; R = R'O) of 1-vinyl*cyclo*hexene. At the commencement of this work no compound of this type was known, although the use of 1-vinyl*cyclo*hexene in the Diels–Alder reaction had been investigated.[5,6] Later, however, Favorskaya and Fedorova [7] reported the preparation of 1-1'-methoxyvinyl- (I; R = OMe) and 1-1'-ethoxyvinyl-*cyclo*hexene (I; R = OEt) by the pyrolysis of the corresponding ketals of 1-acetyl*cyclo*hexene, and described the Diels–Alder reaction of the former with 2 : 5-xyloquinone and hydrolysis of the product (the structure of which was not determined) to a tricyclic triketone. Nazarov [8] has described the preparation of 1-1'-acetoxyvinyl*cyclo*hexene (I; R = OAc) (in 37% yield) by the addition of acetic acid to 1-ethynyl*cyclo*hexene. We have found that this compound is conveniently prepared (in 84% yield) by the action of *iso*propenyl acetate on 1-acetyl*cyclo*hexene in the presence of toluene-*p*-sulphonic acid. The structure of our product was confirmed by its ultraviolet absorption which has a maximum at 232 mμ identical with the value calculated from Woodward's rules [9] and at variance with the value 242 mμ calculated for the alternative structure (II). That enolisation occurs towards the methyl group in the presence of *iso*propenyl acetate has been previously observed by Hagemeyer and Hull [10] and is exemplified by the formation [11] of $\Delta^{16:20}$-enol acetates from Δ^{16}-20-keto-steroids.



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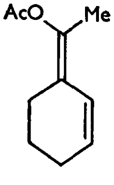

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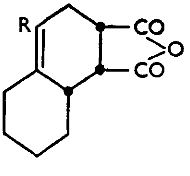

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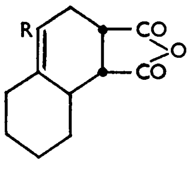

(IV)

The reaction of the acetoxy-diene (I; R = OAc) with maleic anhydride yielded 4-acetoxy-Δ^4-octahydronaphthalene-1 : 2-dicarboxylic anhydride (III; R = OAc) (m. p. 84—86°). Catalytic dehydrogenation was unsuccessful, but dehydrogenation by the

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* Part I, *J.*, 1956, 1238.

† Preliminary communication, *Chem. and Ind.*, 1955, 916.

[1] For reviews see : Norton, *Chem. Rev.*, 1942, **31**, 319; Butz, "Organic Reactions," Vol. V, p. 136.

[2] Sarett, Lukes, Poos, Robinson, Beyler, Vandegrift, and Arth, *J. Amer. Chem. Soc.*, 1952, **74**, 1393.

[3] Robinson and Acheson, *J.*, 1952, 1128.

[4] Newman and McPherson, *J. Org. Chem.*, 1954, **19**, 1717.

[5] Cook and Lawrence, *J.*, 1938, 58.

[6] Robins and Walker, *J.*, 1952, 642, 1610.

[7] Favorskaya and Fedorova, *Z. obshchei Khim.*, 1954, **24**, 242; 1955, **25**, 1477.

[8] Nazarov, Kucherov, Andreyev, and Segal, *Doklady Akad. Nauk S.S.S.R.*, 1955, **104**, 729.

[9] Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72.

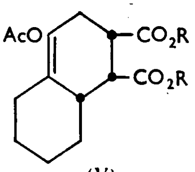
[10] Hagemeyer and Hull, *Ind. Eng. Chem.*, 1949, **41**, 2920.

[11] Moffett and Weisblat, *J. Amer. Chem. Soc.*, 1952, **74**, 2183.

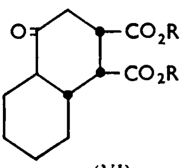
exhaustive bromination method [12] gave 4-acetoxynaphthalene-1 : 2-dicarboxylic anhydride which has an ultraviolet absorption spectrum almost identical with that of naphthalene-1 : 2-dicarboxylic anhydride.

On the basis of Alder and Stein's rules [13] and the mild conditions under which it was prepared we consider that the anydride (III; R = OAc) has the *syn-cis*-configuration shown.* Under more drastic conditions (eight hours in boiling benzene) Nazarov [8] obtained a liquid product to which he assigns the *anti-cis*-structure (IV; R = OAc). In support of the above assignments of configuration it is relevant that similar results have been obtained in the reaction between 1-vinyl*cyclo*hexene and maleic anhydride. Thus, whereas Cook and Lawrence [5] reported the formation of only the solid *syn-cis*-anhydride (III; R = H) when the reaction occurred in a small amount of solvent at room temperature, Nazarov *et al.*[15] found that allowing the exothermic reaction to proceed in the absence of a solvent gave a liquid product together with the crystalline product. Even when the reaction was allowed to proceed at 2—3° for a long period in benzene solution the *syn-cis*-product (55% yield) was accompanied by a liquid containing the *anti-cis*-anhydride (? liquid) (III; R = H). The latter is also formed when the *syn-cis*-anhydride is heated. Thus mild conditions favour the formation of the *syn-cis*-anhydride (III; R = H).

Treatment of the acetoxy-anhydride (III; R = AcO) with 2 : 4-dinitrophenylhydrazine in acidic ethanol gave the 2 : 4-dinitrophenylhydrazone of a half ester of decahydro-4-oxonaphthalene-1 : 2-dicarboxylic acid (VI; R = H), thus establishing the presence of the potential carbonyl group in the original adduct. Hydrolysis of the acetoxy-anhydride (III; R = OAc) with boiling water gave the acid (V; R = H), the melting point of which depended on the rate of heating, perhaps owing to anhydride formation or lactonisation :



(V)



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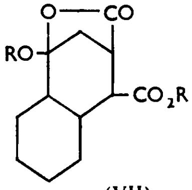

(VII)

on treatment with diazomethane it yielded the sharply melting methyl ester (V; R = Me). Acid or alkaline hydrolysis of the acetoxy-acid (V; R = H) or -anhydride (III; R = AcO) gave decahydro-4-oxonaphthalene-1 : 2-dicarboxylic acid (VI; R = H), whose melting point is variable owing to hydration. Its infrared absorption has an asymmetric maximum at 1703 cm.$^{-1}$ (C=O stretching region), which together with the absence of absorption in the lactonic-carbonyl region (1740—1800 cm.$^{-1}$) indicates that it does not exist in a lactonic form, *e.g.*, (VII; R = H). With diazomethane it gave the sharply melting methyl ester (VI; R = Me) and not the *pseudo*-ester (VII; R = Me), as is shown by its infrared absorption spectrum in which the maxima due to the methoxy-carbonyl and the keto-carbonyl group are just resolved (1730 and 1705 cm.$^{-1}$). The same ester (VI; R = Me), together with a half ester, was also obtained directly from the acetoxy-anhydride (III; R = OAc) by treatment with methanol in the presence of sulphuric acid. This keto-ester readily formed a 2 : 4-dinitrophenylhydrazone. The same compound was also formed, although more slowly, from the acetoxy-ester (V; R = Me).

Conversion of the acetoxy-anhydride (III; R = OAc) into the keto-acid (VI; R = H) or the keto-ester (VI; R = Me) introduces a new centre of asymmetry. If this occurs to give the more stable *trans*-ring junction, as in α-decalone, and no isomerisation occurs at the

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* The dots indicate that hydrogen atoms so denoted are on the side of the carbon skeleton nearer to the reader.[14]

[12] Alder and Schmitz, *Annalen*, 1949, **565**, 123.

[13] Alder and Stein, *Angew. Chem.*, 1937, **50**, 510.

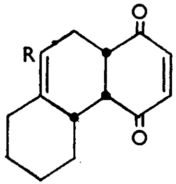
[14] Linstead, *Chem. and Ind.*, 1937, **56**, 510; Linstead and Walpole, *J.*, 1939, 842.

[15] Nazarov, Kucherov, and Andreyev, *Doklady Akad. Nauk S.S.S.R.*, 1955, **102**, 751.

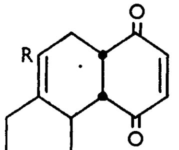
other centres of asymmetry, then the configurations of these compounds are those indicated. Throughout this series of related compounds no evidence was obtained of stereochemical inhomogeneity.

The acetoxy-diene (I; R = AcO) reacted with benzoquinone, in benzene under mild conditions, to give 9-acetoxy-$\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene (VIII; R = AcO), whose ultraviolet absorption spectrum resembled that of $\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene,[6] and, like the latter, it is sensitive to alkali. Its structure was confirmed by reduction with lithium aluminium hydride (two treatments were necessary [16]) followed by dehydration, and dehydrogenation, to yield phenanthrene.

Application of Alder and Stein's rules to the configuration of this compound (VIII; R = AcO) suggests, in view of the mild conditions under which it is formed, that it has the *syn-cis*-configuration as indicated, comparable with that of the adduct (VIII; R = H) obtained from 1-vinyl*cyclo*hexene and benzoquinone.[6] It is not certain whether these rules are applicable to the adduct (VIII; R = AcO) as in some slow diene reactions of this type the *cis*-compound initially formed may undergo easy stereoisomerisation.[17] Moreover, Nazarov [8] has prepared by the same route, but under more drastic conditions (boiling benzene for 7 hr.), an adduct to which he assigns the *anti-cis*-configuration (IX). On the basis of its melting point, however, this compound appears to be identical with ours.



(VIII)



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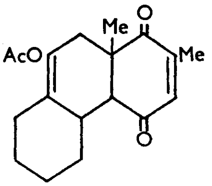

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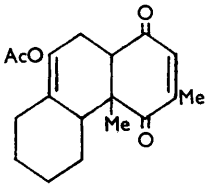

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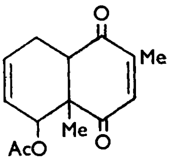

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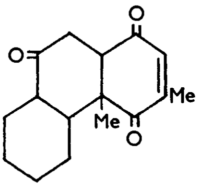

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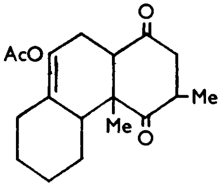

(XIV)

The reaction between 2 : 6-xyloquinone and 1-1′-acetoxyvinyl*cyclo*hexene yielded a homogeneous product which was shown, by degradation to 3-methylphenanthrene, to be 9-acetoxy-$\Delta^{2:9(14)}$-decahydro-3 : 12-dimethyl-1 : 4-dioxophenanthrene (XI) and not the 2 : 11-dimethyl compound (X). An authentic sample of 3-methylphenanthrene was synthesised by a Bogert–Cook synthesis: 4-methyl-1-phenethyl*cyclo*hexanol, from phenethylmagnesium bromide and 4-methyl*cyclo*hexanone, was cyclised with 85% sulphuric acid to 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-3-methylphenanthrene which was then dehydrogenated with selenium. In view of the foregoing discussion and the conditions of formation of the adduct (XI) (21 hours in boiling ethanol or benzene), the use of Alder and Stein's rules to predict the stereochemistry of the product may not be justified. Its ultraviolet spectrum (*cyclo*hexane) shows a general similarity to that of 9-acetoxy-$\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene with a bathochromic shift of the main maximum to 240 mμ (log ε 4·07). This is in good agreement with main maximum (242 mμ; log ε 4·05) (in *cyclo*hexane) recorded by Stein [18] for 5-acetoxy-$\Delta^{2:6}$-hexahydro-2 : 10-dimethyl-1 : 4-dioxonaphthalene (XII), an ene-dione of the same substitution type. Hydrolysis of the adduct (XI) with aqueous-methanolic sulphuric acid gave Δ^{2}-dodecahydro-3 : 12-dimethyl-1 : 4 : 9-trioxophenanthrene (XIII). The ultraviolet absorption spectrum of the

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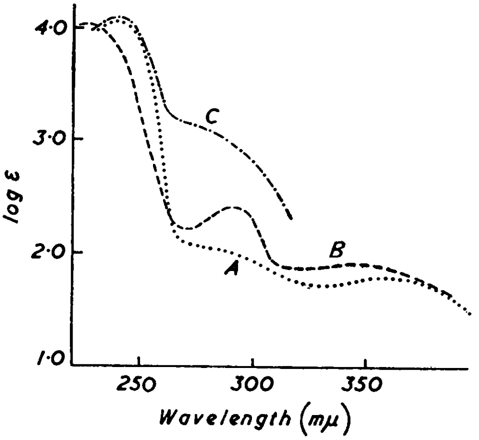
[16] Cf. Dauben and Eastham, *J. Amer. Chem. Soc.*, 1953, **75**, 1718.
[17] Lukes, Poos, and Sarett, *ibid.*, 1952, **74**, 1402.
[18] Stein and Casini, *Gazzetta*, 1955, **85**, 1411.

latter has a single maximum at 241 mμ corresponding to the ene-dione system; the presence of the isolated carbonyl group is indicated by an increase in the intensity of the shoulder in the spectrum to log ε 3·16 (270 mμ) from that of log ε 2·07 (274—275 mμ) in the parent adduct (XI) (see diagram). Reduction of the adduct (XI) with zinc dust in glacial acetic acid at room temperature saturated the conjugated double bond, to yield 9-acetoxy-$\Delta^{9(14)}$-dodecahydro-3 : 12-dimethyl-1 : 4-dioxophenanthrene (XIV).



Absorption spectra of (A) compound (XI) (*in* cyclohexane), (*B*) *compound* (VIII; R = OAc) (*in ethanol*), *and* (*C*) *compound* (XIII) (*in* cyclohexane).

EXPERIMENTAL

1-1′-*Acetoxyvinyl*cyclo*hexene*.—1-Acetyl*cyclo*hexene[19] (62 g.) was added during 15 min. to a boiling mixture of *iso*propenyl acetate (1050 c.c.) and toluene-*p*-sulphonic acid (9·5 g.). The mixture was slowly distilled through a 36″ column packed with Dixon gauzes. After 4½ hr. the theoretical quantity of acetone had been removed and the temperature slowly rose to 97°. Slow distillation was continued for 36 hr. and 650 c.c. of distillate were collected. After cooling, the dark residue was diluted with an equal volume of ether, washed with 10% sodium hydrogen carbonate solution, then with water, and dried (Na_2SO_4). Volatile material, b. p. <40°/15 mm., was removed and the residue distilled from quinol (1·5 g.), to yield after a small fore-run 1-1′-acetoxyvinyl*cyclo*hexene (69·5 g., 83·7%) b. p. 66—71°/1 mm., n_D^{20} 1·4980. A redistilled sample had b. p. 66°/0·7 mm., n_D^{20} 1·4990 (Found: C, 72·0; H, 8·5. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·5%). Nazarov[8] records b. p. 99—100°/10 mm., n_D^{20} 1·4972. This material became viscous on exposure to air and was stored in sealed bottles over quinol. On treatment with 2 : 4-dinitrophenylhydrazine sulphate in alcohol it slowly yielded 1-acetyl*cyclo*hexene 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 199—200°.

4-*Acetoxy*-Δ^4-*octahydronaphthalene*-1 : 2-*dicarboxylic Anhydride*.—A warm solution of redistilled maleic anhydride (2·8 g., 0·029 mole) in dry thiophen-free benzene (30 c.c.) was added to a solution of 1-1′-acetoxyvinyl*cyclo*hexene (5 g., 0·03 mole) in the same solvent (30 c.c.). The mixture developed a transient yellow colour. After 3 days at room temperature the mixture was heated under reflux for 1 hr. Removal of the solvent under reduced pressure left a viscous liquid that solidified on shaking. After being washed with a little ether the crude 4-*acetoxy*-Δ^4-*octahydronaphthalene*-1 : 2-*dicarboxylic anhydride* (6 g., 80%), m. p. 80—85°, was recrystallised twice from ether to give the pure compound (5 g., 67%) as prisms, m. p. 84—86° (Found: C, 63·5; H, 6·2. $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1%). It was unsaturated towards bromine in carbon tetrachloride and neutralised three equivs. of sodium hydroxide on hydrolysis. Treatment with an alcoholic sulphuric acid solution of 2 : 4-dinitrophenylhydrazine gave *ethyl hydrogen* 4-*oxodecahydronaphthalene*-1 : 2-*dicarboxylate* 2 : 4-*dinitrophenylhydrazone*, orange-yellow plates (from alcohol), m. p. 126° (decomp. with resolidification) (Found: C, 53·0; H, 5·8; N, 12·6. $C_{20}H_{24}O_8N_4$ requires C, 53·6; H, 5·4; N, 12·5%).

Neutral Hydrolysis of 4-*Acetoxy*-Δ^4-*octahydronaphthalene*-1 : 2-*dicarboxylic Anhydride*.—The above anhydride (0·5 g.) was boiled with water until dissolved and for a further 30 min. The filtered solution, on cooling, deposited 4-*acetoxy*-Δ^4-*octahydronaphthalene*-1 : 2-*dicarboxylic acid*

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[19] Royals and Henry, *J. Org. Chem.*, 1950, **15**, 1147.

(0·5 g.) as needles, m. p. 190—202° (Found : C, 60·1; H, 6·9. $C_{14}H_{18}O_6$ requires C, 59·6; H, 6·4%). Recrystallisation from water or acetone–light petroleum mixtures did not improve the m. p. which depended on heating conditions and the initial bath-temperature. The acid neutralised three equivs. of sodium hydroxide on hydrolysis. Treatment of the acid with diazomethane in chloroform gave the *dimethyl ester*, m. p. 98—98·5° after recrystallisation from light petroleum (b. p. 40—60°) or methanol (Found : C, 61·8; H, 7·3. $C_{16}H_{22}O_6$ requires C, 61·9; H, 7·2%). This ester with a warm aqueous-methanolic hydrochloric acid solution of 2 : 4-dinitrophenylhydrazine slowly gave the *dimethyl decahydro-*4*-oxonaphthalene-*1 : 2*-dicarboxylate* 2 : 4*-dinitrophenylhydrazone*, golden-yellow plates (from methyl acetate), m. p. 222·5—223·5° (Found : C, 54·0; H, 5·6; N, 12·9. $C_{20}H_{24}O_8N_4$ requires C, 53·6; H, 5·4; N, 12·5%).

Acidic and Alkaline Hydrolysis of 4*-Acetoxy-*Δ^4*-octahydronaphthalene-*1 : 2*-dicarboxylic Anhydride. Decahydro-*4*-oxonaphthalene-*1 : 2*-dicarboxylic Acid.*—The above anhydride (0·4 g.) was heated under reflux with aqueous 0·1N-sodium hydroxide (20 c.c.) for 15 min. The solution was then concentrated to half its bulk under reduced pressure and acidified, to yield the *keto-acid* (0·3 g.). On slow heating, melting (at 157°) was attended by resolidification and final melting at *ca.* 200° (Found : C, 55·9; H, 7·6. $C_{12}H_{16}O_5,H_2O$ requires C, 55·8; H, 7·0%). Recrystallisation from acetone–light petroleum (b. p. 60—80°) followed by prolonged drying (P_2O_5) gave a product, m. p. 191—195° (rapid heating from room temperature) (Found : C, 57·7; H, 7·1. $C_{12}H_{16}O_5$ requires C, 60·0; H, 6·7%). The infrared spectrum had an asymmetric maximum (KBr plate) at 1703 cm.$^{-1}$.

The same product (0·27 g.) was obtained by heating the anhydride (0·4 g.) or 4-acetoxy-Δ^4-octahydronaphthalene-1 : 2-dicarboxylic acid with 0·2N-sulphuric acid (25 c.c.) for 2 hr. All samples, with diazomethane, gave a *dimethyl ester*, m. p. 74—75° (Found : C, 62·9; H, 7·7. $C_{14}H_{20}O_5$ requires C, 62·7; H, 7·5%), whose infrared spectrum had peaks (in CS_2) at 1206, 1705, and 1730 cm.$^{-1}$ (double peak). This ester rapidly gave the 2 : 4-dinitrophenylhydrazone of decahydrodimethyl-4-oxonaphthalene-1 : 2-dicarboxylate (m. p. and mixed m. p. 222·5—223·5°) under conditions described above.

Alcoholysis of 4*-Acetoxy-*Δ^4*-octahydronaphthalene-*1 : 2*-dicarboxylic Anhydride.*—The above anhydride (6·5 g.) was heated in methanol (125 c.c.) and concentrated sulphuric acid (5 g.) for 42 hr. After removal of half the solvent the residue was diluted with an equal volume of ether, washed with 10% sodium hydrogen carbonate solution, then with water, and dried ($MgSO_4$). Removal of the ether left dimethyl decahydro-4-oxonaphthalene-1 : 2-dicarboxylate (3·9 g.), m. p. 73°. Recrystallisation from light petroleum (b. p. 60—80°) gave the pure diester, m. p. 74—75°. The above alkaline extract was made acid and extracted with ether, and the ethereal extract washed with water and dried ($MgSO_4$). Removal of the ether left *methyl hydrogen decahydro-*4*-oxonaphthalene-*1 : 2*-dicarboxylic acid* (2·8 g.), m. p. 137—143°. Recrystallisation from benzene gave needles, m. p. 145—146° (Found : C, 61·6; H, 7·3. $C_{13}H_{18}O_5$ requires C, 61·4; H, 7·2%). It was converted into the diester (m. p. and mixed m. p. 72—73°) by diazomethane in chloroform.

Dehydrogenation of 4*-Acetoxy-*Δ^4*-octahydronaphthalene-*1 : 2*-dicarboxylic Anhydride.*—Bromine (7·3 g.) in glacial acetic acid (16 c.c.) was added during 3 hr. to a solution of the above anhydride (3 g.) dissolved in acetic acid (7 c.c.) at 115°. This temperature was maintained for a further 19 hr., the solution then evaporated under reduced pressure, and the residue heated at 200—220° until evolution of hydrogen bromide ceased (20 hr.). The residue was boiled with acetic anhydride for 3 hr. After removal of the solvent under reduced pressure, 1·4 g. of yellow solid was sublimed from the residue (bath-temp. 160—200°/0·1 mm.). Recrystallisation from benzene gave 4*-acetoxynaphthalene-*1 : 2*-dicarboxylic anhydride*, m. p. 184—186°, pale-buff needles (Found : C, 64·9; H, 3·0. $C_{14}H_8O_5$ requires C, 65·6; H, 3·15%). Treatment of the anhydride with methanol gave a *half-ester*, m. p. 137—138°, needles from benzene (Found : C, 62·4; H, 4·2. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%). Ultraviolet spectra are tabulated.

Naphthalene-1 : 2-dicarboxylic anhydride				4-Acetoxynaphthalene-1 : 2-dicarboxylic anhydride			
mμ	log ε	mμ	log ε	mμ	log ε	mμ	log ε
256	4·74	344	3·54	258	4·67	345	3·61
308	3·59	354	3·45	309	3·58	355	3·56
322	3·56	360	3·50	324	3·67	362	3·59

9*-Acetoxy-*$\Delta^{2:9(14)}$*-decahydro-*1 : 4*-dioxophenanthrene.*—A solution of benzoquinone (2·2 g.) in dry thiophen-free benzene (20 c.c.) was added to a solution of 1-1′-acetoxyvinyl*cyclo*hexene (5 g.) in the same solvent (20 c.c.) containing a few crystals of quinol. The mixture rapidly darkened and after 4 days at room temperature a small amount of precipitate was filtered off. After a further 2 days at room temperature the mixture was heated under reflux for 1 hr. and then evaporated under reduced pressure (15 min.). Addition of light petroleum (b. p. 60—80°) to the partially solid residue completed precipitation of the solid which was filtered off and washed with a little ether, to give 9-*acetoxy*-$\Delta^{2:9(14)}$-*decahydro*-1 : 4-*dioxophenanthrene* (3·2 g.), m. p. 110—118°. Recrystallisation from ether gave pale yellow prisms, m. p. 118—120° (rapid heating). On slow heating it melted at 115—120°, resolidified at a higher temperature, and finally melted at 224° (Nazarov[8] records m. p. 120—121°) (Found: C, 69·9; H, 6·7. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·6%), absorption max. in EtOH at 226, 280, 345 mμ (log ε 4·02, 2·38, 1·90). With acid or alkali it gave dark solutions, and with 2 : 4-dinitrophenylhydrazine (see above) a yellow precipitate which rapidly changed to an amorphous dark red powder.

Degradation of 9-*Acetoxy*-$\Delta^{2:9(14)}$-*decahydro*-1 : 4-*dioxophenanthrene*.—This compound (2·9 g.) was added *via* a Soxhlet extraction apparatus (8 hr. required) to a boiling suspension of lithium aluminium hydride (3 g.) in dry ether (180 c.c.). After cooling, water (30 c.c.) was added followed by ice-cold 10% sulphuric acid (50 c.c.). The aqueous layer was continuously extracted with ether for 24 hr. Evaporation of the dried (K_2CO_3) combined ether extracts left a solid (2·0 g.) containing ketonic material (formed a 2 : 4-dinitrophenylhydrazone). The above procedure was repeatèd with 1·5 g. of lithium aluminium hydride, and the resulting non-ketonic material dehydrated at 180° for 45 min. in a stream of nitrogen with powdered fused potassium hydrogen sulphate (3 g.). After addition of water the product was extracted with ether and dried (K_2CO_3). The ether was replaced by toluene and the solution heated under reflux with sodium. After cooling and filtering, the solvent was removed, and the residue (1·2 g.) boiled with diphenylamine (6 g.) and 5% palladium–charcoal (1·5 g.) in nitrogen for 16 hr., more catalyst (1·0 g.) being added after 8 hr. The cooled mixture was diluted with ether and filtered, and the diphenylamine precipitated with dry hydrogen chloride. The residue obtained on removal of the ether was chromatographed in light petroleum (b. p. 60—80°) on alumina (Peter Spence type " H "). The eluted phenanthrene (0·6 g.), after two recrystallisations from alcohol and sublimation, had m. p. and mixed m. p. 95—96°. The derived picrate had m. p. and mixed m. p. 143—146°.

9-*Acetoxy*-$\Delta^{2:9(14)}$-*decahydro*-3 : 12-*dimethyl*-1 : 4-*dioxophenanthrene*.—A solution of 1-1'-acetoxyvinyl*cyclo*hexene (16·6 g.), 2 : 6-xyloquinone (12·0 g.), and quinol (0·4 g.) in absolute alcohol (130 c.c.) was heated under reflux for 21 hr., then cooled and filtered. Evaporation under reduced pressure (15 mm.) gave 9-*acetoxy*-$\Delta^{2:9(14)}$-*decahydro*-3 : 12-*dimethyl*-1 : 4-*dioxophenanthrene* (13·1 g.), m. p. 108—111° after washing with light petroleum (b. p. 40—60°) and a little ether. Recrystallisation from light petroleum (b. p. 60—80°) raised the m. p. to 112—113° (Found: C, 71·7; H, 7·4. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3%). Ultraviolet absorption maxima (in *cyclo*hexane) were at 240, 274, and 355 mμ (log ε 4·07, 2·07, and 1·79). Extension of the reaction time did not increase the yield. The use of benzene as a solvent reduced the yield.

Degradation of 9-*Acetoxy*-$\Delta^{2:9(14)}$-*decahydro*-3 : 12-*dimethyl*-1 : 4-*dioxophenanthrene*.—This compound (7·8 g.) was reduced and dehydrated as was 9-acetoxy-$\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene. The product (6·0 g.) (a solid sparingly soluble in ether), however, was filtered off. It (4·6 g.) was dehydrogenated by selenium (13 g.) at 350° for 24 hr. The cold residue was extracted with benzene, filtered, and after replacement of the solvent by xylene, heated under reflux with sodium for 45 min., then cooled and filtered. The residue left on removal of the solvent was split by distillation into several arbitrary fractions, b. p. 100—120°/10^{-3} mm., some of which solidified. The solid had m. p. 56—59°, undepressed on admixture with 3-methylphenanthrene, m. p. 61—62°. The whole distillate on treatment with picric acid in benzene gave 3-methylphenanthrene picrate, m. p. 136—137·5° (from alcohol) raised to 137—138·5° on admixture with an authentic specimen (m. p. 138—139·5°).

4-*Methyl*-1-*phenethyl*cyclo*hexan*-1-*ol*.—4-Methyl*cyclo*hexanone (35·9 g.) was added slowly to an ice-cooled solution of the Grignard reagent from phenethyl bromide (54 g.) and magnesium (9·6 g.) in ether (200 c.c.). The mixture was heated under reflux for 3 min., left overnight for 24 hr., and poured on ice and ammonium chloride. The aqueous layer was extracted with ether. Distillation of the dried ($MgSO_4$) combined extracts gave 4-*methyl*-1-*phenethyl*cyclo*hexan*-1-*ol* (34·1 g.), b. p. 104—110°/0·15 mm., n_D^{20} 1·5200—1·5250. A redistilled sample had b. p. 113°/0·1 mm., n_D^{20} 1·5254 (Found: C, 82·7; H, 10·2. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). Bergs *et al.*[21] record b. p. 179°/22 mm. but no analysis.

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-3-*methylphenanthrene*.—The above alcohol (17·1 g.)

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[20] Hirshberg and Jones, *Canad. J. Res.*, 1949, **27**, *B*, 437.
[21] Bergs, Wittfield, and Wildt, *Ber.*, 1934, **67**, 238.

was added slowly with stirring to ice-cold 85% sulphuric acid (36 c.c.). After 15 minutes' stirring at room temperature the mixture was extracted with light petroleum (b. p. 60—80°), and the extract washed with cold 85% sulphuric acid, 10% sodium carbonate solution, and 10% sodium sulphate solution, and dried (K_2CO_3). After removal of the solvent the residue was distilled from sodium, to yield 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-3-*methylphenanthrene* (13·0 g.), b. p. 86°/0·1 mm., n_D^{12} 1·5406 (Found : C, 90·6; H, 9·6. $C_{15}H_{20}$ requires C, 89·9; H, 10·0%).

3-*Methylphenanthrene*.—A mixture of the above octahydromethylphenanthrene (7·4 g.) and selenium (17·4 g.) was heated at 320° for 15 hr. On cooling, the mixture solidified and was extracted with benzene. The filtered solution was concentrated and treated with excess of a benzene solution of picric acid. The picrate formed was filtered off and decomposed by adsorption, from benzene solution, on a column of alumina to yield, by elution with light petroleum (b. p. 40—60°), 3-methylphenanthrene (4·5 g.), m. p. 61·5—62·5° (from aqueous alcohol) (picrate, m. p. 138—139·5). Haworth [22] records m. p. 62—63° and a picrate, m. p. 137—138°.

Δ^2-*Dodecahydro*-3 : 12-*dimethyl*-1 : 4 : 9-*trioxophenanthrene*.—A solution of 9-acetoxy-$\Delta^{2:9(14)}$-dodecahydro-3 : 12-dimethyl-1 : 4-dioxophenanthrene (1 g.) in methanol (125 c.c.), concentrated sulphuric acid (0·5 c.c.), and water (40 c.c.) was boiled for 4 hr. After removal of the methanol, by distillation, the solution was extracted with ether, and the extract washed with sodium hydrogen carbonate solution, then with saturated sodium chloride solution, and dried (K_2CO_3). Evaporation yielded Δ^2-*dodecahydro*-3 : 12-*dimethyl*-1 : 4 : 9-*trioxophenanthrene* (0·6 g.) as a lemon-yellow solid, m. p. 154—159° [from light petroleum (b. p. 60—80°)] (Found : C, 73·7; H, 7·7. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%), absorption max. in *cyclo*hexane at 241, infl. at 270 mμ (log ε 4·08 and 3·16 respectively).

9-*Acetoxy*-$\Delta^{9(14)}$-*dodecahydro*-3 : 12-*dimethyl*-1 : 4-*dioxophenanthrene*.—Zinc powder (1 g.) was added, at room temperature, to a stirred solution of 9-acetoxy-$\Delta^{2:9(14)}$-decahydro-3 : 12-dimethyl-1 : 4-dioxophenanthrene (1 g.) in glacial acetic acid (50 c.c.). After 10 min. the solution was filtered, and the filtrate evaporated under reduced pressure. 9-*Acetoxy*-$\Delta^{9(14)}$-*dodecahydro*-3 : 12-*dimethyl*-1 : 4-*dioxophenanthrene* (0·6 g.), m. p. 131—135°, was extracted from the residue with hot light petroleum (b. p. 100—120°). Crystallisation from methanol raised the m. p. to 136—137° (Found : C, 71·0; H, 8·2. $C_{18}H_{24}O_4$ requires C, 71·0; H, 8·0%).

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[22] Haworth, *J.*, 1932, 1125.