Synthesis of Polycyclic Compounds. Part VIII.[1] Friedel–Crafts Acylation with Anhydrides of Tricarboxylic Acids. Synthesis of 16,17-Dihydro-17-methyl-15*H*-cyclopenta[*a*]phenanthrene

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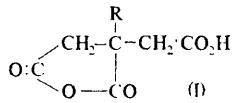
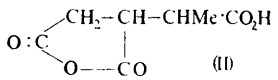
The acylation of naphthalene, 1- and 2-methylnaphthalenes, and 1,2,3,4-tetrahydronaphthalenes with propane-1,2,3-tricarboxylic acid 1,2-anhydride and its 2-methyl derivative is described. 1,2,3,4-Tetrahydro-oxophenanthreneacetic acids have been prepared in good yields by this method. The structures of the intermediates were established by independent syntheses. The keto-acid formed by acylation of naphthalene with 3-methylbutane-1,2,4-tricarboxylic acid 1,2-anhydride has been utilised for a new and improved route to 16,17-dihydro-17-methyl-15*H*-cyclopenta[*a*]phenanthrene (Diels hydrocarbon). The keto-acid from naphthalene and 2-methylpropane-1,2,3-tricarboxylic acid 1,2-anhydride was converted into racemic oestra-1,3,5(10),6,8-pentaen-17-one [*trans*-(±)-3-deoxyequilenin] by known methods.

The Friedel–Crafts succinoylation of aromatic hydrocarbons and phenol ethers and their derivatives has been used for the synthesis of polynuclear compounds.[2-5] However, work hitherto has been restricted to the anhydrides of dibasic acids,[2,3] unsaturated tricarboxylic acids,[3] and the polymeric anhydrides of higher dicarboxylic acids.[2,3] A systematic study of the anhydrides of tricarboxylic acids, *e.g.* propane-1,2,3-tricarboxylic acid [5,6] (Ia), 2-methylpropane-1,2,3-tricarboxylic acid [7] (Ib), and 3-methylbutane-1,2,4-tricarboxylic acid [8] (II),



(I)

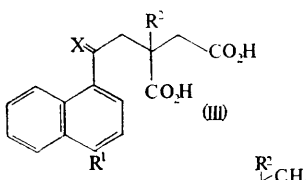
a; R = H
b; R = Me



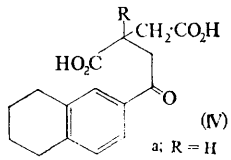
(II)

with napthalene and its alkyl derivatives and 1,2,3,4-tetrahydronaphthalene was therefore considered desirable, particularly in connection with the synthesis of tetracyclic compounds related to 16,17-dihydrocyclopenta[*a*]phenanthrene, which are currently under investigation in these laboratories.

The acylation of naphthalene and its 1- and 2-methyl derivatives, and of 1,2,3,4-tetrahydronaphthalene, with anhydrides (Ia) and (Ib) and the products obtained are described here. The action of the crude anhydride (II) has also been investigated. The structures of the products were substantiated by independent syntheses of the intermediates and by their conversion into known phenanthrene derivatives. The acylation product of naphthalene with anhydride (II), and the conversion of keto-acid (VIa) into 16,17-dihydro-17-methyl-15*H*-cyclopenta[*a*]phenanthrene [9] (Diels Hydrocarbon) is also

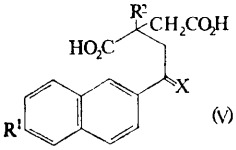


(III)



(IV)

a; R = H
b; R = Me



(V)

	R^1	R^2	X		R^1	R^2	X
a;	H	H	O	e;	H	Me	O
b;	H	H	H_2	f;	H	Me	H_2
c;	Me	H	O	g;	Me	Me	O
d;	Me	H	H_2	h;	Me	Me	H_2

described. The conversion of the keto-acid (IIIe) into oestra-1,3,5(10),6,8,-pentaen-17-one [10] [*trans*-(±)-3-deoxyequilenin] is also described.

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[2] (*a*) A. G. Peto in 'Friedel–Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. III; (*b*) R. D. Haworth, *J. Chem. Soc.*, 1932, 1126; (*c*) P. H. Gore, *Chem. Rev.*, 1955, 229.

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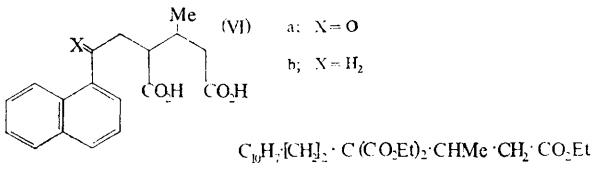
The anhydrides (Ia), (Ib), and (II) perform normal Friedel–Crafts acylation with aromatic and hydroaromatic hydrocarbons to give keto-acids of the types (IIIa), (IVa), (Va), and (VIa); these preparations are difficult or impossible by other methods. Few methods [5,11] are available for the preparation of aroyl alkane-1,2-dicarboxylic acids and the method described here is convenient and more flexible than those of Staudinger [11a] and Clemo *et al.*[11b] Naphthalene in nitrobenzene in the presence of anhydrous aluminium chloride reacted readily with the anhydrides (Ia), (Ib), and (II) to yield the keto-acids (IIIa), (IIIe), and (VIa) as the only isolable products. This is in contrast with the behaviour of the anhydrides of succinic and alkylsuccinic acids, which invariably furnished a mixture of 1- and 2-substituted naphthalenes.[2] The structures assigned to the keto-acids were established by oxidation with alkaline hypobromite to 1-naphthoic acid and by direct syntheses (in very low yield) of (IIIa) and (IIIe) from 1-naphthyl magnesium bromide and the anhydrides (Ia) and (Ib).[12] Better results were obtained for the keto-acid (IIIa) by the condensation of 1-naphthyl chloromethyl ketone [13] with the sodio-derivative of triethyl ethane-1,2,2,-tricarboxylate; [14] the product, after hydrolysis and decarboxylation, gave an acid identical with (IIIa) in all respects. Finally, a complete proof of the structures of the keto-acids (IIIa) and (IIIe) was furnished by the synthesis of the isomeric acids (Va) and (Ve). 1,2,3,4-Tetrahydronaphthalene was condensed with the anhydrides (Ia) and (Ib) in the presence of anhydrous aluminium chloride in nitrobenzene to give the keto-acids (IVa) and (IVb). The esters of (IVa) and (IVb) when dehydrogenated with sulphur, gave products converted by hydrolysis into the isomeric keto-acids (Va) and (Ve). The keto-acids could not be reduced by the Clemmensen–Martin procedure [15] but the diethyl esters are reduced easily. The reduced acids (IIIb), (IIIf), and (VIb) were synthesised independently. The succinic acid (IIIb) was synthesised from diethyl 2-(1-naphthyl)ethylmalonate [16] and ethyl bromoacetate, followed by hydrolysis of the condensation product and decarboxylation. The succinic acid (IIIe) was synthesised [10f] from 4-(1-naphthyl)butan-2-one.[17] The acid (VIb) was prepared by the base-catalysed [18] condensation of diethyl 2-(1-naphthyl)ethylmalonate with ethyl crotonate (VII) followed by hydrolysis and decarboxylation. The acids (IIIb), (IIIf), (Vb), and (Vf) were converted into the tetrahydro-oxophenanthreneacetic acids (VIIIa),[19a] (VIIIc),[19b] (IXa), and (IXc) by 85% sulphuric acid, and then to the known phenanthrenes,[20] by reduction [15] and heating with sulphur or selenium.

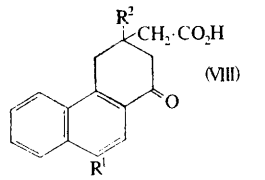


(VI) a; X = O
b; X = H2

$C_{10}H_7[CH_2]_2 \cdot C(CO_2Et)_2 \cdot CHMe \cdot CH_2 \cdot CO_2Et$

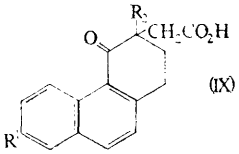
(VII)

Both 1- and 2-methylnaphthalenes were condensed with anhydrides (Ia) and (Ib) to yield the keto-acids (IIIc), (IIIg), (Vc), and (Vg). This parallels the behaviour of succinic and monoalkylsuccinic acids.[20] The keto-acids were converted into the corresponding succinic acids (IIId), (IIIh), (Vd), and (Vh) by reduction,[15] to the keto-acids (VIIIb), (VIIId), (IXb), and (IXd) by cyclisation, and to the known 2,9- and 3,7-dimethylphenanthrenes.[20] Succinic acid (IIIh) was also prepared from 4-(4-methyl-1-naphthyl)butan-2-one, as in the analogous case.



(VIII)

	R^1	R^2		R^1	R^2
a;	H	H	c;	H	Me
b;	Me	H	d;	Me	Me



(IX)

The acid (VIb) was cyclised to the keto-acid (Xa) by 85% sulphuric acid. Reduction by the Huang–Minlon method [21] gave the acid (Xb), the ester of which when heated with sulphur gave the known [9a] phenanthrenebutyric acid (XI). This method for preparing (XI) is simple and convenient and gives an overall yield of above 70%. The acid (XI) was converted by way of the acid chloride and intramolecular cyclisation in the presence of aluminium chloride into the ketone (XIIa). This ketone when reduced [15] gave 16,17-dihydro-17-methyl-15*H*-cyclopenta[*a*]phenanthrene (XIIb); its m. p. and that of its picrate agreed with those for the Diels Hydrocarbon.[9a-c] The advantages of this synthesis are (*a*) the easy availability of starting materials, (*b*) good yields, and (*c*) the avoidance of dehydrogenation at the final stage.

The keto-acid (VIIIc) was converted into the diketone

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[18] Cf. H. Henecka, *Chem. Ber.*, 1948, **81**, 200.

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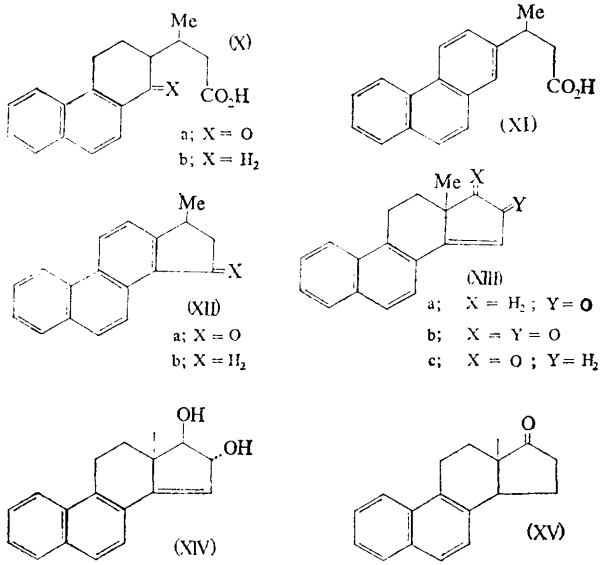
[21] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

(XIIIb) by the method of Wilds.[19b,c] The diketone (XIIIb) was reduced by potassium borohydride to the unsaturated diol (XIV) (90%) in one step only. Earlier, Wilds and his co-workers [19c] had prepared this diol



(XIV) by reduction with lithium aluminium hydride followed by hydrogenation (30% palladium–carbon; acetic acid). The *trans-trans* orientation of the diol (XIV) was shown by hydrogenation to the known saturated diol.[19c] The diol (XIV) was also dehydrated with oxalic acid (20%) to the known unsaturated ketone [10c] (XIIIc) and then hydrogenated to racemic oestra-1,3,5(10),6,8-pentaen-17-one [10e] (XV) [trans-(±)-3-deoxyequilenin].

EXPERIMENTAL

The general methods for anhydrides preparation, Friedel–Crafts acylation, reduction,[15] Grignard reaction of the anhydrides,[12] cyclisation with concentrated sulphuric acid, and dehydrogenation with sulphur were as described for the reactions of naphthalene and 1,2,3,4-tetrahydronaphthalene with anhydride (Ia). Light petroleum had b. p. 40—60°. The phrase 'worked up as usual' means that a reaction mixture was diluted with water, extracted with ether or benzene, washed with water, [aqueous sodium carbonate (5%) for an ester], dried (Na_2SO_4 or $MgSO_4$), and finally distilled under reduced pressure. Nitrite–nitrate bath refers to molten sodium nitrite–sodium nitrate. Yields are above 80% unless otherwise mentioned.

Propane-1,2,3-tricarboxylic acid 1,2-anhydride (Ia) was prepared by heating propane-1,2,3-tricarboxylic acid (5 g.) under reflux with freshly distilled acetic anhydride (5 ml.) for 4 hr. The cooled mixture gave the anhydride as plates (4 g.), m. p. 130—131°. The recommended [6] distillation under reduced pressure was less satisfactory for large amounts (Found: C, 45·6; H, 3·9. Calc. for $C_6H_6O_5$: C, 45·6; H, 3·8%).

Products derived from Naphthalene and Anhydride (Ia)

3-(1-*Naphthoyl*)*propane*-1,2-*dicarboxylic Acid* (IIIa).—(a) *By Friedel–Crafts acylation with anhydride* (Ia) (Method I). To an ice-cold solution of anhydrous aluminium chloride (26·5 g.) in freshly distilled nitrobenzene (75 ml.) an intimate mixture of naphthalene (20 g.) and propane-1,2,3-tricarboxylic acid 1,2-anhydride (15·8 g.) was added during 2 hr. with vigorous shaking. The mixture was set aside in ice for 2 hr. and then left at room temperature overnight, and was finally decomposed with ice–hydrochloric acid. The solvent was removed by steam distillation and the residual brown oil when kept overnight in the cold gave light brown crystals (20 g.), which were collected, washed, dried, and purified by esterification. The crude acid (25 g.) absolute ethanol (200 ml.), and absolute ethanol (20 ml.) saturated with dry hydrogen chloride at 0° were heated under reflux on a water-bath for 10 hr. The mixture was cooled, diluted with water, and extracted with ether, and the extract was washed with dilute sodium carbonate solution and water, and dried. Distillation gave the *keto-ester* as a viscous liquid (24 g.), b. p. 216—218°/6 mm. (Found: C, 70·2; H, 6·6. $C_{20}H_{22}O_5$ requires C, 70·2; H, 6·4%). A mixture of the ester (22 g.), ethanol (50 ml.), water (10 ml.), and potassium hydroxide (9·9 g.) was boiled under reflux for 2 hr. After removal of the neutral products with ether, the alkaline solution was acidified with hydrochloric acid to give the *keto-acid* (IIIa), obtained as prisms, m. p. 142—144° (from aqueous acetic acid) (Found: C, 67·1; H, 4·9. $C_{16}H_{14}O$ requires C, 67·1; H, 4·9%). The *semicarbazone* crystallised from alcohol as nodules, m. p. 260—262° (Found: C, 59·4; H, 4·8; N, 12·1. $C_{17}H_{17}N_3O_5$ requires C, 59·5; H, 5·0; N, 12·25%).

Oxidation of the keto-acid (2·8 g.) with alkaline hypobromite solution, afforded among other products, 1-naphthoic acid, m. p. and mixed m. p. 160°.

(b) *From* 1-*naphthyl chloromethyl ketone and triethyl ethane*-1,2,2-*tricarboxylate*. 1-Naphthyl chloromethyl ketone was prepared by the method of Schröeter *et al.*[13]

Triethyl ethane-1,2,2-tricarboxylate was prepared as follows. To granulated potassium (7·8 g.) covered with anhydrous ether (150 ml.), ethanol (11·5 ml.) diluted with ether (15 ml.) was added during 30 min. without allowing the ether to boil too vigorously; overnight, the liquid become filled with a flocculent precipitate of potassium ethoxide. Ethyl oxalate (29·2 g.) was added, and the clear pale yellow solution was cooled in ice and treated dropwise with diethyl succinate (34·8 g.) in a little dry ether. The mixture was kept at room temperature for 24 hr., after which the yellow potassium salt of the condensation product was decomposed with ice–concentrated hydrochloric acid. The dark red oil thus obtained was extracted into ether and dried (Na_2SO_4). The solvent was then removed and the residue was heated in an oil-bath at 110°/8 mm.; the temperature was then raised to 120° and kept there until a test portion no longer gave a colour with alcoholic ferric chloride. Fractional distillation under reduced pressure gave triethyl ethane-1,2,2-tricarboxylate [14] (37 g., 90%), b. p. 123—125°/6 mm.

To finely divided sodium (0·8 g.) under dry benzene (40 ml.) was added triethyl ethane-1,2,2-tricarboxylate (10·5 g.) with cooling; the mixture was set aside overnight. The yellow solution thus obtained was mixed with 1-naphthyl chloromethyl ketone and heated under reflux on a water-bath for 10 hr. Water was added to the cooled mixture and the product was acidified with acetic acid and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and distilled under reduced pressure to give *triethyl* 3-(1-*naphthoyl*)*propane*-1,2,2-*tricarboxylate* as a viscous oil (5 g.) b. p. 242—245°/8 mm. (Found: C, 66·7;

H, 6·5. $C_{23}H_{26}O_7$ requires C, 66·7; H, 6·3%). The ester was heated under reflux with methanolic potassium hydroxide to give the crude acid which was dried and then decarboxylated at 180° for 2 hr. The cooled product was dissolved in 10% aqueous sodium carbonate and the solution was boiled with animal charcoal, filtered, cooled in ice, and acidified with hydrochloric acid. The oil which separated solidfied to give 3-(1-naphthoyl)propane-1,2-dicarboxylic acid (IIIa) (2·8 g.), m. p. and mixed m. p. with product of (a) 143—144° (from dilute acetic acid) (Found: C, 67·1; H, 5·0. Calc. for $C_{16}H_{14}O_5$: C, 67·1; H, 4·9%).

(c) *From 1-bromonaphthalene* [Grignard reaction with anhydride (Ia)]. A solution of 1-naphthylmagnesium bromide [from magnesium (2·4 g.), 1-bromonaphthalene (20·7 g.), and dry ether (100 ml.)] was added dropwise to a suspension of finely powdered anhydride (Ia) (7·8 g.) in dry ether (200 ml.). The mixture was heated for 4 hr. then cooled, and the product was decomposed with ice–dilute sulphuric acid. The organic layer was separated and washed with dilute aqueous sodium carbonate until effervescence ceased. The alkaline solution was extracted with ether and acidified with dilute hydrochloric acid. The oil which separated quickly solidified and gave 3-(1-naphthoyl)-propane-1,2-dicarboxylic acid (IIIa) (0·5 g.), m. p. 143° (from aqueous acetic acid then benzene–light petroleum) (Found: C, 67·1; H, 5·1. Calc. for $C_{16}H_{14}O_5$: C, 67·1; H, 4·9%).

3-(5,6,7,8-*Tetrahydro-2-naphthoyl*)*propane-1,2-dicarboxylic Acid* (IVa).—*By Friedel–Crafts acylation* (Method II). Redistilled 1,2,3,4-tetrahydronaphthalene (9·5 g.) and anhydride (Ia) (12·5 g.) were dissolved in nitrobenzene (66 ml.) and the clear solution was cooled in a freezing mixture. Coarsely ground anhydrous aluminium chloride (21·5 g.) was gradually introduced with shaking during 30—45 min. The dark brown liquid was kept in an ice-bath for 3 hr. and then at room temperature overnight. Ice and hydrochloric acid were added and the excess of nitrobenzene was removed by steam distillation. The solid residue was dissolved in dilute sodium carbonate solution; the solution was filtered and acidified with hydrochloric acid, and the crystalline solid was collected, washed with water, and dried. The crude acid (15—17 g.), m. p. 145—150° was esterified with 10% ethanolic hydrogen chloride. *Diethyl* 3-(5,6,7,8-*tetrahydro-2-naphthoyl*)*propane-1,2-dicarboxylate* formed a pale yellow viscous oil (16·0 g.), b. p. 200°/6 mm. (Found: C, 69·4; H, 7·7. $C_{20}H_{26}O_5$ requires C, 69·4; H, 7·5%). The *semicarbazone* had m. p. 262—264° (decomp.) (from ethanol) (Found: C, 62·5; H, 7·4; N, 10·4. $C_{21}H_{29}N_3O_5$ requires C, 62·5; H, 7·2; N, 10·4%).

The above ester, when hydrolysed with ethanolic potassium hydroxide (30%), gave the *keto-acid* (IVa), m. p. 152—153° (Found: C, 66·2; H, 6·4. $C_{16}H_{18}O_5$ requires C, 66·2; H, 6·2%).

3-(2-*Naphthoyl*)*propane-1,2-dicarboxylic Acid* (Va).—*By dehydrogenation with sulphur*. The diethyl ester of (IVa) (3·6 g.) was heated with powdered sulphur (0·64 g.) at 190—205° for 4 hr. in a nitrate–nitrite bath. The mixture was distilled under reduced pressure to give the diester of (Va) b. p. 232—234°/8 mm., which was hydrolysed with ethanolic potassium hydroxide to give the *dicarboxylic acid* (Va); this gave prisms, m. p. 170—171° [from dilute acetic acid (charcoal)]; mixed m. p. with the isomeric keto-acid (IIIa) 148° (Found: C, 67·1; H, 4·9. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). The *semicarbazone* had m. p. 261—262° (Found: C, 59·4; H, 4·8; N, 12·1. $C_{17}H_{17}N_3O_5$ requires C, 59·5; H, 5·0; N, 12·25%).

4-(1-*Naphthyl*)*butane-1,2-dicarboxylic Acid* (IIIb).—(a) *From the diethyl ester of* (IIIa). The keto-acid could not be conveniently reduced;[15] therefore the diethyl ester was used. The ester (10 g.), zinc amalgam (50 g.), water (25 ml.), concentrated hydrochloric acid (58 ml.), and toluene (20 ml.) were boiled vigorously under reflux for 45—50 hr. with the addition of aliquot portions of concentrated hydrochloric acid (5 ml.) every 6 hr. The reduced ester (8 g.) was re-esterified with concentrated sulphuric acid (2·5 ml.) in absolute ethanol (25 ml.) under reflux for 8 hr. When subsequently hydrolysed with 20% ethanolic potassium hydroxide, the ester (3·8 g.) gave the *acid* (IIIb) (2·1 g.) in a more pure state, as needles, m. p. 127—128° (from benzene–light petroleum) (Found: C, 70·7; H, 6·0. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%). The anhydride of this acid could not be crystallised. The *carboxyanilide* crystallised from ethanol as needles, m. p. 190—191° (Found: C, 76·1; H, 6·2; N, 4·0. $C_{22}H_{21}NO_3$ requires C, 76·1; H, 6·1; N, 4·05%).

(b) *By the condensation of diethyl* 2-(1-*naphthyl*)*ethylsodiomalonate with ethyl bromoacetate*. To a cold solution of sodium (1·15 g.) in absolute ethanol (20 ml.) was added, with shaking, diethyl 2-(1-naphthyl)ethylmalonate[16] (15·7 g.). After the reaction, ethyl bromoacetate (6 ml.) was added and the mixture was heated under reflux for 10 hr. *Triethyl* 4-(1-*naphthyl*)*butane-1,2,2-tricarboxylate* distilled at 242—245°/8 mm. as a viscous oil (15 g.). The ester was hydrolysed with ethanolic potassium hydroxide (50%) to give the solid crude tricarboxylic acid (9·5 g.), which was decarboxylated at 170—180° (3 hr.), to give the dicarboxylic acid (IIIb), m. p. and mixed m. p. with product of (a) 128—129° (from benzene–light petroleum) (Found: C, 70·7; H, 6·1. Calc. for $C_{16}H_{14}O_4$: C, 70·6; H, 5·9%); carboxyanilide, m. p. and mixed m. p. 190—191°.

1,2,3,4-*Tetrahydro-1-oxo-phenanthrene-2-acetic Acid* (VIIIa).—*By cyclisation*. 4-(1-Naphthyl)butane-1,2-dicarboxylic acid (IIIb), concentrated sulphuric acid (9·0 ml.), and water (3 ml.) were heated on a steam-bath for 1·5 hr. with occasional swirling. The dark mixture was poured on crushed ice and the greenish solid which separated, was washed with water and dried. 1,2,3,4-tetrahydro-1-oxo-phenanthrene-2-acetic acid (VIIIa) gave prisms, m. p. 187—188° [from ethanol or acetic acid (charcoal)] (lit.,[19a] 187—188°) (Found: C, 76·0; H, 5·6. Calc. for $C_{16}H_{14}O_3$: C, 76·0; H, 5·4%). The methyl ester, prepared with 3% methanolic hydrogen chloride, had b. p. 228—230°/3 mm. and gave shining scales, m. p. 107° (from methanol) (lit.,[19a] 105—108°).

2-*Methylphenanthrene*.—The methyl ester of (VIIIa) was reduced[15] and the crude product was heated with sulphur at 240°. 2-Methylphenanthrene thus obtained gave plates, m. p. 55—56° (from ethanol) (Found: C, 94·2; H, 6·2. Calc. for $C_{15}H_{12}$: C, 94·25; H, 6·3%); picrate, m. p. 118—119° (lit.,[2b] 118—119°) (Found: C, 59·8; H, 3·6; N, 9·85. Calc. for $C_{21}H_{15}N_3O_7$: C, 59·85; H, 3·55; N, 10·0%).

4-(2-*Naphthyl*)*butane-1,2-dicarboxylic Acid* (Vb).—The diethyl ester of (Va) when reduced gave the acid (Vb) which gave needles, m. p. 153—155° (from benzene–light petroleum) (Found: C, 70·7; H, 6·0. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%); the *carboxyanilide* gave plates, m. p. 261—262° (decomp.) (from ethanol) (Found: C, 76·1; H, 6·3; N, 4·1. $C_{22}H_{21}NO_3$ requires C, 76·1; H, 6·1; N, 4·05%).

1,2,3,4-Tetrahydro-4-oxophenanthrene-3-acetic Acid (IXa).—Cyclisation of the acid (Vb) gave (IXa) as prisms, m. p. 164—165° (from dilute acetic acid) (Found: C, 76·0; H, 5·6. $C_{16}H_{14}O_3$ requires C, 76·0; H, 5·4%). The ethyl ester could not be crystallised (b. p. 248—250°/8 mm.). The 2,4-dinitrophenylhydrazone gave orange-red prisms, m. p. 220—222° (from glacial acetic acid) (Found: C, 62·4; H, 4·8, N, 12·0. $C_{24}H_{22}N_4O_6$ requires C, 62·3; H, 4·7; N, 12·1%).

3-Methylphenanthrene.—The keto-acid (IXa) was converted [as described for the isomer (VIIIa)] into 3-methylphenanthrene, m. p. 62—63° (lit.,[2a] 62—63°) (Found: C, 94·2, H, 6·22. Calc. for $C_{15}H_{12}$: C, 94·25; H, 6·3%).

Products derived from 1-Methylnaphthalene and Anhydride (Ia)

3-(4-Methyl-1-naphthoyl)propane-1,2-dicarboxylic Acid (IIIc).—1-Methylnaphthalene (9·29 g.) (b. p. 106—108°/8 mm.) and the anhydride (Ia) (11·6 g.) were condensed in the presence of aluminium chloride as described for the Friedel–Crafts acylation of naphthalene. *3-(4-Methyl-1-naphthoyl)propane-1,2-dicarboxylic acid* (IIIc) gave needles, m. p. 171—172° (from acetic acid) (Found: C, 68·0; H, 5·6. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). The diethyl ester had b. p. 294—246°/7 mm. The *semicarbazone* of the ester gave needles, m. p. 274—276° (decomp.) (from ethanol) (Found: C, 63·9; H, 6·6; N, 10·35. $C_{22}H_{27}N_3O_5$ requires C, 63·9; H, 6·5; N, 10·2%).

4-(4-Methyl-1-naphthyl)butane-1,2-dicarboxylic Acid (IIId).—This crystallised from benzene–light petroleum as needles, m. p. 166° (Found: C, 71·3; H, 6·4. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%).

1,2,3,4-Tetrahydro-9-methyl-1-oxophenanthrene-2-acetic Acid (VIIIb).—This formed plates, m. p. 182° (from acetic acid) (Found: C, 76·0; H, 6·1. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·8%). The *methyl ester* gave prisms, m. p. 102° (from methanol) (Found: C, 76·6; H, 6·4. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). The *2,4-dinitrophenylhydrazone* gave deep orange needles, m. p. 242—245° (from acetic acid) (Found: C, 62·9; H, 4·7; N, 12·0. $C_{25}H_{25}N_4O_6$ requires C, 62·9; H, 5·3; N, 11·7%).

2,9-Dimethylphenanthrene.—The keto-acid (VIIIb) was converted into 3-methylphenanthrene, m. p. 56—57° (Found: C, 92·4; H, 6·5. Calc. for $C_{16}H_{14}$: C, 92·7; H, 6·8%). The *picrate* gave red needles, m. p. 138° (from ethanol) (lit.,[20a] 138°) (Found: C, 60·7; H, 3·9; N, 9·6. Calc. for $C_{22}H_{17}N_3O_7$: C, 60·7; H, 3·9, N, 9·6%).

Products derived from 2-Methylnaphthalene and Anhydride (Ia)

3-(6-Methyl-2-naphthoyl)propane-1,2-dicarboxylic acid (Vc).—Acylation was performed as for 1,2,3,4-tetrahydronaphthalene. The *keto-acid* (Vc) was, however, isolated in poor yield (35%), as needles, m. p. 193—194° [from ethanol (or better from acetic acid)] (Found: C, 68·0; H, 5·5. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). The *diethyl ester* had b. p. 220—224°/6 mm. The *semicarbazone* (prepared in ethanol) gave nodules m. p. 294—296° (decomp.) (from ethanol) (Found: C, 63·9; H, 6·6. $C_{22}H_{27}N_3O_5$ requires C, 63·9; H, 6·5%).

4-(6-Methyl-1-naphthyl)butane-1,2-dicarboxylic Acid (Vd).—This compound gave needles, m. p. 159—160° (from benzene–light petroleum) (Found: C, 71·3; H, 6·4. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%).

1,2,3,4-Tetrahydro-7-methyl-4-oxophenanthrene-3-acetic Acid (IXb).—This compound gave *plates*, m. p. 158° (from acetic acid) (Found: C, 76·0; H, 6·2. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·8%). The *methyl ester*, b. p. 250—255°/7 mm., solidified when cool and gave needles, m. p. 131° (from methanol) (Found: C, 76·6; H, 6·4. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). The *2,4-dinitrophenylhydrazone* gave deep red plates, m. p. 272—274° (decomp.) (from glacial acetic acid) (Found: C, 62·4; H, 5·2; N, 12·1. $C_{23}H_{25}N_4O_6$ requires C, 62·9; H, 5·3; N, 11·7%).

3,7-Dimethylphenanthrene.—The methyl ester of (IXb) was converted into the alkyl phenanthrene as described earlier. 3,7-Dimethylphenanthrene, b. p. 150—151/6° mm., gave plates, m. p. 33—34° (from ethanol). The picrate gave yellow needles, m. p. 136° (from methanol) (lit.,[20c] 136°) (Found: C, 60·7; H, 4·1; N, 9·6. Calc. for $C_{22}H_{17}N_3O_7$: C, 60·7; H, 3·9; N, 9·6%).

2-Methylpropane-1,2,3-tricarboxylic Acid 1,2-Anhydride (Ib).—2-Methylpropane-1,2,3-tricarboxylic acid was prepared in large quantities by a modification of the method of Hope and Sheldon.[7] Ethyl cyanoacetate (28·25 ml.), ethyl acetoacetate (32·5 ml.), acetic acid (10 ml.), ammonium acetate (3·85 g.), and dry benzene (50 ml.) were heated in a reflux apparatus provided with a Dean–Stark water separator at 130° in an oil-bath for 4 hr., and the product was worked up as usual. Diethyl 1-cyano-2-methylpropene-1,3-dicarboxylate (35 g.) had b. p. 155—161°/8 mm. Hydrogen cyanide [from potassium cyanide (13 g.) in ethanol (70 ml.) and concentrated hydrochloric acid (20 ml. + 10 ml.)] was added to the above unsaturated cyano-ester to give diethyl 2,3-dicyano-3-methylglutarate, which was then hydrolysed with concentrated hydrochloric acid (sand-bath) for 12 hr. The clear solution was evaporated to dryness and the solid residue was extracted with dry acetone in a Soxhlet apparatus for 8 hr. Evaporation of the solvent left 2-methylpropane-1,2,3-tricarboxylic acid, m. p. 164° (from concentrated hydrochloric acid). The anhydride (Ib), m. p. 139—140° (lit.,[7] 138°), was prepared as described for (Ia).

Products derived from Naphthalene and Anhydride (Ib)

2-Methyl-3-(1-naphthoyl)propane-1,2-dicarboxylic Acid (IIIe).—(a) *By Friedel–Crafts acylation with anhydride* (Ib). *2-Methyl-3-(1-naphthoyl)propane-1,2-dicarboxylic acid* gave prisms, m. p. 150° (from benzene–light petroleum) (Found: C, 68·0; H, 5·6. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). The diethyl ester had b. p. 218—220°/6 mm. The *semicarbazone* of the ester gave prisms, m. p. 234—236° (decomp.) (from ethanol) (Found: C, 63·9; H, 6·4. $C_{22}H_{27}N_3O_5$ requires C, 63·9; H, 6·5%).

(b) *From 1-naphthylmagnesium bromide the anhydride* (Ib). The keto-acid had m. p. and mixed m. p. with product of (a) 149—150°.

The action of 1-naphthoyl chloride on the potassio-salt of diethyl 1-cyano-2-methylpropene-1,3-dicarboxylate did not proceed in the expected manner.

(c) *From 1-naphthoylacetone.* Ethyl acetate (22 ml.) and methyl 1-naphthyl ketone (8·5 g.) were condensed in the presence of sodium ethoxide [from sodium (1·23 g.) and absolute ethyl alcohol (2·66 ml.)] in dry ether. The product was worked up in the usual way and the diketone was purified by way of the crystalline copper derivative. *1-Naphthoylacetone*, b. p. 163—164°/2 mm. showed no tendency to crystallise and gave a violet colouration with ferric chloride (Found: C, 79·3; H, 5·9. $C_{14}H_{12}O$ requires

C, 79·3; H, 5·7%). All attempts to prepare the unsaturated ester $C_{10}H_7$·CO·CH_2·CMe:C(CN)·CO_2Et from this diketone and ethyl cyanoacetate, however, were abortive.

2-Methyl-3-(5,6,7,8-tetrahydro-2-naphthoyl)propane-1,2-dicarboxylic Acid (IVb).—This keto-acid was prepared by Friedel–Crafts acylation (Method II) of 1,2,3,4-tetrahydronaphthalene with the anhydride (Ib). Keto-acid (IVb) gave *needles*, m. p. 162—163° (from ethanol) (Found: C, 67·1; H, 6·7. $C_{17}H_{20}O_5$ requires C, 67·1; H, 6·6%). The diethyl ester had b. p. 210—212°/8 mm. The *2,4-dinitrophenylhydrazone* gave orange needles, m. p. 198—199° (decomp.) (from ethanol) (Found: C, 66·7; H, 6·1. $C_{27}H_{32}N_4O_8$ requires C, 66·7; H, 6·0%).

2-Methyl-3-(2-naphthoyl)propane-1,2-dicarboxylic Acid (Ve).—This keto-acid formed clusters of *needles*, m. p. 181—182° (from dilute acetic acid), mixed m. p. with the isomeric acid (IIIe) 150—160° (Found: C, 68·0; H, 5·6. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%). The diethyl ester could not be crystallised.

2-Methyl-4-(1-naphthyl)butane-1,2-dicarboxylic Acid (IIIf). (a) *From reduction of* (IIIe). The acid crystallised from benzene–light petroleum as needles, m. p. 143° (Found: C, 71·3; H, 6·1. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%). The anhydride, b. p. 198—200°/8 mm., could not be crystallised; the *carboxyanilide* gave plates, m. p. 234° (from ethanol) (Found: C, 76·3; H, 6·5. $C_{23}H_{23}NO_3$ requires C, 76·3; H, 6·4%).

(b) *From 1-chloromethylnaphthalene*. The acid (IIIf) was synthesised essentially as described by Barnes and Miller.[10f] Ethyl acetoacetate (17 g.) was alkylated with 1-chloromethylnaphthalene (17 g.) in the presence of sodium ethoxide [from sodium (2·3 g.) and absolute ethanol (40 ml.)]. The reaction product was worked up as usual. Ethyl (1-naphthyl)methylacetoacetate (20 g.), b. p. 178—180°/5 mm. (lit., 204—206°/12 mm.). This ester was boiled (sand-bath) with 8% aqueous sodium hydroxide solution (120 ml.), for 8 hr.; working up in the usual way gave 4-(1-naphthyl)butan-2-one, b. p. 155—156°/5 mm. The semicarbazone gave plates, m. p. 184—184·5° (from ethanol), (lit.,[10f,17] 176—178°) (Found: C, 70·6; H, 6·8; N, 16·8. Calc. for $C_{15}H_{17}N_3O$: C, 70·6; H, 6·7; N, 16·5%).

Ethyl 2-cyano-3-methyl-5-(1-naphthyl)pent-2-enoate was then synthesised by heating the above ketone (19·6 g.) with ethyl cyanoacetate (11·3 ml.), ammonium acetate (3·8 g.), acetic acid (15 ml.), and dry benzene (100 ml.) for 4 hr. in a Dean–Stark apparatus (140—145°; oil-bath). After the usual work-up, the unsaturated cyano-ester, b. p. 218—220/6 mm., was collected and soon solidified; it gave prisms, m. p. 74—74·5° (from ethanol) (Found: C, 77·9; H, 6·1. Calc. for $C_{19}H_{19}O_2N$: C, 77·8; H, 6·5%).

To this cyano-ester (29·3 g.) in ethanol (120 ml.) was added potassium cyanide (13 g.) in ethanol (70 ml.) followed by hydrochloric acid [concentrated acid (20 ml.) and water (10 ml.)] at 5°. The reaction mixture was poured over dilute hydrochloric acid (5%) and then worked up as usual. The product, ethyl 2,3-dicyano-3-methyl-5-(1-naphthyl)-pentanoate, had b. p. 230—233°/8 mm. (Found: C, 74·9; H, 6·1. Calc. for $C_{20}H_{20}O_2N$: C, 75·0; H, 6·3%).

The dicyano-ester was hydrolysed with concentrated hydrochloric acid, for 90 hr. The crude dicarboxylic acid was esterified (with 10% ethanolic sulphuric acid). Hydrolysis of the diester (20% alcoholic KOH) gave the acid (IIIf) (90%), which gave needles, m. p. and mixed m. p. with product of (a) 143° (from benzene–light petroleum) (lit.,[10f] 140—142) (Found: C, 71·3; H, 6·5%).

1,2,3,4-Tetrahydro-2-methyl-1-oxophenanthrene-2-acetic Acid.—The acid (VIIIc) gave prisms, m. p. 153—155 [19b] (from acetic acid) (Found: C, 76·1; H, 6·1. Calc. for $C_{17}H_{16}O_3$: C, 76·1; H, 6·0%).

2-Methylphenanthrene.—The above keto-acid was reduced, and then heated with selenium (1 g.) for 30 hr. at 300—340°; 2-methylphenanthrene [2b] gave plates, m. p. and mixed m. p. 55—56° (from alcohol) (picrate, m. p. 118—119°).

2-Methyl-4-(2-naphthyl)butane-1,2-dicarboxylic acid (Vf) gave prisms, m. p. 168—169° (from benzene–light petroleum) (Found: C, 71·3; H, 6·5. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%). The anhydride could not be crystallised. The *carboxyanilide* gave needles, m. p. 262—264° (decomp.) (from ethanol) (Found: C, 76·3; H, 6·5. $C_{23}H_{23}NO_3$ requires C, 76·3; H, 6·4%).

1,2,3,4-Tetrahydro-3-methyl-4-oxophenanthrene-3-acetic acid (IXc), gave prisms, m. p. 133° (from acetic acid) (Found: C, 76·1; H, 6·3. $C_{17}H_{16}O_3$ requires C, 76·1, H, 6·0%). The ethyl ester, b. p. 243—245°/6 mm., could not be crystallised. The *2,4-dinitrophenylhydrazone* gave red plates, m. p. 268—270° (decomp.) (from acetic acid) (Found: C, 63·0; H, 5·2. $C_{25}H_{24}N_4O_6$ requires C, 63·0; H, 5·0%).

3-methylphenanthrene,[2a] m. p. 62—63° (picrate, m. p. 138°) was obtained from the above keto-acid as described for (VIIIc).

Products derived from 1-Methylnaphthalene and Anhydride (Ib)

2-Methyl-3-(4-methyl-1-naphthoyl)propane-1,2-dicarboxylic Acid (IIIg).—The acid (IIIg) gave *prisms*, m. p. 169—170° (from acetic acid) (Found: C, 68·0; H, 5·4. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%). The diethyl ester had b. p. 240—242/6 mm. The *semicarbazone* crystallised from ethanol; m. p. 291—292° (decomp.) (Found: C, 66·0; H, 6·9. $C_{23}H_{29}N_3O_5$ requires C, 66·0; H, 6·8%).

2-Methyl-4-(4-methyl-1-naphthyl)butane-1,2-dicarboxylic Acid (IIIh).—(a) *By reduction of* (IIIg). This *acid* had m. p. 152—153° (from benzene–light petroleum) (Found: C, 72·1; H, 6·4. $C_{18}H_{20}O_4$ requires C, 72·1; H, 6·7%). The *diethyl ester* could not be crystallised (b. p. 210—215/6 mm.).

(b) *From 1-chloromethyl-4-methylnaphthalene*. 1-chloromethyl-4-methylnaphthalene was prepared by the method of Darzens and Levy; [22] m. p. 62° (picrate, m. p. 73—74°). *Ethyl (4-methyl-1-naphthyl)methylacetoacetate* was prepared by the procedure described for the analogous compound earlier; b. p. 188—190°/6 mm. (Found: C, 76·1; H, 7·0. $C_{18}H_{20}O_3$ requires C, 76·1; H, 7·0%).

4-(4-Methyl-1-naphthyl)butan-2-one had b. p. 176—178°. The semicarbazone crystallised from ethanol; m. p. 194—195°. *Ethyl 2-cyano-3-methyl-5-(4-methyl-1-naphthyl)pent-2-enoate* had b. p. 212—218°/3 mm. and did not solidify; no attempt was made to crystallise it or to separate the geometrical isomerides (Found: C, 78·2; H, 6·9. $C_{20}H_{21}NO_2$ requires C, 78·2; H, 6·8%). Ethyl 2,3-dicyano-3-methyl-5-(4-methyl-1-naphthyl)pentanoate had b. p. 241—243°/4 mm. and when hydrolysed with concentrated hydrochloric acid gave the dicarboxylic acid (IIIh), m. p. and mixed m. p. 153° (Found: C, 72·2; H, 6·7. Calc. for $C_{18}H_{20}O_4$: C, 72·1; H, 6·7%).

1,2,3,4-Tetrahydro-2,9-dimethyl-1-oxophenanthrene-2-

[22] A. Darzens and G. Levy, *Compt. rend.*, 1936, **202**, 74.

acetic acid (VIIId) gave needles, m. p. 189—190° (from acetic acid) (Found: C, 76·6; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). The ethyl ester had m. p. 102—103° and the 2,4-*Dinitrophenylhydrazone*, m. p. 242—244° (Found: C, 63·7; H, 5·4. $C_{20}H_{26}N_4O_6$ requires C, 63·7; H, 5·6%). 2,9-Dimethylphenanthrene [20a] had m. p. 57° (picrate, m. p. 138°).

Products derived from 2-*Methylnaphthalene*

2-*Methyl*-3-(6-*methyl*-2-*naphthoyl*)*propane*-1,2-*dicarboxylic Acid* (Vg).—Yield of this keto-acid was poor (20%) under the conditions used. The *acid* gave plates or needles, m. p. 212—213° [from ethanol (charcoal)] (Found: C, 68·8; H, 5·9. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%). The diethyl ester had b. p. 248—250°/7 mm. The 2,4-dinitrophenylhydrazone gave deep red plates, m. p. 286—288° (from ethanol).

2-*Methyl*-4-(6-*methyl*-2-*naphthyl*)*butane*-1,2-*dicarboxylic acid* (Vh) gave needles, m. p. 158° (from benzene–light petroleum) (Found: C, 72·1; H, 6·9. $C_{18}H_{20}O_4$ requires C, 72·1; H, 6·7%). 1,2,3,4-*Tetrahydro*-3,7-*dimethyl*-4-*oxophenanthrene*-3-*acetic acid* (IXd) gave prisms, m. p. 135° (from acetic acid) (Found: C, 76·6; H, 6·6. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). 3,7-Dimethylphenanthrene [20c] crystallised from alcohol; m. p. 35° (picrate 135—136°).

Products derived from Naphthalene and Anhydride (II)

3-*Methylbutane*-1,2,4-*tricarboxylic Acid* 1,2-*Anhydride* (II).—3-Methylbutane-1,2,4-tricarboxylic acid was prepared as described by Hope and Perkin,[8] with certain modifications which rendered the isolation of large quantities of the acid a comparatively easy matter. Ethyl crotonate (114 g.) reacted with ethyl sodiocyanoacetate [from ethyl cyanoacetate (113 g.), sodium (23 g.), and dry benzene (300 ml.)]. The product was treated with ethyl bromoacetate (112 ml.) to give triethyl 2-cyano-3-methylbutane-1,2,4-tricarboxylate (200 g.) as a viscous liquid, b. p. 195—198°/8 mm. The cyano-ester (100 g.) was hydrolysed with concentrated sulphuric acid (100 ml.) and water (85 ml.) on a sand-bath for 30 hr. The product was cooled, diluted, neutralised with solid sodium carbonate, concentrated to a small bulk, acidified with conc. hydrochloric acid, and finally evaporated to dryness. The solid residue was worked up as usual. The residual viscous liquid (68 g.), absolute ethanol (150 ml.), and concentrated sulphuric acid (15 ml.) were heated at 110° (oil-bath) for 6 hr. under a fractionating column; alcohol vapour was passed through the flask and the excess of alcohol was allowed to distil off slowly. The cooled product was diluted with water and repeatedly extracted with ether. The extract was washed with 5% aqueous sodium carbonate and water, dried ($CaCl_2$), and evaporated. The residue was distilled under reduced pressure to give triethyl 3-methylbutane1,2,4-tricarboxylate (70 g.), b. p. 160—165°/10 mm. The ester and concentrated hydrochloric acid (200 ml.) were heated under reflux (sand-bath), until the solution became clear (40 hr.). The solution was evaporated to a small bulk, and cooled. Crystals of 3-methylbutane-1,2,4-tricarboxylic acid were collected; m. p. 154—155° (from hydrochloric acid). The acid (20 g.) and acetyl chloride (25 ml.) were boiled on a water-bath until solution was complete and evolution of hydrogen chloride had ceased. The excess of acetyl chloride was removed by leaving overnight in a vacuum dessiccator (KOH). The anhydride (II) showed no tendency to solidify and could not be distilled under reduced pressure without decomposition. When boiled with water in the presence of dioxan, however, it readily yielded 3-methylbutane-1,2,4-tricarboxylic acid, m. p. and mixed m. p. 154°.

2-*Methyl*-4-(1-*naphthoyl*)*butane*-1,3-*dicarboxylic Acid* (VIa).—The keto acid (VIa), prepared by Friedel–Crafts acylation of naphthalene (Method I), crystallised (charcoal) from acetic acid as *prisms*, m. p. 137—138° (Found: C, 68·8; H, 5·9. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%). The diethyl ester had b. p. 230—231°/7 mm.

2-*Methyl*-5-(1-*naphthyl*)*pentane*-1,3-*dicarboxylic Acid* (VIb).—(a) *By reduction of* (VIa). The acid was obtained as uncrystallisable gum; its anhydride had b. p. 218°/7 mm. and was also uncrystallisable. The *carboxyanilide* gave plates, m. p. 116—117° (from benzene) (Found: C, 76·8; H, 6·9. $C_{24}H_{25}NO_3$ requires C, 76·8; H, 6·7%).

(b) *From diethyl* 2-(1-*naphthyl*)*ethylmalonate*. This malonate was prepared by the action of 2-(1-naphthyl)ethyl bromide on diethyl sodiomalonate, or by the condensation of ethyl 4-(1-naphthyl)butyrate [16b] with diethyl oxalate in the presence of potassium ethoxide followed by the elimination of carbon monoxide.

2-(1-Naphthyl)ethylmalonate (15·7 g.) was added to a solution of sodium (0·1 g.) in absolute ethanol (1·5 ml.) and heated at 100° for 2 hr. in a glycerine-bath with stirring. Ethyl crotonate (5·7 g.) was introduced dropwise with stirring, with the temperature maintained at 100 ± 2°. The mixture was then heated at 100—115° for a further 2 hr. with constant stirring. Water (100 ml.) and acetic acid (1·5 ml.) were added to the cooled solution and the product was worked up as usual. The substituted malonic ester (VII) on hydrolysis and decarboxylation (180°) yielded the acid (VIb) as an uncrystallisable gum; *carboxyanilide*, m. p. and mixed m. p. 116—117° (Found: C, 76·8; H, 6·8%).

3-(1,2,3,4-*Tetrahydro*-1-*oxo*-2-*phenanthryl*)*butyric Acid* (Xa).—The acid (VIb) was cyclised to the *keto-acid* (Xa), m. p. 169—170° (Found: C, 76·6; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). The *methyl ester* (b. p. 222—225°/6 mm.) gave scales, m. p. 101—102° (from methanol) (Found: C, 77·0; H, 6·9. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%). The 2,4-*dinitrophenylhydrazone* gave red needles, m. p. 226—228° (from acetic acid) (Found: C, 74·5; H, 8·1. $C_{24}H_{25}N_4O_6$ requires C, 74·5; H, 8·0%).

3-(1,2,3,4-*Tetrahydro*-2-*phenanthryl*)*butyric Acid* (Xb).—The keto-acid (Xa) (2·61 g.), potassium hydroxide (175 g.), hydrazine hydrate (90%; 1·25 g.), and ethylene glycol (13 ml.) were heated (Dean–Stark apparatus) at 160° (oil-bath) for 2 hr. and at 190—200° for 4 hr. after which no more water separated. The liquid was cooled, diluted with water, and extracted with ether, and the alkaline solution was acidified with hydrochloric acid. The crystalline acid was separated and formed *needles*, m. p. 158—159° [from acetic acid (charcoal)] (Found: C, 80·6; H, 7·6. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%). The methyl ester was obtained as a liquid, b. p. 218—220°/6 mm.

3-(2-*Phenanthryl*)*butyric acid* (XI).—The methyl ester of (Xb) (1·42 g.) was heated with a sulphur (0·32 g.) at 200—205° (nitrite–nitrate bath) for 3 hr. and then distilled under reduced pressure. Methyl 3-(2-phenanthryl)butyrate (0·9 g.), b. p. 230—235°/6 mm., formed needles, m. p. 78° (from methanol) (lit.,[9a] 78°) (Found: C, 82·0; H, 6·6. Calc. for $C_{19}H_{18}O_2$: C, 82·0; H, 6·5%). The acid (XI) obtained on hydrolysis, was crystallised from acetic acid; m. p. 127° (lit.,[9a] 127°) (Found: C, 81·7; H, 6·2. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%).

16,17-*Dihydro*-17-*methyl*-15-*oxo*-15H-*cyclopenta*[a]*phenanthrene* (XIIa).—This compound was prepared from the acid (XI), by the procedure described by Bergmann,[9b] as yellow prisms, m. p. 138—139° (lit.,[9b] 135—136°) (Found: C, 87·8; H, 5·7. Calc. for $C_{18}H_{14}O$: C, 87·8; H, 5·6%). Its *oxime*, prepared in pyridine–ethanol, formed plates, m. p. 169—171° (from ethanol) (Found: C, 82·8; H, 5·7. $C_{18}H_{15}NO$ requires C, 82·8; H, 5·8%).

16,17-*Dihydro*-17-*methyl*-15H-*cyclopenta*[a]*phenanthrene* (*Diels hydrocarbon*) (XIIb).—The ketone (XIIa) was reduced to give the hydrocarbon as plates, m. p. 125·5—126° (from ethanol), which agrees with the literature [9] (Found: C, 93·1; H, 6·9. Calc. for $C_{18}H_{16}$: C, 93·1; H, 6·9%). The picrate gave orange-red needles, m. p. 130—131° (from absolute ethanol) (lit.,[9b,c] 130—131°, lit.,[9d] 118—119°) (Found: C, 62·5; H, 4·4. Calc. for $C_{24}H_{19}N_3O_7$: C, 62·8; H, 4·1%).

Conversion of Keto-acid (VIIIc) *into racemic Oestra*-1,3,5(10),6,8-*pentaen*-17-*one* [trans-(±)-3-*deoxyequilenin*] (XV)

Racemic Oestra-1,3,5(10),6,8,14-*hexaene*-16,17-*dione* (XIIIb).—Keto-acid (VIIIc) was converted by way of the derived acylmalonate to 2-acetonyl-1,2,3,4-tetrahydro-2-methyl-1-oxotetrahydrophenanthrene,[19b] m. p. 109° (Found: C, 81·2; H, 6·9. Calc. for $C_{18}H_{18}O_2$: C, 81·2; H, 6·8%). The crude diketone (7·5 g.) was cyclised (aqueous KOH) to racemic oestra-1,3,5(10),6,8,14-hexaen-16-one (XIIIa), (6 g.), m. p. 147—149° (from benzene) (b. p. 210—212°/3 mm.) (Found: C, 87·1; H, 6·6. Calc. for $C_{18}H_{16}O$: C, 87·1; H, 6·5%). The oxime (prepared in pyridine–ethanol) had m. p. 200—202° (from ethanol). The unsaturated ketone (4·1 g.), freshly distilled acetic anhydride (5 ml.), and freshly sublimed selenium dioxide (3 g.) were heated (150—160°; oil bath) for 4 hr. The cooled product was filtered off and recrystallised from a large volume of benzene. The diketone [19b,c] (XIIIb) (3 g.) had m. p. 205—206° (Found: C, 82·4; H, 5·5. Calc. for $C_{18}H_{14}O_2$: C, 82·5; H, 5·3%). The mother liquors when set aside yielded more diketone (1·1 g.), 200—205°.

Oestro-1,3,5(10)6,8,14-*hexaene*-16α,17β-*diol* (XIV).—The diketone (XIIIb), m. p. 205—206°, (500 mg.) was dissolved in methanol (150 ml.) and to it was added methanolic potassium hydroxide (20%; 0·5 ml.). The solution was cooled in ice, and potassium borohydride (0·5 g.) dissolved in methanol (50 ml.) was added. Evolution of hydrogen gas took place and the yellow colour faded. The solution was kept overnight at room temperature, diluted with water (250 ml.) and carefully acidified with dilute hydrochloric acid. The diol which separated in silky needles (500 mg.), showed no i.r. carbonyl absorption; m. p. 150—151° (from ethyl acetate); t.l.c. (silica gel) showed a single compound. A pure sample, prepared by one crystallisation from ethyl acetate and drying in vacuum at 40° for 3 days, had m. p. 152—152·5° (lit.,[19c] m. p. 149—153°) (Found: C, 81·2; H, 6·8. Calc. for $C_{18}H_{18}O_2$: C, 81·2; H, 6·8%). The diacetate, dried at 55° for 3 days *in vacuo*, had m. p. 174—175·5° (from ethyl acetate) (Found: C, 75·4; H, 6·3. Calc. for $C_{22}H_{22}O_4$: C, 75·4; H, 6·3%). The above diol (XIV) (265 mg.; m. p. 151°) was hydrogenated in ethanol (10 ml.) in the presence of palladium chloride (5 mg.), gum arabic (5 mg.), in water (2 ml.). Oestra-1,3,5(10),6,8-pentaene-16α,17β-diol (230 mg.) had m. p. 179—179·5 (lit., 181°), one component on t.l.c. (silica gel) (Found: C, 80·6; H, 7·6. Calc. for $C_{18}H_{20}O_2$: C, 80·6; H, 7·5%). The diacetate had m. p. 191—191·5° (lit.,[19c] 191·6—192·4°) (Found: C, 75·4; H, 6·8. Calc. for $C_{22}H_{24}O_4$: C, 75·4; H, 6·8%). An acetonide could not be prepared even under forcing conditions. Oxidation with periodic acid then with sodium hypobromite gave *trans*-2-carboxy-2-methyl-1,2,3,4-tetrahydrophenanthrene-1-acetic acid, m. p. 183° (lit.,[10c] 182—183°) (Found: C, 72·6; H, 6·2. Calc. for $C_{18}H_{18}O_4$: C, 72·7; H, 6·1%).

Oestra-1,3,5(10)6,8,14-*hexaen*-17-*one* (XIIIc).—The unsaturated diol (XIV), m. p. 151° (266 mg.) and aqueous oxalic acid (20%; 3 ml.) were digested for 3 hr. (water-bath). The mixture was extracted with ether, the extract was washed with water, saturated sodium hydrogen carbonate solution, and water again, dried ($MgSO_4$), and evaporated. The yellow residue (280 mg.) was sublimed (140°/1 mm.) to give the unsaturated ketone [10e] (XIIIc) (220 mg.), m. p. 137—138° [from ethanol (charcoal)] (Found: C, 87·1; H, 6·7. Calc. for $C_{18}H_{16}O$: C, 87·1; H, 6·5%). The semicarbazone (prepared in pyridine) had m. p. 251—252° (Found: C, 74·7; H, 6·4; N, 13·8. Calc. for $C_{19}H_{19}N_3O$: C, 74·75; H, 6·3; N, 13·8%). The saturated diol (100 mg.) with aqueous oxalic acid gave the ketone (XV) (8 mg., 8%) m. p. 188—189, and mixed m. p. 187—189°.

Attempts to dehydrate diol (XIV) with potassium hydrogen sulphate, phosphoryl-chloride, pyridine, toluene-*p*-sulphonyl chloride, and dilute sulphuric acid, however, were unsuccessful.

Oestra-1,3,5(10)6,8-*pentaen*-17-*one* [trans-(±)-3-*deoxyequilenin*] (XV).—The unsaturated ketone (XIIIc) was hydrogenated with palladium–charcoal (30%) in ethyl acetate. The ketone [10e] (XV) had m. p. 190—190·5 (from ethanol) (Found: C, 86·4; H, 7·3. Calc. for $C_{18}H_{18}O$: C, 86·4; H, 7·2%). The semicarbazone had m. p. 256—257 (decomp.) (from ethanol). The picrate had m. p. 153—154 (lit.,[10b] 153—154°) (Found: C, 62·3; H, 4·7; N, 9·1. Calc. for $C_{24}H_{21}N_3O_7$: C, 62·2; H, 4·6; N, 9·1%).

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