71. *Synthesis of Polycyclic Compounds. Part I. A New Synthesis of Alkylphenanthrenes.*

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Ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate was alkylated with a phenethyl bromide and the product (*e.g.*, III) cyclised with sulphuric acid to a naphthalene derivative (*e.g.*, IV); this was converted (Dieckmann) into a hydro-oxophenanthrene (*e.g.*, V), and thence by conventional methods into alkylphenanthrenes. A very flexible new route is thus available which is here used for preparation of several alkylphenanthrenes.

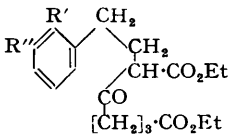
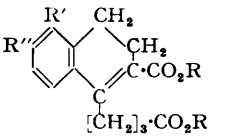
Synthetic 2-ethyl-1 : 8-dimethylphenanthrene was identical with the product, $C_{18}H_{18}$, of dehydrogenation of methyl vinhaticoate and related diterpenoids.[1]

Research, begun in 1936, on the preparation of hydrophenanthrene derivatives useful for the synthesis of œstrogenic ketones,[2] is now being resumed. Such of the earlier work as has not been published from other laboratories will now be reported.

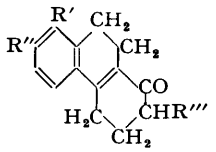
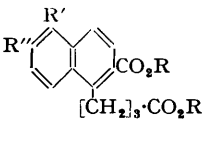
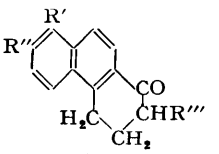
γ-Ethoxycarbonylbutyryl chloride with ethyl sodioacetoacetate gave mainly ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (I), converted by ethanolic sodium ethoxide into ethyl β-oxopimelate (II), albeit in unsatisfactory yield.[3] Nevertheless, the sodio-derivative

$$EtO_2C\cdot[CH_2]_3\cdot COCl \longrightarrow \underset{(I)}{EtO_2C\cdot[CH_2]_3\cdot CO\cdot CHAc\cdot CO_2Et} \longrightarrow \underset{(II)}{EtO_2C\cdot[CH_2]_3\cdot CO\cdot CH_2\cdot CO_2Et}$$

is doubtless formed satisfactorily, for treatment with phenethyl bromide without isolation of the ester (II) afforded a good yield of ethyl β-oxo-α-phenethylpimelate (III; R′ = R″ = H) (for similar reaction see Bouveault and Bongart [4]), which was converted into γ-(2-carboxy-3 : 4-dihydro-1-naphthyl)butyric acid (IV; R = R′ = R″ = H) by means of concentrated sulphuric acid. The derived diethyl ester, on condensation by means of sodium and hydrolysis, gave 1 : 2 : 3 : 4 : 9 : 10-hexahydro-1-oxophenanthrene [5] (V; R′ = R″ = R‴ = H), which was reduced by Clemmensen's method and then dehydrogenated

(III)   (IV)

with selenium to yield phenanthrene.[2] The ester (IV; R = Et, R′ = R″ = H) on dehydrogenation with sulphur and subsequent hydrolysis gave γ-(2-carboxy-1-naphthyl)-butyric acid (VI; R = R′ = R″ = H), converted by acetic anhydride into 1 : 2 : 3 : 4-tetrahydro-1-oxophenanthrene [6] (VII; R′ = R″ = R‴ = H).

 (V)  (VI)  (VII)

By use of 2-*m*-tolylethyl bromide [7] these reactions led to the phenanthrene derivative (VII; R′ = R‴ = H, R″ = Me). 1 : 2 : 3 : 4 : 9 : 10-Hexahydro-7-methyl-1-oxophenanthrene (V; R′ = R‴ = H, R″ = Me) was condensed with methylmagnesium iodide,

[1] (*a*) King and King, *J.*, 1953, 4158; (*b*) King, Godson, and King, *J.*, 1955, 1118.
[2] Bardhan, *Chem. and Ind.*, 1936, 879.
[3] Cf. Birkofer and Storch, *Chem. Ber.*, 1953, **86**, 32; Loewenthal, *J.*, 1953, 3965.
[4] Bouveault and Bongart, *Bull. Soc. chim.*, 1902, **27**, 1100.
[5] Cf. : (*a*) Johnson, Johnson, and Peterson, *J. Amer. Chem. Soc.*, 1946, **68**, 1926; (*b*) Birch and Smith, *J.*, 1951, 1887.
[6] Cf. Haworth, *J.*, 1932, 1130.
[7] Shoesmith and Connor, *J.*, 1927, 1770; Carré, *Compt. rend.*, 1912, **148**, 1109.

and the resultant alcohol dehydrated with anhydrous formic acid and converted by selenium into 1 : 7-dimethylphenanthrene.[8] The tetrahydro-derivative (VII; R′ = R‴ = H, R″ = Me) likewise reacted with an excess of ethylmagnesium bromide affording, by the above reactions, 1-ethyl-7-methylphenanthrene.[8a, 9]

Similarly use of 2-*o*-tolylethyl bromide [8c] yielded 1 : 2 : 3 : 4 : 9 : 10-hexahydro-8-methyl-1-oxophenanthrene (V; R′ = Me, R″ = R‴ = H) and thence 1-ethyl-8-methylphenanthrene, identical with the product recently described by King and King.[10]

The ethyl ester (IV; R = Et, R′ = Me, R″ = H) was condensed by means of sodium, and the resultant product was ethylated and hydrolysed to give 2-ethyl-1 : 2 : 3 : 4 : 9 : 10-hexahydro-8-methyl-1-oxophenanthrene (V; R′ = Me, R″ = H, R‴ = Et), converted by reaction with methylmagnesium iodide, dehydration, and dehydrogenation into 2-ethyl-1 : 8-dimethylphenanthrene. The properties of this hydrocarbon and its picrate and trinitrobenzene derivative corresponded with those recorded for the ethyldimethylphenanthrene and its derivatives which King and King [1] obtained from methyl vinhaticoate, and the constitution suggested by these authors is thereby confirmed.

Lastly, the preceding ester was converted into 1 : 2 : 3 : 4-tetrahydro-8-methyl-1-oxophenanthrene [13] (VII; R′ = Me, R″ = R‴ = H), 1 : 2 : 3 : 4-tetrahydro-8-methyl-1-oxo-2-*iso*propylphenanthrene (VII; R′ = Me, R″ = H, R‴ = Pr^i), and 1 : 2 : 3 : 4-tetrahydro-2 : 8-dimethyl-1-oxophenanthrene [14] (VII; R′ = R‴ = Me, R″ = H), by the methods described for similar cases. The ketone (VII; R′ = Me, R″ = H, R‴ = Pr^i) was reduced by Clemmensen's method and the product dehydrogenated, to yield 1-methyl-7-*iso*propylphenanthrene.[8a, 9] The other two ketones on reaction with *iso*propylmagnesium bromide, under the usual conditions, gave 1-methyl-8-*iso*propyl- [11] and 2 : 8-dimethyl-1-*iso*propylphenanthrene respectively. The last compound differs from a hydrocarbon to which Short and Wang [12] ascribed this formulation.

Experimental

Condensation of γ-Ethoxycarbonylbutyryl Chloride with Ethyl Sodioacetoacetate.—A solution of γ-ethoxycarbonylbutyryl chloride (89 g.) in ether (200 ml.) was added slowly with cooling to a stirred slurry of ethyl sodioacetoacetate [from pulverised sodium (11·5 g.), ethyl acetoacetate (65 ml.), and dry ether (650 ml.)] and set aside overnight, then refluxed for 0·5 hr., and treated with 3N-sulphuric acid (300 ml.) with cooling and stirring. The ethereal extract was washed with water, dried (Na_2SO_4), and distilled. *Ethyl* 4 : 6-*dioxoheptane*-1 : 5-*dicarboxylate* (I) (90 g.), b. p. 152—153°/3 mm., was collected. A middle fraction was analysed (Found: C, 57·1; H, 7·3. $C_{13}H_{20}O_6$ requires C, 57·3; H, 7·4%). The ester which gives a red colour with aqueous-ethanolic ferric chloride is probably contaminated with the corresponding *O*-acyl ester.

Attempts to prepare Ethyl β-Oxopimelate (II).—The preceding ester (9 g.) was added to an ice-cold solution from sodium (0·75 g.) in absolute ethanol (15 ml.), and the resulting solution kept overnight at room temperature, whereafter water and excess of dilute sulphuric acid were added and the oil was collected in ether. On distillation it gave fractions: (*a*) b. p. 140°/4 mm. (5 g.); (*b*) b. p. 146—156°/4 mm. (2·5 g.). Fraction (*a*) showed an intense ferric reaction and was pure ethyl β-oxopimelate [3] (Found: C, 57·2; H, 7·8. Calc. for $C_{11}H_{18}O_5$: C, 57·4; H, 7·8%).

Ethyl β-Oxo-α-phenethylpimelate (III; R′ = R″ = H).—To an ice-cold solution of sodium ethoxide [from sodium (2·3 g.) and absolute ethanol (40 ml.)] was gradually added, with shaking, ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (27·2 g.). Next morning phenethyl bromide (18·5 g.) was added and the whole heated under reflux at 90—92° for 20 hr. It was then diluted with water, acidified, and repeatedly extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and evaporated. *Ethyl β-oxo-α-phenethylpimelate* formed a colourless liquid (15 g.), b. p. 190—193°/4 mm. (Found: C, 68·1; H, 7·8. $C_{19}H_{26}O_5$ requires C, 68·3; H, 7·8%), giving a red colour with ethanolic ferric chloride.

[8] (*a*) Ruzicka and Ballas, *Helv. Chim. Acta*, 1923, **6**, 677; 1924, **7**, 875; (*b*) Haworth, Letsky, and Mavin, *J.*, 1932, 1785; (*c*) Bardhan and Sengupta, *J.*, 1932, 2522.
[9] Haworth, *J.*, 1932, 2719.
[10] King and King, *J.*, 1953, 4167; 1954, 1373.
[11] Short and Wang, *J.*, 1950, 991.
[12] *Idem*, *J.*, 1951, 2980.
[13] Haworth, Mavin, and Sheldrick, *J.*, 1934, 458.
[14] Haworth and Mavin, *J.*, 1932, 2720.

γ-(2-Carboxy-3 : 4-dihydro-1-naphthyl)butyric Acid (IV; R = R′ = R″ = H).—The preceding keto-ester (5 g.) was slowly added with stirring to sulphuric acid (*d* 1·84; 30 ml.) at −10°. Stirring was continued for 3 hr. and then the mixture was poured on ice. The semisolid mass which separated was collected in ether, and the solution washed with water, dried, and evaporated. The brown residue was hydrolysed with potassium hydroxide (3 g.), water (3 ml.), and ethanol (30 ml.). The crude *acid* (3 g.) was purified by repeated crystallisation from dilute acetic acid (charcoal) and formed prisms, m. p. 138° (Found : C, 69·3; H, 6·2. $C_{15}H_{16}O_4$ required C, 69·2; H, 6·1%). The *diethyl ester* had b. p. 194—195°/3 mm. (Found : C, 71·9; H, 7·2. $C_{19}H_{24}O_4$ requires C, 72·1; H, 7·5%).

1 : 2 : 3 : 4 : 9 : 10-*Hexahydro-1-oxophenanthrene* (V; R′ = R″ = R‴ = H).—The preceding ester (3·1 g.) was heated with powdered sodium (0·23 g.) and dry benzene (8 ml.). The reaction which proceeded smoothly at 100° was completed in 2 hr. The viscous mass was decomposed with ice and dilute hydrochloric acid. The benzene extract was separated, washed with sodium carbonate solution, and dried, and the solvent removed under reduced pressure. The residual oil (3 g.) was hydrolysed by heating it with acetic acid (12 ml.) and concentrated hydrochloric acid (6 ml.) for 12 hr. The ketone (V; R′ = R″ = R‴ = H) (1·2 g.) had b. p. 168°/3 mm., m. p. 49° [from light petroleum (b. p. 40—60°)] (Found : C, 84·7; H, 7·1. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·0%) (Johnson *et al.*[8a] record m. p. 49—50°, and Birch and Smith [8b] m. p. 48—49°). The semicarbazone separated in prisms (from ethanol), m. p. 254—255° (decomp.) in agreement with Bardhan;[2] Johnson *et al.*[8a] give m. p. 257—258°, and Birch and Smith [8b] 250—251°.

Phenanthrene.—The foregoing ketone (2 g.) was reduced by Clemmensen procedure to an oil (1·2 g.) which was heated with selenium (2·5 g.) at 300—320° for 20 hr. The product was purified from ethanol (charcoal) and had m. p. 100° alone or mixed with phenanthrene (Found : C, 94·2; H, 5·5. Calc. for $C_{14}H_{10}$: C, 94·4; H, 5·7%).

γ-(2-Carboxy-1-naphthyl)butyric Acid (VI; R = R′ = R″ = H).—The dihydro-ester (IV; R = Et, R′ = R″ = H) (3·1 g.) was heated with powdered sulphur (0·32 g.) at 240—250° for 2 hr., and on distillation in a vacuum gave an oil (3 g.), b. p. 200—205°/4 mm. This on hydrolysis with ethanolic potassium hydroxide in the usual way afforded *γ-(2-carboxy-1-naphthyl)butyric acid* as needles (from aqueous ethanol), m. p. 167° [Found : C, 69·9; H, 5·4%; equiv., 129·0. $C_{15}H_{14}O_4$ (dibasic) requires C, 69·7; H, 5·4%; equiv., 129·0].

1 : 2 : 3 : 4-*Tetrahydro-1-oxophenanthrene* (VII; R′ = R″ = R‴ = H).—The foregoing acid (2 g.) was heated with redistilled acetic anhydride (7 ml.) for 3 hr., the excess of anhydride removed, and the residue distilled in a vacuum. The ketone [9] (VII; R′ = R″ = R‴ = H) separated from light petroleum (b. p. 60—80°) as plates, m. p. 95° (Found : C, 85·7; H, 6·2. Calc. for $C_{14}H_{12}O$: C, 85·7; H, 6·1%).

5-*Oxo-8-phenyloctanoic Acid.*—Ethyl β-oxo-α-phenethylpimelate (III; R′ = R″ = H) (5 g.) was refluxed for 10 hr. in concentrated hydrochloric acid (10 ml.) and acetic acid (20 ml.). The mixture was diluted with water, and the excess of acetic acid removed at 100° as completely as possible and the oil collected in ether. The *keto-acid* (3 g.) had b. p. 205—210°/3 mm. (Found : C, 71·6; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). The *semicarbazone* had m. p. 126° (from ethanol) (Found : C, 61·7; H, 7·2. $C_{15}H_{21}O_3N_3$ requires C, 61·9; H, 7·2%). The *ethyl ester* had b. p. 165°/3 mm. (Found : C, 73·2; H, 8·4. $C_{16}H_{22}O_3$ requires C, 73·3; H, 8·4%).

2-*Phenethyl*cyclo*hexane*-1 : 3-*dione.*—The above ester (5 g.) was heated on the steam-bath with a solution from sodium (0·5 g.) in calcium-dried ethanol (20 ml.) for 20 hr. On cooling, the mixture was diluted with water and extracted with ether. The alkaline solution on acidification afforded the diketone [5b] which crystallised from ethyl acetate–light petroleum (b. p. 60—80°) as plates, m. p. 147° (Found : C, 77·5; H, 7·4. Calc. for $C_{14}H_{16}O_2$: C, 77·8; H, 7·4%).

Ethyl β-*Oxo*-α-(2-m-*tolylethyl*)*pimelate* (III; R′ = H, R″ = Me).—This *ester* was prepared by the condensation of 2-*m*-tolylethyl bromide (20 g.) with ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (27·2 g.) in presence of a solution from sodium (2·3 g.) in absolute ethanol (40 ml.) as described above and had b. p. 190—193°/3 mm. (19 g.) (Found : C, 68·9; H, 8·1. $C_{20}H_{28}O_5$ requires C, 69·0; H, 8·0%).

γ-2-(Carboxy-7-methyl-3 : 4-dihydro-1-naphthyl)butyric Acid (IV; R = R′ = H, R″ = Me).—The preceding keto-ester (32 g.) on cyclisation with sulphuric acid gave the *acid* (IV; R = R′ = H, R″ = Me) (18 g.), prisms, m. p. 154—155° (from aqueous acetic acid) [Found : C, 70·0; H, 6·6%; equiv., 137·0. $C_{16}H_{18}O_4$ (dibasic) requires C, 70·0; H, 6·6%; equiv., 137·0]. The *ethyl ester* boiled at 195°/3 mm. (Found : C, 72·6; H, 8·0. $C_{20}H_{26}O_4$ requires C, 72·7; H, 7·9%).

1 : 2 : 3 : 4 : 9 : 10-*Hexahydro*-7-*methyl*-1-*oxophenanthrene* (V; R′ = R‴ = H, R″ = Me).—The ester (IV; R = Et, R′ = H, R″ = Me) on Dieckmann cyclisation and hydrolysis in the usual way afforded the *ketone* (V; R′ = R‴ = H, R″ = Me), b. p. 160—163°/3 mm. (Found: C, 85·2; H, 7·6. $C_{15}H_{16}O$ requires C, 85·0; H, 7·5%). The *semicarbazone* formed plates (from ethanol), m. p. 254—255° (decomp.) (Found: C, 71·2; H, 7·2. $C_{16}H_{19}ON_3$ requires C, 71·4; H, 7·1%).

1 : 7-*Dimethylphenanthrene* (*Pimanthrene*).—A solution of the preceding ketone (2 g.) in dry ether (30 ml.) was added dropwise at room temperature to methylmagnesium iodide [from magnesium (1 g.), methyl iodide (3 ml.), and dry ether (32 ml.)]. The mixture was refluxed for 4 hr. The product (2 g.) was isolated in the usual way and heated on the water-bath with anhydrous formic acid (4 ml.) for 0·5 hr. and on distillation yielded an oil (1·7 g.), b. p. 155°/3 mm. This on dehydrogenation with selenium (3·5 g.) at 300—320° for 30 hr. gave 1 : 7-dimethylphenanthrene, plates, m. p. 86° (from ethanol) (Found: C, 93·2; H, 6·8. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). The picrate crystallised from ethanol in needles, m. p. 132° (Found: C, 60·4; H, 4·0. Calc. for $C_{16}H_{14},C_6H_3O_7N_3$: C, 60·7; H, 3·9%).[8a,b]

γ-(2-*Carboxy*-7-*methyl*-1-*naphthyl*)*butyric Acid* (VI; R = R′ = H, R″ = Me).—This was prepared by the dehydrogenation of ethyl γ-(2-ethoxycarbonyl-7-methyl-3 : 4-dihydro-1-naphthyl)butyrate (IV; R = Et, R′ = H, R″ = Me) with sulphur in the usual way. The *acid* crystallised from methanol in prisms, m. p. 188—190° (Found: C, 70·2; H, 5·8. $C_{16}H_{16}O_4$ requires C, 70·5; H, 5·9%). The *ethyl ester* had b. p. 198—200°/3 mm. (Found: C, 73·1; H, 7·3. $C_{20}H_{24}O_4$ requires C, 73·2; H, 7·3%).

1 : 2 : 3 : 4-*Tetrahydro*-7-*methyl*-1-*oxophenanthrene* (VII; R′ = R‴ = H, R″ = Me).—Cyclisation of the preceding ester with sodium gave the *ketone*, b. p. 175—178°/3 mm., needles, m. p. 71° [from light petroleum (b. p. 40—60°)] (Found: C, 85·8; H, 6·6. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%). The *semicarbazone* (from ethanol) melts at 259° (decomp.) (Found: C, 71·7; H, 6·4. $C_{16}H_{17}ON_3$ requires C, 71·9; H, 6·4%).

1-*Ethyl*-7-*methylphenanthrene*.—Reaction of ethylmagnesium bromide on the preceding ketone followed by dehydration and dehydrogenation afforded 1-ethyl-7-methylphenanthrene, plates (from ethanol), m. p. 82·5° (Found: C, 92·8; H, 7·4. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). The picrate forms long yellow needles, m. p. 117·5° (Found: C, 61·2; H, 4·3. Calc. for $C_{17}H_{16},C_6H_3O_7N_3$: C, 61·5; H, 4·2%) (cf. refs. 6 and 8).

Ethyl β-*Oxo*-α-(2-o-*tolylethyl*)*pimelate* (III; R′ = Me, R″ = H).—This *ester*, prepared under the standard conditions, had b. p. 195—198°/¼ mm. (Found: C, 68·8; H, 8·1. $C_{20}H_{28}O_5$ requires C, 69·0; H, 8·0%). In sulphuric acid (20 ml.) it (10 g.) gave γ-(2-*carboxy*-5-*methyl*-3 : 4-*dihydro*-1-*naphthyl*)*butyric acid* (IV; R = R″ = H, R′ = Me), which on repeated crystallisation from aqueous acetic acid formed needles, m. p. 168° [Found: C, 69·9; H, 6·5%; equiv., 137·0. $C_{16}H_{18}O_4$ (dibasic) requires C, 70·0; H, 6·6%; equiv., 137·0] [*diethyl ester*, b. p. 200°/4 mm. (Found: C, 72·6; H, 7·9. $C_{20}H_{26}O_4$ requires C, 72·7; H, 7·9%)].

5 : 6 : 7 : 8 : 9 : 10-*Hexahydro*-1-*methyl*-8-*oxophenanthrene* (V; R′ = Me, R″ = R‴ = H).—The ester (IV; R = Et, R′ = Me, R″ = H) (5 g.) was heated with sodium (0·35 g.) in dry benzene (12 ml.), and the product hydrolysed. The *ketone* (2·1 g.), b. p. 175—180°/4 mm., formed plates, m. p. 94°, from light petroleum (b. p. 60—80°) (Found: C, 85·1; H, 7·6. $C_{15}H_{16}O$ requires C, 84·9; H, 7·5%). Its *semicarbazone* formed prisms (from ethanol), m. p. 260—262° (decomp.) (Found: C, 71·4; H, 7·1. $C_{16}H_{19}ON_3$ requires C, 71·4; H, 7·1%).

1-*Ethyl*-8-*methylphenanthrene*.—The above ketone (2·5 g.) was treated in boiling ether (30 ml.) for 3 hr. with excess of ethylmagnesium bromide. The product (2·5 g.) was dehydrated with formic acid and dehydrogenated. 1-Ethyl-8-methylphenanthrene (1·9 g.) formed plates (from ethanol), m. p. 106—107° (Found: C, 93·0; H, 7·3. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). The picrate separated from ethanol in needles, m. p. 125° (Found: C, 61·3; H, 4·4. Calc. for $C_{17}H_{16},C_6H_3O_7N_3$: C, 61·5; H, 4·2%).

2-*Ethyl*-1 : 2 : 3 : 4 : 9 : 10-*hexahydro*-8-*methyl*-1-*oxophenanthrene* (V; R′ = Me, R″ = H, R‴ = Et).—The ester (IV; R = Et, R′ = Me, R″ = H) (6 g.) was treated with sodium (0·42 g.) and ethylated. The product (6 g.), hydrolysed in the usual way, gave a *ketone* (2·2 g.), b. p. 180°/3 mm., needles, m. p. 87—88° [from light petroleum (b. p. 40—60°)] (Found: C, 85·2; H, 8·3. $C_{17}H_{20}O$ requires C, 85·0; H, 8·3%). The *semicarbazone* separated from ethanol in prisms, m. p. 217—218° (Found: C, 72·4; H, 7·7. $C_{18}H_{23}ON_3$ requires C, 72·7; H, 7·7%).

2-*Ethyl*-1 : 8-*dimethylphenanthrene*.—A solution of the ketone (V; R′ = Me, R″ = H, R‴ = Et) (2 g.) in ether (25 ml.) was allowed to react with methylmagnesium iodide [from magnesium (0·8 g.), methyl iodide (2·4 ml.), and ether (30 ml.)]. The product (2 g.) was dehydrated to a hydrocarbon (1·9 g.), b. p. 160—165°/3 mm., which was dehydrogenated with

selenium (4 g.) at 300—320° for 30 hr. 2-Ethyl-1 : 8-dimethylphenanthrene (1·4 g.), b. p. 180—190°/3 mm., on two crystallisations from ethanol formed plates, m. p. 113° (Found : C, 92·1; H, 7·6. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). The picrate formed orange-red needles (from ethanol), m. p. 148—149°. The trinitrobenzene derivative crystallised from ethanol in yellow needles, m. p. 167° (Found : C, 64·3; H, 4·7. Calc. for $C_{18}H_{18},C_6H_3O_6N_3$: C, 64·4; H, 4·7%). King and King [10] give 113°, 148—149°, and 167° as the respective m. p.s.

γ-(2-Carboxy-5-methyl-1-naphthyl)butyric Acid (VI; R = R″ = H, R′ = Me).—The ethyl ester (IV; R = Et, R′ = Me, R″ = H) was dehydrogenated with sulphur and hydrolysed, giving this *acid*, prisms, m. p. 184—185° (from aqueous ethanol) [Found : C, 70·3; H, 5·7%; equiv., 136·2. $C_{16}H_{16}O_4$ (dibasic) requires C, 70·6; H, 5·8%; equiv., 136·0], whose *ethyl ester* had b. p. 200—202°/3 mm. (Found : C, 73·1; H, 7·5. $C_{20}H_{24}O_4$ requires C, 73·2; H, 7·3%).

1 : 2 : 3 : 4-*Tetrahydro-8-methyl-1-oxophenanthrene* (VII; R′ = Me, R″ = R‴ = H).—The ester (VI; R = Et, R′ = Me, R″ = H), on Dieckmann cyclisation and then hydrolysis, afforded this ketone,[13] plates, m. p. 165° [from light petroleum (b. p. 60—80°)] (Found : C, 85·7; H, 6·6. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%). Haworth, Mavin, and Sheldrick [13] give m. p. 164—165°.

1-*Methyl*-8-iso*propylphenanthrene*.—The preceding ketone (3 g.) in benzene (35 ml.) was refluxed with *iso*propylmagnesium bromide [from magnesium (0·72 g.), *iso*propyl bromide (3·7 g.), and ether (30 ml.)] for 4 hr. The product on dehydration and then dehydrogenation yielded 1-methyl-8-*iso*propylphenanthrene, plates (from methanol), m. p. 100° (Found : C, 92·3; H, 7·7. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). The picrate formed orange needles (from ethanol), m. p. 141° (Found : C, 61·7; H, 4·8. Calc. for $C_{18}H_{18},C_6H_3O_7N_3$: C, 62·2; H, 4·5%). Short and Wang [11] give m. p. 101·5—102° and 142·5° respectively.

1 : 2 : 3 : 4-*Tetrahydro-8-methyl-1-oxo-2-iso*propylphenanthrene (VII; R′ = Me, R″ = H, R‴ = Pr^i).—The ester (VI; R = Et, R′ = Me, R″ = H) (4 g.) was allowed to react with powdered potassium (0·5 g.) in benzene, giving a solid potassio-derivative which was refluxed with *iso*propyl iodide (3 ml.) for 20 hr. and then hydrolysed in the usual way. The *ketone* (1·4 g.), b. p. 180°/3 mm., formed needles, m. p. 123—125°, from light petroleum (b. p. 60—80°) (Found : C, 85·4; H, 7·7. $C_{18}H_{20}O$ requires C, 85·7; H, 7·9%).

1-*Methyl*-7-iso*propylphenanthrene* (*Retene*).—The preceding ketone on Clemmensen reduction and then dehydrogenation gave 1-methyl-7-*iso*propylphenanthene,[8b,c] plates (from ethanol), m. p. 99° (Found : C, 92·1; H, 7·6. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). The picrate, orange-yellow needles, m. p. 123—124°, was also prepared (Found : C, 62·1; H, 4·6. Calc. for $C_{18}H_{18},C_6H_3O_7N_3$: C, 62·2; H, 4·5%).

1 : 2 : 3 : 4-*Tetrahydro-2 : 8-dimethyl-1-oxophenanthrene* (VII; R′ = R‴ = Me, R″ = H).—This [14] was prepared from the ester (VI; R = Et, R′ = Me, R″ = H), by sodium-condensation, methylation, and hydrolysis under the usual conditions. The ketone, b. p. 180°/4 mm., crystallised from light petroleum (b. p. 60—80°) as plates, m. p. 108—109° (Found : C, 86·0; H, 7·2. Calc. for $C_{16}H_{16}O$: C, 85·7; H, 7·1%), and gave a semicarbazone, prisms, m. p. 256—257° (decomp.) (Found : C, 72·3; H, 6·7. Calc. for $C_{17}H_{19}ON_3$: C, 72·6; H, 6·8%).

2 : 8-*Dimethyl*-1-iso*propylphenanthrene*.—The action of an excess of *iso*propylmagnesium bromide on the above ketone proceeded normally affording a product which on dehydration and then dehydrogenation gave 2 : 8-*dimethyl*-1-iso*propylphenanthrene*, flakes (from ethanol), m. p. 79° (Found : C, 91·5; H, 8·1. $C_{19}H_{20}$ requires C, 91·9; H, 8·1%). The *picrate* crystallises from ethanol in yellow needles, m. p. 130° (Found : C, 62·6; H, 4·9. $C_{19}H_{20},C_6H_3O_7N_3$ requires C, 62·9; H, 4·8%).

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