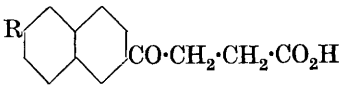
240. *Syntheses of Alkylphenanthrenes. Part II. Pimanthrene,* 1 : 4 : 7 - *Trimethylphenanthrene, Retene, and* 1 : 4 - *Dimethyl* - 7 - iso*propylphen* - *anthrene.*

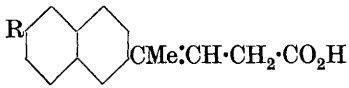
By Robert Downs Haworth, Barnet Mark Letsky, and Cecil Robert Mavin.

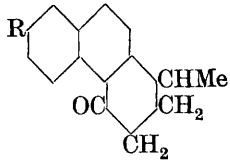
The structure of the hydrocarbon retene has an important bearing on the constitution of abietic acid, from which it is obtained by heating with sulphur (Vesterberg, *Ber.*, 1903, **36**, 4200). The work of Bucher (*J. Amer. Chem. Soc.*, 1910, **32**, 374) and Ruzicka, Schinz, and Meyer (*Helv. Chim. Acta*, 1923, **6**, 1077) leads to the conclusion that retene is 1-methyl-7-*iso*propylphenanthrene. Pimanthrene was first obtained by Ruzicka and Ballas (*Helv. Chim. Acta*, 1923, **6**, 677; 1924, **7**, 875) by dehydrogenating *d*-pimaric acid with sulphur. Later (*ibid.*, 1926, **9**, 962; 1930, **13**, 1402; *Annalen*, 1929, **469**, 147) the same hydrocarbon was prepared by the action of sulphur or selenium on the acids of copal resin. Pimanthrene was shown to be 1 : 7-dimethylphenanthrene by oxidation with alkaline potassium ferricyanide (Ruzicka, Graaf, and Hosking, *Helv. Chim. Acta*, 1931, **14**, 233) to phenanthrene-1 : 7-dicarboxylic acid, the constitution of which was established by the formation of the same acid during the oxidation of retene. Pimanthrene and retene have now been synthesised from β-methyl- and β-*iso*propyl-naphthalene respectively.

β-Methylnaphthalene reacted with succinic anhydride in the presence of anhydrous aluminium chloride to yield β-(6-*methyl*-2-*naphthoyl*)*propionic acid* (I ; R = Me), along with other acids which have not been investigated. The constitution assigned to this acid has been arrived at in the following way. First, it was converted into 2-methylphenanthrene by a series of reactions similar to those described previously (this vol., p. 1125) and the succinic anhydride must therefore have reacted in position 1 or 2. A complete proof of the structure of the acid (I ; R = Me) was obtained from experiments which aimed at oxidation to the corresponding naphthalene-dicarboxylic acid, and alkaline potassium ferricyanide was selected for this purpose, as Weissgerber and Kruber (*Ber.*, 1919, **52**, 352) employed this reagent for oxidation of 1 : 6-dimethylnaphthalene. However, when the keto-acid (I ; R = Me) was oxidised with a quantity of potassium ferricyanide corresponding to thirty atomic proportions of oxygen, it was converted into 6-*methyl*-2-*naphthoic acid*, which was identical with the acid obtained by hydrolysis of 2-cyano-6-methylnaphthalene, produced in small yield when sodium

6-methylnaphthalene-2-sulphonate (Dzieworński, Schoenówna, and Waldmann, *Ber.*, 1925, **58**, 1212) was distilled with potassium ferrocyanide. 6-Methyl-2-naphthoic acid was oxidised by excess of potassium ferricyanide in alkaline solution to naphthalene-2 : 6-dicarboxylic acid.

(I.) 

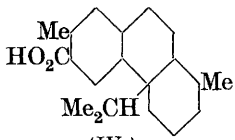
(II.) 



(III.)

β-(6-Methyl-2-naphthoyl)propionic acid (I ; R = Me) was converted into the *methyl* ester, which reacted with methylmagnesium iodide to yield *γ-(6-methyl-2-naphthyl)-Δ$^{\beta}$-pentenoic acid* (II ; R = Me). This acid was reduced by phosphorus and hydriodic acid to γ-(6-methyl-2-naphthyl)valeric acid, which was converted into 4-keto-1 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (III ; R = Me) by means of sulphuric acid. This ketone was reduced by Clemmensen's method and the product was dehydrogenated with selenium to yield 1 : 7-dimethylphenanthrene. The hydrocarbon, picrate, styphnate, quinone, and quinoxaline agree in properties with those of pimanthrene and its derivatives described by Ruzicka and Ballas (*loc. cit.*).

During the conversion of *d*-pimaric acid into pimanthrene, an *iso*propyl group, presumably attached to one of the angular positions, is eliminated, and (IV), (V), and (VI), which neglect the position of the two ethylenic linkages, are the only formulæ consistent with the isoprene rule and the chemistry of *d*-pimaric acid. A determination of the structure of methylpimanthrene obtained by Ruzicka and Ballas (*Helv. Chim. Acta*, 1924, **7**, 818) from *d*-pimaric acid would enable a decision to be made between the three structures, because the third methyl group in this hydrocarbon has been derived from and occupies the same position as the carboxyl group in the resin acid.



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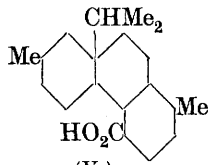

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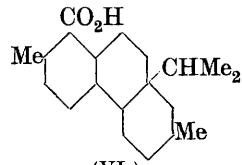


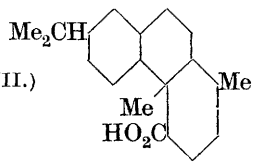
(VI.)

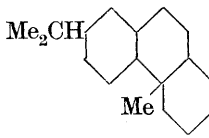
1 : 4 : 7-*Trimethylphenanthrene* has been prepared by dehydration and dehydrogenation of the product of the action of methylmagnesium iodide on the ketone (III ; R = Me), but its properties do not correspond with those of methylpimanthrene obtained from

d-pimaric acid. Structure (V) is therefore excluded and *d*-pimaric acid must have formula (IV) or (VI), and we are engaged in the synthesis of 1 : 2 : 7- and 1 : 6 : 7-trimethylphenanthrene. Further, 1 : 4 : 7-trimethylphenanthrene does not agree in properties with the methylpimanthrene obtained from *iso*agathic dicarboxylic acid (Ruzicka and Hosking, *Helv. Chim. Acta*, 1931, **14**, 203).

Some difficulty was experienced in the preparation of β-*iso*propylnaphthalene which was required for the synthesis of retene. According to Roux (*Bull. Soc. chim.*, 1884, **41**, 379; *Ann. Chim. Phys.*, 1887, **12**, 313; see also Bargellini and Melacini, *Atti R. Accad. Lincei*, 1908, **17**, 26) *n*-propyl bromide condenses with naphthalene in the presence of a small quantity of aluminium chloride to give β-*iso*propylnaphthalene, and we have obtained a liquid hydrocarbon (A) by this reaction. The hydrocarbon reacted with succinic anhydride, giving a crystalline acid, $C_{17}H_{18}O_3$, m. p. 148°, along with inseparable acids. When *iso*propyl bromide was condensed with naphthalene, a liquid hydrocarbon (B) was obtained which gave a picrate melting a few degrees higher than that prepared from hydrocarbon (A), but no appreciable depression in melting point was observed with a mixture of the two picrates. However, hydrocarbon (B) reacted with succinic anhydride to give a mixture of acids, from which a crystalline keto-acid, $C_{17}H_{18}O_3$, m. p. 159°, was isolated, which differed from the isomeric acid obtained from hydrocarbon (A). In view of this anomaly it was obviously desirable to prepare β-*iso*propylnaphthalene by a method which established its structure. This was done by reducing β-*iso*propenylnaphthalene, prepared from 2-naphthyl methyl ketone by Grignard's method (*Bull. Soc. chim.*, 1901, **25**, 498), with phosphorus and hydriodic acid. The ethylene derivative polymerised readily in these circumstances, but a small quantity of β-*iso*propylnaphthalene was obtained, which, condensed with succinic anhydride, yielded a keto-acid, m. p. 159°, identical with the acid obtained from hydrocarbon (B). The β-*iso*propylnaphthalene employed in the following synthetical experiments was therefore prepared from naphthalene and *iso*propyl bromide. The hydrocarbon (A) has not been fully investigated. It probably contains a large quantity of β-propylnaphthalene, and analogy suggests the keto-acid to be β-(6-*propyl*-2-*naphthoyl*)*propionic acid*.

(VII.)





(VIII.)

The keto-acid, m. p. 159°, prepared from succinic anhydride and β-*iso*propylnaphthalene has been proved to be β-(6-iso*propyl*-2-*naphthoyl*)*propionic acid* (I; R = $CHMe_2$) by oxidation with potassium ferricyanide in alkaline solution to 6-iso*propyl*-2-*naphthoic acid*, further oxidation of which yielded naphthalene-2 : 6-dicarboxylic acid. The *methyl* ester of the keto-acid (I; R = $CHMe_2$) was converted successively into γ-(6-iso*propyl*-2-*naphthyl*)-Δ^{β}-*pentenoic acid* (II; R = $CHMe_2$), 4-*keto*-1-*methyl*-7-iso*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (III; R = $CHMe_2$), and 1-methyl-7-*iso*propylphenanthrene by processes similar to those described above in the synthesis of pimanthrene. 1-Methyl-7-*iso*propylphenanthrene gave no depression in melting point with a specimen of retene obtained from abietic acid, and the picrate, styphnate, quinone, and quinoxaline were identical with the corresponding retene derivatives.

In view of the recent work of Ruzicka, Goldberg, Huiser, and Seidel (*Helv. Chim. Acta*, 1931, **14**, 545) the structure for abietic acid has been reduced to two possible formulæ (VII) and (VIII) containing two double bonds, and a determination of the structure of methylretene (Ruzicka and Meyer, *ibid.*, 1922, **5**, 581), in which the second methyl group is derived from the carboxyl group in abietic acid, will enable a decision to be made between these two formulæ. 1 : 4-*Dimethyl*-7-iso*propylphenanthrene* has been prepared by dehydrating and dehydrogenating the product obtained by the action of methylmagnesium iodide on the ketone (III; R = $CHMe_2$). The hydrocarbon does not correspond in properties with methylretene obtained from abietic acid. This synthesis excludes formula (VII) for abietic acid and we are engaged in the synthesis of 1 : 2- and 1 : 3-dimethyl-7-*iso*propylphenanthrenes.

Experimental.

β-(6-*Methyl*-2-*naphthoyl*)*propionic Acid* (I; R = Me).—β-Methylnaphthalene (14 g.) and succinic anhydride (10 g.) were added to a cold solution of aluminium chloride (26 g.) in nitrobenzene (100 c.c.). After 24 hours, the mixture was acidified and steam-distilled, and the residue cooled. The solid acids were crystallised from glacial acetic acid and then from methyl alcohol. The *acid* (I; R = Me) (19 g.) was obtained in colourless plates, m. p. 162° (Found : equiv., 238. $C_{15}H_{14}O_3$ requires equiv., 242).

The *methyl* ester, b. p. 210—212°/12 mm., prepared by the action of methyl-alcoholic hydrogen chloride on the acid, crystallised from methyl alcohol in colourless prisms, m. p. 82—83° (Found : C, 74·9; H, 6·3. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). γ-(6-*Methyl*-2-*naphthyl*)*butyric acid*, obtained by reducing the acid by Clemmen-

sen's method, crystallised from methyl alcohol in colourless plates, m. p. 111—112° (Found : C, 78·6; H, 7·2. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·0%). This acid (2 g.), heated on the water-bath for ½ hour with concentrated sulphuric acid (6 c.c.) and water (2 c.c.), was converted into *4-keto-7-methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, which crystallised from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 62—63° (Found : C, 85·7; H, 6·7. $C_{15}H_{14}O$ requires C, 85·7; H, 6·6%). This ketone was reduced with amalgamated zinc and concentrated hydrochloric acid, and the product dehydrogenated with selenium; 2-methylphenanthrene, m. p. 55°, was obtained and identified by comparison with a specimen obtained by the method previously described (this vol., p. 1133).

6-Methyl-2-naphthoic Acid.—(a) The acid (I; R = Me) (2·4 g.) was warmed on the water-bath with a solution of potassium hydroxide (30 g.) and potassium ferricyanide (150 g.) in water (200 c.c.) for 24 hours. Further quantities of ferricyanide (54 g.) and potassium hydroxide (8 g.) were then added and the mixture was heated for another 24 hours. The solution was cooled, acidified, and saturated with ether, and the inorganic material collected and washed with ether. The filtrate was extracted thoroughly with ether, the extract dried, and the solvent removed. (b) Sodium 6-methylnaphthalene-2-sulphonate (6 g.) and dry potassium ferrocyanide (10 g.) were mixed and heated strongly in a metal retort. The 2-cyano-6-methylnaphthalene (0·2 g.) which sublimed was hydrolysed with boiling acetic acid (6 c.c.) and concentrated hydrochloric acid (6 c.c.) for 12 hours. The solution was diluted with water, and the product collected. In both cases, (a) and (b), the product was crystallised from methyl alcohol or aqueous acetic acid, *6-methyl-2-naphthoic acid*, m. p. 225—227°, being obtained as a micro-crystalline powder (Found : equiv., 190. $C_{12}H_{10}O_2$ requires equiv., 186). The *methyl* ester, prepared from diazomethane and the acid in ether, crystallised from methyl alcohol in colourless needles, m. p. 116—117° (Found : C, 77·6; H, 6·3. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%).

Methyl Naphthalene-2 : 6-dicarboxylate.—6-Methyl-2-naphthoic acid (0·9 g.) was heated for 60 hours with a solution of potassium ferricyanide (54 g.) and potassium hydroxide (8 g.) in water (250 c.c.). The product, isolated as described above in the form of an amorphous powder, was esterified with diazomethane in ethereal solution. The excess of diazomethane was removed by shaking with dilute sulphuric acid and the ethereal solution was washed with sodium carbonate solution, dried, and evaporated. The residue (0·3 g.) crystallised from methyl alcohol in colourless plates, m. p. 188° (Kaufler and Thien, *Ber.*, 1907, **40**, 3258, give 191° corr.) (Found : C, 68·6; H, 5·0. Calc. for $C_{14}H_{12}O_4$: C, 68·8; H, 4·9%).

γ-(6-Methyl-2-naphthyl)-Δ$^{\beta}$-pentenoic Acid (II; R = Me).—Methyl β-(6-methyl-2-naphthoyl)propionate (26 g.) in benzene (100 c.c.) was treated with a solution of methylmagnesium iodide prepared from magnesium (3·6 g.) and methyl iodide (21·5 g.) in ether (50 c.c.). After boiling for 2 hours, the product was decomposed with dilute sulphuric acid, and the benzene layer extracted several times with dilute sodium carbonate solution. Acidification liberated the *acid* (II; R = Me) (22 g.), which crystallised from acetic acid or methyl alcohol in colourless plates (18 g.), m. p. 143—144° (Found: C, 79·5; H, 6·9. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

4-Keto-1 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (III; R = Me).—The acid (II; R = Me) (9 g.) was boiled for 5 hours with red phosphorus (9 g.) and hydriodic acid (*d* 1·7; 45 c.c.), diluted, and cooled, the liquid decanted, and the residue extracted with dilute sodium hydroxide solution. The alkaline extract was acidified, the acid extracted with ether and dried, and the solvent removed. The residual oil (7 g.) was warmed on the water-bath for 1 hour with concentrated sulphuric acid (21 c.c.) and water (7 c.c.), diluted, and extracted with ether. The extract was washed with water and then with aqueous ammonia, dried, and distilled. The ketone (III; R = Me), b. p. 190—192°/0·4 mm., did not solidify. The *semicarbazone* crystallised from alcohol in colourless nodules, m. p. 206—208° (Found: C, 72·8; H, 6·9. $C_{17}H_{19}ON_3$ requires C, 72·6; H, 6·8%).

1 : 7-Dimethylphenanthrene.—The ketone (III; R = Me) (2 g.) was reduced by boiling with amalgamated zinc (10 g.) and concentrated hydrochloric acid (15 c.c.) for 12 hours. The product, isolated with ether, was dehydrogenated with selenium (3 g.) at 300—340° for 30 hours. The selenium was extracted several times with light petroleum (b. p. 40—60°), the solvent removed, the residue distilled over sodium under reduced pressure, and the distillate (1·1 g.) crystallised twice from alcohol; 1 : 7-dimethylphenanthrene separated in plates, m. p. 85—86° (Found: C, 93·0; H, 6·8. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). The picrate crystallised from methyl alcohol in yellow needles, m. p. 132° (Found: N, 9·9. Calc.: N, 9·7%), the styphnate in yellow needles, m. p. 159° (Found: N, 9·5. Calc.: N, 9·3%), the quinone from ethyl alcohol in orange plates, m. p. 165° (Found: C, 81·2; H, 5·2. Calc.: C, 81·4; H, 5·1%), the quinoxaline from acetic acid in pale buff needles, m. p. 192° (Found: N, 9·2. Calc.: N, 9·1%). Ruzicka and Ballas (*loc. cit.*) give 86°, 131°, 159°, 166°, and 194° as the m. p.'s of pimanthrene, its picrate, styphnate, quinone, and quinoxaline respectively.

1 : 4 : 7-Trimethylphenanthrene.—The ketone (III; R = Me) (3 g.) was treated with methylmagnesium iodide from magnesium (0·4 g.),

methyl iodide (2·5 g.), and ether (30 c.c.). After boiling for 3 hours, the mixture was decomposed with dilute sulphuric acid, the product distilled at 0·4 mm., and the distillate (3 g.) dehydrogenated with selenium (4 g.) at 300—340° for 30 hours. 1 : 4 : 7-*Trimethylphenanthrene* crystallised from alcohol in colourless slender prisms, m. p. 72—73° (Found : C, 92·5; H, 7·3. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%). The *picrate* crystallised from methyl alcohol in orange needles, m. p. 141—142° (Found : C, 61·5; H, 4·4. $C_{23}H_{19}O_7N_3$ requires C, 61·5; H, 4·3%), the *styphnate* in yellow needles, m. p. 129—130° (Found : C, 59·4; H, 4·4. $C_{23}H_{19}O_8N_3$ requires C, 59·4; H, 4·1%), the *quinone* from ethyl alcohol in orange prisms, m. p. 170—171° (Found : C, 81·3; H, 5·5. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%), and the *quinoxaline* from alcohol in cream-coloured needles, m. p. 140—141° (Found : N, 8·6. $C_{23}H_{18}N_2$ requires N, 8·7%).

Condensation of (a) iso*Propyl Bromide and* (b) n-*Propyl Bromide with Naphthalene.*—(a) *iso*Propyl bromide (250 g.) and naphthalene (375 g.) were heated on the water-bath during the gradual addition of aluminium chloride (40 g.). The heating was continued for 6 hours, and the product decomposed with dilute hydrochloric acid, extracted with benzene, dried, and fractionated. β-*iso*Propylnaphthalene (200 g.), b. p. 130—135°/12 mm., was obtained; the picrate separated from methyl alcohol in yellow needles, m. p. 93—95° (Found : N, 10·7. Calc. : N, 10·5%).

(b) *n*-Propyl bromide and naphthalene condensed as described in (a) to yield a hydrocarbon, b. p. 130—135°/12 mm.; the picrate crystallised from methyl alcohol in yellow needles, m. p. 89—90° (Found : N, 10·6. Calc. for $C_{19}H_{17}O_7N_3$: N, 10·5%). This hydrocarbon, condensed with succinic anhydride as described below in the case of acid (I; R = $CHMe_2$), yielded an acid, probably β-(6-*propyl*-2-*naphthoyl*)*propionic acid*, which crystallised from glacial acetic acid in colourless needles, m. p. 147—148° (Found : C, 75·5; H, 6·9. $C_{17}H_{18}O_3$ requires C, 75·6; H, 6·6%). A mixture of this acid and acid (I; R = $CHMe_2$) melted at 130—140°.

β-(6-iso*Propyl*-2-*naphthoyl*)*propionic Acid* (I; R = $CHMe_2$).—The crude product obtained from β-*iso*propylnaphthalene (34 g.) as described previously in the case of the acid (I; R = Me) (p. 1787) was mixed with a little ether; the solid obtained crystallised from glacial acetic acid in colourless needles (15 g.), m. p. 159° (Found : C, 75·5; H, 6·7. $C_{17}H_{18}O_3$ requires C, 75·6; H, 6·6%). This acid was also obtained by condensing the small quantity of β-*iso*propylnaphthalene prepared from β-*iso*propenylnaphthalene with succinic anhydride. The *methyl* ester prepared by the action of methyl-alcoholic hydrogen chloride, crystallised from methyl alcohol in

colourless prisms, m. p. 81—82° (Found : C, 75·9; H, 7·2. $C_{18}H_{20}O_3$ requires C, 76·1; H, 7·0%).

6-iso*Propyl*-2-*naphthoic acid* was obtained as an amorphous powder (1·5 g.) by oxidising the acid (I; R = $CHMe_2$) (2·4 g.) with potassium ferricyanide (250 g.) and potassium hydroxide (48 g.) for 24 hours as described in the preparation of 6-methyl-2-naphthoic acid (p. 1788); the *methyl* ester crystallised from methyl alcohol in colourless plates, m. p. 109—110° (Found : C, 78·7; H, 6·8. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·0%). 6-*iso*Propyl-2-naphthoic acid was oxidised to naphthalene-2 : 6-dicarboxylic acid, which was identified by means of its dimethyl ester, m. p. 188—189°.

γ-(6-iso*Propyl*-2-*naphthyl*)-Δ^{β}-*pentenoic acid* (II; R = $CHMe_2$), prepared in 50% yield from methyl β-(6-*iso*propyl-2-naphthoyl)-propionate, was crystallised from glacial acetic acid and then from methyl alcohol; colourless leaflets, m. p. 144°, were obtained (Found : C, 80·4; H, 7·6. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·4%).

4-*Keto*-1-*methyl*-7-iso*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (III; R = $CHMe_2$).—The acid (II; R = $CHMe_2$) was reduced with phosphorus and hydriodic acid. The *keto*-compound (III; R = $CHMe_2$), b. p. 180—185°/0·5 mm., crystallised from light petroleum (b. p. 40—60°) in colourless rhombic plates, m. p. 71—72° (Found : C, 85·4; H, 7·8. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%).

1-*Methyl*-7-iso*propylphenanthrene*.—The cyclic ketone (III; R = $CHMe_2$) (3 g.) was reduced in the usual manner, and the product (3 g.) distilled at 0·5 mm., and dehydrogenated with selenium (5 g.) at 300—340° for 30 hours. 1-Methyl-7-*iso*propylphenanthrene, isolated with light petroleum (b. p. 40—60°), and purified by distillation over sodium under reduced pressure, crystallised from alcohol in colourless plates, m. p. 98—99° (Found : C, 92·5; H, 7·9. Calc. : C, 92·3; H, 7·7%), which showed no depression in melting point on admixture with retene. The picrate separated from alcohol in orange-yellow needles, m. p. 123—124° (Found : N, 9·3. Calc. : N, 9·1%), the styphnate in yellow needles, m. p. 141—142° (Found : N, 8·7. Calc. : N, 8·7%), the quinone in orange-red prisms, m. p. 197—198° (Found : C, 81·7; H, 6·1. Calc. : C, 81·8; H, 6·0%), and the quinoxaline from alcohol–chloroform in pale cream needles, m. p. 163—164° (Found : N, 8·5. Calc. : N, 8·3%).

1 : 4-*Dimethyl*-7-iso*propylphenanthrene*, prepared from the ketone (III; R = $CHMe_2$) as described in the preparation of 1 : 4 : 7-trimethylphenanthrene (p. 1789) and purified by distillation over sodium under reduced pressure, crystallised from alcohol in colourless plates, m. p. 61—62° (Found : C, 91·7; H, 7·8. $C_{19}H_{20}$ requires C, 91·9; H, 8·1%). The *picrate* crystallised from methyl alcohol

in orange needles, m. p. 115° (Found : C, 62·8; H, 4·6. $C_{25}H_{23}O_7N_3$ requires C, 62·9; H, 4·8%), and the *styphnate* in bright yellow needles, m. p. 142—143° (Found : C, 60·7; H, 5·0. $C_{25}H_{23}O_8N_3$ requires C, 60·8; H, 4·7%).

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