374. *Resin Acids. Part I. Synthesis of Phenanthrene Hydrocarbons derived from* d-*Pimaric Acid, and a New Route to Phenanthrene.*

By JOGENDRA C. BARDHAN and SURESH C. SENGUPTA.

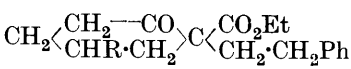
IN a series of investigations on the chemistry of resin acids, Ruzicka and his collaborators (*Helv. Chim. Acta*, 1922, **5**, 585; 1923, **6**, 677, 1082; 1924, **7**, 470, 875), using the Vesterberg–Diels dehydrogenation technique (*Ber.*, 1903, **36**, 4200; *Annalen*, 1927, **459**, 1), isolated retene, a new dimethylphenanthrene (pimanthrene), methylpimanthrene, and methylretene, the additional methyl groups in the last two compounds being derived from the carboxyl groups present in *d*-pimaric acid and abietic acid respectively. From purely analytical experiments, Bucher (*J. Amer. Chem. Soc.*, 1910, **32**, 374) represented retene as 1-methyl-7-*iso*propylphenanthrene. Furthermore, Ruzicka, de Graaff, and Hosking (*Helv. Chim. Acta*, 1931, **14**, 233) have shown that both retene and pimanthrene furnish phenanthrene-1 : 7-dicarboxylic acid on oxidation. Pimanthrene must therefore be 1 : 7-dimethylphenanthrene. The structure of the two remaining phenanthrene derivatives is less definite : although Ruzicka and his collaborators have tentatively represented them as 1 : 4 : 7-trimethyl- and 1 : 4-dimethyl-7-*iso*propylphenanthrenes, numerous alternatives are possible.

In view of the bearing of these phenanthrene derivatives on the orientation of *d*-pimaric and abietic acids, we are endeavouring to synthesise them, and the present communication deals with the products derived from *d*-pimaric acid.

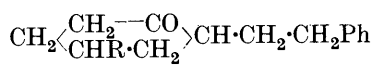
For obvious reasons the classical method of Pschorr (*Ber.*, 1896, **29**, 496) and the modified method of Windaus and Eickel (*Ber.*, 1924, **57**, *B*, 1871, 1875) cannot be conveniently employed for the synthesis of the phenanthrene derivatives described above. On the other hand, Schroeter (*Ber.*, 1924, **57**, *B*, 2025; 1929, **62**, 645) has recently indicated a new synthesis of phenanthrene starting from naphthalene. Owing to the difficulty of obtaining naphthalene derivatives with appropriate substituents (Müller, *Diss.*, Utrecht, 1930) and the difficult questions of orientation involved in the subsequent stages, this method cannot have any wide application (compare, however, Haworth, this vol., p. 1126).

We therefore decided to devise a new synthesis of phenanthrene. In the first instance, we condensed β-phenylethyl bromide with the potassio-derivative of ethyl *cyclo*hexanone-2-carboxylate to give *ethyl* 2-β-*phenylethyl*cyclo*hexanone*-2-*carboxylate* (I; R = H); on hydrolysis, this yielded 2-β-*phenylethyl*cyclo*hexanone* (II; R = H),

and reduction by sodium and moist ether afforded 2-β-*phenylethyl*-cyclo*hexanol* (III; R = H), which, on treatment with phosphorus



(I.)



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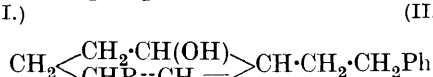
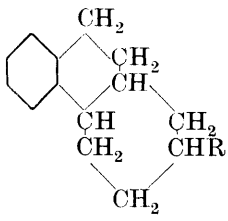


(III.)

pentoxide under certain conditions (p. 2523) readily furnished the desired cyclic condensation product (IV: R = H). That this is



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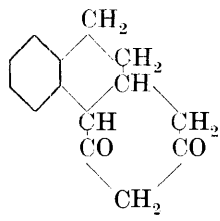

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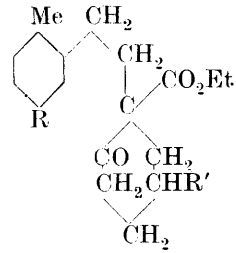


(VI.)

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene follows from a consideration of its physical properties and a rational synthesis from diketo-octahydrophenanthrene (V) (Rabe, *Ber.*, 1898, **31**, 1896) by Clemmensen's method. The same octahydrophenanthrene has been previously prepared by the reduction of phenanthrene by several investigators (Schmidt and Mezger, *Ber.*, 1907, **40**, 4240; Ipatieff, *ibid.*, 1908, **41**, 996; Breteau, *Compt. rend.*, 1910, **151**, 1368; *Bull. Soc. chim.*, 1911, **9**, 764). Since the physical properties of our product did not correspond with those found by previous workers, it is probable that their preparations were not homogeneous. Our formation of octahydrophenanthrene is precisely analogous to the production of methyl*iso*propylhexahydrofluorene by the action of phosphoric oxide on benzylmenthol (Wallach, *Annalen*, 1899, **305**, 261).

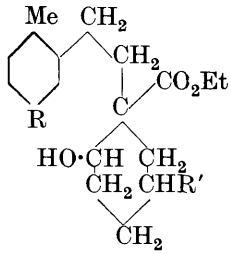
On being heated with selenium at 280—340°, the octahydrophenanthrene readily furnished phenanthrene. This new synthesis of phenanthrene has the advantage that the starting materials are readily accessible in great variety and the yields are excellent throughout; and we have now synthesised 2-methyl-, 1 : 4-dimethyl-, and 1 : 7-dimethyl-phenanthrene with the aid of this method.

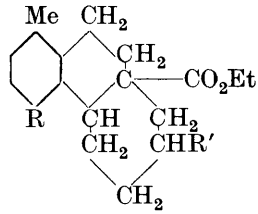
Substitution of ethyl 4-methyl*cyclo*hexanone-2-carboxylate in the above process yielded successively the homologues of (I), (II), (III), and (IV), and finally 2-methylphenanthrene, identical in all

essential respects with the product described by Haworth (*loc. cit.*, p. 1133; compare also Klinckhard, *Annalen*, 1911, **379**, 375).

1 : 4-*Dimethylphenanthrene.*—2 : 5-*Dimethylbenzyl chloride* was prepared from *p*-xylene by an extension of the method of Blanc (*Bull. Soc. chim.*, 1923, **33**, 313). This was converted, by way of the *cyanide*, into *ethyl* 2 : 5-*dimethylphenylacetate*, which was reduced by Bouveault's method, a good yield of β-2 : 5-*dimethylphenylethyl alcohol* being obtained. The alcohol was converted into the *bromide*, and the latter condensed with ethyl *cyclo*hexanone-2-carboxylate to give the *keto-ester* (VI; R = Me, R′ = H). This could not be hydrolysed to the ketone, so it was directly reduced to the *hydroxy-ester* (VII; R = Me, R′ = H), which was converted into the cyclic product (VIII; R = Me, R′ = H) by means of phosphoric oxide.

(VII.)





(VIII.)

Dehydrogenation by selenium gave 1 : 4-*dimethylphenanthrene*, with the extrusion of the carbethoxyl group. Owing to the small amount produced we could not definitely establish the constitution of this product, but the production of phenanthrene in good yield by reduction of the keto-ester (I; R = H), cyclisation, and dehydrogenation leaves no doubt as to the correctness of our view.

1 : 7-*Dimethylphenanthrene.*—By a precisely analogous method, β-*o*-tolylethyl bromide and ethyl 4-methyl*cyclo*hexanone-2-carboxylate yielded successively (VI; R = H, R′ = Me), (VII; R = H, R′ = Me), and thence 1 : 7-dimethylphenanthrene, identical with a specimen of pimanthrene prepared by the selenium dehydrogenation of *d*-pimaric acid. Its identity was further established by the formation of the picrate and the styphnate.

We have also prepared by the general method 1 : 4 : 7-trimethylphenanthrene, which differs from methylpimanthrene. An account of this, together with the corresponding products derived from abietic acid, will be communicated to the Society shortly.

Whilst our work was in progress, the preliminary notice of work on similar lines by Haworth and his co-workers appeared. We, therefore, place on record the results which we have obtained independently and almost simultaneously by a method which, we believe, is quite different from that used by them.

EXPERIMENTAL.

A. *Synthesis of* 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenanthrene and of Phenanthrene.—Ethyl* 2-*β*-*phenylethyl*cyclo*hexanone*-2-*carboxylate* (I; R = H). Many unsuccessful attempts were made to bring about the interaction of *β*-phenylethyl bromide and the Na derivative of ethyl *cyclo*hexanone-2-carboxylate; combination readily took place, however, when the corresponding K derivative was employed: K (7 g.) was finely powdered under xylene, the latter was replaced by dry C_6H_6 (100 c.c.), and the ester (29 g.; Kötz and Michels, *Annalen*, 1906, **350**, 210; 1908, **358**, 198) was added. When the formation of the K derivative was complete, the mixture was treated with a slight excess of *β*-phenylethyl bromide (35 g.) and the whole heated under reflux on the water-bath for 28 hrs. After cooling, H_2O was added, and the C_6H_6 layer was separated, washed with H_2O, dried, and distilled, the bulk passing over at 180—190°/7 mm. (yield, 23 g.), and redistilling at 184—185°/6 mm. (Found: C, 74·3; H, 8·3. $C_{17}H_{22}O_3$ requires C, 74·4; H, 8·0%). The *ester* is a colourless viscous oil of pleasant odour and gives no coloration with $FeCl_3$.

2-*β*-*Phenylethyl*cyclo*hexanone* (II; R = H). The foregoing keto-ester (20 g.) was boiled with 10% KOH aq. (150 c.c.) for 23 hrs. under reflux; the product was cooled, slightly acidified with HCl, and distilled in steam. The distillate was saturated with NaCl and repeatedly extracted with Et_2O. The solvent was removed, and the crude ketone directly converted into *semicarbazone* (8 g.), which crystallised from abs. EtOH, in which it is sparingly sol., in minute prisms, m. p. 179—180° (decomp.) (Found: C, 69·9; H, 8·4. $C_{15}H_{21}ON_3$ requires C, 69·5; H, 8·2%). The *ketone* was regenerated from the semicarbazone by gently warming it with dil. HCl aq. and collected in Et_2O; it was a perfectly colourless, mobile liquid of characteristic agreeable smell, b. p. 154°/6 mm. (Found: C, 83·0; H, 9·0. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%).

2-*β*-*Phenylethyl*cyclo*hexanol* (III; R = H). The ketone (14 g.), dissolved in Et_2O (50 c.c.), was placed in a flask connected with a condenser, and Na (14 g., in very thin slices) gradually added. The mixture was then stirred mechanically, and H_2O slowly added from a dropping funnel, further Et_2O being added if necessary. When all the Na had dissolved (*ca.* 4 hrs.) the ethereal solution was separated, washed (H_2O) until no longer alkaline, dried (anhydrous K_2CO_3), and the Et_2O evaporated. On distilling the residue under reduced press., a colourless viscous oil (11 g.) was collected, b. p. 158—160°/6 mm. (Found: C, 82·6; H, 9·8. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%). It did not solidify when cooled to —10° in a freezing mixture. The *phenylurethane*, prep. in the usual way, crystallised from MeOH or light petroleum (b. p. 80—90°) in stellate clusters of minute prisms, m. p. 115—116° (Found: N, 4·5. $C_{21}H_{25}O_2N$ requires N, 4·3%).

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenanthrene* (IV; R = H). (i) *From* 2-*β*-*phenylethyl*cyclo*hexanol*. The alcohol (5 g.) was heated with P_2O_5 (10 g.) for 20 mins. under 6 mm. in a metal-bath to 135—140°. The temp. was then gradually raised to 160—170° and a fraction (4·5 g.) distilled over. This was dried and purified by distillation over Na. It had b. p. 135°/9 mm., $d_4^{32.5°}$ 0·997325, $n_D^{32°}$ 1·548575 (Found: C, 90·5; H, 9·4. Calc. for $C_{14}H_{18}$: C, 90·3; H, 9·7%). It is stable to $KMnO_4$ and does not decolorise Br in $CHCl_3$.

(ii) *From diketo-octahydrophenanthrene.* The diketo-compound (10 g.; Rabe, *loc. cit.*) was reduced by boiling with conc. HCl (150 c.c.) and amalgamated Zn (100 g.). gaseous HCl being passed into the mixture towards the end of the process. When the greater part of the Zn had dissolved, the liquid was cooled and extracted with Et_2O. The crude octahydrophenanthrene was repeatedly distilled over Na, giving a mobile oil (3 g.), b. p. 130°/7 mm., $d_{4^\circ}^{30^\circ}$ 0·9990, $n_D^{30^\circ}$ 1·54940.

Phenanthrene. The octahydrophenanthrene (4·6 g.) was heated with powdered Se (10 g.) at 300—320° for 20 hrs., then cooled and thoroughly extracted with Et_2O; the residue of crude phenanthrene (2 g.) was converted into its picrate, long yellow needles, m. p. 145° (Found : C, 59·3; H, 3·1. Calc. : C, 59·0; H, 3·0%) after repeated crystn. from EtOH. The regenerated phenanthrene had m. p. 100° (Found : C, 94·5; H, 5·4. Calc. : C, 94·4; H, 5·6%). The identities of phenanthrene and its picrate were confirmed by mixed m. p.'s with an authentic specimen (Merck) and its picrate.

Ethyl 2-*β*-*phenylethyl*cyclo*hexanol*-2-*carboxylate.* The keto-ester (I; R = H) (10 g.) was dissolved in EtOH and mixed with H_2O until a faint turbidity was produced; the solution was then treated, in a porcelain beaker fitted with a mechanical stirrer, with 6 times the theo. quantity of 3% Na amalgam, a rapid stream of CO_2 being passed during the operation. The product was separated from $NaHCO_3$ by extraction with Et_2O and obtained as a light brown oil (8 g.). This was again reduced exactly as before. *Ethyl* 2-*β*-*phenylethyl*-cyclo*hexanol*-2-*carboxylate* was collected as a thick colourless oil, b. p. 182—183°/3 mm. (Found : C, 73·3; H, 8·3. $C_{17}H_{24}O_3$ requires C, 73·9; H, 8·7%). The dehydration of the hydroxy-ester with P_2O_5 was carried out as usual, giving an oil, b. p. 145—147°/4 mm. This was directly treated with Se as described above, and the product identified as phenanthrene (m. p. 100°; picrate, m. p. 144°).

B. *Synthesis of* 2-*Methylphenanthrene.*—*Ethyl* 2-*β*-*phenylethyl*-4-*methyl*cyclo*hexanone*-2-*carboxylate* (I; R = Me). This was prepared exactly as described on p. 2523 [K, 5·8 g.; ethyl 4-methyl*cyclo*hexanone-2-carboxylate (Kötz and Michels, *Annalen*, 1906, **348**, 95), 27 g.; *β*-phenylethyl bromide, 30 g.]. The *keto-ester* (20 g.) boiled at 175—178°/3 mm. (Found : C, 75·3; H, 8·4. $C_{18}H_{24}O_3$ requires C, 75·0; H, 8·3%).

2-*β*-*Phenylethyl*-4-*methyl*cyclo*hexanone* (II; R = Me). The *ketone* obtained on hydrolysis of the keto-ester, when purified in the usual way, boiled at 145—147°/3 mm. (Found : C, 83·7; H, 9·5. $C_{15}H_{20}O$ requires C, 83·3; H, 9·2%). The *semicarbazone* separated from EtOH in small prisms, m. p. 187° (decomp.) (Found : N, 15·2. $C_{16}H_{23}ON_3$ requires N, 15·4%).

2-*β*-*Phenylethyl*-4-*methyl*cyclo*hexanol* (III; R = Me), prep. as described above, was obtained as a colourless, thick oil, b. p. 157—160°/6 mm. (Found : C, 82·1; H, 10·0. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%).

2-*Methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene* (IV; R = Me) formed a colourless liquid, b. p. 137°/6 mm. (Found : C, 89·4; H, 10·1. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%).

2-*Methylphenanthrene.* The crude hydrocarbon obtained on heating the foregoing compound with Se was converted into the picrate; small yellow needles, m. p. 117—118° (Found : C, 59·7; H, 3·9. Calc. : C, 59·9; H, 3·6%), from EtOH. 2-Methylphenanthrene, regenerated from the pure picrate, separated from MeOH in colourless plates, m. p. 54—55° (Found : C, 94·0; H, 6·3. Calc. : C, 93·7; H, 6·2%). Haworth (*loc. cit.*) gives m. p.

118—119° and 55—56° respectively, and Klinckhard (*loc. cit.*) gives m. p. 52—53° for the hydrocarbon.

C. *Synthesis of* 1 : 4-*Dimethylphenanthrene.*—2 : 5-*Dimethylbenzyl chloride.* A mixture of *p*-xylene (200 g.), freshly fused powdered $ZnCl_2$ (40 g.) and CH_2O (45 g. of 40%) was stirred mechanically in a flask fitted with an inlet for dry HCl, an efficient stirrer passing through a mercury seal, and an outlet tube connected with a reflux condenser. A rapid current of HCl was passed through the reaction mixture, which was kept at 60° during the whole time. The gas was rapidly absorbed and in ½ hr. the reaction was complete. The product was poured into H_2O, the xylene layer separated, washed successively with H_2O, dil. NaOH aq., and H_2O, dried, and fractionated, the portion of b. p. 110—130°/25 mm. being collected (yield; 60 g.). On redistn. practically the whole of the 2 : 5-*dimethylbenzyl chloride* boiled at 85—86°/7 mm. (Found : Cl, 22·4. $C_9H_{11}Cl$ requires Cl, 22·9%). *p*-Xylene (140 g.) was recovered, and a residue, evidently of higher chlorinated products, was not further examined.

2 : 5-*Dimethylbenzyl cyanide.* KCN (32 g.) and H_2O (22 c.c.) were placed in a flask connected with a reflux condenser and a solution of the above chloride (60 g.) in EtOH (76 c.c.) was slowly added from a dropping funnel. The mixture was finally heated on the steam-bath for 4 hrs. The EtOH was then distilled off, the residue diluted with H_2O, and the *cyanide* extracted by ether, dried, and distilled; b. p. 115—119°/6 mm. (yield, 40 g.) (Found : N, 9·9. $C_{10}H_{11}N$ requires N, 9·6%).

Ethyl 2 : 5-*dimethylphenylacetate* was prepared by boiling a mixture of the foregoing cyanide (58 g.), abs. EtOH (96 c.c.), and conc. H_2SO_4 (42 c.c.) on an oil-bath at 130° for 5 hrs. The ester had b. p. 114°/4 mm. (Found : C, 75·1; H, 8·6. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

β-2 : 5-*Dimethylphenylethyl alcohol.* A solution of the ester (22·5 g.) in abs. EtOH (150 c.c., distilled over Ca) was reduced with Na (35 g.) in the apparatus described by Rupe and Langer (*Helv. Chim. Acta*, 1920, **3**, 272), more EtOH (100 c.c.) being added from time to time to dissolve the last traces of Na. H_2O was then added cautiously and the whole heated to boiling for 15 mins. EtOH was distilled off, and the alk. layer extracted with Et_2O. β-2 : 5-*Dimethylphenylethyl alcohol* formed a colourless, viscous oil, b. p. 110—113°/5 mm. (Found : C, 80·1; H, 9·4. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%).

β-2 : 5-*Dimethylphenylethyl bromide.* The alcohol (10 g.) was heated in a sealed tube with 30% HBr in glac. AcOH (80 c.c.) at 100° for 16 hrs. The cooled liquid was poured into H_2O, and the *bromide* extracted by ether and purified as usual; b. p. 104—106°/5 mm. (yield, 12 g.) (Found : Br, 37·0. $C_{10}H_{13}Br$ requires Br, 37·5%).

Ethyl 2-(β-2′ : 5′-*dimethylphenylethyl*)cyclo*hexanone*-2-*carboxylate* (VI; R = Me, R′ = H). The keto-ester was prepared exactly as described on p. 2523 (K, 4·9 g.; ethyl *cyclo*hexanone-2-carboxylate, 21·2 g.; bromide, 28·5 g.). The *keto-ester* formed a colourless oil, b. p. 192—194°/4 mm. (yield, 12·5 g.) (Found : C, 75·3; H, 8·2. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%).

Ethyl 2-(β-2′ : 5′-*dimethylphenylethyl*)cyclo*hexanol*-2-*carboxylate* (VII; R = Me, R′ = H). The above keto-ester was twice reduced with Na amalgam in the usual manner. The *hydroxy-ester* was obtained as a viscous oil, b. p. 195—198°/4 mm. (Found : C, 75·3; H, 9·1. $C_{19}H_{28}O_3$ requires C, 75·0; H, 9·2%).

1 : 4-*Dimethylphenanthrene.* Ethyl dimethyloctahydrophenanthrenecarb-

oxylate (VIII; R = Me, R′ = H) was readily obtained when this hydroxy-ester (5 g.) was heated with P_2O_5 in the usual way. The crude distillate (2 g.), b. p. 170—174°/4 mm., was heated with Se (6 g.) at 300—320° for 20 hrs. The product, isolated in the usual way, was converted into *picrate*, which separated from EtOH, in which it is difficultly sol., in small orange needles, m. p. 155° (Found: C, 60·6; H, 3·9. $C_{22}H_{17}O_7N_3$ requires C, 60·7; H, 4·0%).

1 : 4-*Dimethylphenanthrene*, regenerated from the picrate, crystallised from methyl alcohol in long needles, m. p. 77° (Found: C, 92·9; H, 6·5. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%).

D. *Synthesis of* 1 : 7-*Dimethylphenanthrene* (*Pimanthrene*).—*Ethyl* 2-(β-o-*tolylethyl*)-4-*methyl*cyclo*hexanone*-2-*carboxylate* (VI; R = H, R′ = Me). Shoesmith and Connor (J., 1927, 1770) prepared β-*o*-tolylethyl alcohol from *o*-bromotoluene by Grignard's method (*Compt. rend.*, 1905, **141**, 44), but the following procedure is more convenient for preparing large quantities. *o*-Xylene was converted by known methods (Atkinson and Thorpe, J., 1907, **91**, 1695) into ethyl *o*-tolylacetate, and the latter reduced by Bouveault's method to give β-*o*-tolylethyl alcohol (yield, 50%), b. p. 105—108°/5 mm. A large amount of *o*-tolylacetic acid was recovered, which yielded more of the alcohol. Shoesmith and Connor were unable to prepare the bromide by using HBr, but we readily obtained it (b. p. 94—95°/2 mm.) by the method described on p. 2525. The condensation with ethyl 4-methylcyclohexanone-2-carboxylate was carried out in the usual manner (K, 3·4 g.; ester, 16·1 g.; bromide, 15 g.). *Ethyl* 2-(β-o-*tolylethyl*)-4-*methyl*cyclo*hexanone*-2-*carboxylate* formed a thick, colourless liquid, b. p. 185—187°/2 mm. (yield, 10 g.) (Found: C, 75·2; H, 8·6. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%).

Ethyl 2-(β-o-*tolylethyl*)-4-*methyl*cyclo*hexanol*-2-*carboxylate* (VII; R = H, R′ = Me), prepared by reducing the above keto-ester with Na–Hg, was collected as a viscous oil, b. p. 195—197°/2 mm. (Found: C, 74·7; H, 8·9. $C_{19}H_{28}O_3$ requires C, 75·0; H, 9·2%). It (95 g.) was treated with P_2O_5 (12 g.) according to the standard method (p. 2523), and the crude cyclisation product (2 g.), b. p. 175—185°/2 mm., collected.

1 : 7-*Dimethylphenanthrene*. The foregoing product (2 g.) was heated with excess of Se at 280—300° for 8 hrs. and then at 335—340° for a further 12 hrs. 1 : 7-Dimethylphenanthrene partly sublimed in the flask and was purified by distillation over Na in a high vac.; it crystallised from EtOH in colourless plates (Found: C, 93·1; H, 6·8. Calc.: C, 93·2; H, 6·8%). These had the appearance of phenanthrene and had m. p. 86°, unaltered when mixed with an equal amount of pimanthrene prep. from *d*-pimaric acid. Its identity was further established by preparing the picrate, long yellow needles, m. p. 131—132° (Found: C, 60·7; H, 3·9. Calc.: C, 60·7; H, 4·0%), and the styphnate, fine yellow needles, m. p. 159° (Found: C, 58·4; H, 3·6. Calc.: C, 58·5; H, 3·8%), and by direct comparison with the corresponding products obtained from pimanthrene.

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UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
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