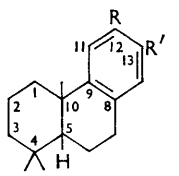
821. *Synthetical Studies in the Diterpene Series. Part II.*[1] *Synthesis of (±)-Sugiyl Methyl Ether and Related Compounds.**

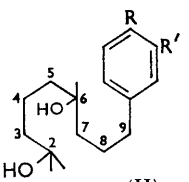
By D. Nasipuri and (Miss) Maya Guha.

A synthesis of the podocarpa-8,11,13-triene system (I) by a concerted double cyclisation of appropriately substituted ω-arylalkanols (*e.g.*, II and III) is described. The method has been employed for the synthesis of (±)-sugiyl methyl ether (VII) and (±)-xanthoperyl methyl ether (VIII). A few related products, *e.g.*, reten-6-ol and 6-methoxyretene have also been synthesised.

In 1957, we reported [2] a synthesis of podocarpa-8,11,13-triene (I; R = R′ = H) by cyclodehydration of the alcohols (II and III; R = R′ = H), and hoped to extend it to the synthesis of some related tricyclic phenolic diterpenes.[3] The work, however, was interrupted and the method has since then been used in other laboratories [4] for similar purposes. A study [5] of the stereochemistry of the cyclised product has shown it to be a mixture of *cis*- and *trans*-fused isomers. An observation by Wenkert and Jackson [6] that oxidation of the *trans*-isomer by chromic acid affords a monoketone (as VII) and the *cis*-isomer a diketone (as VIII), easily separable by chromatography, has greatly improved the usefulness of the method, allowing preparation of each or both isomers in a series. In the present paper we report the synthesis of (±)-sugiyl methyl ether (VII) and (±)-xanthoperyl methyl ether (VIII) and some related degradation products.



(I)



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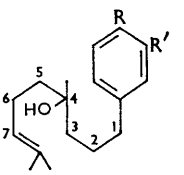

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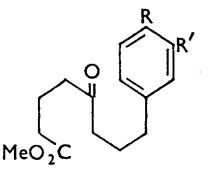

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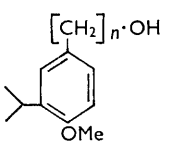

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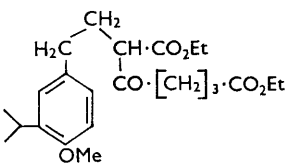

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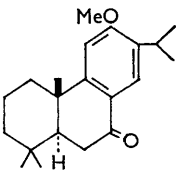

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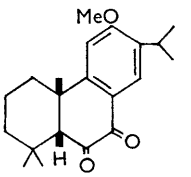


(VIII)*

* One enantiomer only is shown.

It was shown earlier [3] that 2,6-dimethyl-9-phenylnonane-2,6-diol (II; R = R′ = H) [obtained by the action of methylmagnesium iodide on methyl 5-oxo-8-phenyloctanoate [7] (IV; R = R′ = H)] and 4,8-dimethyl-1-phenylnon-7-en-4-ol (III; R = R′ = H) [obtained by condensing 3-phenylpropylmagnesium bromide with methylheptenone] were cyclised by polyphosphoric acid to the same stereoisomeric mixture of *cis*- and *trans*-(±)-podocarpa-8,11,13-triene (I; R = R′ = H). The products were each oxidised by chromic

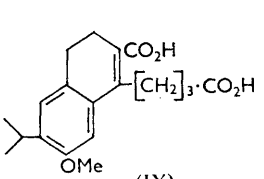
* A preliminary account of this work appeared in *Chem. and Ind.*, 1957, 425, and *J. Sci. Ind. Res. India*, 1962, **21**, *B*, 96, 199.

[1] Part I, Nasipuri and Chaudhuri, *J.*, 1958, 2579.
[2] Nasipuri, *Chem. and Ind.*, 1957, 425.
[3] See Tsutsui and Tsutsui, *Chem. Rev.*, 1959, **59**, 1031, for other syntheses.
[4] Fétizon and Delobelle, *Compt. rend.*, 1958, **246**, 2774; 1960, **251**, 2048; *Tetrahedron Letters*, 1960, No. 9, 16.
[5] Fétizon and Delobelle, *Bull. Soc. chim. France*, 1961, 1632.
[6] Wenkert and Jackson, *J. Amer. Chem. Soc.*, 1958, **80**, 211.
[7] Bardhan and Nasipuri, *J.*, 1956, 350.

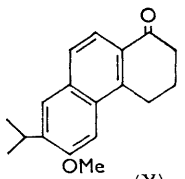
acid [6] and (±)-*trans*-podocarpa-8,11,13-trien-7-one and (±)-*cis*-podocarpa-8,11,13-triene-6,7-dione were isolated in each case, in almost identical proportions. Before applying this method to the synthesis of sugiyl methyl ether and allied compounds, a good supply of 3-isopropyl-4-methoxyphenethyl alcohol (V; $n = 2$) was required. The alcohol does not seem to have been reported before and the following method was found to be most satisfactory.

p-Bromoanisole and isopropyl alcohol in presence of 80% sulphuric acid gave 4-bromo-2-isopropylanisole in good yield, the structure of the product being settled by its conversion into 3-isopropyl-4-methoxybenzoic acid [8] by the action of carbon dioxide on the derived Grignard reagent. The bromide was converted into 3-isopropyl-4-methoxyphenethyl alcohol (V; n = 2) and thence into the propanol (V; $n = 3$) and their respective bromides by standard procedure.

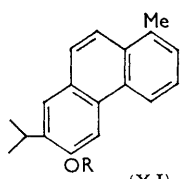
Ethyl α-(3-isopropyl-4-methoxyphenethyl)-β-oxopimelate (VI), obtained by alkylation of ethyl β-oxopimelate,[9] was hydrolysed by alkali and the resultant acid esterified to give the oxo-ester (IV; R = OMe, R′ = Pr^i). This was treated with an excess of methylmagnesium iodide and the resulting diol (II; R = OMe, R′ = Pr^i) cyclised by polyphosphoric acid, to furnish a stereoisomeric mixture of (±)-13-isopropyl-12-methoxypodocarpa-8,11,13-trienes (I; R = OMe, R′ = Pr^i) in 80% yield. The same mixture was obtained by cyclisation of the unsaturated alcohol (III; R = OMe, R′ = Pr^i), prepared by the action of 3-(3-isopropyl-4-methoxyphenyl)propylmagnesium bromide on methylheptenone. The podocarpatriene derivative (I; R = OMe, R′ = Pr^i) was oxidised by chromic acid in acetic acid and the product resolved into two fractions by chromatography. The major fraction was (±)-sugiyl methyl ether [10] (VII), m. p. 125—127°, and the minor fraction, the methyl ether (VIII), m. p. 205°, of (±)-xanthoperol,[11] the identities being established by comparison of ultraviolet and infrared absorption spectra.



(IX)



(X)



(XI)

In other experiments, the substituted β-oxopimelate (VI) was cyclised by concentrated sulphuric acid, and the resultant dihydronaphthalene derivative (IX) was converted into 1,2,3,4-tetrahydro-7-isopropyl-6-methoxy-1-oxophenanthrene (X) and thence into 6-methoxyretene (XI; R = Me) and reten-6-ol (XI; R = H) by methods described elsewhere.[7] These phenanthrenes and their derivatives compared well with those derived from natural sources.[10b, 12]

Experimental

M. p.s are corrected. Ultraviolet absorption spectra were recorded for ethanolic solutions on a Beckman spectrophotometer, unless otherwise stated. Light petroleum refers to the fraction of b. p. 40—60°.

2,6-*Dimethyl*-1-*phenylnonane*-2,6-*diol* (II; R = R′ = H).—To a Grignard reagent prepared from magnesium (5 g.), methyl iodide (15 ml.), and dry ether (100 ml.), was added with stirring a solution of methyl 5-oxo-8-phenyloctanoate (10 g.) in ether (20 ml.). The mixture was gently refluxed for 1 hr., then cooled, and decomposed with cold dilute sulphuric acid. The ethereal layer was separated, washed with water, dried (Na_2SO_4), and evaporated. The residue was

[8] Sengupta, Biswas, and Bhattacharya, *J. Indian Chem. Soc.*, 1959, **36**, 659.
[9] Guha, Rakshit, and Nasipuri, *J. Indian Chem. Soc.*, 1960, **37**, 267.
[10] (*a*) Keimatsu, Ishiguro, and Fukui, *J. Pharm. Soc. Japan*, 1937, **57**, 92; (*b*) Huzii and Tikamori, *ibid.*, 1939, **59**, 124; (*c*) Brandt and Thomas, *J.*, 1952, 2442; (*d*) Sengupta, Chaudhuri, and Khastgir, *Tetrahedron*, 1960, **10**, 45.
[11] (*a*) Brendenberg and Gripenberg, *Acta Chem. Scand.*, 1956, **10**, 1511; (*b*) Briggs, Cambie, Seelye, and Warth, *Tetrahedron*, 1959, **7**, 270.
[12] Keimatsu and Ishiguro, *J. Pharm. Soc. Japan*, 1935, **55**, 45; Brandt and Neubauer, *J.*, 1939, 1031; Campbell and Todd, *J. Amer. Chem. Soc.*, 1940, **62**, 1287.

distilled, to give the *diol* (II; R = R′ = H) (10 g.), b. p. 170°/0·01 mm., n_D^{36} 1·5030 (Found: C, 77·6; H, 10·3. $C_{17}H_{28}O_2$ requires C, 77·3; H, 10·6%).

4,8-*Dimethyl*-1-*phenylnon*-7-*en*-4-*ol* (III; R = R′ = H).—A solution of methylheptenone (20 g.) in ether (40 ml.) was added dropwise to a stirred solution of Grignard reagent prepared from magnesium (4 g.), 3-phenylpropyl bromide (30 g.), and ether (100 ml.) at such a rate that gentle refluxing was maintained. The mixture was heated on the water-bath for 1 hr., then decomposed with cold dilute sulphuric acid, and the product was worked up as above. The unsaturated alcohol (III; R = R′ = H) was obtained as a viscous oil (26·8 g.), b. p. 145—150°/0·01 mm., n_D^{36} 1·5030 (Found: C, 83·0; H, 10·8. Calc. for $C_{17}H_{26}O$: C, 82·9; H, 10·6%). Fétizon and Delobelle record $n_D^{22·5}$ 1·5078.

(±)-*Podocarpa*-8,11,13-*triene* (I; R = R′ = H).—The above two alcohols were cyclised under identical conditions with practically the same result, as follows: (*a*) The alcohol (8 g.) was added to stirred polyphosphoric acid [13] [from phosphorus pentoxide (10 g.) and 89% phosphoric acid (50 ml.)] and heated at 160—170° for 3 hr., then cooled, poured on ice, and extracted repeatedly with ether. The ethereal solution was washed with dilute sodium hydroxide solution, dried (Na_2SO_4), and evaporated, and the residue distilled over sodium, to give the hydrocarbon (I; R = R′ = H) (5 g.), b. p. 140°/2 mm., n_D^{37} 1·5390 (Found: C, 89·4; H, 10·5. Calc. for $C_{17}H_{24}$: C, 89·5; H, 10·5%), $\lambda_{max.}$ 264 and 272 mμ (log ε 2·80 and 2·72, respectively).[14]

(*b*) The alcohol (5 g.) was heated with polyphosphoric acid [from phosphorus pentoxide (62 g.) and 89% phosphoric acid (40 ml.)] at 160° for 3 hr. The hydrocarbon (I) (3 g.), b. p. 140°/2 mm., n_D^{37} 1·5410, was obtained. Perbenzoic acid titration showed unsaturation to the extent of 10—12% in the cyclised product from both the alcohols. Dehydrogenation with selenium at 300—350° for 40 hr. gave 1-methylphenanthrene,[15] m. p. and mixed m. p. 118—119° (picrate, m. p. 136°).

Oxidation of (±)-*Podocarpa*-8,11,13-*triene by Chromic Acid* (I; R = R′ = H).—The preceding hydrocarbon (10 g.) in acetic acid (100 ml.) was mixed with a solution of chromic acid (13 g.) in 80% acetic acid (75 ml.) in the cold. After 24 hr. at room temperature, the mixture was diluted with water, extracted thoroughly with ether, washed with sodium carbonate solution, dried, and evaporated. The residue (7 g.) was taken up in light petroleum and passed on to a column of alumina (300 g.). After an initial fraction (2 g.) of unoxidised material, eluted by light petroleum, (±)-*trans*-podocarpa-8,11,13-trien-7-one was obtained by benzene and subsequently distilled, affording a viscous sweet-smelling liquid (3·8 g.), b. p. 160°/1 mm., n_D^{36} 1·5530 (Found: C, 84·3; H, 9·0. Calc. for $C_{17}H_{22}O$: C, 84·3; H, 9·1%), $\lambda_{max.}$ 253 mμ (log ε 4·02). The dinitrophenylhydrazone crystallised from benzene–methanol in red needles, m. p. 218° (lit.,[5] 212°) (Found: C, 65·6; H, 6·1; N, 13·0. Calc. for $C_{23}H_{26}N_4O_4$: C, 65·4; H, 6·1; N, 13·3%). The chromatogram was further eluted with methanol; the product so obtained, on rechromatography and crystallisation from light petroleum, gave yellow needles, m. p. 120° (lit.,[5] 119—122°) (Found: C, 79·3; H, 8·0. Calc. for $C_{17}H_{20}O_2$: C, 79·7; H, 7·8%), $\lambda_{max.}$ 315 mμ (log ε 3·82).

4-*Bromo*-2-*isopropylanisole*.—A mixture of *p*-bromoanisole (83 g.), isopropyl alcohol (20·6 g.), and 80% sulphuric acid (300 g.) was stirred at 75—80° for 3·5 hr., then cooled, decomposed with ice, and extracted with ether (3 × 100 ml.). The extract was washed with water, dried (Na_2SO_4), and distilled through a column. The fraction (66 g.), b. p. 105—107°/7 mm., n_D^{34} 1·5340 (Found: C, 52·5; H, 5·6. $C_{10}H_{13}BrO$ requires C, 52·5; H, 5·7%), was 4-*bromo*-2-*isopropylanisole*. Attempts to oxidise the compound to 5-bromo-2-methoxybenzoic acid failed.

3-*Isopropyl*-4-*methoxybenzoic Acid*.—A slow stream of dry carbon dioxide was passed into a cooled solution of Grignard reagent from 4-bromo-2-isopropylanisole (5 g.), magnesium (1·2 g.), and ether (25 ml.), during 1 hr. The solid complex formed was decomposed with ice and dilute sulphuric acid. The ethereal solution was separated and extracted with sodium hydrogen carbonate solution, and the extract acidified to furnish 3-isopropyl-4-methoxybenzoic acid (2 g.) which crystallised from aqueous methanol in thin needles, m. p. and mixed m. p. 163—164° (cf. ref. 8) (Found: C, 67·9; H, 7·2%; equiv., 196. Calc. for $C_{11}H_{14}O_3$: C, 68·0; H, 7·2%; equiv., 194).

3-*Isopropyl*-4-*methoxyphenethyl Alcohol* (V; *n* = 2).—A mixture of 4-bromo-2-isopropylanisole (50 g.), ethyl bromide (1 ml.), and ether (170 ml.) was added dropwise during 30 min.

[13] Ansell and Shelleck, *J.*, 1956, 1238.
[14] Askew, *J.*, 1935, 512.
[15] Haworth, *J.*, 1932, 1125.

to a suspension of magnesium (6 g.) in ether (50 ml.). Thiophen-free benzene (100 ml.) was added, the mixture was refluxed for 1 hr., then cooled to 0°, and ethylene oxide (20 g.) in ether (100 ml.) was introduced with stirring. Next day, the mixture was gently refluxed on the water-bath for 1 hr., cooled, and decomposed with ice and 10% sulphuric acid. The organic layer was separated, dried (K_2CO_3), and distilled, to give 3-*isopropyl*-4-*methoxyphenethyl alcohol* (26 g.), b. p. 150—153°/2 mm., n_D^{33} 1·5180 (Found: C, 74·1; H, 9·1. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%). The 3,5-*dinitrobenzoate* crystallised from ethanol in yellow prismatic needles, m. p. 105—106° (Found: C, 58·4; H, 5·0. $C_{19}H_{20}N_2O_7$ requires C, 58·8; H, 5·2%). 3-*Isopropyl*-4-*methoxyphenethyl bromide*, b. p. 135°/3 mm., was prepared [16] by the action of phosphorus tribromide in carbon tetrachloride.

3-(3-*Isopropyl*-4-*methoxyphenyl*)*propan*-1-*ol* (V; $n = 3$).—The above bromide (31·9 g.) was refluxed with sodium cyanide (25 g.), sodium iodide (4·6 g.), and 95% ethanol (150 ml.) for 7 hr., giving 3-*isopropyl*-4-*methoxyphenethyl cyanide* (19 g.), b. p. 145—155°/6 mm. The latter was dissolved in methanol (60 ml.), saturated with hydrogen chloride at 0°, and heated on the water-bath for 6 hr. in a stream of dry hydrogen chloride. *Methyl* β-(3-*isopropyl*-4-*methoxyphenyl*)-*propionate* (20 g.) had b. p. 143—145°/10 mm. The derived *acid* crystallised from aqueous methanol in needles, m. p. 79—81° (Found: C, 70·2; H, 8·0. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%).

The preceding ester (17 g.) was reduced by lithium aluminium hydride (4·2 g.) in ether (150 ml.), giving 3-(3-*isopropyl*-4-*methoxyphenyl*)*propan*-1-*ol* (13 g.), b. p. 140—145°/6 mm. (Found: C, 75·1; H, 9·5. $C_{13}H_{20}O_2$ requires C, 75·0; H, 9·6%). The corresponding bromide, prepared by phosphorus tribromide had b. p. 135°/6 mm.

Ethyl α-(3-*Isopropyl*-4-*methoxyphenethyl*)-β-*oxopimelate* (VI).—Ethyl β-oxopimelate (7 g.) and 3-isopropyl-4-methoxyphenethyl bromide (7 g.) were heated with sodium (0·65 g.) in ethanol (20 ml.) at 90° for 20 hr., to give the β-oxo-ester (VI) (6 g.), b. p. 210—215°/0·01 mm.

Methyl 8-(3-*Isopropyl*-4-*methoxyphenyl*)-5-*oxo*-*octanoate* (IV; R = OMe, R′ = Pr^i).—The β-oxo-ester (VI) (8 g.) was heated with sodium hydroxide (4 g.) in water (160 ml.) for 6 hr. The mixture was cooled and extracted once with ether, and the alkaline solution acidified. The gummy acid, thus set free, was esterified by 3% methanolic hydrogen chloride, to give the *ester* (IV; R = OMe, R′ = Pr^i) (5·3 g.), b. p. 180—185°/2 mm. (Found: C, 71·0; H, 8·9. $C_{19}H_{28}O_4$ requires C, 71·3; H, 8·8%). The derived acid did not solidify but gave a *semicarbazone*, m. p. 136° (Found: C, 62·6; H, 7·8. $C_{19}H_{29}N_3O_4$ requires C, 62·8; H, 8·0%).

9-(3-*Isopropyl*-4-*methoxyphenyl*)-2,6-*dimethylnonane*-2,6-*diol* (II; R = OMe, R′ = Pr^i).—A solution of the preceding ester (5·3 g.) in thiophen-free benzene (20 ml.) was slowly added to a Grignard reagent prepared from magnesium (2·7 g.), methyl iodide (8 ml.), and ether (60 ml.). The mixture was heated on the water-bath for 1 hr., then worked up as above to give the crude diol (5·8 g.) which was used for cyclisation.

1-(3-*Isopropyl*-4-*methoxyphenyl*)-4,8-*dimethylnon*-7-*en*-4-*ol* (III; R = OMe, R′ = Pr^i).—This was prepared as described for the analogous parent compound. 3-(3-Isopropyl-4-methoxyphenyl)propyl bromide (11·5 g.) and methylheptenone (6 g.), on condensation, gave the unsaturated alcohol (III; R = OMe, R′ = Pr^i) (11 g.) after the removal of lower-boiling fraction at 140°/2 mm.

(±)-13-*Isopropyl*-12-*methoxypodocarpa*-8,11,13-*triene* (I; R = OMe, R′ = Pr^i).—The above two alcohols (II and III; R = OMe, R′ = Pr^i) were cyclised as follows. The alcohol (5 g.) was mixed with warm polyphosphoric acid [from phosphorus pentoxide (62 g.) and 89% phosphoric acid (40 ml.)] and kept at 80—100° for 1 hr. with stirring. The deep red solution was cooled, decomposed with ice, and worked up as above, and the *product* distilled. The fraction (3·2—4 g.) of b. p. 145—150°/0·1 mm. was collected. A redistilled sample was analysed (Found: C, 84·2; H, 11·0. $C_{21}H_{32}O$ requires C, 84·0; H, 10·7%). The use of higher temperature (160—170°) and a longer period (3 hr.) did not improve the quality of the product. The cyclised product was not appreciably affected when shaken with an aqueous solution of potassium permanganate in acetone.[5]

(±)-*Sugiyl Methyl Ether* (VII).—The above cyclised product (2·3 g.) was dissolved in glacial acetic acid (25 ml.) and added to a solution of chromic acid (3 g.) in 80% acetic acid (25 ml.). After 24 hr. at the room temperature, the solution was diluted with water, and the product worked up in the usual way. The crude product was chromatographed in light petroleum on activated alumina (100 g.) and eluted successively with light petroleum, benzene, and ethanol.

[16] Hewett, *J.*, 1936, 50.

The petroleum fraction consisted of non-ketonic material (0·3—0·4 g.) and was neglected. The benzene fraction (1·1 g.), on being kept in the refrigerator in contact with a little methanol, slowly deposited crystals, m. p. 120—123°. These were collected and on further crystallisation from aqueous methanol afforded (±)-*sugiyl methyl ether* (VII) as plates, m. p. 125—127° (Found: C, 80·4; H, 9·8. $C_{21}H_{30}O_2$ requires C, 80·2; H, 9·6%), $\lambda_{max.}$ 228 and 277 mμ (log ε 4·31 and 4·13, respectively). The ultraviolet and infrared absorption spectra were identical with those of (+)-sugiyl methyl ether,[10d] m. p. 137—138°. The synthetic ketone gave a dark red *dinitrophenylhydrazone* (from ethyl acetate–methanol), m. p. 244—246° (Found: C, 65·4; H, 6·8; N, 11·4. $C_{27}H_{34}N_4O_5$ requires C, 65·6; H, 6·9; N, 11·3%), $\lambda_{max.}$ (in $CHCl_3$) 401 mμ (log ε 4·47). The mother-liquor from (±)-sugiyl methyl ether afforded a new *dinitrophenylhydrazone*, m. p. 205—207° (from ethyl acetate–methanol), having the same elemental analysis (Found: C, 65·7; H, 6·9; N, 11·6%) and $\lambda_{max.}$ 396 mμ (log ε 4·44) which might be the *cis*-isomer.

(±)-*Xanthoperyl Methyl Ether* (VIII).—The ethanolic eluate from the above experiment, on evaporation, afforded a yellow solid (0·4 g.), m. p. 180—193°. It crystallised from aqueous methanol in yellow needles, m. p. 205° and gave correct analyses for the *diketone* (VIII) (Found: C, 76·7; H, 8·6. $C_{21}H_{28}O_3$ requires C, 76·8; H, 8·5%), and $\lambda_{max.}$ 225, 250, and 349 mμ (log ε 3·95, 3·78, and 4·01, respectively). The ultraviolet and infrared absorption spectra were identical with those of xanthoperyl methyl ether, m. p. 190—192°, prepared by us from (+)-xanthoperol,[11a] m. p. 255—270°, with dimethyl sulphate–potassium carbonate–acetone. Though the compound (VIII) has been represented as having the *cis*-ring junction, it might well be the stable *trans*-isomer owing to equilibration during working-up (see, however, Brendenberg [17]).

γ-(2-Carboxy-3,4-dihydro-6-isopropyl-7-methoxy-1-naphthyl)butyric Acid (IX).—Ethyl α-(3-isopropyl-4-methoxyphenethyl)-β-oxopimelate (VI) (6 g.) was cyclised by concentrated sulphuric acid (18 ml.) at 0° during 30 min. The product was worked up in the usual way and hydrolysed to the *dihydronaphthalene* (IX) (3·2 g.), m. p. 211—213° (Found: C, 68·7; H, 7·1%; equiv., 168. $C_{19}H_{24}O_5$ requires C, 68·7; H, 7·2%; equiv., 166). The dimethyl ester, b. p. 200—205°/0·01 mm. was dehydrogenated [7] with sulphur to the corresponding aromatic ester, b. p. 205—207°/0·01 mm.

1,2,3,4-*Tetrahydro-7-isopropyl-6-methoxy-1-oxophenanthrene* (X).—The above dimethyl aromatic ester (4 g.) was heated with finely powdered sodium (0·3 g.) in thiophen-free benzene (14 ml.) for 5 hr. on the water-bath. The resultant β-oxo-ester was hydrolysed by refluxing acetic acid (80 ml.), hydrochloric acid (40 ml.), and water (7 ml.), for 30 min. under carbon dioxide. The product was worked up in the usual way; the *ketone* (X) (0·82 g.), b. p. 200—210°/1 mm., crystallised from benzene–light petroleum in plates, m. p. 144—145° (Found: C, 80·7; H, 7·3. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%) [*semicarbazone* (from ethanol), nodules, m. p. 270° (Found: N, 13·0. $C_{19}H_{23}N_3O_2$ requires N, 12·9%)].

6-*Methoxyretene* (XI; R = Me) and *Reten-6-ol* (XI; R = H).—A solution of the preceding ketone (0·5 g.) in dry benzene (20 ml.) was treated with methylmagnesium iodide (3 mol.), and the resultant alcohol (0·5 g.) heated with 10% palladium–charcoal (350 mg.) at 300—320° for 2 hr. 7-Isopropyl-6-methoxy-1-methylphenanthrene (XI; R = Me), so obtained, crystallised from benzene–light petroleum in plates, m. p. 80° (Found: C, 86·3; H, 7·7. Calc. for $C_{19}H_{20}O$: C, 86·4; H, 7·6%) [*trinitrobenzene derivative*, m. p. 187° (Found: C, 62·7; H, 5·0. $C_{25}H_{23}N_3O_7$ requires C, 62·9; H, 4·8%); quinone, m. p. 208—209° (Found: C, 77·3; H, 6·1. Calc. for $C_{19}H_{18}O_3$: C, 77·6; H, 6·1%)]. Reten-6-ol (XI; R = H) obtained on demethylation of the ether crystallised from benzene–light petroleum in plates, m. p. 178° (Found: C, 86·3; H, 7·1. Calc. for $C_{18}H_{18}O$: C, 86·4; H, 7·2%) [acetate, m. p. 91° (Found: C, 82·1; H, 6·9. Calc. for $C_{20}H_{20}O_2$: C, 82·2; H, 6·8%); picrate, m. p. 177° (Found: N, 8·6. Calc. for $C_{24}H_{21}N_3O_8$: N, 8·7%)]. M. p.s of all these compounds agree well with those reported in the literature.[10b, 12]

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[17] Brendenberg, *Acta Chem. Scand.*, 1960, **14**, 385; Brendenberg and Shoolery, *ibid.*, 1960, **14**, 556.