

245. The Synthesis of Some Substituted Hexahydro-12-methyl-2-oxophenanthrenes.

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3 : 4-Dihydro-1-methylnaphthalene with perbenzoic acid (cf. ref. 1) gives 1-methyl-2-tetralone, which has been converted into 2 : 3 : 4 : 9 : 10 : 12-hexahydro-12-methyl-2-oxophenanthrene.² The method has been shown to be applicable to several derivatives.

THE Robinson ring-extension gives a good yield when applied to 1-methyl-2-tetralones, and is a satisfactory way of making intermediate substances for the synthesis of several natural products.³⁻⁶ However, although 2-tetralones are easily made, monomethylation is difficult by ordinary methods.^{3,4,6,7} Cornforth and Robinson have avoided this difficulty in the case of 5-hydroxy-1-methyl-2-tetralone (I) which has been made directly by the reduction of 6-methoxy-5-methyl-1-naphthol,⁷ but the starting material is not easy to obtain, and some of the stages are limited in scale.

An interesting approach is the oxidation of 4-alkyl-1 : 2-dihydronaphthalenes, first explored by Ghosh and Robinson⁸ and lately described by Newhall *et al.*⁵ in the specific case of 5-hydroxy-8-methoxy-1-methyl-2-tetralone. Both groups found perbenzoic acid

¹ English and Cavaglieri, *J. Amer. Chem. Soc.*, 1943, **65**, 1085.

² Zwahlen, Horton, and Fujimoto, *J. Amer. Chem. Soc.*, 1957, **79**, 3131.

³ Cornforth and Robinson, *J.*, 1946, 676.

⁴ Grob and Jundt, *Helv. Chim. Acta*, 1952, **35**, 2111.

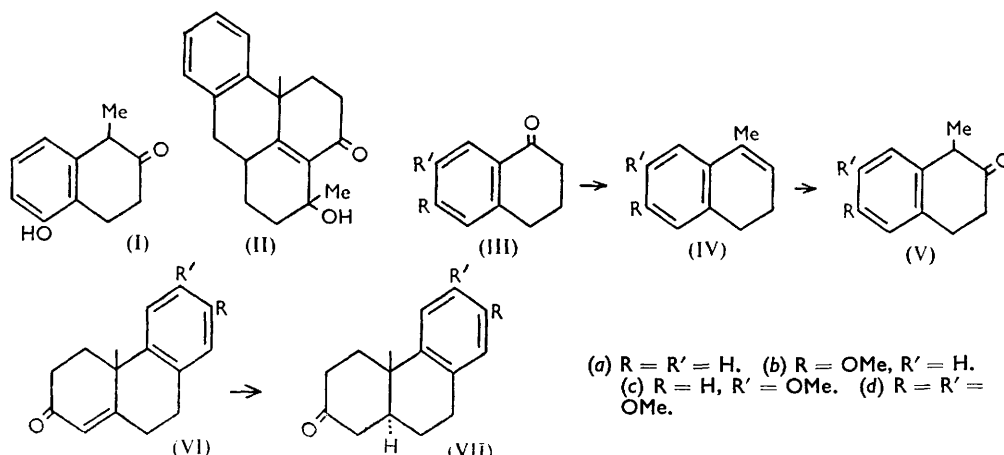
⁵ Newhall, Harris, Holly, Johnston, Richter, Walton, Wilson, and Folkers, *J. Amer. Chem. Soc.*, 1955, **77**, 5646.

⁶ Stork and Schulenberg, *ibid.*, 1956, **78**, 250.

⁷ Cornforth, Kauder, Pike, and Robinson, *J.*, 1955, 3348.

⁸ Ghosh and Robinson, *J.*, 1944, 506.

unsatisfactory; Ghosh and Robinson got a low yield with hydrogen peroxide in acetic acid, while the Merck group found red lead in acetic acid very satisfactory. English and Cavaglieri¹ described the oxidation of 1:2-dihydro-4-methylnaphthalene to 1-methyl-2-tetralone with perbenzoic acid, and we found this a very good preparative method. It is stated that the oxidation yields the ketone directly without accompanying epoxide, but we find the product often gives only a little semicarbazone, although a dinitrophenylhydrazone is formed in good yield. As our crude product has a roughly constant boiling point (the



same as that of the ketone), we suppose the non-ketonic material is the epoxide and not the glycol monobenzoate. It is easily converted into the ketone by dilute acid. Performic acid, perphthalic acid, and red lead in acetic acid gave unsatisfactory results.

For the ring extension of 1-methyl-2-tetralone, we found alkylation with 4-chlorobutan-2-one in the presence of sodium hydride in light petroleum gave the best yield, a method which seems not to have been used before. Ring extension, using the Mannich base, gave also a by-product, $C_{19}H_{22}O_2$, m. p. 166°. The spectrum of this shows that it is an $\alpha\beta$ -unsaturated ketone. It may have the structure (II) and arise from dialkylation of 1-methyl-2-tetralone.

We have reduced 2:3:4:9:10:12-hexahydro-12-methyl-2-oxophenanthrene (VIa) in several ways. Lithium in liquid ammonia gave a 60% yield of a crystalline ketone (VIIa) which we suppose is the more stable *trans*-isomer. With lithium aluminium hydride this gave an oily alcohol, having a crystalline benzoate in which the hydroxyl group should have the more stable equatorial 2β -conformation. Catalytic reduction of the ketone (VIa) gave oils containing more or less of the *cis*-isomer; on further reduction with lithium aluminium hydride a crystalline alcohol was obtained to which we assign the 2α -*cis*-structure. Re-oxidation of this gave the oily *cis*-ketone, isolated as its semicarbazone. The nuclear structure of this alcohol was confirmed by dehydrogenation to phenanthrene over a palladium catalyst.

6-Methoxy-1-tetralone, 7-methoxy-1-tetralone, and 6:7-dimethoxy-1-tetralone are readily obtained. We have converted them into the corresponding 1-methyl-2-tetralones without difficulty. The structure of the crystalline 1:2-dihydro-6:7-dimethoxy-4-methylnaphthalene (IVd) was proved by acetylation to the known 3-acetyl derivative. 6:7-Dimethoxy-1-methyl-2-tetralone (Vd) was also obtained crystalline, and an attempt was made to prove the structure by reaction with ethylmagnesium bromide and dehydrogenation to 2-ethyl-6:7-dimethoxy-1-methylnaphthalene. Only 6:7-dimethoxy-1-methyl-2-naphthol was obtained, so it seems that the ketone reacted with the Grignard reagent completely in the enolic form.

Ring extension of these three 2-tetralones then gave respectively the oxophenanthrenes

(VIb, c, and d), the best yield in each case being obtained by the Mannich base method. Reduction with lithium in liquid ammonia gave the *trans*-ketones (VIIb, c, and d), of which only the 6-methoxy-compound (VIIc) crystallised. All the alcohols have remained amorphous. The use of these compounds in the preparation of substances related to natural products will be described shortly.

This method also affords 5-methoxy-1-methyl-2-tetralone, which has interest as the intermediate in the Robinson–Cornforth steroid synthesis. This substance is, however, not difficult to prepare by other methods, in contrast to 5-methoxy-1-tetralone.^{9,10}

EXPERIMENTAL

1-Methyl-2-tetralone.—1 : 2-Dihydro-4-methylnaphthalene (130 g.) in acetone (400 ml.) was added slowly with shaking to perbenzoic acid (130 g.) in acetone (1 l.) at 0°. After 2½ hr., the solvent was evaporated and ether added. The solution was washed until neutral and the ether evaporated. A sample of the residue gave only a low yield of semicarbazone, although a dinitrophenylhydrazone was readily formed. The residue was refluxed for 4 hr. with ethanol (800 ml.), concentrated sulphuric acid (100 ml.), and water (600 ml.), cooled, and extracted with ether. After being washed until neutral, the ether was evaporated and the residue distilled. 1-Methyl-2-tetralone (107 g.), collected at 128°/14 mm., had n_D^{20} 1.5568. The semicarbazone, m. p. 202°, was formed in nearly quantitative yield.

2 : 3 : 4 : 9 : 10 : 12-Hexahydro-12-methyl-2-oxophenanthrene (VIa).—(a) 4-Dimethylaminobutan-2-one (20.5 g.) in dry ether (25 ml.) was stirred at 0° while methyl iodide (9 ml.) in ether (10 ml.) was added. After a further hour's stirring, the ether was evaporated under reduced pressure at 0°, and to the residue was added 1-methyl-2-tetralone (22 g.) in dry benzene (100 ml.) and then potassium (7 g.) in ethanol (100 ml.), then the whole was stirred for 2 hr. at 0° and 10 min. on the steam-bath. Dilute sulphuric acid and ether were added, and the organic layer was washed until neutral. Evaporation of the solvent and distillation of the residue gave 2 : 3 : 4 : 9 : 10 : 12-hexahydro-12-methyl-2-oxophenanthrene, b. p. 144–146°/0.05 mm., which crystallised from light petroleum (b. p. 60–80°) as prisms, m. p. 90° (3.5 g.) (Zwahlen *et al.*² give m. p. 90–91°) (Found: C, 84.5; H, 7.4. Calc. for $C_{15}H_{16}O$: C, 84.8; H, 7.6%), ν 1669 cm^{-1} (in Nujol). The semicarbazone formed prisms, m. p. 220–224°, from ethanol (Found: C, 72.0, 71.3; H, 7.3, 6.9; N, 15.6. $C_{16}H_{19}ON_3$ requires C, 71.3; H, 7.1; N, 15.6%). A fraction, collected at 150–200°/0.05 mm., crystallised from acetone–light petroleum (b. p. 60–80°), giving a substance as prisms (1.2 g.), m. p. 166° (Found: C, 80.3; H, 7.9. $C_{19}H_{22}O_2$ requires C, 80.8; H, 7.8%), λ_{max} , 247 $m\mu$ (log ϵ 4.15 in EtOH), ν 1669 cm^{-1} (in Nujol). The semicarbazone formed very insoluble crystals, m. p. 268–270°, from ethanol (Found: C, 71.2; H, 7.7. $C_{20}H_{25}O_2N_3$ requires C, 70.8; H, 7.4%). A third substance (200 mg.), obtained by storing the residues in light petroleum (b. p. 60–80°), had m. p. 198° (from benzene) (Found: C, 77.1; H, 6.9. $C_{18}H_{20}O_3$ requires C, 77.0; H, 6.8%), ν 1720 cm^{-1} .

(b) 1-Methyl-2-tetralone (16 g.) was added to sodium hydride (2.5 g.) in light petroleum (b. p. 60–80°; 100 ml.). The suspension was stirred while 4-chlorobutan-2-one (11 g.) was added rapidly. After the initial reaction was over, refluxing was continued for 15 min., the whole was cooled, and sodium hydride (2.5 g.) added. After ½ hour's refluxing, dilute hydrochloric acid was added, the organic layer separated and evaporated, and the residue distilled. The tricyclic ketone was collected at 160°/0.1 mm. and formed colourless prisms (11.0 g.), m. p. and mixed m. p. 90°, from light petroleum (b. p. 60–80°). Chromatography of the mother-liquors gave a further amount (total 70%).

Reduction of the Tricyclic Ketone (VIa).—(a) Over palladised calcium carbonate. The ketone (300 mg.) in ethanol (10 ml.) was shaken with hydrogen over palladised calcium carbonate for 2 hr. Filtration, evaporation, and recrystallisation from light petroleum (b. p. 60–80°) gave *trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-12-methyl-2-oxophenanthrene (VIIa) (15 mg.) as plates, m. p. 106–107° (Found: C, 83.9; H, 8.3. $C_{15}H_{18}O$ requires C, 84.1; H, 8.5%). The semicarbazone formed needles, m. p. 229–231° (decomp.), from ethanol (Found: C, 71.4, 70.8; H, 7.4, 7.2; N, 15.6. $C_{16}H_{21}ON_3$ requires C, 70.8; H, 7.8; N, 15.5%).

⁹ Lockett and Short, *J.*, 1939, 787.

¹⁰ Papa, Schwenk, and Breiger, *J. Org. Chem.*, 1949, **14**, 366.

(b) *Over palladised alumina.* The tricyclic ketone (600 mg.), reduced in ethanol (25 ml.) and concentrated hydrochloric acid (3 drops) over palladised alumina, gave the *trans*-ketone (110 mg.), m. p. 106–107°, undepressed on admixture with the previous sample.

(c) *With lithium in liquid ammonia.* Lithium (300 mg.) was dissolved in liquid ammonia (100 ml.), and the tricyclic ketone (1.5 g.) in dry ether (50 ml.) added. After 15 min. ammonium chloride was added, and then, after evaporation of most of the ammonia, also ether and water. Evaporation of the ether layer left crystals which gave the *trans*-ketone (900 mg. 60%), m. p. and mixed m. p. 106°, from light petroleum (b. p. 60–80°). The use of calcium in place of lithium gave similar results.

trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-2 β -hydroxy-12-methylphenanthrene.—Reduction of the *trans*-ketone (500 mg.) with lithium aluminium hydride in ether gave an oily alcohol which on benzylation gave *trans-2 β -benzoyloxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-12-methylphenanthrene* (500 mg.) as prisms, m. p. 160° (Found: C, 81.9, 82.4; H, 7.4, 7.3. C₂₂H₂₄O₂ requires C, 82.5; H, 7.5%). This benzoate (195 mg.) was also obtained on hydrogenation of the *trans*-ketone (200 mg.) over Adams catalyst.

cis-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-2 α -hydroxy-12-methylphenanthrene.—The amorphous saturated ketone obtained by hydrogenation at neutral palladium [see (a) above] (7.0 g.) was reduced with lithium aluminium hydride in ether. The product crystallised slowly from light petroleum (b. p. 60–80°); recrystallisation gave *cis-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-2 α -hydroxy-12-methylphenanthrene* (1.9 g.) as needles, m. p. 75–77° (Found: C, 83.5; H, 9.4. C₁₈H₂₀O requires C, 83.3; H, 9.3%). The *benzoate* crystallised from ethanol in prisms, m. p. 155–156°, giving a large depression with the *trans*-benzoate (Found: C, 82.4; H, 7.6%). This benzoate (50%) was also obtained on hydrogenation of the unsaturated ketone over Adams catalyst or Raney nickel in ethanol.

cis-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-12-methyl-2-oxophenanthrene.—Oxidation of the *cis*-alcohol with chromic acid in acetone by the procedure of Bowers *et al.*¹¹ gave the oily *cis*-ketone which gave a *semicarbazone* as prisms, m. p. 196–198° (decomp.), from ethanol (Found: C, 71.0; H, 7.7; N, 15.7. C₁₆H₂₁ON₃ requires C, 70.8; H, 7.8; N, 15.5%).

Dehydrogenation of the Crude cis-Alcohol.—This alcohol (500 mg.) was heated for 4 hr. with 30% palladised charcoal (100 mg.) at 400°. Chromatography and sublimation, followed by two crystallisations from ethanol, gave phenanthrene (12 mg.), m. p. and mixed m. p. 98–100°.

6 : 7-Dimethoxy-1-tetralone (III d).— γ -(3 : 4-Dimethoxyphenyl)butyric acid (96 g.), benzene (500 ml.), and phosphorus pentachloride (100 g.) were refluxed for 1 hr., and the solution was washed until neutral and evaporated. Crystallisation of the residue from light petroleum (b. p. 60–80°) gave *6 : 7-dimethoxy-1-tetralone* as prisms, m. p. 96°. The method of Haworth and Mavin¹² gave, in our hands, a product difficult to purify.

1 : 2-Dihydro-6 : 7-dimethoxy-4-methylnaphthalene (IV d) (cf. ref. 12).—*6 : 7-Dimethoxy-1-tetralone* (70 g.) in benzene (250 ml.) was added to a solution prepared from magnesium (12 g.) and excess of methyl bromide in ether (700 ml.). After $\frac{1}{2}$ hour's refluxing, saturated ammonium chloride solution was added, and the ether layer separated and evaporated. Heating the residual alcohol dehydrated it and then crystallisation from light petroleum (b. p. 60–80°) gave *1 : 2-dihydro-6 : 7-dimethoxy-4-methylnaphthalene* (60 g.), prisms, m. p. 70–72° (Found: C, 76.6; H, 7.9. C₁₈H₁₆O₂ requires C, 76.4; H, 7.9%). Heating the alcohol with formic acid gave *6 : 7-dimethoxy-1-methylnaphthalene*, needles (from methanol), m. p. 114°. A sample made by decarboxylation of *6 : 7-dimethoxy-1-methylnaphthalene-2-carboxylic acid*¹³ with copper bronze in quinoline had m. p. and mixed m. p. 114° (Found: C, 77.2; H, 7.0. Calc. for C₁₈H₁₄O₂: C, 77.2; H, 7.0%). Haworth and Mavin give m. p. 110–111°.

2-Acetyl-3 : 4-dihydro-6 : 7-dimethoxy-1-methylnaphthalene.—*1 : 2-Dihydro-6 : 7-dimethoxy-4-methylnaphthalene* (4.0 g.) was treated in nitrobenzene (10 ml.) with acetyl chloride (1.5 ml.) and aluminium chloride (2.7 g.) in nitrobenzene (10 ml.). After being kept overnight the solution was poured into ice and hydrochloric acid, ether added, and the organic layer washed to neutrality and distilled. The fraction collected at 160–170°/0.5 mm. was taken up in ethanol, whereupon it crystallised. Recrystallisation gave *2-acetyl-3 : 4-dihydro-6 : 7-dimethoxy-1-methylnaphthalene* (300 mg.) as pale yellow plates, m. p. 109°, alone or mixed with an authentic specimen¹³ (Found: C 73.4; H, 7.3. Calc. for C₁₈H₁₈O₃: C, 73.1; H, 7.4%).

¹¹ Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.

¹² Haworth and Mavin, *J.*, 1932, 1485.

¹³ Howell and Taylor, *J.*, 1956, 4252.

6 : 7-Dimethoxy-1-methyl-2-tetralone (Vd).—1 : 2-Dihydro-6 : 7-dimethoxy-4-methylnaphthalene (35 g.) in chloroform (100 ml.) was treated with perbenzoic acid (36 g.) in chloroform (360 ml.). After storage overnight the solution was washed neutral and the residue distilled. The fraction collected at 160—175°/0.1 mm. crystallised from methanol, to give 6 : 7-dimethoxy-1-methyl-2-tetralone (26 g.) as prisms, m. p. 87° (Found: C, 71.2; H, 6.95. $C_{13}H_{16}O_3$ requires C, 70.9; H, 7.3%). The semicarbazone formed needles, m. p. 200° (decomp.), from ethanol (Found: C, 60.6; H, 7.1; N, 15.1. $C_{14}H_{19}O_3N_3$ requires C, 60.6; H, 6.9; N, 15.15%). A fraction collected at 180—200°/0.1 mm. crystallised from methanol, giving 6 : 7-dimethoxy-1-methyl-2-naphthol (500 mg.), needles, m. p. 223° (Found: C, 71.6; H, 6.6. $C_{13}H_{14}O_3$ requires C, 71.5; H, 6.5%).

6 : 7-Dimethoxy-1-methyl-2-naphthol.—6 : 7-Dimethoxy-1-methyl-2-tetralone (900 mg.) in ether (50 ml.) was added to a Grignard solution prepared from magnesium (0.5 g.) and ethyl bromide (2 ml.) in ether (30 ml.). After 15 minutes' refluxing, the product was isolated and heated at 300° for $\frac{1}{2}$ hr. with 30% palladised charcoal (100 mg.). The solid product recrystallised from methanol, yielding 6 : 7-dimethoxy-1-methyl-2-naphthol (600 mg.), m. p. and mixed m. p. 223°.

2-Ethyl-6 : 7-dimethoxy-1-methylnaphthalene.—2-Acetyl-6 : 7-dimethoxy-1-methylnaphthalene¹³ (400 mg.) in toluene (10 ml.) was refluxed with amalgamated zinc (6 g.) in hydrochloric acid (9.0 ml.) and water (11 ml.) for 6 hr. Ether-extraction and evaporation gave a solid which was sublimed and then recrystallised from light petroleum (b. p. 60—80°). 2-Ethyl-6 : 7-dimethoxy-1-methylnaphthalene (300 mg.) formed plates, m. p. 92—93° (Found: C, 78.2; H, 8.1. $C_{18}H_{18}O_2$ requires C, 78.2; H, 7.9%).

2 : 3 : 4 : 9 : 10 : 12-Hexahydro-6 : 7-dimethoxy-12-methyl-2-oxophenanthrene (VIId).—4-Dimethylaminobutan-2-one (14 g.) was dissolved in dry ether (50 ml.) and methyl iodide (8 ml.) added with stirring at 0°. After 1 hr. the ether was removed under reduced pressure at 0°, and 6 : 7-dimethoxy-1-methyl-2-tetralone (26 g.) in benzene (130 ml.) added. A solution of sodium (5.5 g.) in methanol (130 ml.) was added at 0° with stirring in a nitrogen atmosphere, and the mixture stirred for 2 hr., then refluxed for 10 min. Ether and dilute sulphuric acid were added, the organic layer was washed until neutral, and distilled. An oil (23 g.) was collected at 184—186°/0.01 mm. Crystallisation from ether gave 2 : 3 : 4 : 9 : 10 : 12-hexahydro-6 : 7-dimethoxy-12-methyl-2-oxophenanthrene (19.2 g., 60%) as yellow prisms, m. p. 105—106° (Found: C, 74.5; H, 7.85. $C_{17}H_{20}O_3$ requires C, 75.0; H, 7.4%). The semicarbazone formed orange prisms, m. p. 232° (decomp.), from ethanol (Found: C, 65.5; H, 7.3; N, 12.85. $C_{18}H_{23}O_3N_3$ requires C, 65.6; H, 7.0; N, 12.8%).

2 : 3 : 4 : 6 : 10 : 12-Hexahydro-6 : 7-dihydroxy-12-methyl-2-oxophenanthrene.—The dimethoxy-compound (1.0 g.) was refluxed for $\frac{1}{2}$ hr. with acetic acid (20 ml.) and 55% hydriodic acid (4.0 ml.; prepared by refluxing over red phosphorus and filtering). Ether and water were added, and the ether layer was washed with aqueous sodium hydrogen sulphite solution and with water, and evaporated. The residue crystallised from a little ether, and recrystallisation from methanol-ether gave 2 : 3 : 4 : 9 : 10 : 12-hexahydro-6 : 7-dihydroxy-12-methyl-2-oxophenanthrene (300 mg.) as unstable yellow prisms, m. p. 200° (decomp.), giving an intense green colour with ferric chloride (Found: C, 72.7; H, 6.7. $C_{16}H_{16}O_3$ requires C, 73.75; H, 6.6%).

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-6 : 7-dimethoxy-12-methyl-2-oxophenanthrene (VIIId).—The dimethoxy-compound (500 mg.) in dioxan (20 ml.) and ether (20 ml.) was added slowly to a solution of lithium (100 mg.) in liquid ammonia (50 ml.). After 15 min. ammonium chloride was added, the ammonia was evaporated, and ether and water were added. The ether layer was washed until neutral and evaporated; the oily residue gave the semicarbazone of the octahydro-compound as plates, m. p. 213—215° (decomp.), from ethanol (Found: C, 65.5; H, 7.7; N, 13.05. $C_{18}H_{25}O_3N_3$ requires C, 65.2; H, 7.6; N, 12.7%).

7-Methoxy-1-tetralone (IIIc).—Succinic anhydride (100 g.), suspended in nitrobenzene (200 ml.) and anisole (108 g.), was added with shaking to a solution of aluminium chloride (266 g.) in nitrobenzene (600 ml.) at 0°. After storage overnight at room temperature, the solution was heated at 45° for 1 hr., then poured into ice and hydrochloric acid. The solid which separated was filtered off and reprecipitated from sodium carbonate solution. The acid obtained was reduced in the usual way by the Clemmensen method using toluene; distillation then gave γ -*p*-methoxyphenylbutyric acid (149 g.), b. p. 153—154°/0.05 mm., which was cyclised as described by Haworth and Sheldrick.¹⁴ 7-Methoxy-1-tetralone (105 g., 60% calc. on anisole) was obtained as prisms, m. p. 66°.

¹⁴ Haworth and Sheldrick, *J.*, 1934, 1950.

1 : 2-Dihydro-6-methoxy-4-methylnaphthalene (IVc).—7-Methoxy-1-tetralone (50 g.) in ether (400 ml.) was added slowly with stirring to a Grignard solution from methyl iodide (30 ml.) and magnesium (11 g.) in ether (400 ml.). After addition of saturated ammonium chloride solution the ether layer was removed and evaporated. The residue was heated with potassium hydrogen sulphate (50 g.) at 120° for 2 hr. The product was isolated with ether and distilled, 1 : 2-dihydro-6-methoxy-4-methylnaphthalene (43 g.) being collected at 145—148°/14 mm.

7-Methoxy-1-methyl-2-tetralone (Vc).—1 : 2-Dihydro-6-methoxy-4-methylnaphthalene (43 g.) was dissolved in chloroform (100 ml.), and perbenzoic acid (43 g.) in chloroform (600 ml.) added slowly with stirring at 0°. After being kept overnight at 0°, the solution was washed with sodium hydroxide solution and water and evaporated. The residue was refluxed in ethanol (300 ml.), water (250 ml.), and sulphuric acid (50 ml.) for 3 hr., then concentrated under reduced pressure. Ether was added and the solution washed until neutral and distilled. 7-Methoxy-1-methyl-2-tetralone (34 g., 71%) was collected at 120—122°/0.1 mm. (Found: C, 75.5; H, 7.5. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%). The semicarbazone crystallised from ethanol in needles, m. p. 197° (decomp.) (Found: C, 63.4; H, 6.6; N, 16.9. $C_{13}H_{17}O_2N_3$ requires C, 63.1; H, 6.9; N, 17.0%).

2 : 3 : 4 : 9 : 10 : 12-Hexahydro-6-methoxy-12-methyl-2-oxophenanthrene (VIc).—4-Dimethylaminobutan-2-one (21 g.) in ether (75 ml.) was cooled to 0° and methyl iodide (11.5 ml.) in ether (15 ml.) added with stirring in 15 min. After 1 hour's stirring at 0°, the solution was evaporated under reduced pressure, and 7-methoxy-1-methyl-2-tetralone (34 g.) in benzene (200 ml.) was added under nitrogen. A solution from sodium (8.2 g.) and methanol (200 ml.) was added in 5 min. and the whole stirred for 2 hr. at 0°, then 10 min. at the b. p. Ether and dilute sulphuric acid were added, and the ether layer was washed until neutral and distilled. A pale yellow oil (31.4 g.) was collected at 186—187°/0.01 mm., which crystallised from ether-light petroleum (b. p. 60—80°) to give 2 : 3 : 4 : 9 : 10 : 12-hexahydro-6-methoxy-12-methyl-2-oxophenanthrene (21.7 g., 50%) as prisms, m. p. 63° (Found: C, 79.8; H, 7.8. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%). The semicarbazone formed prisms, m. p. 218—220° (decomp.), from ethanol (Found: C, 68.2; H, 7.0; N, 14.5. $C_{17}H_{21}O_2N_3$ requires C, 68.2; H, 7.1; N, 14.0%).

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-6-methoxy-12-methyl-2-oxophenanthrene (VIIc).—The preceding ketone (10 g.) in ether (200 ml.) was added to liquid ammonia (400 ml.) containing lithium (1 g.). After 5 min. ammonium chloride was added, the ammonia evaporated, and the ether solution washed until neutral and evaporated. The residue, crystallised from ether, gave the octahydro-ketone (7.8 g.) as prisms, m. p. 130° (Found: C, 78.4; H, 8.3. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25%). The semicarbazone formed plates, m. p. 208—210° (decomp.), from ethanol (Found: C, 67.3; H, 7.4; N, 14.1. $C_{17}H_{23}O_2N_3$ requires C, 67.75; H, 7.7; N, 13.9%).

2 : 3 : 4 : 9 : 10 : 12-Hexahydro-6-hydroxy-12-methyl-2-oxophenanthrene.—The preceding hexahydro-methoxy-ketone (500 mg.) was heated in acetic acid (9 ml.) and 55% hydriodic acid (1 ml.; cf. above) for $\frac{1}{2}$ hr. Treatment with ether, washing with sodium hydrogen sulphite solution, removal of the phenol with sodium hydroxide solution, and its sublimation at 160—170°/0.02 mm. and crystallisation from ether afforded 2 : 3 : 4 : 9 : 10 : 12-hexahydro-6-hydroxy-12-methyl-2-oxophenanthrene (340 mg.) as bright yellow plates, m. p. 202° (Found: C, 78.7; H, 7.2. $C_{16}H_{16}O_2$ requires C, 78.9; H, 7.1%).

6-Methoxy-1-methyl-2-tetralone (Vb).—To a Grignard solution from magnesium (6 g.) and methyl iodide (15 ml.) in ether (500 ml.), 6-methoxy-1-tetralone (27 g.) in ether (400 ml.) was added slowly with stirring. The complex was decomposed with saturated ammonium chloride solution, and the ether layer washed with water and evaporated. The residue was heated with potassium hydrogen sulphate (30 g.) for 2 hr. at 120—130°, ether and water were added, the ether layer was washed and evaporated, and the residue distilled. 1 : 2-Dihydro-7-methoxy-4-methylnaphthalene (20.2 g.) was collected at 148—154°/14 mm. This was treated in chloroform (75 ml.) with perbenzoic acid (28 g.) in chloroform (280 ml.) at 0°. The solution was kept overnight at 0°, washed, and evaporated. The residue was refluxed for 3 hr. with water (125 ml.), ethanol (150 ml.), and concentrated sulphuric acid (25 ml.), and the product isolated with ether and distilled. 6-Methoxy-1-methyl-2-tetralone (10 g.) was collected at 120—128°/0.05 mm. The semicarbazone formed needles, m. p. 218—220° (decomp.), from ethanol (Found: C, 63.2; H, 6.7; N, 16.4. $C_{13}H_{17}O_2N_3$ requires C, 63.1; H, 6.9; N, 17.0%). A fraction, b. p. 130—170°/0.01 mm., crystallised from aqueous ethanol to give 6-methoxy-1-methyl-2-naphthol (600 mg.), needles, m. p. 154° (Found: C, 76.5; H, 6.6. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%).

2 : 3 : 4 : 9 : 10 : 12-Hexahydro-7-methoxy-12-methyl-2-oxophenanthrene (VIb).—4-Dimethylaminobutan-2-one (6 g.) in ether (20 ml.) was cooled to 0° and methyl iodide (3.3 ml.) in ether (10 ml.) was added in 15 min. After 1 hour's stirring at 0°, the ether was removed under reduced pressure and 6-methoxy-1-methyl-2-tetralone (9.8 g.) was added in benzene (60 ml.) under nitrogen. A solution of sodium (2.4 g.) in methanol (60 ml.) was added in 5 min., and the whole stirred for 2 hr. at 0° and then for 10 min. at the b. p. The product (5.4 g.) had b. p. 180—188°/0.3 mm. and gave 2 : 3 : 4 : 9 : 10 : 12-hexahydro-7-methoxy-12-methyl-2-oxophenanthrene (2.9 g.) as pale yellow prisms, m. p. 106—108°, from ether (Found: C, 79.1; H, 7.7. $C_{18}H_{18}O_2$ requires C, 79.3; H, 7.5%). The semicarbazone formed plates, m. p. 233—236° (decomp.), from ethanol (Found: C, 68.0; H, 6.85; N, 14.2. $C_{17}H_{21}O_2N_3$ requires C, 68.2; H, 7.1; N, 14.0%). The *trans*-octahydro-derivative, prepared with lithium and liquid ammonia in the usual way, failed to crystallise, but its semicarbazone formed prisms, m. p. 232—233° (decomp.), from ethanol (Found: C, 67.85; H, 7.6; N, 14.2. $C_{17}H_{23}O_2N_3$ requires C, 67.75; H, 7.7; N, 13.9%).

2 : 3 : 4 : 9 : 10 : 12-Hexahydro-8-methoxy-12-methyl-2-oxophenanthrene.—5-Methoxy-1-tetralone (1 g.) was added to a Grignard solution prepared from magnesium (1 g.) and methyl iodide (1 ml.) in ether (20 ml.). The complex was decomposed with aqueous ammonium chloride, and the ether layer evaporated. The residue was heated for 2 hr. at 130° with potassium hydrogen sulphate (1 g.), and the product isolated with ether and distilled. 1 : 2-Dihydro-8-methoxy-4-methylnaphthalene (850 mg.) was collected at 180° (bath) /15 mm. This was added in chloroform (10 ml.) to perbenzoic acid (1 g.) in chloroform (20 ml.). After being kept overnight at 0° the solution was washed to neutrality and evaporated. The residue was refluxed for 3 hr. with ethanol (25 ml.), water (25 ml.), and sulphuric acid (2.5 ml.), and the product isolated with ether. Distillation gave 5-methoxy-1-methyl-2-tetralone, b. p. 220° (bath)/15 mm. Potassium (200 mg.) was dissolved in *tert*-butyl alcohol (200 ml.), and the tetralone added, followed by 4-chlorobutan-2-one (316 mg.). After $\frac{1}{2}$ hour's refluxing, dilute hydrochloric acid was added and the product isolated with ether and chromatographed on alumina (12 g.; Spence type "H"). *cyclo*Hexane containing 10% of benzene eluted an oil which, crystallised from *cyclo*hexane, gave 2 : 3 : 4 : 9 : 10 : 12-hexahydro-8-methoxy-12-methyl-2-oxophenanthrene (80 mg.) as pale yellow prisms, m. p. and mixed m. p. 119° with an authentic specimen kindly provided by Dr. J. W. Cornforth. The infrared spectra of the two samples were identical (Found: C, 79.0; H, 7.6. Calc. for $C_{18}H_{18}O_2$: C, 79.3; H, 7.5%).

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