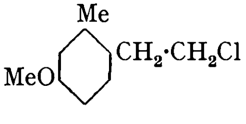
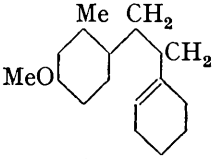
114. *Syntheses in the Phenanthrene Series. Part VI. 3-Methoxy-1-methylphenanthrene.*

By Peter Hill, W. F. Short, H. Stromberg, and A. E. Wiles.

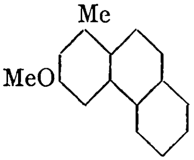
For the reason explained in Part V (this vol., p. 263) 3-*methoxy*-1-*methylphenanthrene* has been synthesised by two methods. In the first of these, interaction between the Grignard compound of 6-bromo-*m*-tolyl methyl ether and β-chloroethyl toluene-*p*-sulphonate afforded β-(5-*methoxy*-o-*tolyl*)*ethyl chloride* (I) in 36% yield. The pairing of the magnesium compound of (I) with *cyclo*hexanone produced 1-β-(5′-methoxy-*o*-tolyl)ethyl*cyclo*hexanol, which was dehydrated to 1-β-(5′-*methoxy*-o-*tolyl*)*ethyl*-Δ^1-cyclo*hexene* (II). The synthesis of 3-methoxy-1-methylphenanthrene (III) was completed by treating the unsaturated compound with aluminium chloride and dehydrogenating the resulting mixture with sulphur.



(I.)

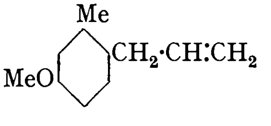


(II.)

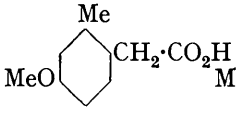


(III.)

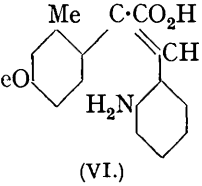
In the alternative method, 6-*allyl*-m-*tolyl methyl ether* (IV), prepared from allyl bromide and the Grignard compound of 6-bromo-*m*-tolyl methyl ether, was first oxidised to 5-*methoxy*-o-*tolylacetic acid* (V). Condensation of the potassium salt of this acid with *o*-nitrobenzaldehyde furnished 2-*nitro*-α-(5′-*methoxy*-o-*tolyl*)*cinnamic acid*, which was reduced to the *amino-acid* (VI). 3-*Methoxy*-1-*methylphenanthrene*-10-*carboxylic acid* (VII) was obtained when the amino-acid was diazotised and warmed with alkali, and decarboxylation was smoothly effected by heating with copper powder. The resulting 3-methoxy-1-methylphenanthrene was demethylated to the corresponding phenol. 3-*Hydroxy*-1 *methylphenanthrene*, its methyl ether, and the *picrate* of the latter melt at almost the same temperatures as the isomeric compounds obtained by the dehydrogenation of podocarpic acid (Sherwood and Short, *Rep. Austral. Assoc. Sci.*, 1933, **31**, 38), but there is a considerable depression in melting point on admixture of the respective pairs.



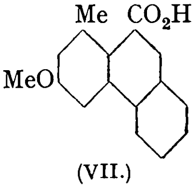
(IV.)



(V.)



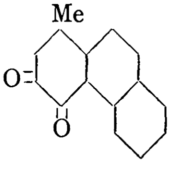
(VI.)

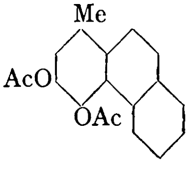


(VII.)

3-Hydroxy-1-methylphenanthrene coupled with diazotised sulphanilic acid to produce a red dye and, owing to the fixation of the double bonds in the phenanthrene system, reaction doubtless occurred at position 4. Reduction of the dye with sodium hyposulphite furnished an unstable amino-phenol, which was successively oxidised (chromic anhydride) to 1-*methylphenanthra*-3 : 4-*quinone* (VIII) and reduced by Thiele's method to 3 : 4-*diacetoxy*-1-*methylphenanthrene* (IX).

(VIII.)





(IX.)

EXPERIMENTAL.

6-*Bromo*-m-*tolyl Methyl Ether*.—The bromination of *m*-cresol was effected as described by Darzens and Lévy (*Compt. rend.*, 1931, **193**, 292), but the phenol was dissolved in a mixture of acetic acid and chloroform (4 : 1 by vol.). The yield of 6-bromo-*m*-cresol, b. p. 120—131°/10 mm. (mostly at 123—125°/10 mm.), s. p. 48°, was 67% and methylation with methyl sulphate (1·3 mols.) in 10% sodium hydroxide solution afforded the phenol ether, b. p. 119—122°/18 mm., in 66% yield.

β-(5-*Methoxy*-o-*tolyl*)*ethyl Chloride* (I).—β-Chloroethyl toluene-*p*-sulphonate (1 mol.), dissolved in benzene (5·5 mols.), was added to a Grignard solution prepared from the preceding bromo-ether (1 mol.), magnesium (1 atom), and ether (6 mols.), and the mixture boiled for 3 hours. Decomposition with ice-cold dilute hydrochloric acid and careful fractionation afforded a 36% yield of β-(5-*methoxy*-o-*tolyl*)*ethyl chloride*, b. p. 134—135°/10 mm. (Found : Cl, 19·5. $C_{10}H_{13}OCl$ requires Cl, 19·25%).

1-β-(5′-*Methoxy*-o-*tolyl*)*ethyl*-Δ^1-cyclo*hexene* (II).—The aforesaid chloride (1 mol.) was slowly added to magnesium (3 atoms) and ether (15 mols.), the mixture boiled for ½ hour, and the liquid decanted from the excess of magnesium. *cyclo*Hexanone (1·9 mols.) was slowly added to the Grignard solution with mechanical stirring and cooling in a freezing mixture and, after 12 hours, the complex was decomposed with ice-cold ammonium chloride solution. Distillation afforded a fraction, b. p. 200—240°/20 mm., which deposited crystals, m. p. 87°, when dissolved in methyl alcohol and strongly cooled, and recrystallisation from acetone gave αδ-*di*-(5-*methoxy*-o-*tolyl*)*butane*, m. p. 89° (Found : C, 80·4; H, 8·5. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·7%). Removal of the methyl alcohol and distillation of the residue furnished a viscous liquid, b. p. 210—227°/23 mm., which still contained some of the butane derivative and was dehydrated by heating at 165° for 1 hour with 1½ parts of potassium hydrogen sulphate. Fractionation afforded the cyclo*hexene* (II) in 22% yield as a colourless liquid, b. p. 192—195°/18 mm. (Found : C, 83·2 ; H, 9·4. $C_{16}H_{22}O$ requires C, 83·5 ; H, 9·6%).

6-*Allyl*-m-*tolyl methyl ether* (IV), b. p. 102—120°/10 mm., was obtained in 63% yield by adding allyl bromide (1·1 mols.) to a Grignard solution prepared from 6-bromo-*m*-tolyl methyl ether (1 mol.), magnesium (1 atom), and ether (5 mols.). A middle fraction, b. p. 107—108°/10 mm., was analysed (Found : C, 81·7 ; H, 8·7. $C_{11}H_{14}O$ requires C, 81·5 ; H, 8·6%).

5-*Methoxy*-o-*tolylacetic Acid* (V).—5% Potassium permanganate solution (6340 c.c.) was added with vigorous stirring to an emulsion of the preceding allyl compound (136 g.) in ice-water (500 c.c.) and glacial acetic acid (342 c.c.), cooled in a freezing mixture so that the temperature remained below 0°. Distillation with steam removed the unchanged allyl compound (45%) and the residue was made alkaline and filtered. The liquid was concentrated to 1 l. and acidified at 0°. The solid was exhaustively extracted with ligroin, and the extract recrystallised from the same solvent, giving long hexagonal plates, m. p. 106·5—107° (Found : C, 66·7 ; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·7 ; H, 6·7%). Yield, 15%. Extraction of the aqueous layer with ether gave acetic acid and a small quantity of 5-methoxy-*o*-toluic acid, which separated from acetic acid in long rods, m. p. 177—178°.

2-*Nitro*-α-(5′-*methoxy*-o-*tolyl*)*cinnamic Acid*.—The dry potassium salt (23 g.) of the preceding acid, *o*-nitrobenzaldehyde (16 g.), and acetic anhydride (83 c.c.) were maintained at 100° for 16 hours and then poured into hot water. The precipitate was warmed with sodium hydroxide solution and freed from neutral impurities by extraction with ether. When the crude acid, obtained by acidifying the alkaline layer, was extracted with chloroform, 0·5 g. of *o*-nitrocinnamic acid remained undissolved. Recrystallisation of the soluble portion from chloroform–light petroleum (b. p. 60—80°) gave a 27% yield of 2-*nitro*-α-(5′-*methoxy*-o-*tolyl*)*cinnamic acid*, which crystallised in radiating prisms, m. p. 169·5—170° (Found : C, 64·9 ; H, 4·9. $C_{17}H_{15}O_5N$ requires C, 65·2 ; H, 4·8%).

2-*Amino*-α-(5′-*methoxy*-o-*tolyl*)*cinnamic Acid* (VI).—The nitro-acid was reduced in the usual way with ferrous sulphate (7·7 mols.) and ammonia. The crude amino-acid is unstable and should be diazotised immediately. A portion of the crude *acid*, recrystallised from ligroin, formed small citron-yellow needles, m. p. 171—172° (Found : C, 72·2 ; H, 5·9. $C_{17}H_{17}O_3N$ requires C, 72·1 ; H, 6·0%).

3-*Methoxy*-1-*methylphenanthrene*-10-*carboxylic Acid* (VII).—Sodium nitrite solution (2 mols.) was rapidly added to a mechanically stirred suspension of the amino-acid in excess of dilute hydrochloric acid at 50°, and the mixture maintained at this temperature for ½ hour. Excess of urea was then added, the mixture filtered and the filtrate made alkaline and warmed at 90° for a few minutes. The solution was acidified at 0°, kept for 12 hours, and the solid collected. Recrystallisation from acetic acid furnished the *acid* in faintly coloured, long rods, m. p. 199—200° (Found : C, 76·8 ; H, 5·4. $C_{17}H_{14}O_3$ requires C, 76·7 ; H, 5·3%).

3-*Methoxy*-1-*methylphenanthrene* (III).—(1) Aluminium chloride (32 g.) was gradually added to an ice-cold solution of 1-β-(5′-methoxy-*o*-tolyl)ethyl-Δ^1-*cyclo*hexene (20 g.) in carbon disulphide (340 c.c.). After 12 hours at room temperature, the mixture was decomposed with ice-cold hydrochloric acid, and the carbon disulphide layer washed, dried, and evaporated. The residue (17 g.) was dehydrogenated at 180—240° with sulphur (6 g.) and distilled under diminished pressure. The distillate solidified and recrystallisation from alcohol furnished cream-coloured plates, m. p. 90°, of 3-*methoxy*-1-*methylphenanthrene* (Found : C, 86·3 ; H, 6·5. $C_{16}H_{14}O$ requires C, 86·5 ; H, 6·3%). The *picrate* separated from absolute alcohol in red needles, m. p. 147° (Found : C, 58·3 ; H, 3·85. $C_{22}H_{17}O_8N_3$ requires C, 58·5 ; H, 3·8%). (2) 3-Methoxy-1-methylphenanthrene-10-carboxylic acid (0·24 g.) was decarboxylated by heating at 230° for 1 hour with quinoline (1·2 c.c.) and copper powder (0·12 g.). The product melted at 90° after recrystallisation from alcohol and did not depress the m. p. of the methyl ether prepared by method (1). Demethylation of the phenol ether (0·2 g.) by boiling for 3½ hours with hydriodic acid (4 c.c., *d* 1·7) and acetic acid (4 c.c.) afforded 3-*hydroxy*-1-*methylphenanthrene*, which separated from benzene–light petroleum in almost white, radiating needles, m. p. 161° (Found : C, 86·3 ; H, 5·95. $C_{15}H_{12}O$ requires C, 86·5 ; H, 5·8%). This phenol gives a faint green colour with aqueous ferric chloride.

1-*Methylphenanthra*-3 : 4-*quinone* (VIII).—A solution of 3-hydroxy-1-methylphenanthrene (0·43 g.) in sodium hydroxide (0·74 g.) and water (5 c.c.) was added at 0° to a diazonium suspension prepared from sulphanilic acid (0·43 g.), and the mixture stirred for 10 minutes. The suspension of the red azo-dye was reduced by warming with a solution of sodium hyposulphite (1·0 g.), and the flocculent precipitate collected and extracted with two 10 c.c. portions of boiling dilute (1 : 1) hydrochloric acid containing sulphur dioxide. Addition of concentrated hydrochloric acid precipitated the amine hydrochloride as a white powder, m. p. *ca.* 210°, which rapidly turned brown in air. A solution of this hydrochloride (0·11 g.) in acetic acid (1·5 c.c.) was slowly added to an ice-cold solution of chromic anhydride (0·05 g.) in water (0·1 c.c.) and after being stirred for 10 minutes the solution was poured into water. The orange *quinone* was collected and washed with hot water. It decomposed at 300° without melting (Found: C, 80·8; H, 4·8. $C_{15}H_{10}O_2$ requires C, 81·1; H, 4·5%).

3 : 4-*Diacetoxy*-1-*methylphenanthrene* (IX).—The quinone (0·2 g.), dissolved in acetic anhydride (1·0 c.c.) and pyridine (3 drops), was stirred with zinc dust until the solution became pale yellow. The mixture was diluted with acetic acid (1·0 c.c.), filtered from excess of zinc, and diluted with water, and the solid collected. The *diacetate* separated from benzene–light petroleum in colourless plates, m. p. 138·5—139° (Found: C, 73·9; H, 5·3. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%).

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