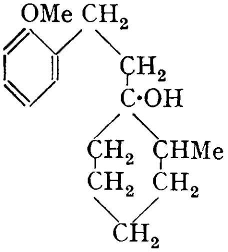
339. *Syntheses in the Phenanthrene Series. Part VIII.* 8-*Methoxy*-1-*methylphenanthrene*.

By Peter Hill, W. F. Short, and H. Stromberg.

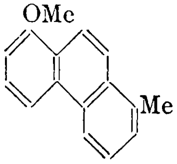
8-Methoxy-1-methylphenanthrene has been synthesised by the Bogert–Cook and by the Schroeter method. A novel case of ring fission of a hydroaromatic ring ketone by hydrobromic acid is described.

The first method employed for the synthesis of 8-*methoxy*-1-*methylphenanthrene* (II) involved the preparation of 1-β-o-*anisylethyl*-2-*methyl*cyclo*hexan*-1-*ol* (I) from the Grignard compound of β-o-*anisylethyl chloride* and 2-methyl*cyclo*hexanone. The unsaturated *com-*

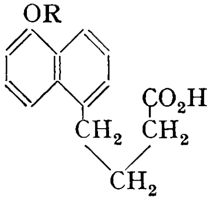
pound obtained by dehydration of this carbinol was treated with aluminium chloride, and the product dehydrogenated with sulphur to yield 8-methoxy-1-methylphenanthrene.



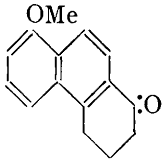
(I.)



(II.)



(III.)



(IV.)

In the alternative synthesis we first prepared γ-5-methoxy-1-naphthylbutyric acid (III; R = Me) (Kon and Ruzicka, J., 1936, **191**) by an improved method. Kon and Ruzicka reported that this acid was converted into " 1-keto-8-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene," m. p. 137°, by the action of stannic chloride, but that an abnormal product, m. p. 88—89°, was produced when the corresponding acid chloride was treated with aluminium chloride. They state that the isomeride, m. p. 88—89°, did not react with semicarbazide and on demethylation gave a phenol $C_{14}H_{14}O_3$ (instead of $C_{14}H_{12}O_2$) which was not converted into the original methoxy-compound on methylation. By the action of phosphoric oxide on the acid we obtained the product, m. p. 88—89°, in good yield, and the same compound was produced in lower yield by the action of stannic chloride; no trace of the compound, m. p. 137°, could be isolated in either instance. We regard the isomeride of lower melting point as 1-*keto*-8-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IV), since it formed a *semicarbazone* and a 2 : 4-*dinitrophenylhydrazone*. Demethylation of the methoxy-ketone with hydrobromic–acetic acid afforded the phenol $C_{14}H_{14}O_3$, m. p. 155°, described by Kon and Ruzicka and we find that the same compound is also produced by the demethylation of the acid (III; R = Me). It is therefore evident that the phenol is γ-5-*hydroxy*-1-*naphthylbutyric acid* (III; R = H) and that the action of hydrobromic–acetic acid on the methoxy-ketone (IV) causes ring fission as well as demethylation. There are many examples of the removal of a carbonyl side chain from aromatic compounds by the action of hydrobromic acid (Hill and Short, J., 1935, 1123), but there is no previous record of the fission of a hydroaromatic ring ketone by this reagent: 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (Butenandt and Schramm, *Ber.*, 1935, **68**, 2083) and 6-methoxy-1-tetralone (Haberland, *Ber.*, 1936, **69**, 1380) undergo normal demethylation. Interaction between the cyclic ketone and methylmagnesium iodide afforded 8-*methoxy*-1-*methyl*-3 : 4-*dihydrophenanthrene*, dehydrogenation of which furnished 8-methoxy-1-methylphenanthrene (II) identical with that obtained by the first method.

EXPERIMENTAL.

The experimental methods were identical with those recorded in Parts I—VII and details are given only in those cases where modifications were necessary.

β-o-*Anisylethyl Chloride*.—Phenol (500 g.) was brominated at 170—175° by passing into it a mixture of nitrogen and bromine vapour (1 mol.) for 12 hours. The *o*- and the *p*-isomer were separated by fractionation and conversion of the former into the picrate (compare von Goedike, *Ber.*, 1893, **26**, 3042). In spite of this wasteful purification 24% of pure *o*-bromophenol was obtained. Holleman and Rinkes (*Rec. trav. chim.*, 1911, **30**, 48), who brominated phenol at 180° during 3 days, arrived at the *o* : *p* ratio 23 : 77 by thermal analysis. The higher *o* : *p* ratio obtained in our experiments is probably due to the greater speed of bromination (compare Hewitt, Kenner, and Silk, J., 1904, **85**, 1225; Skraup and Beifuss, *Ber.*, 1927, **60**, 1077). Methylation with methyl sulphate (1·3 mols.) and 10% aqueous sodium hydroxide (1·4 mols.) gave *o*-bromoanisole, b. p. 110°/20 mm., from which a 50% yield of β-*o*-anisylethyl alcohol, b. p. 126—127°/5 mm., was obtained by treating the Grignard reagent with ethylene oxide (compare Shoesmith and Connor, J., 1927, 2233; Bogert and Hamann, *Amer. Perf.*, 1930, **25**, 19). Thionyl chloride (1·2 mols.) was slowly added with mechanical stirring to a solution of the alcohol (1 mol.) in pyridine (1·5 mols.) cooled in a freezing mixture. The resulting pasty mass was warmed at 80—100° until no more gas was evolved, and the product isolated in the usual manner. β-o-*Anisylethyl chloride*, b. p. 117—119°/8 mm., was obtained in 62% yield as an almost colourless oil (Found: Cl, 20·65. $C_9H_{11}OCl$ requires Cl, 20·8%).

1-β-o-*Anisylethyl*-2-*methyl*cyclo*hexan*-1-*ol* (I).—The Grignard compound of the preceding chloride and 2-methyl*cyclo*hexanone afforded the tertiary *alcohol* as a viscous liquid, b. p. 175—176°/7 mm. (Found: C, 77·1; H, 9·5. $C_{16}H_{24}O_2$ requires C, 77·4; H, 9·7%), and dehydration with potassium hydrogen sulphate yielded 1-β-o-*anisylethyl*-2-*methyl*cyclo*hexene*, b. p. 155—156°/6 mm. (Found: C, 83·45; H, 9·4. $C_{16}H_{22}O$ requires C, 83·5; H, 9·6%).

8-*Methoxy*-1-*methylphenanthrene*, obtained by treatment with aluminium chloride and dehydrogenation with sulphur, separated from 50% alcohol in small clustered needles, m. p. 96—97° (Found: C, 86·2; H, 6·2. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). The *picrate* separated from alcohol in orange-red needles, m. p. 141·5—142·5° (Found: C, 58·0; H, 3·75. $C_{16}H_{14}O,C_6H_3O_7N_3$ requires C, 58·6; H, 3·8%). Demethylation of the methyl ether with hydrobromic–acetic acid furnished 8-*hydroxy*-1-*methylphenanthrene*, which separated from 40% methyl alcohol in white plates, m. p. 144—145° (Found: C, 86·2; H, 5·55. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%).

β-5-*Methoxy*-1-*naphthoylpropionic Acid*.—Bromination of α-nitronaphthalene at 95—100° with the theoretical quantity of bromine and a little iron powder furnished 1-bromo-5-nitronaphthalene in 56% yield (compare Ullmann and Consonno, *Ber.*, 1902, **35**, 2804). The best yield (65%) of 5-bromo-α-naphthylamine was obtained by reducing the nitro-compound with zinc and ammonium chloride as described by Fries and Köhler (*Ber.*, 1924, **57**, 504), and 5 : 5′-*dibromo*-α-*azoxynaphthalene*, m. p. 211·5—212° (decomp.), was isolated as a by-product (Found: C, 52·9; H, 2·9; N, 6·1; Br, 35·5. $C_{20}H_{12}ON_2Br_2$ requires C, 52·6; H, 2·6; N, 6·1; Br, 35·1%). Kon and Ruzicka (*loc. cit.*) obtained 5-bromo-α-naphthol in 20% yield by decomposing the diazonium salt with 9% sulphuric acid. The yield was raised to 41—44% by the following modification: A solution of the naphthylamine in acetic acid (14 mols.) was poured into 24% sulphuric acid (7·5 mols.) and diazotised at 5—7° with 17% aqueous sodium nitrite (1·3 mols.). Nitrous acid was destroyed by adding excess of urea, and the resulting clear solution added as rapidly as possible to boiling 40% sulphuric acid (13 mols.). The liquid was boiled for ½ hour, cooled, and filtered. The naphthol was extracted from the tar by boiling with dilute sodium hydroxide solution. Methylation with methyl sulphate (1·3 mols.) and 10% sodium hydroxide solution (1·4 mols.) at 30—70° afforded the methyl ether, b. p. 175°/10 mm., m. p. 67·5—68°, in 79% yield, and 9% of naphthol was recovered.

A Grignard solution prepared from 1-bromo-5-methoxynaphthalene (40 g.), benzene (100 c.c.), activated magnesium (4·16 g.), and ether (144 c.c.) was added during 1 hour to a boiling solution of succinic anhydride (17·3 g.) in benzene (346 c.c.). The yellow paste was boiled for an hour, cooled, and decomposed with dilute sulphuric acid, and the solvent layer extracted with dilute alkali. The oily acid solidified on trituration with methyl alcohol and recrystallisation from the same solvent afforded β-5-*methoxy*-1-*naphthoylpropionic acid*, m. p. 153·5—154° (Found: C, 69·8; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4%). The yield was 27% and another 3% was obtained by esterifying the acid in the mother-liquors and saponifying the fraction, b. p. 200—220°/1·5 mm.

γ-5-*Methoxy*-1-*naphthylbutyric Acid*.—Reduction of the keto-acid by Clemmensen's method, Martin's technique (*J. Amer. Chem. Soc.*, 1936, **58**, 1438) being used, gave a 51% yield of the butyric acid, which melted at 143° as recorded by Kon and Ruzicka (*loc. cit.*) (Found: C, 73·7; H, 6·7. Calc. for $C_{15}H_{16}O_3$: C, 73·8; H, 6·6%). Demethylation of the acid (0·5 g.) by boiling for 4½ hours with hydrobromic acid (28 c.c.; *d* 1·5) and acetic acid (22·5 c.c.) afforded γ-5-*hydroxy*-1-*naphthylbutyric acid*, which crystallised from dilute acetic acid in felted needles, m. p. 155—156° (Found: C, 72·95; H, 6·2. $C_{14}H_{14}O_3$ requires C, 73·05; H, 6·1%). Alcoholic ferric chloride produced first a dull red-green and then a bluish-violet coloration and remethylation afforded the methoxy-acid, m. p. and mixed m. p. 143°.

1-*Keto*-8-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—This compound was obtained in *ca.* 40% yield from the acid and stannic chloride (Kon and Ruzicka, *loc. cit.*) and in better yield by the action of phosphoric oxide on the acid in benzene solution (compare J., 1936, 321). It separated from light petroleum (b. p. 60—80°) in plates, m. p. 88—89° (Found: C, 79·6; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·2%). The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene–ethyl acetate in crimson grains, m. p. 250—251° (decomp.) (Found: C, 61·9; H, 4·6; N, 14·0. $C_{21}H_{18}O_5N_4$ requires C, 62·1; H, 4·4; N, 13·8%). The ketone afforded a very sparingly soluble *semicarbazone*, m. p. 221° (decomp.) (Found: C, 68·1; H, 6·1; N, 14·7. $C_{16}H_{17}O_2N_3$ requires C, 67·8; H, 6·0; N, 14·8%), and when boiled with hydrobromic–acetic acid furnished γ-5-hydroxy-1-naphthylbutyric acid, m. p. and mixed m. p. 155—156°.

8-*Methoxy*-1-*methyl*-3 : 4-*dihydrophenanthrene*.—Interaction between the cyclic ketone and methylmagnesium iodide (3 mols.) afforded 8-*methoxy*-1-*methyl*-3 : 4-*dihydrophenanthrene*, which separated from methyl alcohol in irregular plates, m. p. 104—105° (Found : C, 85·65; H, 7·5. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). Much of the product was an oil, which doubtless consisted of a mixture of the dihydrophenanthrene with the corresponding tertiary alcohol. Dehydrogenation of this oil with palladium–charcoal afforded 8-methoxy-1-methylphenanthrene, isolated as the picrate, which was identical with that obtained in the first method, but the yield was poor.

Addendum : Professor L. F. Fieser has pointed out to us that β-4 : 8-dimethoxy-1-naphthoylpropionic acid, γ-4 : 8-dimethoxy-1-naphthylbutyric acid and its methyl ester, which were described as new compounds in Part VII (this vol., p. 937), had already been prepared by Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1936, **58**, 2382). We regret that we had overlooked the priority of these authors. Our experiments were completed in January, 1936, but publication was delayed until the orientation experiments described in Part VII had been performed.

We thank the Chemical Society for a grant and Imperial Chemical Industries Ltd. (Dyestuffs Group) for various gifts of chemicals.

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[*Received, August* 30*th*, 1937.]