

**166.** *Syntheses of Polycyclic Compounds related to the Sterols.*  
*Part VII. The Cyclisation of  $\gamma$ -5-Methoxy-1-naphthylbutyric Acid.*

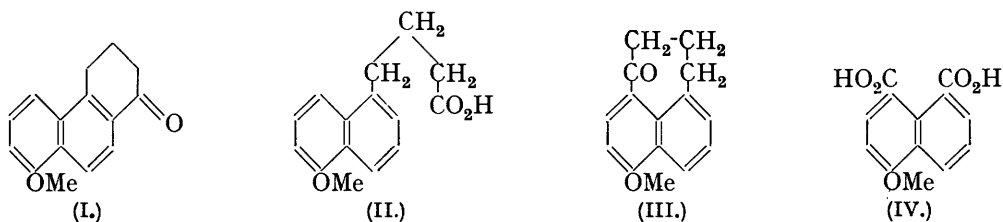
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The ketone, m. p. 137°, obtained by the cyclisation of  $\gamma$ -5-methoxy-1-naphthylbutyric acid (II) (Kon and Ruzicka, J., 1936, 187) was originally formulated as (I) and this structure has now been confirmed by its conversion into 8-methoxy-1-methylphenanthrene. The isomeric ketone, m. p. 88—89°, is shown to be 7-keto-4-methoxy-7 : 8-dihydrohomophenalene (III), formed from the acid by *peri*-ring closure.

IN Part V (*loc. cit.*) it was stated that  $\gamma$ -5-methoxy-1-naphthylbutyric acid could be converted by means of stannic chloride into a ketone, m. p. 137°, which was regarded as the tetrahydrophenanthrene derivative (I); the action of aluminium chloride on the chloride of the acid gave an isomeric compound, m. p. 88—89°, the structure of which was not determined but it was shown that it was demethylated to a phenolic substance which on methylation gave a compound differing from the starting material. This was shown by Hill, Short, and Stromberg (J., 1937, 1619) to be the methoxy-acid (II), so ring fission must have accompanied demethylation; the ketone of lower melting point was the only product obtained by them and they regarded it as having the structure (I). From this compound they prepared what was thought to be 8-methoxy-1-methylphenanthrene.

These reactions have now been reinvestigated. The preparation of the ketone, m. p. 137°, is very uncertain and sometimes fails for no apparent reason and we were unable to work out the exact conditions for its formation, but we obtained a sufficient amount to treat it with methylmagnesium iodide and to dehydrogenate the crude product with palladised charcoal; the crystalline 8-methoxy-1-methylphenanthrene thus produced in good

yield was identical with the compound prepared by Lockett and Short (preceding paper) by an alternative method and different from that prepared by Hill, Stromberg, and Short (*loc. cit.*). The constitution originally assigned to the ketone (I) is thus fully confirmed.



The ketone, m. p. 88—89°, which is evidently the principal product of the cyclisation of the acid (II), was oxidised with chromic acid, whereby 4-methoxynaphthalene-1 : 8-dicarboxylic acid (IV) was obtained in the form of its anhydride (Dziewoński, Galitzerówna, and Kocwa, *Bull. Acad. Polonaise*, 1926, A, 209). A specimen of this anhydride was also synthesised from 5-nitroacenaphthene and found to be identical with that obtained above.

It therefore follows that *peri*-ring closure must have taken place in the formation of the lower-melting ketone, a possibility first suggested to the authors by Dr. W. F. Short in a private communication, and the ketone must in that case be 7-keto-4-methoxy-7 : 8-dihydrohomophenylene (III). The formation of a seven-membered ring in preference to a six-membered ring has been recorded by Fieser and Peters (*J. Amer. Chem. Soc.*, 1932, **54**, 4347) and Fieser and Fieser (*ibid.*, 1933, **55**, 3342).

#### EXPERIMENTAL.

**1-Keto-8-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (I).**—The action of stannic chloride on  $\gamma$ -5-methoxy-1-naphthylbutyric acid was variable; on one or two occasions the ketone, m. p. 137°, was obtained practically pure, but generally a mixture, m. p. 78—84°, was produced and the desired compound could only be isolated from it with great difficulty and in poor yield by fractional crystallisation from petroleum. A better result was achieved by diluting the stannic chloride with toluene : 0.5 g. of the acid, 1 c.c. of toluene, and 1 c.c. of stannic chloride were warmed on the steam-bath for 1 hour and the product was isolated by addition of dilute hydrochloric acid and dissolved in ether. The dried ethereal solution was evaporated, and the toluene solution kept; the ketones gradually separated in large crystals, amongst which those of the high-melting ketone could easily be recognised and picked out. On a larger scale the crystals were hand-picked and recrystallised from methyl alcohol, but the yields were always poor.

An attempt was made to effect a separation by subjecting the mixture of ketones, from which most of the high-melting ketone had been mechanically separated, to the action of hydrobromic acid in acetic acid in the hope that the ketone, m. p. 137°, would undergo demethylation, whereas the isomeride, m. p. 88—89°, would be reconverted into the acid (Hill, Short, and Stromberg, *loc. cit.*). The product was then remethylated and boiled with alkali to hydrolyse any ester formed; the yield of the desired product was, however, small.

**8-Methoxy-1-methylphenanthrene.**—A solution of 0.95 g. of the ketone, m. p. 137°, in 11 c.c. of benzene was added to an ice-cold Grignard reagent, prepared from 1.2 c.c. of methyl iodide in ether and decanted from the excess of magnesium. The reaction was completed by warming for 1 hour, and the product isolated by addition of ice and dilute sulphuric acid and dissolved in ether. After removal of the solvent the residual oil was heated with 0.7 g. of 10% palladised charcoal for 2 hours at a bath temperature of 300—330°. The dehydrogenation product was extracted with about 250 c.c. of light petroleum (b. p. 60—80°), and the solution percolated through a column of activated alumina, which was then thoroughly washed with the pure solvent. On evaporation of the solution 0.3 g. of 8-methoxy-1-methylphenanthrene was obtained; it crystallised from methyl alcohol in fine needles, m. p. 121—121.5° (Found : C, 86.5; H, 6.4.  $C_{16}H_{14}O$  requires C, 86.5; H, 6.3%). The *picrate* formed orange plates from alcohol, m. p. 153—154° (Found : C, 58.7; H, 3.8.  $C_{16}H_{14}O, C_6H_3O_7N_3$  requires C, 58.5; H, 3.8%); the *s*-trinitrobenzene compound formed long yellow needles, m. p. 177—178° (Found : C, 60.4; H, 3.8.  $C_{16}H_{14}O, C_6H_3O_6N_3$  requires C, 60.7; H, 3.9%), and the *styphnate*, orange needles, m. p. 179—180° (Found : C, 56.8; H, 3.7.  $C_{16}H_{14}O, C_6H_3O_8N_3$  requires C, 56.5; H, 3.7%).

**Oxidation of the Ketone (III).**—0.84 G. of coarsely powdered sodium dichromate was added in

small portions to a warm solution of 0.1 g. of the ketone in 1.5 c.c. of acetic acid, and the mixture boiled for 2½ hours; long yellow needles separated. The product, precipitated in an amorphous form on addition of 10 c.c. of warm water, was collected when cold and washed with water. When it was boiled with 10% sodium carbonate solution, the amorphous portion gradually dissolved, leaving fine yellow needles, m. p. 255—257°. The alkaline solution was acidified and the precipitated solid recrystallised from ethyl acetate–alcohol and finally sublimed, more of the compound, m. p. 255—257°, being obtained. This was identified as 4-methoxynaphthalic anhydride by analysis (Found: C, 68.5; H, 3.6. Calc.: C, 68.4; H, 3.5%) and by comparison (m. p. and mixed m. p.) with a specimen prepared as described below.

*5-Methoxyacenaphthene*.—5.7 G. of 5-aminoacenaphthene (Fleischer and Schranz, *Ber.*, 1922, 55, 3253) in 28 c.c. of acetic acid were poured with vigorous stirring into an ice-cold solution of 13.7 c.c. of sulphuric acid in 78 c.c. of water, and the suspension diazotised at 2—3° with 3 g. of sodium nitrite in 14 c.c. of water. The excess of nitrous acid was destroyed with urea, and the olive-green solution poured in a thin stream into a boiling solution of 24 c.c. of sulphuric acid in 64 c.c. of water; after ½ hour's boiling, the precipitated tar was washed with water and extracted by boiling for 10 minutes with 20 c.c. of 10% sodium hydroxide solution. The cold solution was filtered and warmed with 5 c.c. of methyl sulphate; *5-methoxyacenaphthene* (2.5 g.) was isolated by extraction with ether and had b. p. 174°/13 mm. It solidified and formed pale buff, flattened needles, m. p. 66°, from methyl alcohol (Found: C, 84.7; H, 6.6. C<sub>13</sub>H<sub>12</sub>O requires C, 84.7; H, 6.6%).

*4-Methoxynaphthalic Anhydride*.—5-Methoxyacenaphthene was oxidised exactly as described above and the product was purified in the same way; it formed yellow needles from acetic acid, m. p. 255—256°, giving a fine blue fluorescence in alcoholic solution.

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