CCCVII.—*The Synthesis of* 1-*Phenanthrol.*

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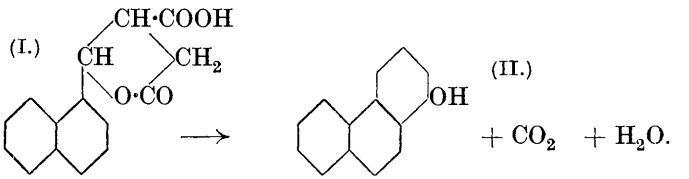
1-PHENANTHROL (II) is the only one of the five theoretically possible monohydroxy-derivatives of phenanthrene not described in the literature. It has been obtained by heating *α-naphthylparaconic acid* (I), loss of carbon dioxide and ring closure with elimination of water taking place as follows :



α-Naphthaldehyde was prepared (*a*) in a yield of 33% by the catalytic reduction of α-naphthoyl chloride, m. p. 22°, b. p. 158°/12 mm., by Rosenmund's method (*Ber.*, 1918, **51**, 591)—it is noteworthy that in absence of solvent during this reduction the side chain was completely removed and naphthalene produced in quantity—and (*b*) in a yield of 25% by the action of ethyl orthoformate in ethereal solution on magnesium naphthyl bromide in the usual manner. The second is the more convenient method although the yield is somewhat smaller. By both methods the aldehyde was obtained as an oil, b. p. 173—174°/35 mm.; p-*nitrophenylhydrazone*, scarlet needles from acetic acid, m. p. 233—235°.

α-Naphthylparaconic Acid.—α-Naphthaldehyde (7·5 g.), succinic anhydride (5 g.), and anhydrous sodium acetate (6 g.) were heated together under reflux for 6 hours at 122° (a higher temperature causes formation of tarry by-products which render the subsequent purification of the acid difficult); excess of α-naphthaldehyde was

removed from the reaction product in a current of steam, and the residue filtered hot, cooled, extracted with ether, and acidified. The precipitated *α-naphthylparaconic acid* (2 g.) was recrystallised from aqueous alcohol (water 2 parts, alcohol 1 part), from which it separated in well-defined, white, rectangular prisms, m. p. 169° (evolution of carbon dioxide) (Found: C, 70·2; H, 4·7. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%).

1-*Phenanthrol.*—α-Naphthylparaconic acid was heated in a distillation flask immersed in a metal-bath at 180—200° until evolution of carbon dioxide had ceased (30 minutes). The temperature of the bath was then rapidly raised to about 340° and distillation of the vapour prevented by impinging a blast of cold air on the neck of the flask. After 15—20 minutes the temperature was raised again and distillation allowed to proceed. The red oil which distilled over solidified and was dissolved in ether; the ethereal solution was extracted with sodium carbonate to remove carboxylic acids and then with aqueous sodium hydroxide. The latter extract was saturated with carbon dioxide, the precipitate extracted with ether, and the ether evaporated; the 1-*phenanthrol* so obtained was crystallised from light petroleum, separating as colourless, prismatic needles, m. p. 156° (Found: C, 85·9; H, 5·2. $C_{14}H_{10}O$ requires C, 86·6; H, 5·2%); yield, 5%. In another experiment crude α-naphthylparaconic acid was used, and the yield of 1-phenanthrol increased to about 15%; this observation is similar to that of Fittig and Erdmann (*Annalen*, 1885, **227**, 242), who found that crude phenylparaconic acid gives a better yield of α-naphthol than does the pure acid.

1-Phenanthrol is stable in air and in solution (contrast the 9-isomeride, which is very unstable, Japp and Findlay, J., 1897, **71**, 1115). It resembles α-naphthol in giving a deep blue coloration on warming with chloroform in alkaline solution, but differs in giving no coloration with glucose solution and concentrated sulphuric acid (compare Molisch's test for carbohydrates). It dissolves in concentrated sulphuric acid with a yellow colour, the solution slowly becoming red and finally colourless when heated. Its alkaline solution gives dyes with diazotised aniline, etc. The picrate crystallises in orange-red, feathery needles, m. p. 182°, from methyl alcohol.

In order to characterise the compound further it was methylated as follows. To 1-phenanthrol (0·8 g.) dissolved in 8 c.c. of methyl alcohol, 4 c.c. of 10% methyl-alcoholic potassium hydroxide and 8 c.c. of a 13% solution of methyl sulphate in methyl alcohol were added, and the solution was heated on the steam-bath for 1 hour, after which it was diluted with water, extracted with ether, the

ethereal solution extracted with alkali to remove unchanged phenanthrol, and the 1-methoxyphenanthrene left on evaporation was recrystallised from methyl alcohol; yield, 50%. The colourless prismatic needles had m. p. 105°, and were found to be identical in all respects with a sample of 1-methoxyphenanthrene prepared by the method described by Pschorr, Wolfes, and Buckow (*Ber.*, 1900, **33**, 170).

The authors wish to acknowledge the grant of a Carnegie Teaching Fellowship to one of them (J. B. S.) during the tenure of which the investigation was carried out.

EDINBURGH UNIVERSITY. [*Received, June 28th,* 1928.]