Synthesis of 2,3-Dihydrophenalene-2-carboxylic Acid (Perinaphthane-2-carboxylic Acid)

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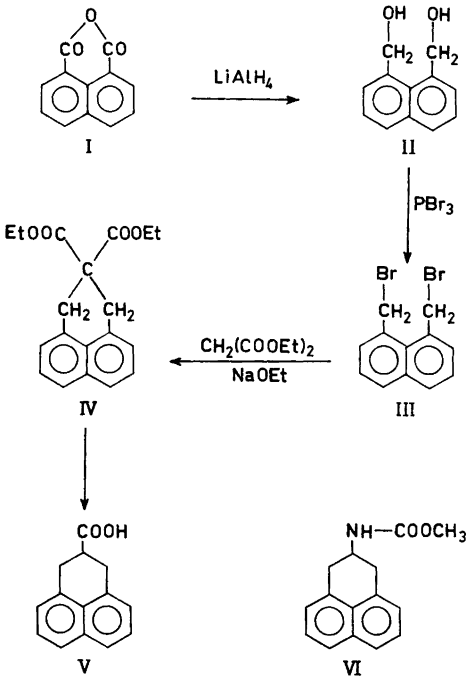
In connection with studies of rearrangements in partially aromatic hydrocarbons, we have investigated some synthetic methods applied to 2,3-dihydrophenalene derivatives. During this work we synthesized the 2-carboxylic acid (V), and since this simple derivative has not been described in the literature, we will briefly report its synthesis here.



The anhydride (I) of naphthalene-1,8-dicarboxylic acid was reduced to 1,8-bis-(hydroxymethyl)-naphthalene (II) which in turn was converted to 1,8-bis-(bromomethyl)-naphthalene (III) using previously published methods. A malonic ester synthesis gave (IV) which on hydrolysis and decarboxylation afforded the 2,3-dihydrophenalene-2-carboxylic acid (V). The amide of (V) was also prepared in the usual way via the acid chloride. A Hoffman reaction in methanol (the amide is insoluble in water) gave the urethane (VI) in 70 % yield from the amide. This, and further reactions will be described later.

Experimental. *1,8-Bis-(hydroxymethyl)-naphthalene (II)*, was prepared from naphthalic anhydride (I) by reduction with $LiAlH_4$ according to Mitchell *et al.*[1]

1,8-Bis-(bromomethyl)-naphthalene (III), was synthesized from (II) and PBr_3 according to Bergmann *et al.*[2]

2,3-Dihydrophenalene-2-carboxylic acid (V). Diethylmalonate (40 g, 0.25 mole) was added to a sodium ethylate solution prepared from 11.5 g (0.50 mole) of sodium and 500 ml of absolute ethanol. The dibromide III (78.5 g, 0.25 mole), dissolved in 250 ml of ethanol, was then added dropwise to half of the above sodium diethylmalonate solution at reflux temperature. Simultaneously, the other part of the malonate solution was added dropwise to the reaction mixture. After the addition, the mixture was refluxed for 2 h, poured onto excess water and extracted with ether. The crude ester (IV) resulting after evaporation of the ether was hydrolyzed by boiling for 3 h with excess sodium hydroxide in 350 ml of water and 20 ml of methanol. The dicarboxylic acid (m.p. 206-208°. decomp.) precipitated when the cooled mixture was acidified with hydrochloric acid. The acid was decarboxylated by heating to 210° for 1 h. Recrystallization from benzene gave 32.8 g (62 %) of 2,3-dihydrophenalene-2-carboxylic acid, m.p. 175—177°. (Found: C 79.23; H 5.68; equiv.wt. 210.1. Calc. for $C_{14}H_{12}O_2$ (212.24): C 79.22; H 5.70; equiv.wt. 212.24).

Acknowledgements. The authors wish to express their gratitude to Professor Arne Fredga for all the facilities placed at their disposal. The analyses were carried out at the Analytical Department of the Chemical Institute.

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2. Bergmann, E. D. and Szmuszkovicz, J. *J. Am. Chem. Soc.* **75** (1953) 2760.

Received March 13, 1965.