180. *Imidochlorides. Part V. Synthesis of Hydroxycarbethoxyphenyl-α- and -β-naphthaquinolines.*

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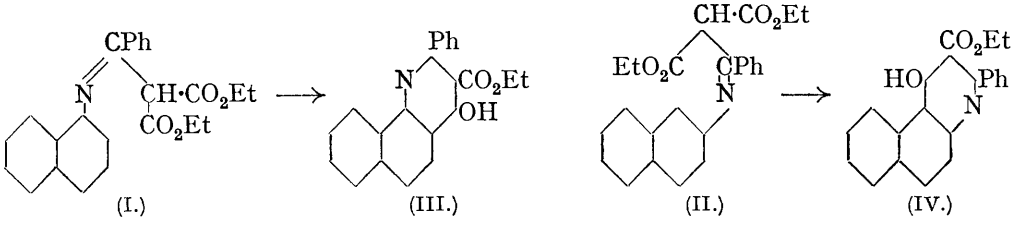
Ethyl α- and β-naphthyliminobenzylmalonate (I and II respectively), prepared by the authors' modification (J., 1936, 428) of Just's method (*Ber.*, 1886, **19**, 984, 987), have been cyclised by the action of heat to *ethyl* 4-*hydroxy*-2-*phenyl*-α-*naphthaquinoline*-3-*carboxylate* (III) and *ethyl* 1-*hydroxy*-3-*phenyl*-β-*naphthaquinoline*-2-*carboxylate* (IV) respectively.



(I.) (III.) (II.) (IV.)

As β-naphthylamine usually undergoes ring closure in the α-position (Lellmann and Schmidt, *Ber.*, 1887, **20**, 3154; von Braun and Gruber, *Ber.*, 1922, **55**, 1710), the β-naphthaquinoline derivative has been assigned the structure (IV).

A mixture of benz-α-naphthalide imidochloride [from benz-α-naphthalide (30 g.; 1 mol.) and phosphorus pentachloride (30·5 g.; 1·2 mols.)], ethyl malonate (23 g.; 2 mols.), and sodium (1·5 g.; 1 atom) was refluxed in anhydrous toluene at 120—130° for 2 hours and treated with water; the product extracted by ether was heated at 120—125°/30—40 mm. to remove toluene and the excess of malonic ester; the residual ethyl α-naphthyliminobenzylmalonate, after solidifying, crystallised from alcohol in needles, m. p. 146—148° (Just, *loc. cit.*, gives m. p. 144°). Yield, 8 g. (17·5%).

This ester (1·5 g.) was heated at 185—195° until the evolution of bubbles of ethyl alcohol could be noticed. The resulting *ethyl* 4-*hydroxy*-2-*phenyl*-α-*naphthaquinoline*-3-*carboxylate* (III) crystallised from ethyl acetate in needles, m. p. 228—230° (Found: N, 4·3. $C_{22}H_{17}O_3N$ requires N, 4·0%), difficultly soluble in hot methyl and ethyl alcohols and chloroform, and insoluble in benzene, toluene, and light petroleum.

Ethyl β-naphthyliminobenzylmalonate, prepared from benz-β-naphthalide imidochloride (19 g.; 1 mol.), ethyl malonate (23 g.; 2 mols.), and sodium (1·5 g.; 1 atom), crystallised from alcohol in needles, m. p. 141—142° (Just, *loc. cit.*, gives m. p. 140°). Yield, 8 g. (29·6%).

This ester (4 g.), heated at 185—195°, gave *ethyl* 1-*hydroxy*-3-*phenyl*-β-*naphthaquinoline*-2-*carboxylate* (IV), which crystallised from alcohol in needles (3 g.), m. p. 280—282° (Found: N, 4·3%), and resembled the α-naphthaquinoline derivative in solubility. It gave, on hydrolysis with aqueous alcoholic caustic soda, the *acid*, which crystallised from alcohol in needles, m. p. 248—250° (Found: N, 4·4. $C_{20}H_{13}O_3N$ requires N, 4·5%), and, when refluxed with alcoholic picric acid for 3 hours, formed a *picrate*, which separated in orange needles, m. p. 179—181°, on cooling (Found: N, 10·1. $C_{22}H_{17}O_3N,C_6H_3O_7N_3$ requires N, 9·8%).

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