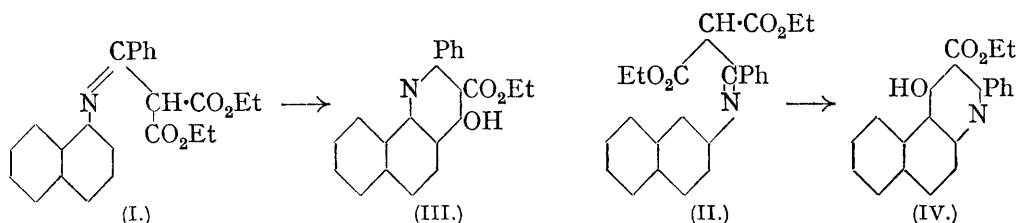


180. Imidochlorides. Part V. Synthesis of Hydroxycarbethoxy-phenyl- α - and - β -naphthaquinolines.

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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.



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. C₂₂H₁₇O₃N 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. C₂₀H₁₅O₃N 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. C₂₂H₁₇O₃N.C₆H₃O₇N₃ requires N, 9.8%).

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