98. *Di-imidochlorides. Part I. Synthesis of Derivatives of 6 : 6′-Diquinolyl and Phenanthroline from Di-imidochlorides.*

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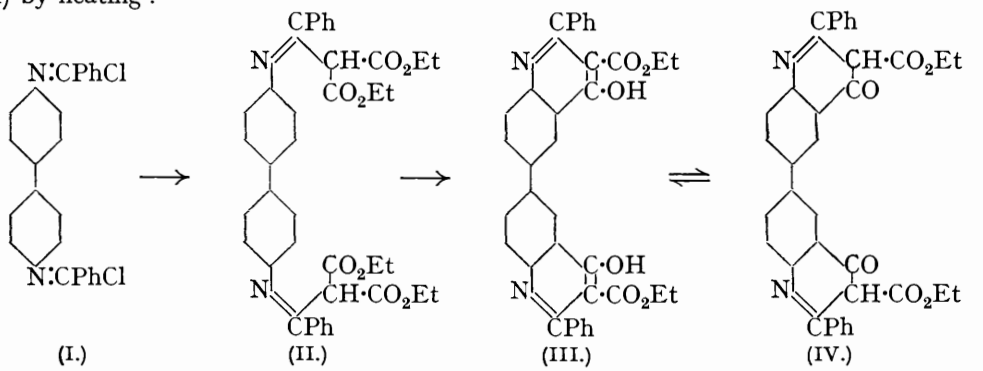
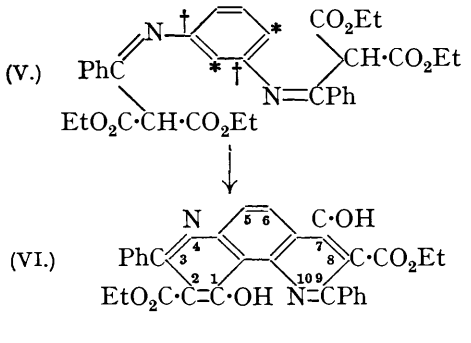
Dibenzbenzididedi-imidochloride on condensation with ethyl sodiomalonate yields a product which gives a derivative of 6 : 6′-diquinolyl on heating. Di-imidochlorides from the benzoyl derivatives of *m*- and *p*-phenylenediamine give phenanthroline derivatives on similar treatment.

A new diquinolyl (III) synthesis is provided by condensing dibenzbenzididedi-imidochloride (I) (J., 1937, 1643) with ethyl sodiomalonate by Just's method (*Ber.*, 1885, **18**, 2623) as modified by Shah and Heeramaneck (J., 1936, 428) and cyclising the product (II) by heating:

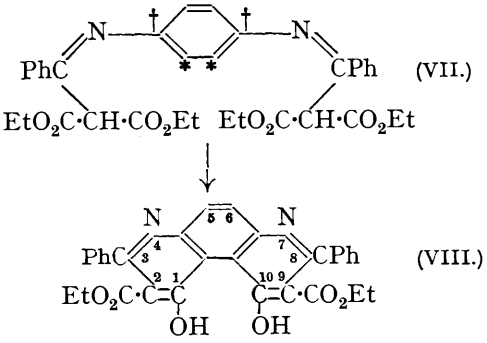


(I.) (II.) (III.) (IV.)

New derivatives of phenanthroline (VI) and *ψ*-phenanthroline (VIII) have been similarly prepared from the di-imidochlorides derived from *m*- and *p*-phenylenediamine respectively (J., 1937, 1643):



(V.)



(VII.)

(VI.)

(VIII.)

These diquinolyl and phenanthroline derivatives have been formulated as hydroxy-compounds, but are probably tautomeric, as is ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate (Heeramaneck and Shah, *Proc. Indian Acad. Sci.*, 1937, **5**, 442). Some part of the water of constitution which the diquinolyl derivatives contain may be attached to the keto-group.

It is assumed by analogy with the Skraup synthesis of phenanthrolines from diamines that cyclisation occurs so that the nitrogen-containing rings have one direct link without an intervening carbon atom (Skraup and Vortmann, *Monatsh.*, 1882, **3**, 570; Smith, *J. Amer. Chem. Soc.*, 1930, **52**, 397). This follows also if one assumes that the cyclisation reaction always involves the ring carbon atom (*) which is doubly linked to the ring carbon atom (†) attached to nitrogen as shown in (V) and (VII).

Experimental.

Reaction of Dibenzbenzidided-imidochloride with Ethyl Sodiomalonate.—A mixture of the di-imidochloride (4 g.), toluene (20 c.c.), ethyl sodiomalonate (from 2 atoms of sodium), and ethyl malonate (3·5 g.) was refluxed (calcium chloride guard-tube) for 4 hours and diluted with water. Ether extracted an oily product, which on heating for several hours at 100° yielded NN′-*bis*-(α-*dicarbethoxymethylbenzylidene*)*benzidine* as a paste. This, crystallised from alcohol, had m. p. 189° (Found: C, 71·2; H, 5·9. $C_{40}H_{40}O_8N_2$ requires C, 71·0; H, 5·9%). When heated at 200—210°, it was converted into *ethyl* 4 : 4′-*dihydroxy*-2 : 2′-*diphenyl*-6 : 6′-*diquinolyl*-3 : 3′-*dicarboxylate*, which after crystallisation from pyridine melted above 300° (Found: C, 69·6; H, 5·2; loss at 160°, 6·0. $C_{36}H_{28}O_6N_2,2H_2O$ requires C, 69·7; H, 5·2; H_2O, 5·8%). This ester was hydrolysed by 10% alcoholic sodium hydroxide to the corresponding *acid*, which, being insoluble in most organic solvents, was purified by repeated precipitation from alkaline solution; it had m. p. above 300° (Found: C, 63·3; H, 4·7; loss at 160°, 11·8. $C_{32}H_{20}O_6N_2,4H_2O$ requires C, 64·0; H, 4·7; H_2O, 12·0%). The ester was converted, by treatment with hydrochloric acid (1 : 1) in a sealed tube at 170—180°, into 4 : 4′-*dihydroxy*-2 : 2′-*diphenyl*-6 : 6′-*diquinolyl*, which was purified by washing with hot pyridine, alcohol, and acetone, as it was insoluble in all the usual solvents: this may explain the somewhat unsatisfactory analysis, which also gave 0·6% of residue (Found: C, 79·4; H, 4·8; loss at 160°, 4·2. $C_{30}H_{20}O_2N_2,H_2O$ requires C, 78·6; H, 4·8; H_2O, 3·9%). The compound melted above 300°.

The condensation products of the di-imidochlorides derived from *m*- and *p*-phenylenediamines with ethyl sodiomalonate were prepared and cyclised to the corresponding phenanthrolines by the method described above.

NN′-*Bis*-(α-*dicarbethoxymethylbenzylidene*)-m-*phenylenediamine*, crystallised from alcohol, had m. p. 131° (Found: C, 67·9; H, 6·1. $C_{34}H_{36}O_8N_2$ requires C, 68·0; H, 6·0%). *Ethyl* 1 : 7-*dihydroxy*-3 : 9-*diphenylphenanthroline*-2 : 8-*dicarboxylate*, crystallised from alcohol, had m. p. 264° (Found: C, 70·9; H, 4·9. $C_{30}H_{24}O_6N_2$ requires C, 70·8; H, 4·7%). 1 : 7-Dihydroxy-3 : 9-diphenylphenanthroline melted above 300°, but could not be purified, as it separated as a jelly from the usual organic solvents.

NN′-*Bis*-(α-*dicarbethoxymethylbenzylidene*)-p-*phenylenediamine* melted at 186° (Found: C,

67·8; H, 6·0. $C_{34}H_{36}O_8N_2$ requires C, 68·0; H, 6·0%), *ethyl* 1 : 10-*dihydroxy*-3 : 8-*diphenyl*-ψ-*phenanthroline*-2 : 9-*dicarboxylate* at 218° (Found : C, 70·7; H, 4·8. $C_{30}H_{24}O_6N_2$ requires C, 70·8; H, 4·7%), and 1 : 10-*dihydroxy*-3 : 8-*diphenyl*-ψ-*phenanthroline* above 300° (Found : C, 78·7; H, 4·5. $C_{24}H_{16}O_2N_2$ requires C, 79·1; H, 4·4%). All three compounds were crystallised from alcohol.

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