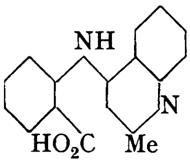
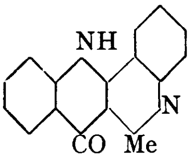
104. *The Condensation of Anthranilic Acid with 4-Chloroquinaldine and with 2-Chlorolepidine.*

By O. G. Backeberg.

When 4-chloroquinaldine is refluxed with anthranilic acid in acetic acid solution, the hydrochloride of 4-o-*carboxyphenylaminoquinaldine* (I) is formed. The free base is converted by concentrated sulphuric acid at 100° into 7-*keto*-6-*methyl*-7 : 10-*dihydro*-8 : 9-*benzquinoquinoline* (II). This base, which is given an acridone in preference to an anthranil structure on account of its yellow colour and its stability to alkalis, yields 6-*methyl*-8 : 9-*benzquinoquinoline* on distillation with zinc dust.

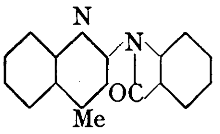
(I.)



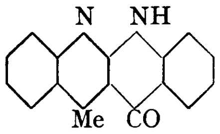


(II.)

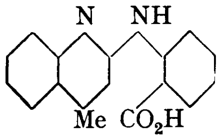
The corresponding reaction between anthranilic acid and 2-chlorolepidine investigated by Ephraim (*Ber.*, 1892, **25**, 2710) gave a colourless compound, which he suggested was *N*-(2-lepidyl)anthranil (III) rather than the acridone (IV) on the ground that an acidic product, which he does not describe, is formed by the action of alcoholic potash. The same condensation is referred to in E.P. 321738, the reaction being carried out in nitrobenzene solution, and the product is said to be 2-*o*-carboxyphenylaminolepidine (V). It has, however, been found that the product is the same whether the reactants are heated together alone, in acetic acid or in nitrobenzene solution, giving rise to the compound (III) described by Ephraim. The ready hydrolysis of this compound to the acid (V) by aqueous-alcoholic caustic soda establishes its anthranil structure, as suggested by Ephraim. It has not been found possible to convert (V) into the acridone (IV); heating alone or refluxing with acetic anhydride—operations which have no action on (I)—reconvert (V) into the anthranil (III), and heating with sulphuric acid produces a complex substance containing sulphur, whose structure has not been elucidated.



(III.)



(IV.)



(V.)

(Analyses were carried out by Pregl's micro-methods.)

4-o-*Carboxyphenylaminoquinaldine* (I).—4-Chloroquinaldine (1 mol.) and anthranilic acid (1 mol.) were refluxed for 3 hr. in AcOH. Conc. HCl was added to the cooled solution diluted with H_2O. The hydrochloride of (I), which separated as a gelatinous mass, crystallised from dil. HCl in long, yellow, silky needles, which lost HCl on drying over P_2O_5. The *base* crystallised from dil. AcOH in cream-coloured needles, m. p. 309—310° (decomp.) (Found: C, 73·6; H, 4·9. $C_{17}H_{14}O_2N_2$ requires C, 73·4; H, 5·0%).

7-*Keto*-6-*methyl*-7 : 10-*dihydro*-8 : 9-*benzquinoquinoline* (II).—The reddish-brown solution with a strong blue fluorescence obtained by heating (I) at 100° with an equal wt. of conc. H_2SO_4 for 30 min. was poured into H_2O, a cream-coloured *sulphate*, unmolten below 320° and insol. in all ordinary solvents except alc. or aq.-alc. alkali, being pptd. (Found: H_2SO_4, 15·5. $2C_{17}H_{12}ON_2,H_2SO_4$ requires H_2SO_4, 15·9%). The *base*, pptd. from a cooled solution of the sulphate in aq.-alc. NaOH by AcOH, crystallised from EtOH or dil. pyridine in yellow needles, m. p. 295—296° (decomp.) (Found: C, 78·45; H, 4·5. $C_{17}H_{12}ON_2$ requires C, 78·5; H, 4·6%). Picrate, chars at 270—280°.

6-*Methyl*-8 : 9-*benzquinoquinoline*.—When a mixture of 2 g. of (II) and 50 g. of Zn dust was heated in a current of dry H, a *base* (0·3 g.) distilled which solidified in yellow needles, m. p. 137° after recrystn. from dil. EtOH (Found: C, 83·5; H, 5·1; *M*, by micro-Rast, 248·9. $C_{17}H_{12}N_2$ requires C, 83·6; H, 4·9%; *M*, 244). It was easily sol. in EtOH, C_6H_6, and Et_2O, the solutions having a green fluorescence, and readily sol. in mineral acids, giving an intense green fluorescence with conc. H_2SO_4. The *chloroplatinate* was pptd. from alc. solution as an orange-coloured solid which darkened without melting at 325° (Found: Pt, 21·9. $2C_{17}H_{12}N_2,H_2PtCl_6$ requires Pt, 21·7%). Picrate, m. p. 234° (decomp.).

2-o-*Carboxyphenylaminolepidine* (V).—The compound (III), prepared according to Ephraim (*loc. cit.*), was crystallised from Ac_2O; m. p. 217° (Found: C, 78·5; H, 4·6. Calc. for $C_{17}H_{12}ON_2$: C, 78·5; H, 4·6%). Picrate, m. p. 223° (Ephraim gives 213° and 217° respectively for the base and the picrate). Crystallised from hot dil. HCl, the *hydrochloride* formed colourless needles, m. p. 222° (decomp.): drying at 110° appeared to cause partial dissociation (Found: Cl, 10·6. $C_{17}H_{12}ON_2,HCl$ requires Cl, 11·3%). The base was unchanged by distillation with Zn dust as well as by heating with conc. H_2SO_4 at 100°. It was converted into (V) by refluxing it with aq.-alc. NaOH for 30 min. and acidifying the clear cooled solution with AcOH; a pale yellow solid separated, insol. in all ordinary org. solvents except AcOH, which was washed, and dried over P_2O_5; m. p. 202° with shrinking at 175—180° (Found: C, 73·3; H, 5·15. Calc. for $C_{17}H_{14}O_2N_2$: C, 73·4; H, 5·0%).

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