XLVIII.—*Condensations involving Reactive Methyl Groups in Heterocyclic Bases.*

By James Ernest Humphries.

The reactions described below, *viz.*, the condensation of quinaldine, *p*-toluquinaldine, and α-picoline and of their quaternary salts with Michler's hydrol and a nitrosoamine, are further examples of the reactivity of methyl and methylene groups towards the groups $:C:O$ and $\cdot N:O$. Fosse (*Ann. Chim. Phys.*, 1906, **8**, 18) found that, in presence of acetic acid as condensing agent, Michler's hydrol (4 : 4′-tetramethyldiaminobenzhydrol) reacted with the methylene group of such compounds as acetoacetic ester, acetylacetone, etc. Quinaldine and α-picoline condense readily with the hydrol under the same conditions, yielding the compounds

$$C_9H_6N\cdot CH_2\cdot CH(C_6H_4\cdot NMe_2)_2 \text{ and } C_5H_4N\cdot CH_2\cdot CH(C_6H_4\cdot NMe_2)_2.$$

The condensations can also be effected by zinc chloride. The methiodides of the heterocyclic bases react more readily than the bases themselves and under conditions in which the latter are not affected, *viz.*, in alcoholic solution. The condensation products are similar to the *leuco*-compounds of the triphenylmethane dyes and are readily oxidised by lead peroxide and acetic acid to red dyes.

The quaternary salts do not react with benzenediazonium sulphate, but condense readily with *p*-nitrophenylnitrosoamine, in cold alcoholic solution. The resulting compounds were phenylhydrazones, *e.g.*, $C_9H_6N(MeI)\cdot CH:N\cdot NH\cdot C_6H_4\cdot NO_2$. This reaction differs from that of Adams (*Chem. Zentr.*, 1923, **94**, I, 1591), who added simultaneously solutions of potassium hydroxide and diazotised aniline to an aqueous solution of quinaldine methiodide and obtained the azo-compound, $C_9H_6N\cdot CH_2\cdot N:N\cdot C_6H_5$.

The bases themselves and their hydrochlorides do not react with the nitrosoamine, so that in both reactions the reactivity of the α-methyl group is enhanced by converting the tertiary base into a quaternary compound.

EXPERIMENTAL.

Condensations with Michler's Hydrol.—(1) *Quinaldine.* A solution of equimolecular quantities of the hydrol and quinaldine in glacial acetic acid was warmed on a water-bath until the intense blue colour changed to deep red (1 hour). Ammonium hydroxide then precipitated a dark green oil which, isolated by means of ether, was obtained in pale-yellow needles, m. p. 131° (Found: N, 10·7. $C_{27}H_{29}N_3$ requires N, 10·6%).

The condensation product (1 mol.) was dissolved in hydrochloric acid (3 mols.) and enough water to make a 2% solution; acetic acid (2 mols.) was added and the whole cooled to 0°. Then, with rapid stirring, freshly prepared lead peroxide (1 mol.) was quickly added. The solution became intensely red. The lead was removed as sulphate, and the oxidation product obtained by addition of sodium hydroxide and extraction with chloroform. A red, amorphous powder was precipitated from the dried chloroform extract on adding ether. The *oxalate* was analysed (Found: N, 8·0. $C_{30}H_{32}O_6N_3$ requires N, 7·95%).

The oxidation product dyes silk violet. Its salts are red, but the pseudo-base, $C_9H_6N\cdot CH{:}C(C_6H_4\cdot NMe_2)_2$, is brown.

(2) p-*Toluquinaldine.* The condensation product (m. p. 152°) was similar to that formed from quinaldine (Found: N, 10·1. $C_{28}H_{31}N_3$ requires N, 10·3%).

(3) α-*Picoline.* The condensation was carried out as in (1) and pale yellow crystals, m. p. 187°, were obtained (Found: N, 12·1. $C_{23}H_{27}N_3$ requires N, 12·2%).

(4) p-*Toluquinaldine methiodide.* The condensation, which also proceeds in glacial acetic acid, was effected by boiling an alcoholic solution of the reactants for a few minutes. On concentrating the solution, copper-red needles, m. p. 160° (decomp.), were obtained (Found: I, 23·2; N, 7·6. $C_{29}H_{34}N_3I$ requires I, 23·05; N, 7·6%).

The corresponding methochloride, obtained by condensing *p*-toluquinaldine methochloride and the hydrol, was oxidised as in (1), but the deep-red, amorphous dye which was formed could not be obtained pure.

Condensations with p-*Nitrophenylnitrosoamine.*—When equal molecular quantities of benzenediazonium sulphate and *p*-toluquinaldine methiodide were mixed in alcoholic solution at the ordinary temperature, the solution turned red and golden-yellow plates, m. p. 133°, of the *periodide* of *p*-toluquinaldine methiodide immediately began to separate (Found: N, 2·55; I, 69·1. $C_{12}H_{14}NI_3$ requires N, 2·5; I, 68·9%). This was readily reduced to the methiodide by sulphur dioxide or stannous chloride, and was also formed by warming the methiodide and iodine in glacial acetic acid.

No condensation took place when the methiodide was replaced by the methonitrate of *p*-toluquinaldine.

(1) p-*Toluquinaldine methiodide.* The nitrosoamine was prepared by Schraube and Schmidt's method (*Ber.*, 1894, **27**, 514). Equimolecular quantities of the nitrosoamine and the methiodide, each in alcoholic solution, were mixed at 0°. The crystalline precipitate was recrystallised from methyl alcohol, reddish-brown needles, m. p. 244°, being thus obtained (Found : N, 12·3; I, 28·6. $C_{18}H_{19}O_2N_4I$ requires N, 12·5; I, 28·35%).

That the new compound was the p-*nitrophenylhydrazone* of 2-formyl-6-methylquinoline was proved in the following way. *p*-Toluquinaldine methiodide was condensed with *p*-nitrosodimethylaniline (Kaufmann and Vallette, *Ber.*, 1912, **45**, 1738), yielding the Schiff's base, $C_{10}H_{10}N(MeI){\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NMe_2$, in green needles, m. p. 207 (decomp.). This was hydrolysed by boiling with dilute hydrochloric acid, and *p*-nitrophenylhydrazine added. The hydrazone so found was identical with the product of the nitrosoamine condensation.

(2) *Quinaldine methiodide.* The product formed red needles, m. p. 250° (Found : I, 29·4. $C_{17}H_{15}O_2N_4I$ requires I, 29·3%).

(3) *Quinaldine ethiodide* gave red needles, m. p. 262° (Found : I, 28·5. $C_{18}H_{17}O_2N_4I$ requires I, 28·3%).

(4) *α-Picoline methiodide* gave yellow needles, m. p. 260° (Found : I, 33·4. $C_{13}H_{13}O_2N_4I$ requires I, 33·1%).

In the last three cases the identity of the product was confirmed as in the case of (1).

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