390. *Some Aminotetrahydroquinolines.*

By ISIDORE E. BALABAN.

ALTHOUGH attempts (Balaban, J., 1930, 2346) to prepare aminotetrahydroquinolines from certain nitro- and amino-methyl- and -dimethyl-hydroxyquinolines by reduction with sodium and alcohol were unsuccessful, 2-chloro-6-nitro-4-methylquinoline has now been found to yield very small quantities of *dl*-6-amino-4-methyl-1 : 2 : 3 : 4-tetrahydroquinoline (isolated as *dipicrate*) on reduction with these reagents or with tin and hydrochloric acid.

Since this series of chloroquinolines was unfavourable for the required purpose, five aminomethoxyquinolines were prepared, and their reduction with tin and hydrochloric acid examined. Of these, only two gave the desired derivatives, viz., 5-*amino*-6-*methoxy*- and 5-*amino*-8-*methoxy*-1 : 2 : 3 : 4-*tetrahydroquinolines*, isolated as *dihydrochlorides*. The respective bases were immediately oxidised when solutions of these salts were basified. 8-Amino-6-methoxy-, 6-amino-8-methoxy-, and 8-*amino*-7-*methoxy-quinoline* gave only intensely purple solutions on reduction.

8-Methoxyquinoline on nitration yields the 5-nitro-derivative, whilst 7-methoxyquinoline gives two nitro-derivatives, mainly 8-*nitro*-7-*methoxyquinoline*.

EXPERIMENTAL.

The aminomethoxyquinolines were all prepared by the method of Jacobs and Heidelberger (*J. Amer. Chem. Soc.*, 1920, **42**, 2278).

dl-6-*Amino*-4-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline Dipicrate*.—5 G. of 2-chloro-6-nitro-4-methylquinoline, abs. EtOH (25 c.c.), Sn (40 g.), and conc. HCl (100 c.c.) were heated for 60—70 hrs. on the steam-bath. After removal of Sn and concentration of the filtrate, the base was obtained in Et_2O as usual, and purified as *picrate*; brown, irregular plates, m. p. 173° (decomp.); yield 1·3 g. (Found : $C_6H_3O_7N_3$, 75·0; N, 16·1. $C_{10}H_{14}N_2,2C_6H_3O_7N_3$ requires

$C_6H_3O_7N_3$, 73·9; N, 18·1%). Reduction by Na and EtOH was less satisfactory.

5-Amino-6-methoxyquinoline was prepared from the nitro-compound (Decker and Engler, *Ber.*, 1909, **42**, 1740); the *picrate* crystallised from dil. EtOH or H_2O, in which it is very sparingly sol., in brick-red needles, m. p. 225° (Found : $C_6H_3O_7N_3$, 56·6. $C_{10}H_{10}ON_2,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 56·8%).

5-Amino-6-methoxy-1 : 2 : 3 : 4-tetrahydroquinoline.—5·2 G. of the hydrochloride of the foregoing base were reduced with Sn (30 g.), EtOH (25 c.c.), and conc. HCl (100 c.c.) for 70 hrs. The *dihydrochloride* was obtained as *monohydrate*, colourless plates, m. p. 247° (decomp.), from 2*N*-HCl (yield 2·7 g.) (Found, in material dried at 100° : Cl, 26·7, 26·8; N, 10·1. $C_{10}H_{10}ON_2,2HCl,H_2O$ requires Cl, 26·4; N, 10·4%). The dipicrate crystallises from H_2O in dark irregular plates, m. p. 147°.

8-Amino-6-methoxyquinoline.—8-Nitro-6-methoxyquinoline (8 g.; from 3-nitro-4-aminoanisole) gave on reduction 2·1 g. of hydrochloride, golden-yellow needles, m. p. 228°, from dil. HCl. The *picrate* crystallises from H_2O, in which it is sparingly sol., in golden needles, m. p. 221° (decomp.) (Found : $C_6H_3O_7N_3$, 56·9. $C_{10}H_{10}ON_2,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 56·8%).

5-Amino-8-methoxyquinoline.—5·7 G. of 8-methoxyquinoline (prep. from *o*-anisidine) were added to fuming HNO_3 (11·5 c.c.) in ice; after 20 mins., *5-nitro-8-methoxyquinoline nitrate* was separated, and recryst. from H_2O as *monohydrate*, very pale yellow prisms, m. p. 177° (eff.) [Found, in air-dried material : loss at 100°, 6·6. $C_{10}H_8O_3N_2,HNO_3,H_2O$ requires H_2O, 6·3. Found, in dried material : HNO_3 (by nitron) 23·5. $C_{10}H_8O_3N_2,HNO_3$ requires HNO_3, 23·6%]. The base had m. p. 155°, alone or mixed with an authentic specimen (from 4-nitro-2-aminoanisole).

20 G. of the above nitro-compound in boiling 95% EtOH (150 c.c.) and conc. HCl (2 c.c.) were reduced with Fe powder (20 g.) for 4 hrs.; the solution was filtered and concentrated, and the deposited material dried and extracted with C_6H_6. The amino-compound was obtained in golden-yellow needles, m. p. 156°. The *picrate* crystallised from H_2O, in which it is moderately sol., in brown glistening needles, m. p. 126° (Found : $C_6H_3O_7N_3$, 56·8. $C_{10}H_{10}ON_2,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 56·8%).

5-Amino-8-methoxy-1 : 2 : 3 : 4-tetrahydroquinoline.—5 G. of the above amino-compound gave on reduction (as above) 2·9 g., m. p. 250° (decomp.), of *dihydrochloride* of the tetrahydro-base, which crystallises from abs. EtOH in colourless, stout, hexagonal prisms, m. p. 258—260° (decomp.) (Found, in material dried at 100° : Cl, 27·4; N, 10·4. $C_{10}H_{14}ON_2,2HCl,\frac{1}{2}H_2O$ requires Cl, 27·3; N, 10·8%). With conc. H_2SO_4 and HNO_3 this salt gives an intense bluish-purple colour, and its alc. solution has a green fluorescence.

6-Amino-8-methoxyquinoline.—5·5 G. of the 6-nitro-compound (from 5-nitro-2-aminoanisole) gave on reduction 1·8 g. of the required amino-compound, m. p. 169° (softening from 165°) [Fourneau, Trefouel, and Benoit (*Ann. Inst. Pasteur*, 1930, **44**, 748) give m. p. 168°] (Found : N, 16·0. Calc. for $C_{10}H_{10}ON_2$: N, 16·1%); the sparingly sol. *picrate* forms long glistening orange needles, m. p. 224° (softening), from water (Found : $C_6H_3O_7N_3$, 55·6. $C_{10}H_{10}ON_2,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 56·8%).

8-Nitro-7-methoxyquinoline.—10 G. of 7-methoxyquinoline (Späth and Brunner, *Ber.*, 1924, **57**, 1243) were added to HNO_3 (*d* 1·52; 21 c.c.) at 0° in very small amounts; after 20 mins., the mixture was poured into ice-water

(400 c.c.). Purification of the solid, and of the material obtained from the mother-liquor by basification and extraction with $CHCl_3$, successively through nitrate, base, and picrate, yielded 4·8 g., m. p. 178°, of the 8-nitro-derivative; 0·4 g., m. p. 200°, of an isomeric nitro-compound; and 9·6 g., m. p. 231°, of 7-methoxyquinoline picrate. 8-*Nitro*-7-*methoxyquinoline* crystallises from $CHCl_3$ in long, stout, thick, pale yellow prisms, m. p. 178°, or from C_6H_6 in colourless, glistening, rectangular plates (solubility *ca.* 4% in hot solution, 0·5% in cold) (Found : N, 13·9. $C_{10}H_8O_3N_2$ requires N, 13·7%). The nitrate crystallises in bright yellow prismatic needles, m. p. 155—156° (eff.). ?-*Nitro*-7-*methoxyquinoline* crystallises from abs. EtOH in long, colourless, prismatic needles, m. p. 200° (Found : N, 13·5. $C_{10}H_8O_3N_2$ requires N, 13·7%).

8-*Amino*-7-*methoxyquinoline*.—The corresponding nitro-compound (10·2 g.) gave on reduction by the method of Jacobs and Heidelberger (*loc. cit.*) 4·5 g. of the *base*, which crystallises from 50% EtOH (charcoal) in yellow, glistening, prismatic needles, m. p. 108°, and volatilises at 100° (Found : N, 15·8. $C_{10}H_{10}ON_2$ requires N, 16·1%). The *picrate* crystallises from dil. EtOH, in which it is very sparingly sol., in terra-cotta-coloured needles, m. p. 226° (decomp.) (Found : $C_6H_3O_7N_3$, 56·9. $C_{10}H_{10}ON_2$,$C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 56·8%).

RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LTD.,
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