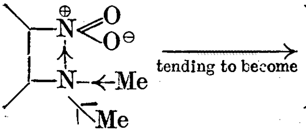
LXIX.—3-*Halogeno*-6-*nitro*- *and* -6-*amino-dimethylanilines.*

By HERBERT HENRY HODGSON and ARNOLD KERSHAW.

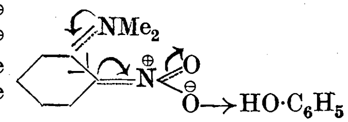
THE 2 : 4-dihalogenonitrobenzenes have been found to react readily with an alcoholic solution of dimethylamine in the absence of a catalyst, and in every case it is the 2-halogeno-substituent that is easily and exclusively replaced by the dimethylamino-group, this being in accordance with the well-known promotion of mobility of halogens by an adjacent nitro-group. Further, the ease of replacement of one halogen only, indicates considerable satisfaction of the electronic demands of the nitro-group by one dimethylamino-group (compare the ease with which sodium methoxide replaces both halogens in a 2 : 4-dihalogenonitrobenzene, a further illustration of the fact that $NMe_2 > OMe$ as a potential electron-source). It is noteworthy also that in 4-chloro-2-iodonitrobenzene the iodine only is replaced by dimethylamine under the same conditions, a fact which indicates that the 2-carbon atom is more positive than the

4-carbon atom, notwithstanding the greater positivity produced by chlorine as compared with iodine, and therefore that the general effect of the nitro-group (Allan, Oxford, Robinson, and Smith, J., 1926, 401) is much greater on the 2-carbon than on the 4-carbon atom.

Most unsubstituted 2-nitrodialkylanilines are liquids at the ordinary temperature, but the derivatives now under consideration are solids of low m. p., and since the *p*-nitrodialkylanilines have high m. p.'s (*e.g.*, 4-nitrodimethylaniline has m. p. 168°), it is probable that the low m. p.'s of the *o*-compounds are due to co-ordination of a similar type (I) to that described by Bennett and Willis (J., 1929, 256).



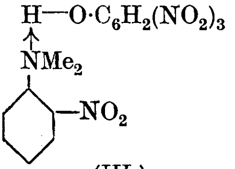
(I.)



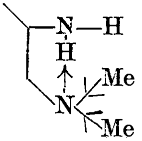
(II.)

The 3-halogeno-6-nitrodimethylanilines are not sufficiently basic to form salts except with strong acids, and these are immediately hydrolysed by water. In non-dissociating solvents such as light petroleum and naphthalene, 1% solutions are yellow, and the molecular weight of 3-chloro-6-nitrodimethylaniline in naphthalene is about 10% above that of the single molecule (compare the discussion of similar cases by Sidgwick, " Electronic Theory of Valency," 1927, p. 149 *et seq.*, who considers that such cryoscopic evidence of association must be interpreted with caution). Very deep red 1% solutions are formed in phenol, the product being unimolecular, which might reasonably indicate a change of structure produced by co-ordination of solvent (II). Anisole does not give this colour change.

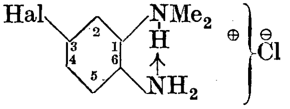
The picrates of the 3-halogeno-6-nitrodimethylanilines are stable, with m. p.'s below those of the 3-halogeno-6-aminodimethylanilines : these are true salts soluble in water, so the diminution of melting point may be due to chelation (III)—a point of view which is supported by the fact that the more salt-like is the picrate of a 3-halogeno-6-nitrodimethylaniline the higher is its m. p.; *e. g.*, iodo- (104°), bromo- (85°), and chloro- (70°), a series conforming with the well-known order of the general effects of the halogens, Cl>Br>I.



(III.)



(IV.)



(V.)

The 3-halogeno-6-aminodimethylanilines are all liquids at the ordinary temperature, owing doubtless to chelate union (IV) (compare Sidgwick and Callow, J., 1924, **125**, 527), which should be stronger than in the case of *o*-phenylenediamine (m. p. 102°), since the dimethylamino-nitrogen is more negative than the amino-nitrogen atom. Moreover, the free bases, including *o*-aminodimethylaniline itself, are much more stable in air than *p*-aminodimethylaniline and much less soluble in water : this is further evidence of the great stability associated with 5-membered chelate rings.

All the above substances form stable monohydrochlorides; but only the halogeno-compounds give dihydrochlorides, which diminish in stability from the chloro- to the iodo-compound. It would appear that salt formation produces in the monohydrochloride of *o*-aminodimethylaniline a 5-membered chelate ring, by the sharing of a hydrogen ion between the amino-groups (V) (compare Sidgwick's discussion on hydrofluoric acid, *op. cit.*, p. 72), which is sufficiently stable to prevent further salt-formation at the amino-nitrogen atom; but that when the 3-halogeno-atom is introduced, its general (inductive) effect on the chelating electrons of the *p*-amino-nitrogen atom is a weakening of their union to such an extent that, under the influence of the powerful kationoid reagent (a second molecule of hydrochloric acid), the dimethylamino-group captures the hydrogen atom and thus enables further salt formation to take place at the released amino-group. This salt formation is facilitated by the alternating (tautomeric) effect of the halogen substituent, now rendered available (compare the greater positivity of the 3-carbon atom in comparison with the 4-carbon atom in activated 1-chloro-3 : 4-dinitrobenzene, due to the alternating effect of the chlorine atom). Since the order of the general effect of the halogens is $Cl > Br > I$, it follows that 3-chloro-6-aminodimethylaniline dihydrochloride will be the most easily formed and, in consequence, be the most stable of the analogues.

Only the free bases mentioned above give violet colours with ferric chloride; the salts, however, do so with stronger oxidising agents (*e.g.*, chromic acid).

3-Chloro-6-aminodimethylaniline was recovered unchanged after repeated treatment with Caro's acid under widely varying conditions : this resistance to oxidation is probably due to chelation both in the free base and in the salt (compare the ready oxidation of *o*-anisidine and *o*-nitroaniline to the corresponding nitroso-derivatives, and the instantaneous destruction of *p*-aminodimethylaniline under the same conditions).

EXPERIMENTAL.

Action of Dimethylamine on the 2 : 4-*Dihalogenonitrobenzenes.*—The 2 : 4-dihalogenonitrobenzene (10 g.) was boiled under reflux with 10% more than the theoretical quantity of a solution of dimethylamine (1 g.-mol.) in ordinary alcohol (400 c.c.) to which an equal volume of the solvent had been added. The chloro- and bromo-compounds were refluxed for 10 hours and the iodo-analogue for 15 hours, the alcohol then being removed by steam; the oily reaction product solidified on cooling [compare Weissenberger (*Monatsh.*, 1912, **33**, 821), who in a similar reaction with *o*-chloronitrobenzene used absolute alcohol and copper powder, both of which have now been found unnecessary].

3-*Chloro*-6-*nitrodimethylaniline* crystallises from light petroleum in short, stout, dull yellow prisms, often almost cubes, m. p. 49° (Found: Cl, 17·5; *M*, cryoscopic in phenol, 185·9, 187·8; *M*, cryoscopic in naphthalene, 199·5, 210·5. $C_8H_9O_2N_2Cl$ requires Cl, 17·7%; *M*, 188·5), which are fairly readily volatile in steam. The constitution of this compound was confirmed by its preparation (as above) from 4-chloro-2-bromo- and also from 4-chloro-2-iodonitrobenzene. The *picrate*, prepared from the compound (0·6 g.) and picric acid (0·7 g.) in boiling alcohol (7 c.c.), is deposited, on cooling, in bright yellow, flat prisms, m. p. 70° (Found: Cl, 8·1. $C_8H_9O_2N_2Cl,C_6H_3O_7N_3$ requires Cl, 8·3%).

3-*Bromo*-6-*nitrodimethylaniline* separates from light petroleum in crystals, m. p. 58·5°, resembling those of the chloro-analogue (Found: Br, 32·4. $C_8H_9O_2N_2Br$ requires Br, 32·6%). The *picrate* melts at 85° (Found: Br, 16·6. $C_8H_9O_2N_2Br,C_6H_3O_7N_3$ requires Br, 16·9%). Their constitutions follow from their identity (mixed m. p., etc.) with the compound and its picrate made from 2-chloro-4-bromonitrobenzene by the general process above. The 2-chloro-4-bromonitrobenzene was obtained from 3-chloro-4-nitroaniline by means of the Sandmeyer reaction.

3-*Iodo*-6-*nitrodimethylaniline* crystallises from light petroleum in long orange prisms, m. p. 52° (Found: I, 43·7. $C_8H_9O_2N_2I$ requires I, 43·5%). It was also obtained from 2-chloro-4-iodonitrobenzene, prepared from 3-chloro-4-nitroaniline by the usual iodination process. The *picrate* melts at 104° (Found: I, 24·2. $C_8H_9O_2N_2I,C_6H_3O_7N_3$ requires I, 24·4%). All the 3-halogeno-6-nitrodimethylanilines are precipitated on dilution of their colourless solutions in concentrated sulphuric acid. o-*Nitrodimethylaniline picrate* crystallises from alcohol in long yellow prisms, m. p. 103° (Found: N, 18·0. $C_8H_{10}O_2N_2,C_6H_3O_7N_3$ requires N, 17·7%).

Reduction of the 3-*Halogeno*-6-*nitro- to the* 3-*Halogeno*-6-*aminodimethylanilines.*—Each of the above nitro-compounds is readily reduced by iron powder and 50% aqueous acetic acid to the corresponding amine, which is then removed by steam distillation from the reaction mixture, made alkaline. The amines are colourless viscous oils of a not unpleasant odour and are volatile in steam. The chloro- and bromo-compounds are conveniently isolated from the steam distillates directly as hydrochlorides, but the iodo-compound, on account of its ready decomposition when boiled with hydrochloric acid, is extracted with ether prior to its conversion into the hydrochloride.

3-*Chloro*-6-*aminodimethylaniline* (Found: Cl, 20·6. $C_8H_{11}N_2Cl$ requires Cl, 20·8%) forms a *monohydrochloride*, which crystallises from water in long needles (Found: Cl, 34·1. $C_8H_{11}N_2Cl,HCl$ requires Cl, 34·3%). The *dihydrochloride* separates from concentrated hydrochloric acid solution in colourless prisms (Found: ionisable Cl, 29·1; total Cl, 43·5. $C_8H_{11}N_2Cl,2HCl$ requires ionisable Cl, 29·1; total Cl, 43·7%). The *picrate* separates from a hot alcoholic solution of equimolecular quantities of the amine and picric acid in bright yellow prisms, m. p. 151° (to a brown-red liquid) (Found: Cl, 8·7. $C_8H_{11}N_2Cl,C_6H_3O_7N_3$ requires Cl, 8·9%).

3-*Bromo*-6-*aminodimethylaniline* (Found: Br, 37·0. $C_8H_{11}N_2Br$ requires Br, 37·2%) forms a *monohydrochloride* (Found: Cl, 14·1. $C_8H_{11}N_2Br,HCl$ requires Cl, 14·1%) and a *dihydrochloride* (Found: Cl, 24·6. $C_8H_{11}N_2Br,2HCl$ requires Cl, 24·6%). The *picrate* crystallises from alcohol in bright yellow prisms, m. p. 137° (Found: Br, 17·9. $C_8H_{11}N_2Br,C_6H_3O_7N_3$ requires Br, 18·0%).

3-*Iodo*-6-*aminodimethylaniline* (Found: I, 48·2. $C_8H_{11}N_2I$ requires I, 48·5%) forms a *monohydrochloride* (Found: Cl, 11·8. $C_8H_{11}N_2I,HCl$ requires Cl, 11·9%) and a *dihydrochloride* (Found: Cl, 20·0. $C_8H_{11}N_2I,2HCl$ requires Cl, 21·2%). The latter analysis indicates the presence of monohydrochloride (compare the theoretical discussion). The *picrate* crystallises in thin, bright yellow plates, m. p. 167° (Found: I, 25·6. $C_8H_{11}N_2I,C_6H_3O_7N_3$ requires I, 25·9%).

o-*Aminodimethylaniline* is prepared as above by reduction of *o*-nitrodimethylaniline and has b. p. 212° (Found: N, 20·7. $C_8H_{12}N_2$ requires N, 20·6%). Its *monohydrochloride* separates from concentrated hydrochloric acid in long colourless prisms (Found: Cl, 20·9. $C_8H_{12}N_2,HCl$ requires Cl, 20·6%). The *picrate* crystallises in bright yellow prisms, m. p. 136° (Found: N, 19·3. $C_8H_{12}N_2,C_6H_3O_7N_3$ requires N, 19·2%).

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