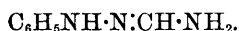


LXXXVI.—*A Method for Preparing the Formyl
Derivatives of the Aromatic Amines.*

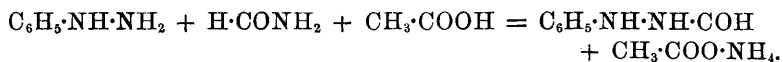
By HENRY R. HIRST and JULIUS B. COHEN, Ph.D., Yorkshire College.

IN studying the constitution of the acid amides, it was thought possible that formamide might react like an aldehyde, combining with phenylhydrazine to form a hydrazone of the formula



On mixing formamide and phenylhydrazine in molecular proportion dissolved in glacial acetic acid and allowing the mixture to remain in the cold, crystals soon began to be deposited, and in a few hours formed a nearly solid mass.

The substance proved to be formylphenylhydrazine,* the action being as follows.



As the yield in this case amounted to 82 per cent. of the theoretical, we thought that the reaction, if generally applicable, might furnish an easy method for preparing formyl derivatives of the amines. This has so far proved to be the case with all the primary

* Compare Just (*Ber.*, 1886, 19, 1201), who prepared this compound by heating phenylhydrazine with formamide at 130°.

830 FORMYL DERIVATIVES OF THE AROMATIC AMINES.

aromatic amines experimented on, the action taking place in the cold. The secondary aromatic amines containing an alkyl radicle only react on heating, whilst diphenylamine does not combine even on continued boiling. The formyl derivatives of the following bases have been prepared. Aniline, ortho- and para-toluidine, α - and β -naphthylamine, phenylhydrazine, orthotolylhydrazine, methylaniline, ethylaniline, paraphenylenediamine, and benzidine.

The yield in all cases was very satisfactory, so that only a few grams of the base are required for the experiment. The product, after one recrystallisation, was usually quite pure.

Formanilide.—Four grams of aniline and 2 grams of formamide dissolved in 4.8 grams of glacial acetic acid gave 3.2 grams of pure formanilide, m. p. 45–47°.

0.2079 gave 21.4 c.c. moist nitrogen at 14° and 746 mm. $N = 11.9$.
 C_7H_7NO requires $N = 11.6$ per cent.

Formylorthotoluide, obtained as above, melted at 57–59°.

0.2585 gave 23.4 c.c. moist nitrogen at 12° and 757 mm. $N = 10.7$.
 C_8H_9NO requires $N = 10.4$ per cent.

Formylparatoluide, after one crystallisation, melted at 50–53°. It was not analysed.

Formyl- α -naphthalide melted at 137.5°, and gave the following results on analysis.

0.2407 gave 16.6 c.c. moist nitrogen at 12° and 751.5 mm. $N = 8.1$.
 $C_{11}H_9NO$ requires $N = 8.2$ per cent.

Formyl- β -naphthalide melted at 120–123°.

0.2085 gave 15.4 c.c. moist nitrogen at 16° and 748 mm. $N = 8.4$.
 $C_{11}H_9NO$ requires $N = 8.2$ per cent.

Formylphenylhydrazide melted at 140°.

0.1610 gave 29.8 c.c. moist nitrogen at 19° and 748 mm. $N = 20.6$.
 $C_7H_8N_2O$ requires $N = 20.9$ per cent.

Formylorthotolylhydrazide.—This substance, which has not yet been described, crystallises from alcohol in colourless needles, melting at 119°.

0.1910 gave 31.2 c.c. moist nitrogen at 13.5° and 733.5 mm. $N = 18.6$.
 $C_8H_{10}N_2O$ requires $N = 18.7$ per cent.

Formylmethylanilide.—Three grams of methylaniline, 1.5 gram of formamide, and 3.6 grams of glacial acetic acid were heated for six hours, the liquid poured into water, neutralised with ammonium carbonate, and extracted with ether. 2.7 grams of liquid were obtained, of which the portion boiling at 240–243° (1.1 gram) was analysed.

0.3640 gave 32.6 c.c. moist nitrogen at 14.5° and 749.5 mm. $N = 10.36$.
 C_8H_9NO requires $N = 10.4$ per cent.

Formylethylanilide.—Three grams of ethylaniline, treated in the same way as methylaniline, gave 2.4 grams of liquid boiling at $240-250^{\circ}$.

0.1983 gave 16 c.c. moist nitrogen at 15° and 751 mm. $N = 9.3$.
 $C_8H_{11}NO$ requires $N = 9.3$ per cent.

Diformylparaphenylenediamine.—1.3 gram of paraphenylenediamine, 1 gram of formamide, and 2.4 grams of glacial acetic acid were left to stand, and the product crystallised from water. 1.2 gram of a greyish crystalline powder was obtained, melting at $205-207^{\circ}$. The disodium compound of this substance was obtained as a fine white powder by adding a strong solution of caustic soda in alcohol to the alcoholic solution of the formyl compound.

0.1005 gave 0.0665 Na_2SO_4 . $Na = 21.43$.
 $C_8H_6N_2O_2Na_2$ requires 22.11 per cent.

Orthophenylenediamine, under similar conditions, appears to form phenyleneformamidine, melting at $168-170^{\circ}$.

Diformylbenzidine, prepared as above, formed a crystalline powder which did not melt at 240° . It was converted into the disodium compound, which was analysed with the following result.

0.0525 gave 0.0278 Na_2SO_4 . $Na = 16.9$.
 $C_{17}H_{10}N_2O_2Na_2$ requires $Na = 16.19$.
