LXXXIII.—*A New Method for Preparing Substituted Diphenylamines.*

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SUBSTITUTED diphenylamines are frequently difficult to prepare, especially if the two groups attached to the nitrogen atom are different. Direct substitution in diphenylamine or one of its derivatives may be employed, but such reactions are limited in number and do not reveal the constitution of the product. Even Ullmann's method (*Annalen*, 1907, **355**, 312; compare also Gibson and collaborators, J., 1927, 247; 1928, 2204) has a restricted application, and the process of heating an aromatic amine with an amine salt is mainly useful for the production of diphenylamines similarly substituted in both nuclei.

The author has recently shown (J., 1925, **127**, 1992; 1927, 1743) that *N*-arylaryliminoaryl ethers (II), when heated at 200—300°, are converted quantitatively into acyl derivatives of the corresponding diphenylamines (III). In this conversion the migrating group becomes attached to the nitrogen atom by means of the nuclear carbon atom that was originally attached to the oxygen atom.

$$R'NH_2 \xrightarrow{R\cdot COCl} R\cdot CO\cdot NHR' \xrightarrow{PCl_5} R\cdot CCl{:}NR' \xrightarrow{R''ONa} \underset{\text{(I.)}}{} R\cdot C(OR''){:}NR' \xrightarrow{\text{heat}} \underset{\text{(II.)}}{} R\cdot CO\cdot NR'R'' \xrightarrow{KOH} \underset{\text{(III.)}}{} NHR'R''$$

It has now been found that the acyl compounds thus obtained can be hydrolysed readily with alcoholic potash to the corresponding diphenylamines in yields of about 80% of those calculated. The imino-ethers can be prepared easily from the corresponding amines ($R'NH_2$) and phenols (R''OH) through the anilideiminochlorides (I) (J., 1922, **121**, 1676). In the typical case of *N*-*p*-chlorophenyl-

benzimino-2 : 4 : 6-trichlorophenyl ether, the yields of anilide, anilideiminochloride, and imino-ether were respectively 53, 88, and 80% of the theoretical.

A convenient means is therefore available for preparing diphenylamines with similar or different substituents in the two nuclei and of known constitution. The presence of " negative " substituents in the phenol facilitates the rearrangement of the imino-ether, whereas in the amine their presence retards the change. It is therefore preferable, if the alternative amines and phenols are available, to employ the more acidic phenol and the more basic amine, so that the rearrangement may occur at the lowest possible temperature. The approximate time and temperature of heating required can be estimated from the known effects of substituents on the velocity of the change (J., 1927, 1750).

Hitherto, the constitution of Gnehm's tetrachlorodiphenylamine, first prepared by direct chlorination of diphenylamine in glacial acetic acid solution, has remained unknown (*Ber.*, 1875, **8**, 1040). In view of the method of preparation it was probably 2 : 4 : 2′ : 4′-, 2 : 4 : 6 : 2′-, or 2 : 4 : 6 : 4′-tetrachlorodiphenylamine. These three compounds were therefore synthesised respectively from 2 : 4-dichlorophenol and 2 : 4-dichloroaniline, 2 : 4 : 6-trichlorophenol and *o*-chloroaniline, and 2 : 4 : 6-trichlorophenol and *p*-chloroaniline, through the corresponding benzanilides, benzanilideiminochlorides, benzimino-ethers, and benzoyldiphenylamines. Comparison with Gnehm's compound left no doubt of its identity with the 2 : 4 : 2′ : 4′-derivative.

Experimental.

The imino-ethers were prepared from the corresponding iminochlorides and sodium phenoxides by the method described for the preparation of *N*-phenylbenzimino-*m*-hydroxyphenyl ether (J., 1922, **121**, 1676). The imino-ethers and benzoyldiphenylamines all crystallised well from alcohol, in which they were moderately easily soluble when hot, but only sparingly soluble in the cold.

N-o-*Chlorophenylbenzimino*-2 : 4 : 6-*trichlorophenyl ether*, from benz-*o*-chloroanilideiminochloride and 2 : 4 : 6-trichlorophenol, formed colourless plates or prisms, m. p. 99—100° (Found : Cl, 34·7. $C_{19}H_{11}ONCl_4$ requires Cl, 34·5%), and was converted by heating for 2 hours at 250—270° into *benzoyl*-2 : 4 : 6 : 2′-*tetrachlorodiphenylamine*, prisms, m. p. 131—132° (Found : Cl, 34·5%).

N-p-*Chlorophenylbenzimino*-2 : 4 : 6-*trichlorophenyl ether*, from benz-*p*-chloroanilideiminochloride and 2 : 4 : 6-trichlorophenol, formed pale yellow leaflets, m. p. 121—122° (Found : Cl, 34·3%), and underwent rearrangement into *benzoyl*-2 : 4 : 6 : 4′-*tetrachloro*-

diphenylamine (needles, m. p. 154°. Found : Cl, 34·5%) in 2 hours at 250—270°.

N-2 : 4-*Dichlorophenylbenzimino*-2 : 4-*dichlorophenyl ether*, from benz-2 : 4-dichloroanilideiminochloride and 2 : 4-dichlorophenol, was obtained as a viscous oil that did not crystallise even after standing for several weeks, but underwent isomeric change into *benzoyl*-2 : 4 : 2′ : 4′-*tetrachlorodiphenylamine* (plates, m. p. 153—154°. Found : Cl, 34·7%) on heating at 280—300° for 2 hours.

Numerous preliminary experiments showed that benzoyldiphenylamine itself and its substituted derivatives were best hydrolysed as follows : The benzoyl compound (10 g.) was boiled under reflux with a mixture of potassium hydroxide (50 c.c. of 50% aqueous solution) and alcohol (125 c.c.), and hydrolysis was complete in 2 hours. The mixture was then evaporated to dryness on the steam-bath, extracted with water, filtered, and the residue washed with water and crystallised from alcohol.

2 : 4 : 6 : 2′-*Tetrachlorodiphenylamine* formed stout prisms, m. p. 87—88°, sparingly soluble in alcohol (Found : Cl, 46·1. $C_{12}H_7NCl_4$ requires Cl, 46·2%).

2 : 4 : 6 : 4′-*Tetrachlorodiphenylamine* was readily soluble in alcohol and crystallised in prisms, m. p. 63—64° (Found : Cl, 46·3%).

2 : 4 : 2′ : 4′-*Tetrachlorodiphenylamine* crystallised in fine needles, m. p. 141—142°, very sparingly soluble in alcohol (Found : Cl, 46·3%).

2 : 4 : 6-*Trichlorodiphenylamine*, prepared from its benzoyl derivative, formed plates, m. p. 43—44°, readily soluble in alcohol (Found : Cl, 39·1. $C_{12}H_8NCl_3$ requires Cl, 38·7%).

Chlorination of Diphenylamine.—A rapid current of dry chlorine was passed into a solution of diphenylamine (50 g.) in glacial acetic acid (250 g.) under a reflux condenser. The chlorine was completely absorbed, hydrogen chloride was evolved, the solution became hot, and after the flask and contents had gained 40 g. in weight, the solution began to fill with long needle-shaped crystals. It was allowed to stand for an hour and filtered. The residue (55 g.), consisting of practically pure 2 : 4 : 2′ : 4′-tetrachlorodiphenylamine (m. p. 136—138°), crystallised from alcohol to a constant m. p. of 141—142° (Gnehm gives m. p. 133—134°); its identity with the tetrachlorodiphenylamine obtained as above was established by analysis (Found : Cl, 46·3%) and by mixed melting-point determination. When the chlorination was continued until chlorine was no longer absorbed (gain in weight = 60 g.), another substance separated, sparingly soluble in alcohol, m. p. 138—139° (Found : Cl, 56·6. $C_{12}H_5NCl_6$ requires Cl, 56·6%). It was therefore a *hexachlorodiphenylamine*, probably the 2 : 4 : 6 : 2′ : 4′ : 6′-compound. The

orientation could not be confirmed, however, as all attempts to hydrolyse benzoyl-2 : 4 : 6 : 2′ : 4′ : 6′-hexachlorodiphenylamine (J., 1927, 1747) or to benzoylate the amine were unsuccessful, no doubt owing to the intense steric hindrance of the four ortho-chlorine atoms.

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