238. *A Ring Closure Reaction in the Triarylamidine Series. A New Source of Disecondary* ortho-*Diamines.*

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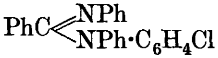
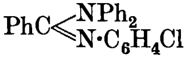
IN the course of investigations upon the molecular rearrangement of substituted triarylbenzenylamidines (J., 1930, 2462; preceding paper) the three *o*-chloro-substituted compounds (I), (II), and (III) were prepared; but it was not possible to study their interconversion, as another reaction occurred at a lower temperature.


$\mathrm{PhC}{<}\begin{matrix}\mathrm{NPh}\\ \mathrm{NPh{\cdot}C_6H_4Cl}\end{matrix}$

(I.)

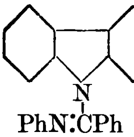

$\mathrm{PhC}{<}\begin{matrix}\mathrm{NPh_2}\\ \mathrm{N{\cdot}C_6H_4Cl}\end{matrix}$

(II.)

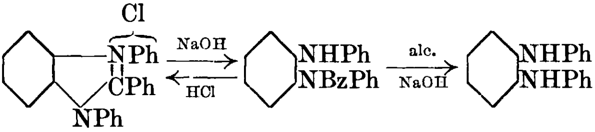

$\mathrm{PhC}{<}\begin{matrix}\mathrm{N{\cdot}C_6H_4Cl}\\ \mathrm{NPh{\cdot}C_6H_4Cl}\end{matrix}$

(III.)

When (I) was heated at temperatures of 200° and over it fused and in a few minutes began to solidify again, becoming finally a hard crystalline mass. The new compound did not melt at 300° and was readily soluble in water. Its aqueous solution contained chloride ions amounting, in a specimen heated at 267—269° for 30 minutes, to more than 96% of the chlorine of the original amidine. When the aqueous solution was rendered alkaline a new substance, m. p. 152°, was obtained which redissolved with some difficulty in concentrated hydrochloric acid. This was at first believed to be a carbazole derivative (IV) formed by the condensation of the two aromatic nuclei on the one nitrogen atom, but analysis indicated that it was *benzoyl-NN′-diphenyl-*o*-phenylenediamine* (VI), and this constitution was established by hydrolysis of the compound to *NN′*-diphenyl-*o*-phenylenediamine (VII). The primary product of heating amidine (I) must therefore have been 1 : 2 : 3-triphenylbenziminazolium chloride (V) and the ready solubility of this compound in water compared with the relatively slow solution of (VI) in concentrated hydrochloric acid (when V is re-formed) are thus explained (compare Meyer and Jacobson, " Lehrbuch der Organischen Chemie," 1920, II, 3, 489).



(IV.)



(V.) (VI.) (VII.)

The dichloro-substituted amidine (III) also underwent ring closure, but more slowly, 90% of the calculated amount of chlorine becoming ionic after 2 hours at 267—279°. The retardation was evidently due to the less basic character of the nitrogen atom caused by the introduction of the extra chlorine atom.

Compound (II) was unchanged after heating at 267—269° for ½ hour, but after ½ hour at 330—333° a small yield of (VI) was isolated from the product. Rearrangement of (II) into (I) evidently preceded ring closure.

In view of the comparative ease with which the required triarylamidines may be prepared it seems likely that the ring closure reaction here described will furnish a convenient method for the preparation of substituted disecondary *o*-diamines of known constitution which might otherwise be only difficulty accessible.

EXPERIMENTAL.

The amidines were prepared from the corresponding anilideiminochlorides and secondary amines by the method previously described (J., 1929, 2136). The substituted diphenylamines were obtained from the corresponding imino-ethers (J., 1929, 569).

NN'-*Diphenyl*-N-o-*chlorophenylbenzenylamidine* (I) formed lemon-yellow crystals, m. p. 171°, from acetone–alcohol (Found: Cl, 9·2. $C_{25}H_{19}N_2Cl$ requires Cl, 9·3%). On hydrolysis with concentrated hydrochloric acid for 6 hours at 200—230° it yielded *o*-chlorodiphenylamine and aniline, identified as their benzoyl derivatives, m. p. 95—96° and 159—161° respectively.

N-*Diphenyl*-N'-o-*chlorophenylbenzenylamidine* (II) formed pale yellow crystals, m. p. 94,° from light petroleum or alcohol (Found: Cl, 9·15%).

NN'-*Di*-o-*chlorophenyl*-N-*phenylbenzenylamidine* (III) was crystallised from light petroleum, m. p. 142° (Found: Cl, 16·9. $C_{25}H_{18}N_2Cl_2$ requires Cl, 17·0%). The complete condensation of benz-*o*-chloroanilideiminochloride and *o*-chlorodiphenylamine required 3 hours at 150°.

Condensation of benzanilideiminochloride and 2 : 2′-dichlorodiphenylamine to yield *N*-di-*o*-chlorophenyl-*N′*-phenylbenzenylamidine was found to be difficult and attempts to prepare this amidine were abandoned when the ring closure reaction was discovered. The following new intermediate compounds were, however, obtained.

N-o-*Chlorophenylbenzimino*-o-*chlorophenyl ether*, from benz-*o*-chloroanilideiminochloride and *o*-chlorophenol, separated from alcohol in pale yellow crystals, m. p. 75—76° (Found : Cl, 20·65. $C_{19}H_{13}ONCl_2$ requires Cl, 20·75%).

Benzoyl-2 : 2′-*dichlorodiphenylamine*, m. p. 149° (Found : Cl, 20·7%).

2 : 2′-*Dichlorodiphenylamine*, m. p. 30—31°, b. p. 200—202°/27 mm. (Found : Cl, 29·3. $C_{12}H_9NCl_2$ requires Cl, 29·8%).

Numerous experiments were conducted on *NN′*-diphenyl-*N*-*o*-chlorophenylbenzenylamidine (I), of which the following is typical. 10 G. of the amidine were heated for 15 minutes at 300—305°, the hard mass of interlacing crystals of 1 : 2 : 3-triphenylbenziminazolium chloride (V) was broken out of the tube and dissolved in hot water (150 c.c.), hydrochloric acid (10 c.c.) added, and the solution filtered from a little tarry matter and made alkaline with caustic potash; the copious white precipitate formed was washed with water and crystallised from alcohol, yielding 7·7 g. (81% of the calculated amount) of *benzoyl*-NN′-*diphenyl*-o-*phenylenediamine* (VI) as colourless needles, m. p. 152° [Found : C (micro), 82·2; H (micro), 5·6; N, 7·9. $C_{25}H_{20}ON_2$ requires C, 82·5; H, 5·5; N, 7·7%].

Hydrolysis of (VI) with alcoholic potash (compare J., 1929, 569) yielded *NN′*-diphenyl-*o*-phenylenediamine (m. p. 107—108°, not depressing the m. p. of an authentic specimen kindly provided for comparison by Professor C. S. Gibson. Acetyl derivative, m. p. 282°; compare Clemo, Perkin, and Robinson, J., 1924, **125**, 1781; Gibson and Johnson, J., 1928, 1988). 25 G. of amidine (I) yielded after heating, hydrolysis, and distillation under reduced pressure 11 g. of crude amine (m. p. 98° upwards) melting at 107—108° after repeated crystallisation from light petroleum. The crude amine was very sensitive to atmospheric oxidation.

5 G. of *NN′*-di-*o*-chlorophenyl-*N*-phenylbenzenylamidine (III) were heated at 267—269° for 2 hours, in the course of which it set to a mass of crystals. The material was dissolved in water, the solution made alkaline, and the precipitate crystallised from alcohol, in which it was readily soluble, yielding 1·7 g. of *benzoyl*-N-*phenyl*-N′-o-*chlorophenyl*-o-*phenylenediamine* in crusts, m. p. 124—126° [Found (micro) : C, 75·3; H, 4·85. $C_{25}H_{19}ON_2Cl$ requires C, 75·3; H, 4·8%]. The mother-liquors yielded an uncrystallisable syrup.

N-Diphenyl-*N′*-*o*-chlorophenylbenzenylamidine (II) (5 g.) charred badly when heated at 330° for an hour, but about 0·1 g. of benzoyl-*NN'*-diphenyl-*o*-phenylenediamine was obtained from the heated material by the process described above; m. p. 148°; mixed with specimen from compound (I), m. p. 148—152°.

The microanalyses were performed by Dr. A. Schoeller.

We wish to express our thanks to the Research Fund Committee of the Chemical Society for a grant to one of us (A. W. C.) that has defrayed part of the cost of this investigation.

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[*Received, April 5th,* 1932.]