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HALOGENATIONS IN THE DIPHENYLAMINE SERIES

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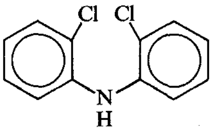
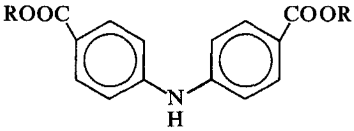
Abstract—The preparation of substituted dibenz[b.f]azepin required several substituted diphenylamines, especially 2,2′-dichloro-diphenylamine (I) and its derivatives. The observations made in this investigation are believed to be of some general interest.

BROMINATION of diphenylamine-4,4′-dicarboxylic acid (II, R = H)[1] and its methyl ester (II, $R = CH_3$)[2] in glacial acetic acid at low temperature gave 2,2′-dibromodiphenylamine-4,4′-dicarboxylic acid (III, R = H) and its dimethyl ester as the most probable structures in analogy with the following chlorination experiments. As it proved impossible to decarboxylate the acid III, which tended to carbonize, the chlorination in glacial acetic acid at 10° was undertaken. The product contained *five* chlorine atoms, one of which was bound to the nitrogen and could be eliminated by treatment with sodium iodide. The chlorination products, according to the rules of substitution, would, therefore, be IV and V, respectively. Both were decarboxylated by copper bronze in boiling quinoline to the same 2,2′,6,6′-tetrachlorodiphenylamine (VI).

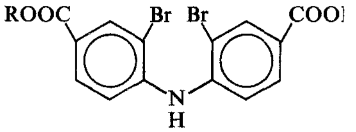
In order to limit the extent of chlorination of II (R = H), we employed t-butyl



I



II $R = CH_3, H$



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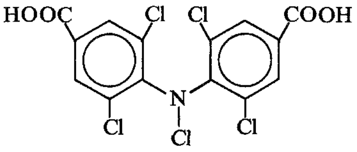

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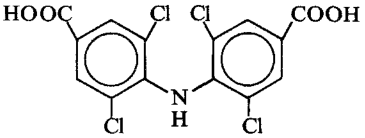

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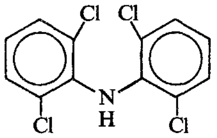

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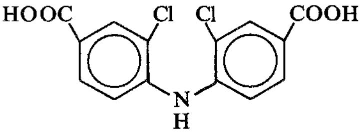

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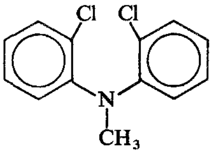
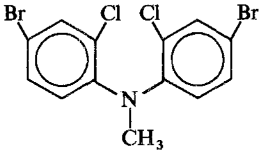


VIII



IX

hypochlorite and N-chlorosuccinimide. Whilst the latter gave a quantitative yield of 2,2′-dichlorodiphenylamine-4,4′-dicarboxylic acid (VII) and by subsequent decarboxylation the known, 2,2′-dichlorodiphenylamine (I, 80% yield),[3] compound IV yielded 95% of VII and 5% of IV which could not be separated; but their decarboxylation products I and VI were separated by column chromatography on alumina.

The structure of compound I was confirmed by its NMR spectrum which is typical of an *ortho*-disubstituted benzene.

A second route to the system VIII which lends itself to large-scale preparations, starts from the easily accessible[4] 4,4′-dibromo-N-methyldiphenylamine. Its chlorination with t-butyl hypochlorite gave 4,4′-dibromo-2,2′-dichloro-N-methyldiphenylamine (IX), which could be selectively debrominated to VIII either with triphenylstannan[5] or by magnesium in the presence of ethylene dibromide.[6] The latter method gives a more easily purifiable product.

The NMR spectrum of VIII is sufficiently similar to that of I to make formula VIII unequivocal.

EXPERIMENTAL

Dimethyl diphenylamine-4,4′-dicarboxylate (II, R = CH_3)

Diphenylamine-4,4′-dicarboxylic acid[1] was stirred with excess $SOCl_2$ for 4 hr at room temp and for 2 hr at the boiling temp of $SOCl_2$. Excess of the latter was distilled off *in vacuo* and the residue dissolved in cold MeOH and refluxed for 2 hr. The reaction mixture was poured into water and the solid product filtered and recrystallized from aqueous EtOH as colorless crystals, m.p. 177° (lit.[2] 177°); yield, 95%.

2,2′-Dibromodiphenylamine-4,4′-dicarboxylic acid (III, R = H)

Bromine (5 g) in 50 ml AcOH was added with stirring at 5° to a soln of 8 g of II (R = H) in 100 ml of the same solvent. The mixture was kept at this temp for 2 hr and poured into water. The solid product was dissolved in 10% $NaHCO_3$aq, refluxed with active carbon, filtered and isolated by acidification, giving from aqueous alcohol, m.p. above 300° a quantitative yield. (Found: C, 41·0; H, 2·6; N, 3·4; Br, 38·2. Calc. for $C_{14}H_9Br_2NO_4$: C, 40·5; H, 2·2; N, 3·4; Br, 38·6%).

The *dimethyl ester* (III, R = CH_3) was obtained analogously from II (R = CH_3) in 89% yield, from aqueous alcohol, m.p. 219°. (Found: C, 43·6; H, 3·1; N, 3·0; Br, 35·7. Calc. for $C_{16}H_{13}Br_2NO_4$: C, 43·3; H, 3·1; N, 3·2; Br, 36·1%).

N *2,2′,6,6′-Pentachlorodiphenylamine-4,4′-dicarboxylic acid* (IV)

At a temp not exceeding 10°, a current of chlorine was passed through a soln of 5 g of II (R = H) in glacial AcOH until the absorption of the gas ceased. After 12 hr at room temp, the soln was poured into water and the ppt filtered off and purified from aqueous alcohol, m.p. > 300°; yield, 90%. (Found: C, 38·8; H, 1·8; N, 3·2; Cl, 40·5. Calc. for $C_{14}H_6Cl_5NO_4$: C, 38·8; H, 1·8; N, 3·2; Cl, 40·9%).

2,2′,6,6′-Tetrachlorodiphenylamine-4,4′-dicarboxylic acid (V)

A mixture of 4·5 g of IV, 2 g NaI, 100 ml AcOH and 60 ml benzene was kept at room temp for 24 hr, poured into water and treated with $NaHSO_3$aq. The solid product, resulting from the evaporation of the benzene layer, was precipitated from bicarbonate soln with acid and melted above 300°, yield, 90%. To obtain an analytically pure product, trituration with aqueous alcohol proved sufficient. (Found: C, 41·9; H, 2·0; N, 3·5; Cl, 36·0. Calc. for $C_{14}H_7Cl_4NO_4$: C, 42·5; H, 1·8; N, 3·5; Cl, 35·9%).

2,2′,6,6′-Tetrahclorodiphenylamine (VI)

A soln of 4 g of IV or V in 100 ml freshly distilled quinoline was refluxed with 0·5 g copper bronze until the evolution of CO_2 ceased. The mixture was poured into water, the biphasic liquid filtered from the copper, and the aqueous layer extracted with benzene. The benzene extract was then washed twice with 5% HCl, dried and concentrated *in vacuo*, and the residue dissolved in a little fresh benzene and chromatographed on alumina. A mixture of hexane–benzene (2:1) served as eluent. Yield, 70–75%; m.p. 94°. (Found: C, 46·6; H, 2·5; N, 4·3; Cl, 47·0. Calc. for $C_{12}H_7Cl_4N$: C, 46·9; H, 2·3; N, 4·5; Cl, 46·3%).

2,2′-*Dichlorodiphenylamine*-4,4′-*dicarboxylic acid* (VII)

(a) A soln of 4·5 g t-butyl hypochlorite in 50 ml glacial AcOH[7] was added, at 5° with stirring, to 5 g of II (R = H), dissolved in 100 ml of the same solvent. After a further 6 hr at 5°, the mixture was poured into water, and the product was filtered, yield, 100%. The analysis showed that the product contained a small amount of V.

(b) Similarly, 5 g of II (R = H) was treated with 5 g N-chlorosuccinimide. The mixture was poured into water, heated at 50° and filtered. The product was recrystallized repeatedly from aqueous alcohol (active carbon) and melted above 300°, yield, quantitative. (Found: C, 51·0; H, 2·6; N, 4·0; Cl, 22·5. Calc. for $C_{14}H_9Cl_2NO_4$: C, 51·5; H, 2·7; N, 4·3; Cl, 22·0%).

2,2′-*Dichlorodiphenylamine* (I)

Decarboxylation of VII in the manner described above gave an oil which was chromatographed on alumina and eluted with hexane, m.p. 32–33° (lit.[3]: 32°); yield, 80%.

4,4′-*Dibromo*-N-*methyldiphenylamine*

In the manner described for diphenylamine,[3] N-methyldiphenylamine was brominated and the product (yield, quantitative), recrystallized from EtOH; m.p. 120°. (Found: C, 45·2; H, 3·4; N, 4·1; Br, 48·0. Calc. for $C_{13}H_{11}Br_2N$: C, 45·7; H, 3·2; N, 4·1; Br, 47·0%).

4,4′-*Dibromo*-2,2′-*dichloro*-N-*methyldiphenylamine* (IX)

At 5°, a soln of 4·5 g t-butyl hypochlorite in 50 ml AcOH was added slowly to a soln of 7 g of the foregoing compound in 150 ml of the same solvent. After 12 hr at room temp, the mixture was diluted with water, and the solid which precipitated was recrystallized from alcohol; m.p. 103°; yield, 90%. (Found: C, 37·9; H, 2·2; N, 3·0. Calc. for $C_{13}H_9Cl_2Br_2N$: C, 38·0; H, 2·2; N, 3·1%).

2,2′-*Dichloro*-N-*methyldiphenylamine* (VIII)

(a) When a mixture of 8 g of IX and 10 g triphenylstannan was heated slowly to 140°, an exothermic reaction caused the temp to rise to 190°. The heating was interrupted, and the temp maintained at 150° for 1·5 hr. The mass was refluxed with 50 ml MeOH for 30 min and after addition of 6 g MeI for another 10 min. Then 5 g KOH was added and the heating continued for 10 min. The product was diluted with water and extracted with benzene. The residue of this extract was a mixture of solid and a liquid which was taken up in MeOH. Distillation under 0·5 mm press gave at 170–175° an oil (yield, 70%) which was separated from some triphenylstannol by chromatography on alumina and eventually melted at 40°. (Found: C, 61·9; H, 3·8; N, 5·5; Cl, 28·0. Calc. for $C_{13}H_{11}Cl_2N$: C, 62·0; H, 4·4; N, 5·6; Cl, 28·1%).

(b) To a suspension of 11·0 g Mg in 200 ml ether, 4 g of 1,2-dibromoethane was added at such a rate that the heat of reaction kept the ether boiling. In the same way a soln of 8 g of IX and 4 g dibromoethane in 200 ml ether was added gradually. The reaction mixture was refluxed for 1 hr and decomposed with 10% HCl, and the ethereal layer was dried and concentrated, b.p. 170–180° (0·5 mm). The product, m.p. 42°, was purified by chromatography, as indicated above.

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