## 345. *Amidines. Part II. Diamidines from Di-imidochlorides derived from Diamines.*

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Diamidines of the types NRR′·CPh:N·$C_6H_4$·$C_6H_4$·N:CPh·NRR′ and NRR′·CPh:N·$C_6H_4$·N:CPh·NRR′ have been prepared.

Di-imidochlorides, from diamines, and the corresponding diamidines have hitherto been unknown. The dibenzoyl derivatives of benzidine and of *m*- and *p*-phenylenediamines have now been converted into the corresponding *di-imidochlorides*, which have been condensed, by Shah's modified method (*J. Indian Inst. Sci.*, 1924, **7**, 215), with a number of amines to yield *diamidines* of the types NRR′·CPh:N·$C_6H_4$·$C_6H_4$·N:CPh·NRR′ and NRR′·CPh:N·$C_6H_4$·N:CPh·NRR′.

*Dinitriles* also have been obtained from the di-imidochlorides derived from benzidine

and *p*-phenylenediamine, by treating them with potassium cyanide (cf. Mumm, Volquartz, and Hesse, *Ber.*, 1914, **47**, 751).

*Dibenzbenzididedi-imidochloride*.—A mixture of dibenzoylbenzidine (25 g.), phosphorus pentachloride (30 g.), and nitrobenzene (30 c.c.) was heated under reflux (calcium chloride guard-tube) until a clear liquid was produced. The yellow crystals (22 g.) obtained at room temperature after 12 hours were washed with light petroleum and kept under reduced pressure over phosphoric oxide and paraffin wax for 24 hours; m. p. 212° (Found: Cl, 16·6. $C_{26}H_{18}N_2Cl_2$ requires Cl, 16·6%).

NN′-*Di*-(α-o-*chloroanilinobenzylidene*)*benzidine*.—A mixture of the di-imidochloride (5 g.), *o*-chloroaniline (3·2 g.), and diethylaniline (10 c.c.) which had been heated at 100° for 2 hours was poured into excess of dilute hydrochloric acid (1 : 1), and after 2 hours the insoluble hydrochloride was decomposed with concentrated aqueous ammonia at 100°; the *base* crystallised from toluene in yellowish clusters of needles, m. p. 234° (Found: Cl, 11·3. $C_{38}H_{28}N_4Cl_2$ requires Cl, 11·6%). The yellow *picrate* separated slowly from mixed solutions of the base and picric acid in hot chlorobenzene; m. p. 229—230° (decomp.) (Found: Cl, 6·9. $C_{38}H_{28}N_4Cl_2,2C_6H_3O_7N_3$ requires Cl, 6·6%).

The following di-amidines were similarly prepared. They were yellowish in colour and were crystallised from chlorobenzene or toluene: *Di*-(α-*methylanilinobenzylidene*)*benzidine*, m. p. 234° (Found: N, 10·1. $C_{40}H_{34}N_4$ requires N, 9·8%); *picrate*, m. p. 248° (decomp.) (Found: N, 13·7. $C_{40}H_{34}N_4,2C_6H_3O_7N_3$ requires N, 13·6%). *Di*-(α-*ethylanilinobenzylidene*)-*benzidine*, m. p. 203° (Found: N, 9·6. $C_{42}H_{38}N_4$ requires N, 9·4%); *picrate*, m. p. 235° (decomp.) (Found: N, 13·2. $C_{42}H_{38}N_4,2C_6H_3O_7N_3$ requires N, 13·3%). *Di*-(α-*benzylanilinobenzylidene*)*benzidine*, m. p. 174° (Found: C, 86·6; H, 6·2. $C_{52}H_{42}N_4$ requires C, 86·4; H, 5·8%); *picrate*, m. p. 185° (decomp.) (Found: N, 11·8. $C_{52}H_{42}N_4,2C_6H_3O_7N_3$ requires N, 11·9%). *Di*-(α-*diphenylaminobenzylidene*)*benzidine*, m. p. 262° (Found: N, 8·6. $C_{50}H_{38}N_4$ requires N, 8·1%); *picrate*, m. p. 234° (Found: N, 11·5. $C_{50}H_{38}N_4,2C_6H_3O_7N_3$ requires N, 12·1%). *Di*-(α-*ethyl*-o-*toluidinobenzylidene*)*benzidine*, m. p. 200° (Found: C, 84·5; H, 6·8. $C_{44}H_{42}N_4$ requires C, 84·4; H, 6·7%). *Di*-(α-*ethyl*-p-*toluidinobenzylidene*)*benzidine*, m. p. 221° (Found: C, 84·2; H, 6·5; N, 8·8. $C_{44}H_{42}N_4$ requires C, 84·4; H, 6·7; N, 8·9%). The picrates separate as oils in the last two cases.

NN′-*Di*-(α-*aminobenzylidene*)*benzidine*, obtained by shaking a mixture of the di-imidochloride (20 g.) and a concentrated solution of ammonia in methyl alcohol (150 c.c.) for 48 hours, crystallised from pyridine in yellow needles, m. p. 252° (Found: C, 79·8; H, 5·9; N, 14·0. $C_{26}H_{22}N_4$ requires C, 80·0; H, 5·6; N, 14·3%).

*Dibenz*-p-*phenylenediamidedi-imidochloride* was prepared from a mixture of dibenzoyl-*p*-phenylenediamine (50 g.), phosphorus pentachloride (75 g.), and nitrobenzene (40 c.c.), washed with dry light petroleum, and dried as before; m. p. 176° (Found: Cl, 21·0. $C_{20}H_{14}N_2Cl_2$ requires Cl, 20·1%).

The following diamidines were prepared as described above. NN′-*Di*-(α-*methylanilinobenzylidene*)-p-*phenylenediamine*, m. p. 264° (Found: N, 10·8. $C_{34}H_{30}N_4$ requires N, 11·3%); *picrate*, m. p. 243° (decomp.) (Found: N, 14·5. $C_{34}H_{30}N_4,2C_6H_3O_7N_3$ requires N, 14·7%). *Di*-(α-*benzylanilinobenzylidene*)-p-*phenylenediamine*, m. p. 203° (Found: C, 85·7; H, 6·0; N, 8·9. $C_{46}H_{38}N_4$ requires C, 85·4; H, 5·9; N, 8·7%); *picrate*, m. p. 220° (decomp.) (Found: N, 12·8. $C_{46}H_{38}N_4,2C_6H_3O_7N_3$ requires N, 12·7%). *Di*-(α-*methyl*-o-*toluidinobenzylidene*)-p-*phenylenediamine*, m. p. 227° (Found: C, 82·7; H, 6·7; N, 10·8. $C_{36}H_{34}N_4$ requires C, 82·8; H, 6·5; N, 10·7%); *picrate*, m. p. 236° (decomp.) (Found: N, 13·7. $C_{36}H_{34}N_4,2C_6H_3O_7N_3$ requires N, 14·3%). *Di*-(α-*ethyl*-o-*toluidinobenzylidene*)-p-*phenylenediamine*, m. p. 186° (Found: C, 83·0; H, 6·9. $C_{38}H_{38}N_4$ requires C, 82·9; H, 6·9%); *picrate*, m. p. 237° (decomp.) (Found: N, 14·0. $C_{38}H_{38}N_4,2C_6H_3O_7N_3$ requires N, 13·9%).

When the clear solution obtained by heating a mixture of dibenzoyl-*m*-phenylenediamine (10 g.) and phosphorus pentachloride (14 g.) was cooled, *dibenz*-m-*phenylenediamidedi-imidochloride* (6 g.) crystallised in greyish clusters of needles. It was washed with dry light petroleum and dried as usual; m. p. 86° (Found: Cl, 19·5. $C_{20}H_{14}N_2Cl_2$ requires Cl, 20·1%).

*Di*-(α-*benzylanilinobenzylidene*)-m-*phenylenediamine* had m. p. 129—130° (Found: C, 84·8; H, 6·2. $C_{46}H_{38}N_4$ requires C, 85·4; H, 5·9%); the picrate separated as a paste.

NN′-*Di*-(α-*cyanobenzylidene*)*benzidine* was obtained by heating a mixture of dibenzbenzididedi-imidochloride (2·5 g.) and methyl-alcoholic potassium cyanide (2 g. in 100 c.c.) under reflux for about 15 minutes; crystallised from toluene, it had m. p. 252° (Found: C, 82·0; H, 4·6. $C_{28}H_{18}N_4$ requires C, 81·9; H, 4·4%).

NN′-*Di*-(α-*cyanobenzylidene*)-p-*phenylenediamine*, prepared from dibenz-*p*-phenylenediamide-di-imidochloride as described above and crystallised from toluene, had m. p. 236° (Found : C, 78·6; H, 4·2. $C_{22}H_{14}N_4$ requires C, 79·0; H, 4·2%).

The authors' thanks are due to Dr. R. C. Shah for his valuable advice.

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