LXXXVIII.—N-*Alkylated Amidines.*

By MONMOHAN SEN and JÑANENDRA NATH RÂY.

IN connexion with certain investigations relating to glyoxaline alkaloids, it became necessary to prepare and study the behaviour of a number of *N*-alkylated amidines. The methods already available for the preparation of these substances (Wallach, *Ber.*, 1879, **12**, 328; 1882, **15**, 208; 1883, **16**, 357, 1647; Strecker, *Annalen*, 1857, **103**, 328) are not entirely satisfactory. Hofmann (*Jahresber. Fort. Chem.*, 1865, 414; *Monatsberichte Berl. Akad.*, 1865, 640) obtained diphenylacetamidine and diphenylbenzamidine by condensing aniline with acetanilide and benzanilide, respectively, in presence of phosphorus trichloride or pentachloride. This rather convenient method seems to have been little investigated and it was deemed desirable to study it systematically. It is of very general applicability and by its means a number of new amidines have been prepared, in good yield in most cases. Phosphorus trichloride is the most suitable condensing agent for the purpose, although phosphoric oxide in boiling xylene may advantageously replace it in some cases.

A mixture of the requisite quantities of an amine and an acylamine in about ten times the weight of phosphorus trichloride is heated at 110—120° for about 3 hours. The completion of the reaction is indicated by a drop of the reaction mixture giving a clear solution in water. The product is dissolved in cold water and basified; the amidine is then precipitated in a crystalline condition.

The method is applicable to a secondary amine like diphenylamine and an acylamine. On the other hand, acetomethylanilide condenses with *m*-toluidine, hence the reaction is represented as taking place as follows:

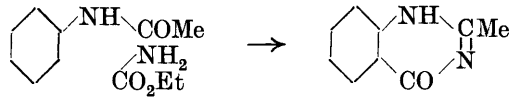
$$NH_2R + R'\cdot CO\cdot NHR'' \rightarrow NHR\cdot CR'(OH)\cdot NHR'' \xrightarrow{-H_2O} NR{:}CR'\cdot NHR'' \text{ or } NHR\cdot CR'{:}NR''.$$

But no isomeric forms can be isolated, as the amidines show virtual tautomerism (compare von Pechmann, *Ber.*, 1895, **28**, 869). By altering the order of combination the same product was isolated (A) from acetanilide and *m*-toluidine and from aceto-*m*-toluidine and aniline, and (B) from acetanilide and *p*-nitroaniline and from *p*-nitroacetanilide and aniline. The result (B) is interesting, as here a strongly negative group in the molecule has not impaired the mobility of the hydrogen atom in any way.

With a view to prepare hydrazidines, we attempted to condense an acylamine with phenylhydrazine by this method. The product

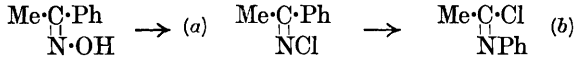
of interaction of acetanilide and phenylhydrazine, on being rendered alkaline, evolved ammonia and diphenylacetamidine was obtained in more than 70% yield.

Next, we attempted to prepare cyclic amidines by using urethane in place of an amine. Phosphoric oxide acting on molar proportions of acetanilide and urethane in boiling xylene solution gave rise to the compound (I), which will be described along with others of the same series in a subsequent communication.



(I.)

A further point of interest is in connexion with the Beckmann transformation of acetophenoneoximė. The transformation may be represented as taking place through the phases (*a*) and (*b*) :



Both (*a*) and (*b*) represent reactive chloro-compounds capable of condensing with aniline to form acetophenonephenylhydrazone and diphenylacetamidine respectively. The actual amounts of each would depend on the relative reactivity of the two chlorine atoms in (*a*) and (*b*). Actually, the amidine was produced and no trace of acetophenonephenylhydrazone could be detected. This result may, of course, be due to the smaller reactivity of the chlorine atom in the group C:NCl as compared with N:CCl, but it may also be taken to indicate that the intermediate phase (*a*) exists only for a very short period of time.

EXPERIMENTAL.

Some properties of the amidines that have been prepared are tabulated below. Unless stated otherwise, the amidines were crystallised from alcohol. The values in brackets in column 3 are the calculated percentages of nitrogen. An amidine X:NY was prepared from the components XO and NH_2Y; *e.g.*,

$NHPh{\cdot}CMe{:}N{\cdot}C_6H_4Me$

from $NHPh{\cdot}COMe$ and $C_6H_4Me{\cdot}NH_2$, and so on.

Formula.	M. p.	N %.	Remarks.
$NHPh{\cdot}CMe{:}N{\cdot}C_6H_4Me$ (*m*).	103°	*12·7 (12·5)	Needles.
,, (*p*).	90	12·7	,,
,, (*o*).	138	12·9	Buff-coloured needles.
$NHPh{\cdot}CMe{:}N{\cdot}C_6H_4{\cdot}NO_2$ (*p*).	189	16·9 (16·5)	Yellow, prismatic needles.†
$NHPh{\cdot}CMe{:}N{\cdot}C_6H_4{\cdot}OEt$ (*p*).	102	11·3 (11·0)	Colourless needles.

* C, 80·2 (80·3); H, 7·3 (7·1). † From methyl alcohol.

Formula.	M. p.	N %.	Remarks.
$NPh{:}CMe{\cdot}NPh_2$.	92	10·1 (9·8)	Prismatic needles.
(*m*) $C_6H_4Me{\cdot}NH{\cdot}CMe{:}NPh$.	103	12·8 (12·5)	Identical with the first.
(*m*) $C_6H_4Me{\cdot}NH{\cdot}CMe{:}N{\cdot}C_6H_4Me$(*o*).	101	12·1 (11·8)	Rectangular plates.
(*p*) ,, (*p*).	120	11·5	Needles.*
(*p*) $C_6H_4Me{\cdot}NH{\cdot}CMe{:}N{\cdot}C_6H_4{\cdot}NO_2$ (*m*).	134	15·9 (15·6)	Product boiled with water before crystallisation. Yellow needles.*
(*p*) $C_6H_4Me{\cdot}N{:}CMe{:}NPh_2$.	122	9·4 (9·3)	Needles.
(*p*) $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CMe{:}N{\cdot}C_6H_4{\cdot}OEt$ (*p*).	117	9·6 (9·6)	,,
$NHPh{\cdot}CPh{:}N{\cdot}C_6H_4Me$ (*o*).	107	10·0 (9·8)	,,
(*p*) $C_6H_4Br{\cdot}NH{\cdot}CMe{:}N{\cdot}C_6H_4Me$ (*o*).	122	9·4 (9·2)	Elongated needles.
$NPhMe{\cdot}CMe{:}N{\cdot}C_6H_4Me$ (*m*). (picrate)	157	15·2 (15·0)	The base is an oil. Isolated as the picrate. Bright yellow needles. The free base regenerated from the picrate is an oil which could not be solidified.
(*p*) $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CMe{:}NPh$.	189	—	Mixed with the fourth compound, no lowering of m. p. observed.
$NHPh{\cdot}CMe{:}NPh$.	—	—	From acetanilide and phenylhydrazine.

* From dilute alcohol.

We wish to thank Professor R. Robinson, F.R.S., for his kind help in the preparation of the manuscript.

THE UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.
THE UNIVERSITY, MANCHESTER. [*Received, November 28th,* 1925.]