166. N-*Nitro*-N′-2 : 4-*dinitrophenylurea. A Reagent for Primary and Secondary Amines.*

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N-Nitro-*N*′-2 : 4-dinitrophenylurea (I) was first prepared by Reudler (*Rec. trav. chim.*, 1914, **33**, 35) by nitration of phenylurea; he described the decomposition of (I) with ammonia in anhydrous ether to give 2 : 4-dinitrophenylurea, with aqueous ammonia and alkali to give 2 : 4-dinitroaniline, and with ethanol to give 2 : 4-dinitrophenylurethane. Kniphorst (*Rec. trav. chim.*, 1925, **44**, 693) prepared *N*-2 : 4-dinitrophenyl-*N*′-ethyl (and methyl) nitrourea and showed that these, and (I), with aniline, *p*-toluidine, phenylhydrazine or hydrazine in ether yielded *s*.-ureas. There appears, however, to have been no attempt to utilise (I) as a reagent for the characterisation of primary and secondary amines, a use to which it is particularly adapted on account of ease of preparation, simplicity of use and ease of purification of the derivatives.

Since (I) behaves as a moderately strong acid, salts are formed with amines. These salts, insoluble in hydrocarbon solvents, are readily decomposed by boiling in xylene suspension, nitrous oxide and water being formed; the *s*.-urea dissolves in the xylene from which it crystallises on cooling, or from which it may be precipitated with light petroleum. *Salts* prepared are listed in Table I.

Table I.

Salts of N-*Nitro*-N′-2 : 4-*dinitrophenylurea and amines.*

Amine.	M. p. of salt.	Formula.	Analysis. Found N%.	Required N%.
Piperidine	133°	$C_{12}H_{16}O_7N_6$	23·5	23·6
Aniline	175	$C_{13}H_{12}O_7N_6$	23·4	23·1
Diethylamine	130	$C_{11}H_{17}O_7N_6$	24·1	24·4
Methylaniline	207	$C_{14}H_{14}O_7N_6$	22·1	22·2

A simpler method of preparing the ureas is addition of (I) to a boiling alcoholic solution of the amine. The ureas, which normally begin to separate from the hot solution, are formed in high yield, are well crystalline and easily recrystallised. They show a wide range of m. p.'s. 2 : 4-*Dinitrophenylureas* have been prepared from the amines listed in Table II.

The reagent may be used with amines in aqueous solution although this procedure is not, in general, so satisfactory and is occasionally accompanied by some tar formation. Finally, it is necessary to add a note of warning that (I) is an explosive of rather lower power than picric acid, but possessing slightly greater sensitiveness to friction and impact. It should not be stored in bottles with ground-in stoppers.

TABLE II.

Amine.	M. p. of urea.	Analysis. Found N%.	Required N%.
Methylamine	208*	22·8	23·3
Ethylenediamine	258	23·4	23·4
Dimethylamine	203	21·7	22·0
Ethylamine	161	21·8	22·0
β-Hydroxyethylamine	162	20·4	20·7
Diethylamine	123	19·7	19·8
Piperidine	140	18·8	19·0
Morpholine	172	19·0	18·9
Dibutylamine	98	16·6	16·6
*cyclo*Hexylamine	170	17·9	18·2
n-Amylamine	114	19·5	19·0
β-Dimethylaminoethylamine	153	23·4	23·6
2 : 4-Dimethyl-3-pentylamine	155	17·2	17·2
Aniline	189 *	18·2	18·5
N-Methylaniline	204	17·8	17·7
o-Toluidine	200	18·1	17·7
m-Toluidine	213	18·3	17·7
o-Anisidine	201	17·1	16·9
p-Anisidine	204	17·4	16·9
α-Naphthylamine	207	15·9	15·9
β-Naphthylamine	230	16·0	15·9

* Kniphorst (*loc. cit.*) gives m. p. 194°.

EXPERIMENTAL.

(Analyses by Mr. E. S. Morton. M. p.'s are uncorrected.)

N-*Nitro*-N'-2 : 4-*dinitrophenylurea*.—This was prepared according to Reudler (*loc. cit.*)

Aniline salt of N-*nitro*-N'-2 : 4-*dinitrophenylurea*. The details of the preparation of this are given as an example. To a solution of the reagent (5 g.) in the minimum quantity of cold acetone, aniline (1·7 g.) was added. On cooling and scratching a pale yellow crystalline powder (6·4 g.) separated, which was collected and washed with cold acetone; m. p. 175° (Found : N, 23·4. $C_{13}H_{12}O_7N_6$ requires N, 23·1%).

N-2 : 4-*Dinitrophenyl*-N'-*phenylurea*.—*Method* (a), *by decomposition of the salt*. The salt (above) was suspended in a little xylene and boiled under reflux during five minutes. There was vigorous effervescence, and the solid gradually dissolved. The solution on cooling deposited a solid which, recrystallised from alcohol, gave yellow needles, m. p. 189° (Found : N, 18·2. Calc. for $C_{13}H_{10}O_5N_4$: N, 18·5%). *Method* (b), *by direct preparation*. To a solution of aniline (4·65 g.) in boiling ethanol (50 c.c.), the reagent (13·65 g.) was added during 20 minutes. Each addition was accompanied by vigorous effervescence and caution was necessary. The clear solution was boiled for five minutes during which crystallisation commenced and, on cooling to 20°, a semi-solid magma of yellow crystals was formed, which was collected, washed with alcohol (25 c.c.) and dried (13·2 g.). The crude material had m. p. 182—185°; recrystallised from alcohol, it gave yellow needles m. p. 189°, undepressed by admixture with that formed under (*a*) above.

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