N-Aminoisocyanides by 1,1-Elimination from Formimidoyl Chloride

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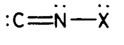
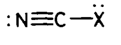
The *N*-aminoisocyanide (**6**) has been observed in solution and trapped by rate determining nucleophilic attack to give formamides and formamidines.

Although isocyanides have attracted increasing attention as synthetic intermediates,[1] those isocyanides which carry a heteroatom on nitrogen (**1**, X = –NHPh, –OPh, –NMeAr) have not been isolated or described in detail, presumably because they undergo rapid subsequent reactions. Thus Wentrup[2] has shown that (**1**, X = –NHPh) generated by flash vacuum pyrolysis rearranges rapidly to the corresponding cyanamide (**2**, X = –NHPh) even at −100 °C and also polymerises at higher temperatures. This instability appears to be shared also by many heterocumulenes (such as ketenimines) when they are similarly substituted by a heteroatom.

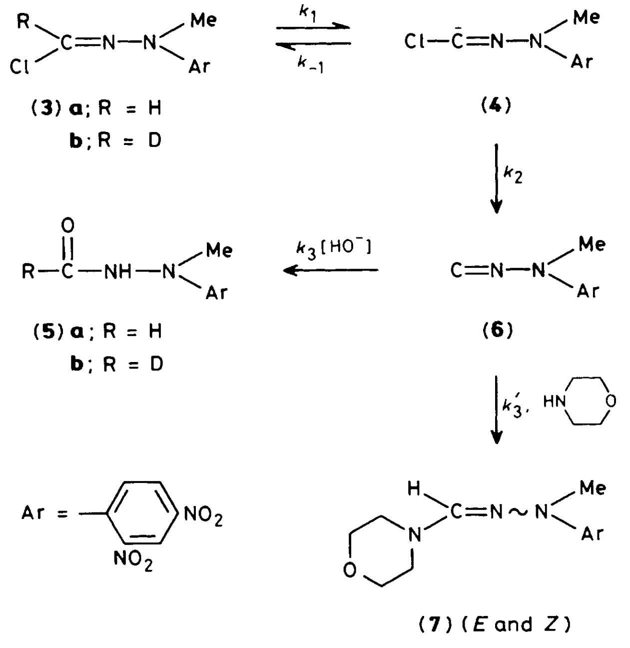
We have now synthesised *N*-(2,4-dinitrophenyl)-*N*-methylformohydrazonoyl chloride (**3a**) from the reaction of the hydrazide (**5a**) with PCl$_5$.† Although formimidoyl halides of the type (**3**) have previously been proposed as intermediates in the synthesis of isocyanides, they have not been isolated; previous attempts to isolate such halides have yielded dimeric products[3] because of the susceptibility of the formimidoyl halide system to direct nucleophilic attack.



(**1**)



(**2**)



When (**3a**) is treated in aqueous solution at high pH it undergoes two successive reactions, both of which are base catalysed. The first reaction is 1,1-elimination to form the isocyanide (**6**); the rate of this reaction is proportional to [HO$^-$] over the pH range 9—13 giving an observed second-order rate constant of 7.6 mol^{-1} dm^3 s^{-1} at 25 °C.‡ The second reaction is the hydration of the isocyanide (**6**) to give as final product the formamide (**5a**). That elimination–addition is occurring is confirmed by the observation that when the reaction is carried out in D$_2$O–DO$^-$, the product isolated is the deuterioformamide (**5b**); preliminary experiments established that (**5a**) did not exchange deuterium under the reaction conditions.

There is a fine balance between reprotonation of the carbanion by water (k_{-1}) and loss of Cl$^-$ to give (**6**) (k_2) since (i) formation of (**6**) does not show appreciable base catalysis by amine or carbonate buffers; *i.e.* the reaction is dependent only on pH; (ii) addition of [Cl$^-$] (1.0 M) shows a small rate depression (*ca.* 30%) relative to [NO$_3^-$] or [ClO$_4^-$] at pH 12; (iii) the deuterio analogue (**3b**) reacts 17% slower than (**3a**) at the same pH.

The rate of reaction of (**6**) with HO$^-$ occurs at a rate *ca.* 150-fold less than the rate of formation of (**6**) under the same conditions (k_3 = 3.8 × 10^{-2} mol^{-1} dm^3 s^{-1} at 25 °C). This reaction involves direct nucleophilic attack on the isocyanide. Secondary amines also react with isocyanide (**6**) to give amidines. Thus the reaction with morpholine is proportional to the concentration of morpholine free base (k_3' = 6.7 × 10^{-2} mol^{-1} dm^3 s^{-1}) and interestingly the initial kinetic product isolated was a 1 : 1 mixture of the *E* and *Z* isomers (**7**); (*Z*)-(**7**) was converted into (*E*)-(**7**) on standing or (more rapidly) in the presence of acid.

Although the formation and trapping of (**6**) by nucleophiles in solution has been successfully carried out, attempts to concentrate or acidify solutions of (**6**) led to decomposition; the only product isolated from (**6**) under these conditions was *N*-methyl-2,4-dinitroaniline.

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References

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2 W. Reichen and C. Wentrup, *Helv. Chim. Acta*, 1976, **59**, 2618; C. Wentrup and H.-W. Winter, *J. Org. Chem.*, 1981, **46**, 1045.

3 I. Ugi, 'Isonitrile Chemistry,' Academic Press, New York, 1971, Ch. 2.

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† Equimolar quantities of (**5a**) and finely powdered PCl$_5$ were treated together in the absence of solvent initially at 0 °C and subsequently at 80 °C for 1 h. The POCl$_3$ formed was removed by distillation with dry benzene and the chloride (which showed a C, H, N, Cl analysis consistent with the structure) was separated by chromatography on silica gel. N.m.r. (**3a**) δ (CDCl$_3$) 3.44 (s, Me), 7.58 (s, H–C=N), 7.58 (d, 6-H′, *J* 9 Hz), 8.42 (dd, 5-H′, *J* 9, 2 Hz), 8.67 (d, 3-H′, *J* 2 Hz).

‡ The reactions were followed at 25 °C in water (ionic strength = 1.0 M, KClO$_4$) by observing changes in the u.v. spectra [(**3a**) has $\lambda_{max.}$ 375 nm and (**4**) has $\lambda_{max.}$ 317 nm].