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

## Anthony F. Hegarty\* and Ian Cunningham

Chemistry Department, University College Dublin, Belfield, Dublin 4, Ireland

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,<sup>1</sup> 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<sup>2</sup> 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)-Nmethylformohydrazonoyl chloride (3a) from the reaction of the hydrazide (5a) with PCl<sub>5</sub>.<sup>†</sup> 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<sup>3</sup> because of the susceptibility of the formimidoyl halide system to direct nucleophilic attack.

$$:C = \ddot{N} - \ddot{X} \qquad :N \equiv C - \ddot{X}$$
(1)
(2)

$$R > C = N - N < Me \qquad \frac{k_1}{k_{-1}} \qquad C_1 - \bar{C} = N - N < Me \qquad Ar$$
(3) a; R = H
(4)
b; R = D

 $\mathbf{b}; \mathbf{R} = \mathbf{D}$ 



<sup>†</sup> Equimolar quantities of (5a) and finely powdered PCl<sub>5</sub> were treated together in the absence of solvent initially at 0 °C and subsequently at 80°C for 1 h. The POCl<sub>3</sub> 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<sub>3</sub>) 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).

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 secondorder rate constant of 7.6 mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> at 25 °C.<sup>‡</sup> 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  $D_2O-DO^-$ , 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<sup>-</sup> 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<sup>-</sup>] (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<sup>-</sup> occurs at a rate ca. 150-fold less than the rate of formation of (6) under the same conditions  $(k_3 = 3.8 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \text{ at } 25 \text{ °C})$ . 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  $(k_3' = 6.7 \times 10^{-2})$  $mol^{-1}$  dm<sup>3</sup> s<sup>-1</sup>) 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.

Received, 16th May 1986; Com. 663

## References

- 1 H. Walborsky and M. P. Perlasmay, 'The Chemistry of Triple-Bonded Functional Groups,' eds. S. Patai and Z. Rappoport, Wiley, New York, 1983, Part 2, p. 835.
- 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.

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