

sisted of an equimolar mixture of 10-2,4,4- $d_3$  and 10-3,4,4- $d_3$ .

These results are consistent with the migration of the imide hydrogen of maleimide to a  $\beta$ -carbon during the reduction. Analysis of 2-pyrrolidinone (5) isolated from the reaction mixture suggests that this migration precedes the reduction of at least one of the carbonyl groups (Scheme I). GC-MS of the trifluoroacetyl derivative showed that three deuterium atoms have been incorporated. The mass spectrum of a derivative of its hydrolysis product (6) indicated that 5 was 2-pyrrolidinone-3,4,4- $d_3$ .

A mechanism consistent with these results is presented in Scheme I. The first step of the reaction involves attack at the most electropositive carbon<sup>6</sup> which results in the reduction of one of the carbonyl groups by 1,2-addition.<sup>7</sup>  $\Delta^3$ -Pyrrolin-2-one (2) thus formed could then undergo 1,4-reduction to yield the intermediate 3. The enamine 3 rearranges to the more stable imine<sup>9</sup> 4 with the migration of a hydrogen atom from N to C-3. Further reduction of the lactim salt 4 leads to pyrrolidine (7).

Regardless of the mechanism, it is obvious that the reaction has involved a transfer of hydrogen from nitrogen to carbon, since the reduction of N-deuterated maleimide (prepared by recrystallization from  $D_2O$ ) with  $LiAlH_4$  gave exclusively pyrrolidine-3- $d$ .<sup>10</sup>

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Registry No. 1, 541-59-3;  $LiAlH_4$ , 16853-85-3.

(6) Matsuo, T. *Bull. Chem. Soc. Jpn.* 1968, 38, 557-562.

(7) This is analogous to the addition of Grignard reagents to N-substituted maleimide. Equimolar amounts of the reactants results in 5-substituted-5-hydroxy-2-pyrrolinones.<sup>8</sup>

(8) Queen, A.; Reipas, A. *J. Chem. Soc. C* 1967, 245-246.

(9) Alt, G. H. "Enamines"; Cook, G. A., Ed.; Marcel Dekker, Inc.: New York, 1969; pp 115-168.

(10) The mass spectrum of the N-trifluoroacetyl derivative showed the presence of one deuterium. No  $(M - D)^+$  could be detected, indicating the label was not on C-2.

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### Isocyanamines, R-NH-NC<sup>1</sup>

**Summary:** Secondary isocyanamines, R-NH-NC, are obtained by flash vacuum pyrolysis of 3-methyl-4-(aryl-hydrazono)isoxazol-5(4H)-ones.

**Sir:** Isocyanamines are little known compounds. "Isodiazomethane",  $H_2NNC$ ,<sup>2</sup> and a few N,N-dialkyl derivatives,  $R_2NNC$ ,<sup>3</sup> and N-isocyanimines,  $R_2C=N-NC$ ,<sup>4</sup> are

(1) This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Mr. L. A. J. Köhler for construction of the pyrolysis apparatus.

(2) Müller, E.; Kästner, P.; Beutler, R.; Rundel, W.; Suhr, H.; Zeeh, B. *Justus Liebigs Ann. Chem.* 1968, 713, 87-95. Müller, E.; Beutler, R.; Zeeh, B. *Ibid.* 1968, 719, 72-79.

(3) Bredereck, H.; Föhlich, B.; Walz, K. *Justus Liebigs Ann. Chem.* 1965, 686, 92-101.

(4) Hagedorn, I.; Eholzer, U. *Angew. Chem.* 1962, 74, 499; *Angew. Chem., Int. Ed. Engl.* 1962, 1, 514. Jakobsen, P. *Acta Chem. Scand.*, Ser. B 1976, 30, 995-996. See also: Anselme, J.-P. *J. Chem. Educ.* 1977, 54, 296-298.

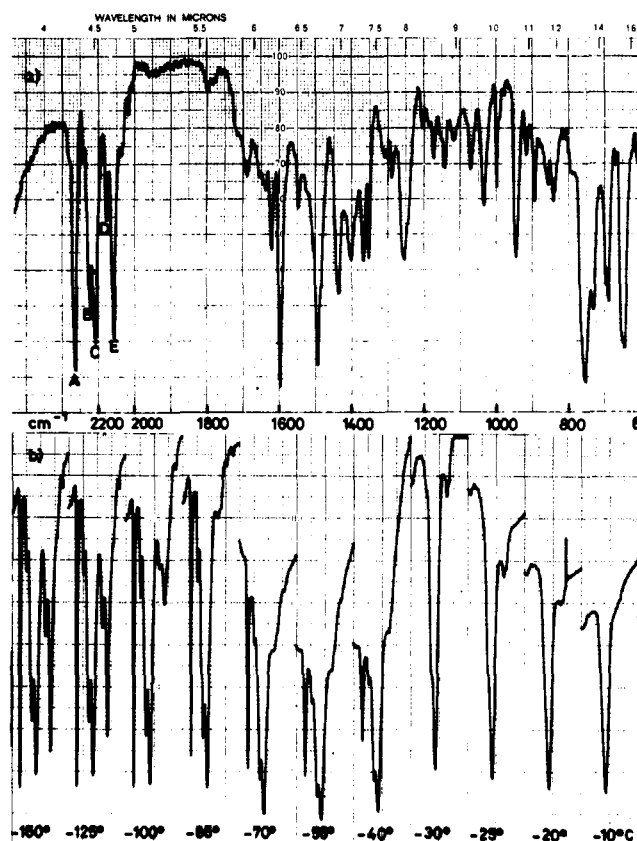
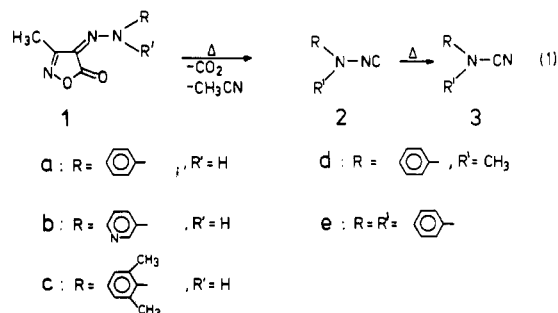


Figure 1. (a) Infrared spectrum ( $-196^\circ C$ ) of the pyrolyzate formed from 1a at  $600^\circ C$  ( $10^{-4}$  torr). The marked peaks are as follows; A,  $CO_2$ ; B,  $CH_3CN$ ; C, phenylcyanamide (3a); D and E, phenylisocyanamine (2a). (b) Repetitive scanning of the  $2400-2000\text{-cm}^{-1}$  region during warm-up.

known. However, no aromatic isocyanamines have been prepared, and the entire class of secondary amine derivatives,  $R-NH-NC$ , is unknown. We now report direct spectroscopic evidence for the formation of these extremely unstable compounds by pyrolysis of 4-hydrazonoisoxazol-5(4H)-one derivatives.<sup>5</sup>

Flash vacuum pyrolyses were carried out at ca.  $10^{-4}$  torr, and the products were collected directly on a turnable KBr disk attached to a liquid nitrogen cryostat and mounted in a vacuum shroud equipped with KBr windows for infrared spectroscopy. The pyrolysis of 1a at  $600^\circ C$  gave a product showing intense isocyanide absorptions at 2120 and  $2155\text{ cm}^{-1}$ , together with phenylcyanamide (3a) ( $2220\text{ cm}^{-1}$ ) and  $CO_2$  ( $2330\text{ cm}^{-1}$ ) (Figure 1a). Acetonitrile, a byproduct of the reaction shown in eq 1, lies partly under

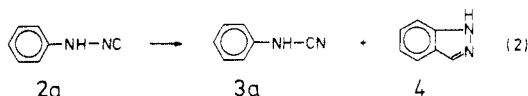


the phenylcyanamide peak but is a weaker absorber. The  $2250\text{-cm}^{-1}$  absorption is clearly visible in Figure 1a. This peak is seen to decrease on warming (Figure 1b) due to the

(5) Reichen, W.; Wentrup, C. *Helv. Chim. Acta* 1976, 59, 2618-2620.

evaporation of acetonitrile which could be distilled off and identified. The isocyanide absorptions at 2120–2155  $\text{cm}^{-1}$  decreased markedly already at  $-100^\circ\text{C}$  and had almost entirely disappeared at  $-85^\circ\text{C}$  (Figure 1b). The disappearance of the isocyanide does not significantly affect the intensity of the cyanamide absorption. Thus, phenylamino isocyanide (**2a**) is transformed, presumably by polymerization,<sup>6</sup> at ca.  $-85^\circ\text{C}$ , and the cyanamide (**3a**) is formed in the gas phase during the pyrolysis. These assertions are supported by pyrolyses at lower temperatures (500 and 450  $^\circ\text{C}$ ) where the isocyanide absorptions increased relative to the cyanamide absorptions. However, under these pyrolytic conditions most of the starting material (**1a**) was recovered unchanged. Conversely, pyrolyses at higher temperatures (700  $^\circ\text{C}$ ) resulted in increased formation of **3a** at the expense of **2a**.

As previously reported,<sup>5</sup> indazole (**4**) is a further gas-phase rearrangement product of **2a** (eq 2). The yields of



a preparative pyrolysis of **1a** at 550  $^\circ\text{C}$  ( $10^{-3}$  torr) were 58% **3a** and 37% **4**.<sup>7</sup>

The pyrolysis of **1b** was analogous to that of **1a**, giving a mixture of an isocyanide and a cyanamide absorbing in the same frequency range as found for **2a** and **3a**. The use of the 2,6-dimethylphenyl substituent in **1c** caused a retardation of the isocyanide–nitrile rearrangement, so that a very strong spectrum of the isocyanide **2c** (complex band with maxima at 2120–2140  $\text{cm}^{-1}$ ) together with a weaker band due to the cyanamide **3e** (2220  $\text{cm}^{-1}$ ) was obtained from a pyrolysis at 600  $^\circ\text{C}$ . The sterically blocking methyl groups do not, however, prevent the isocyanide **2c** from polymerizing, for the compound disappeared on warming to  $-120^\circ\text{C}$ .

The opposite effect of a methyl group was found in **1d** which, at 600  $^\circ\text{C}$ , gave mainly the cyanamide **3d** [2200 (w), 2220 (s)  $\text{cm}^{-1}$ ] and much weaker absorptions at 2120–2140  $\text{cm}^{-1}$  due to the isocyanide **2d**. The latter disappeared on warming to  $-90^\circ\text{C}$ . A preparative pyrolysis of **1d** at 550  $^\circ\text{C}$  ( $10^{-2}$  torr) gave a 77% yield of **3d**.<sup>7</sup> 1-Methylindazole was not detectable. Therefore, the disubstituted amino group in **2d** accelerates the isocyanide–nitrile rearrangement to such an extent that the competing cyclization observed in **2a** (eq 2) does not occur. This effect is even more pronounced in the case of the diphenylamino group in **1e**. This compound did not give any detectable isocyanide at 600  $^\circ\text{C}$ , only the cyanamide **3e** being formed (2210  $\text{cm}^{-1}$ ). Previous attempts to prepare **2e** also met with failure.<sup>8</sup>

In conclusion, the flash vacuum pyrolysis technique coupled with low-temperature spectroscopy allows the identification of the elusive isocyanides **2a–d**.<sup>9</sup> Chemical evidence that the absorptions are due to **2** is

provided by the thermal isomerization to stable, isolable cyanamides (**3**). In some cases, indazoles (e.g., **4**) are also formed.

**Registry No.** **1a**, 6017-59-0; **1b**, 51186-92-6; **1c**, 5670-06-4; **1d**, 5777-08-2; **1e**, 76334-34-4; **2a**, 61743-02-0; **2b**, 76346-76-4; **2c**, 76346-77-5; **2d**, 61700-67-2; **3a**, 622-34-4; **3b**, 76334-35-5; **3c**, 20922-60-5; **3d**, 18773-77-8; **3e**, 27779-01-7; **4**, 271-44-3;  $\text{Me}_2\text{NCON}_3$ , 13750-17-9;  $\text{Ph}_2\text{NCON}_3$ , 17223-83-5;  $\text{Me}_2\text{NN}=\text{C}=\text{O}$ , 10270-13-0;  $\text{Ph}_2\text{NN}=\text{C}=\text{O}$ , 67500-29-2.

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### Organic Fulminates, R-O-NC<sup>1</sup>

**Summary:** Organic fulminates are generated by flash vacuum pyrolysis and matrix photolysis of 4-oximinoisoxazol-5(4H)-ones.

**Sir:** The realization that silver cyanate and silver fulminate have the same chemical composition played an important role in the development of the concept of isomerism.<sup>2</sup> Yet, not all the isomeric RCNO species are known. The cyanates (ROCN), isocyanates (RNCO), and nitrile oxides (RCNO) are known compounds, but no organic fulminate (RO-NC; O-ester of fulminic acid)<sup>3</sup> has yet been reported. For almost 100 years chemists have attempted the preparation of such compounds by reacting metal fulminates with alkyl or acyl halides, or by treating O-substituted derivatives of hydroxylamine under conditions normally used for the preparation of isocyanides. Although an isonitrile odor was recorded in some cases, no evidence for a fulminate was ever found.<sup>6,7</sup>

In the accompanying communication we report the preparation of unstable isocyanatoamines (RNH-NC and R<sub>2</sub>N-NC) by thermal decomposition of 4-arylhydrazonoisoxazol-5(4H)-ones.<sup>8</sup> Since isocyanatoamines are isoelec-

(1) Fulminates. Part 2. Part 1: Wentrup, C.; Gerecht, B.; Briehl, H. *Angew. Chem.* 1979, 91, 503; *Angew. Chem., Int. Ed. Engl.* 1979, 18, 467. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Degussa AG for a gift of starting materials and Mr. H. Müller-Stärke for some experiments.

(2) Liebig, J.; Gay-Lussac, J. L. *Ann. Chim. Phys.* 1824, [2] 25, 285; Wöhler, F. *Ibid.* 1824, [2] 27, 196.

(3) We use the name "fulminate" (IUPAC rule C-833) for compounds of the structure R<sub>2</sub>NCN, the isomers RCNO being nitrile oxides, even though fulminic acid itself has the structure HCNO.<sup>4</sup> In a similar manner, cyanates (ROCN) are derivatives of HOCN, although the compound often referred to as "cyanic acid" is mainly—if not exclusively—HNCN.<sup>5</sup>

(4) Beck, W.; Swoboda, P.; Feld, K.; Tobias, R. S. *Chem. Ber.* 1971, 104, 533–543.

(5) Groving, N.; Holm, A. *Acta Chem. Scand.* 1965, 19, 1768–1769.

(6) Grundmann, C.; Grünanger, P. "The Nitrile Oxides"; Springer-Verlag: Heidelberg, 1971.

(7) Carstanjen, E.; Ehrenberg, A. *J. Prakt. Chem.* 1882, [2] 25, 232–248. Steiner, A. *Ber. Dtsch. Chem. Ges.* 1883, 16, 1484–1486, 2419–2420. Calmels, G. C. R. *Hebd. Seances Acad. Sci.* 1884, 49, 794–797. *J. Prakt. Chem.* 1884, [2] 30, 319–321. Schöll, R. *Ber. Dtsch. Chem. Ges.* 1890, 23, 3505–3519. Holleman, A. F. *Ibid.* 1890, 23, 2998–3001. Nef, J. U. *Justus Liebigs Ann. Chem.* 1894, 280, 339 (291–342). Biddle, H. C. *Am. Chem. J.* 1905, 33, 68; *Ibid.* 1906, 35, 349. Palazzo, F. C.; Tamburello, A. *Gazz. Chim. Ital.* 1907, 37, 1–45. Jones, L. W.; Neuffer, L. J. *Am. Chem. Soc.* 1917, 39, 659–668. See also: Wieland, H.; Rosenfeld, B. *Justus Liebigs Ann. Chem.* 1930, 484, 236–245. Wieland, H.; Höchtien, A. *Ibid.* 1933, 505, 237–247. Biddle's experiments were reinvestigated by Grundmann et al. (ref 6, p 41) and by Harder (Dissertation, Universität de Lausanne, Switzerland, 1976, Chapter 5) who found no evidence for alkyl fulminates.

(6) For poly- and oligomerization of isocyanides, see: Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* 1979, 12, 30–35 and references therein.

(7) The preparative pyrolyses require lower temperatures than those used in conjunction with spectroscopy because of different apparatus design (30 × 2 cm quartz tube in the preparative apparatus; 10 × 1 cm quartz tube for low-temperature spectroscopy).

(8) Koga, N.; Anselme, J.-P. *Tetrahedron* 1970, 26, 1909–1915.

(9) Using the same technique, we have also been able to observe the elusive isocyanatoamines (2220  $\text{cm}^{-1}$ ; dimerizing at ca.  $-40^\circ\text{C}$ ) in the following reaction (Lukosch, H.; Wentrup, C., unpublished results).

