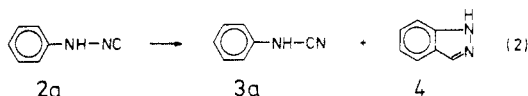


evaporation of acetonitrile which could be distilled off and identified. The isocyanide absorptions at 2120–2155 cm^{-1} decreased markedly already at -100°C and had almost entirely disappeared at -85°C (Figure 1b). The disappearance of the isocyanide does not significantly affect the intensity of the cyanamide absorption. Thus, phenylamino isocyanide (**2a**) is transformed, presumably by polymerization,⁶ at ca. -85°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,⁵ 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**.⁷

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 cm^{-1}) together with a weaker band due to the cyanamide **3e** (2220 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°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) cm^{-1}] and much weaker absorptions at 2120–2140 cm^{-1} due to the isocyanide **2d**. The latter disappeared on warming to -90°C . A preparative pyrolysis of **1d** at 550 $^\circ\text{C}$ (10^{-2} torr) gave a 77% yield of **3d**.⁷ 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 cm^{-1}). Previous attempts to prepare **2e** also met with failure.⁸

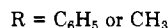
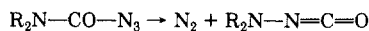
In conclusion, the flash vacuum pyrolysis technique coupled with low-temperature spectroscopy allows the identification of the elusive isocyanides **2a–d**.⁹ Chemical evidence that the absorptions are due to **2** is

(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 cm^{-1} ; dimerizing at ca. -40°C) in the following reaction (Lukosch, H.; Wentrup, C., unpublished results).



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; Me_2NCON_3 , 13750-17-9; Ph_2NCON_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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Received December 9, 1980

Organic Fulminates, R-O-NC¹

Summary: Organic fulminates are generated by flash vacuum pyrolysis and matrix photolysis of 4-oximinoisoxazol-5(4*H*)-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.² 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)³ 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.^{6,7}

In the accompanying communication we report the preparation of unstable isocyanatoamines (RNH-NC and R₂N-NC) by thermal decomposition of 4-arylhydrazonoisoxazol-5(4*H*)-ones.⁸ Since isocyanatoamines are isoelec-

(1) Fulminates. Part 2. Part 1: Wentrup, C.; Gerech, 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 RONC, the isomers RCNO being nitrile oxides, even though fulminic acid itself has the structure HCNO.⁴ 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.⁵

(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.

ated glass cell of the spectrometer.^{13a} In contrast, the major products from **6b** were fulminic acid (HCNO) and ethylene (eq 2). Fulminic acid was identified by its IR spectrum (2198 cm⁻¹ in the gas phase;⁴ 2180 cm⁻¹ in the solid state at -196 °C) and by millimeter wave spectroscopy.^{13b}

A similar pyrolysis of **6c** resulted in benzaldehyde and HCN (eq 3) together with a small amount of benzyl isocyanate (**9**, eq 4). The formation of **9** is indicative of an initial isomerization of benzyl fulminate (**7c**) to benzyl cyanate (**8**). **8** cannot be isolated under the conditions used, since it is known to rearrange to **9** below room temperature.¹⁴

Theoretical calculations¹⁵ have indicated that alkyl fulminates should be stable under conditions disfavoring intermolecular reactions because no low-energy intramolecular isomerization pathways were found. The most facile intramolecular process was the isomerization to cyanates with an activation energy of ca. 43 kcal/mol.¹⁵ This agrees well with our observation that cyanates are formed only in low yields in our reactions. The chemistry summarized in eq 1-4 demonstrates, however, that the favored intramolecular reaction pathways of the alkyl fulminates are elimination reactions which had not previously been considered. It is particularly interesting that

ethyl fulminate (**7b**) apparently undergoes an "ester pyrolysis" leading to fulminic acid, a reaction which is not possible for **7a** and **7c**.

In conclusion, we have presented chemical and spectroscopic evidence for the formation of organic fulminates by photolysis and thermolysis of isoxazolones of the types **2** and **6**. The CN stretching vibration of the fulminates appears in the region 2108-2160 cm⁻¹ in matrix or in the solid state at -196 °C. This is the same range as observed for the isoelectronic isocyanamines under the same conditions.⁸

Registry No. 1, 18438-56-7; 2, 76347-03-0; 3, 67249-97-2; 4, 1122-85-6; 5, 273-53-0; **6a**, 76347-04-1; **6b**, 76347-05-2; **6c**, 76347-06-3; **7a**, 67347-39-1; **7b**, 76347-07-4; **7c**, 76347-08-5; 8, 75403-69-9; 9, 3173-56-6; diphenyliodonium chloride, 1483-72-3; benzaldehyde, 100-52-7; HCN, 74-90-8.

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Received December 8, 1980

(13) (a) Winnewisser, M.; Winnewisser, B. P. *Z. Naturforsch.*, A 1974, 29, 633-664. (b) Winnewisser, M.; Winnewisser, B. P. *Ibid.* 1971, 26, 128-131.

(14) Jensen, K. A.; Holm, A.; Wolff-Jensen, J. *Acta Chem. Scand.* 1969, 23, 1567-1572.

(15) Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* 1978, 100, 3674-3685. Cf. also: Poppinger, D.; Radom, L.; Pople, J. A. *Ibid.* 1977, 99, 7806-7816.