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 "C) where the isocyanide absorptions increased relative to the cyanamide absorptions. However, under these pyrolytic conditions most of the starting material (la) was recovered unchanged. Conversely, pyrolyses at higher temperatures (700 "C) resulted in increased formation of 3a at the expense of 2a.

As previously reported,⁵ indazole (4) is a further gasphase rearrangement product of 2a (eq 2). The yields of

a preparative pyrolysis of 1a at 550 °C (10^{-3} torr) were 58% 3a and 37% **4.7**

The pyrolysis of 1**b** was analogous to that of 1**a**, 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 IC 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 $3e(2220 \text{ cm}^{-1})$ was obtained from a pyrolysis at 600 "C. The sterically blocking methyl groups do not, however, prevent the isocyanoamine 2c from polymerizing, for the compound disappeared on warming to -120 °C.

The opposite effect of a methyl group was found in Id which, at 600 $^{\circ}$ C, gave mainly the cyanamide 3d [2200 (w), 2220 (s) cm⁻¹ and much weaker absorptions at $2120-2140$ $cm⁻¹$ due to the isocyanoamine 2d. The latter disappeared on warming to -90 "C. **A** preparative pyrolysis of Id at 550 °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 le. This compound did not give any detectable isocyanide at 600 "C, only the cyanamide **3e** being formed (2210 cm-I). 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 isocyanoamines 2a-d.⁹ Chemical evidence that the absorptions are due to 2 is

$$
R_2N - CO - N_3 \rightarrow N_2 + R_2N - N = C = 0
$$

 $R = C_6H_5$ or CH_3

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

Registry **No. la, 6017-59-0; lb, 51186-92-6; IC, 5670-06-4; Id,** 5777-08-2; le, 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; Me₂NCON₃, 13750-17-9; Ph₂NCON₃, 17223-83-5; Me₂NN=C=0, 10270-13-0; Ph₂NN=C=0, **67500-29-2.**

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Organic Fulminates, **R-0-NC'**

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.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 0 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 isocyanoamines (RNH-NC and R_2N-NC) by thermal decomposition of 4-arylhydrazono $isoxa$ zol-5(4H)-ones.⁸ Since isocyanoamines are isoelec-

0022-3263/81/1946-1046\$01.25/0 *0* 1981 American Chemical Society

⁽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 $(30 \times 2 \text{ cm} \text{ quartz}$ tube in the preparative apparatus; $10 \times 1 \text{ cm}$ design $(30 \times 2 \text{ cm}$ quartz tube in the preparative apparatus; $10 \times 1 \text{ cm}$ 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-'; dimerizing at ca. **-40** "C) in the following reaction (Lukosch, H.; Wentrup, C., unpublished results).

⁽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. Miiller-Starke for some experiments. **(2)** Liebig, J.; Gay-Lussac, J. L. *Ann. Chim. Phys.* **1824, [2] 25, 285;** WBhler, 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 (ROC ner, cyanates (ROCN) are derivatives of HOCN, although the compound often referred to as "cyanic acid" is mainly-if not exclusively-HNCO.⁵

⁽⁴⁾ Beck, W.; Swoboda, P.; Feldl, 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.

Verlag: Heidelberg, 1971.

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^{2419–2420.} Calmels, G. C. R. Hebd. Seances Acad. Sci. 1884, 49, 794–797,
J. Prakt. Chem. 1884, [2] 30, 319–321. Scholl, 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. Ph,** F. C.; Tamburello, A. Gazz. Chim. Ital. 1907, 37, 1-45. Jones, L. W.; Naugza, F. C.; Hamoureno, 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 L alkyl fulminates.

tronic with fulminates, we planned to generate the latter using a similar procedure. $9\degree$ We now report direct evidence for the formation of organic fulminates in such reactions.

The phenyl fulminate precursor **2** (Scheme I) was prepared by phenylation of **3-methyl-4-oximinoisoxazol-5-** $(4H)$ -one (1) with diphenyliodonium chloride in acetone at -10 °C in the presence of K_2CO_3 .¹⁰

2 was subjected to flash vacuum pyrolysis at 300 $^{\circ}$ C (10⁻⁴) torr), collecting the products on a KBr target at -196 °C. The IR spectrum of the pyrolyzate $(-196 \degree C)$ showed the formation of $CO₂$, acetonitrile, and two further absorption maxima $(2120-2140 \text{ cm}^{-1})$ in the region expected for the isocyano group.⁸ A peak at 2080 cm⁻¹ was identified as HCN by comparison with an authentic sample and by isolation in the preparative experiments to be described below. When the pyrolysis of **2** was carried out at 500 "C, the $2120-2140\text{-cm}^{-1}$ bands had almost disappeared, suggesting that they belong to a thermally unstable compound.

No fulminate could be isolated when these pyrolyses were carried out under preparative conditions and worked up at room temperature. **A** GLC-mass spectrometry analysis of the distillable pyrolysis products demonstrated the presence of small amounts of phenyl cyanate (4) and benzisoxazole **(5)** (Scheme I), identified by comparison with authentic materials. These products constitute *strong* evidence for the intermediate formation of phenyl fulminate **(3),** particularly since isoelectronic cyanamides and indazoles are formed by thermal isomerization of isocyanoamines in a completely analogous reaction.8 However, the major pyrolysis products recovered from the pyrolyses of **2** at either 300 or 500 "C were phenol and HCN. These products are indicative of a fragmentation into phenoxy and cyano radicals, followed by hydrogen abstraction.¹¹

Further evidence for the formation of phenyl fulminate was obtained by photolysis ($\lambda \approx 360$ nm) of 2, matrix isolated in **Ar** at 10 K. The IR spectrum of **2** (Figure la) disappeared rapidly and was replaced by a double absorption at 2108-2134 cm⁻¹ (Figure 1b). The similarity of

Figure 1. (a) Infrared spectrum of 3-methyl-4-(0-phenyl **oximino)isoxazo1-5(4H)-one (2),** matrix isolated in *Ar* at 10 **K.** (b) Product of photolysis of **2** at 10 **K.**

the absorptions obtained by thermolysis and photolysis of **2** suggests that the same compound is formed under both conditions. The complexity of the fulminate absorption (Figure 1b) is reminiscent of the cyanates (ROCN), which normally show several intense maxima around 2250 cm^{-1} .¹² Also isocyanoamines show double absorptions in the region $2120-2155$ cm⁻¹ at low temperatures.⁸ The development of the 2108-2134-cm⁻¹ band of **3** (Figure lb) was accompanied by the formation of **COz.** The other fragmentation product, acetonitrile, is barely visible in the **IR** spectrum at the concentrations used here; however, acetonitrile was isolated and identified from a photolysis of 2 in an organic matrix at -196 °C.

Flash pyrolysis of the 0-alkyloximes **6a** and **6b** between 300 and 600 "C resulted in medium absorptions near 2160 cm⁻¹ (-196 °C), which disappeared above ca. -100 °C and may be ascribed to the corresponding alkyl fulminates **7a** and **7b.** The alkyl fulminates are, however, even more

unstable than phenyl fulminate, undergoing facile elimination reactions under the conditions necessary for their generation. The major thermolysis products of **6a** were HCN and formaldehyde (eq 1), identified both by IR and
 CH_3-0-NC - CH₂O + HCN (1) HCN and formaldehyde (eq l), identified both by IR and

$$
CH_3-O-NC \longrightarrow CH_2O + HCN
$$
 (1)

$$
CH_3-O-NC \longrightarrow CH_2O + HCN
$$
\n
$$
7Q
$$
\n
$$
C_2H_5O-NC \longrightarrow C_2H_4 + HCNO
$$
\n(1)

 \Diamond сно + нсм (3)

$$
\begin{array}{ccc}\n\textcircled{0}-\text{CH}_{2}-\text{ONC} & \xrightarrow{\smile} & \textcircled{0}-\text{CH}_{2}-\text{OCN}\n\end{array}
$$
\n
$$
\begin{array}{ccc}\n\textcircled{3} & \textcircled{4} & \textcircled{5}-\text{CH}_{2}-\text{NCO} & \textcircled{4} \\
\textcircled{8} & \textcircled{9}\n\end{array}
$$

millimeter wave spectroscopy. In the latter case, the pyrolysis products were introduced directly into the evacu-

⁽⁸⁾ Wentrup, C.; Winter, **H.-W.** *J.* Org. Chem., preceding paper in this issue.

⁽⁹⁾ Wentrup, C.; Reichen, W. *Helu. Chim. Acta* 1976,59,2615-2617. (10) 2 was obtained as a pure isomer (presumably of E configuration):
mp 128–129 °C; ¹H NMR (CDCl₃) δ 2.58 (s, CH₃), 7.46 (m, 5 H); ¹³C NMR
(CDCl₃) δ 163 (C-5), 158 (phenyl C-1), 153 (C-3), 139 (C-4), 12 ortho), 125.7 (phenyl para), 114.8 (phenyl meta), 15.2 (CH₃); IR, see Figure la; mass spectrum, m/e 204.0535 (M⁺; calcd for C₁₀H₈N₂O₃ 204.0535).

⁽¹¹⁾ Evidence that the isocyanide-nitrile rearrangement can, in certain cases, take place via free radicals has been presented: Yamada, S.; Ta-
kashima, K.; Sato, T.; Terashima, S. *Chem. Commun.* 1969, 811. The formation of phenol and HCN is formally a hydrogenation and could be a wall-catalyzed process (cf.: Becker, J.; Wentrup, C.; Katz, E.; Zeller, K.-P. J. *Am.* Chem. *SOC.* 1980,102, 5110-5112).

⁵¹²⁾ Groving, N.; Holm, A. *Acta Chem. Scand,* 1965, *19,* 443-450. Reich, P.; Martin, D. *Chem. Ber.* 1965,98, 2063-2069.

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 $(2198 \text{ cm}^{-1} \text{ in the gas phase}; 42180 \text{ cm}^{-1} \text{ in the}$ 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** kca1/mol.l5 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-l in matrix or in the solid state at -196 °C. This is the same range as observed for the isoelectronic isocyanoamines 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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⁽¹³⁾ (a) Winnewisser, M.; Winnewisser, B. P. **Z.** *Naturforsch., A* **1974, 29, 633-664.** (b) Winnewisser, M.; Winnewisser, B. P. *Ibid.* **1971, 26,**

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⁽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.**