(8) E. A. Chandross and C. J. Dempster, *J. Am. Chem Soc.*, **92**, 3586 (1970).
(9) P. Avouris, J. Kordas, and M. A. El-Bayoumi, *Chem. Phys. Lett.*, **26**, 373 (1974).
(10) Although the absorption coefficient of DNP at 337 nm is very small, a laser pulse was strong enough to excite DNP (probably a laser pulse may excite hot bands of the naphthyl molety). As for the effect of any impurity which has a large ϵ at 337 nm, there was no difference between the steady-state fluorescence spectrum excited at 337 nm and that excited at a shorter wavelength band.
(11) T. J. Chuang and K. B. Eisenthal, *J. Chem. Phys.*, **59**, 2140 (1973); T. J. Chuang, R. J. Cox, and K. B. Eisenthal, *J. Am. Chem. Soc.*, **96**, 6828 (1974).
(12) T. J. Chuang and K. B. Eisenthal, *J. Chem. Phys.*, **62**, 2213 (1975).
(13) J. B. Birks, "Photophysics of Aromatic Molecule", Wiley-Interscience, New York, N.Y., 1970.
(14) W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968).
(15) T. Mimura and M. Itoh, *Chem. Phys. Lett.*, submitted for publication.

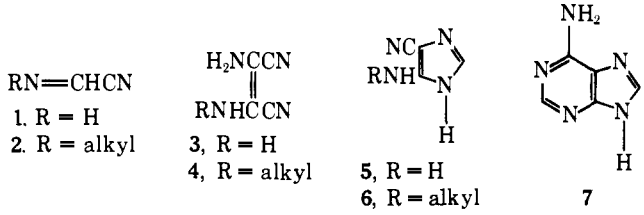
N-Alkylformimidoyl Cyanides and Isocyanides[1]

Joseph H. Boyer* and Johannes Kooi

Contribution from the Chemistry Department, University of Illinois, Chicago Circle Campus, Chicago, Illinois 60680. *Received June 18, 1975*

Abstract: An *N*-chloro derivative (**11**), from an *N*-alkylaminoacetonitrile (**10**) and calcium hypochlorite, was dehydrochlorinated by calcium hydroxide into (*E*)- and (*Z*)-*N*-alkylformimidoyl cyanides (**2**) and the isomeric isocyanide **12**; similar dehydrochlorination gave an *N*-alkylchloroformimidoyl cyanide (**13**) from the α,*N*-dichloro-*N*-alkylaminoacetonitrile. Both diethyl azodicarboxylate and *o*-chloranil dehydrogenated the amine **10d** (R = $(CH_3)_3C$) into the imidoyl cyanide **2d** (R = $(CH_3)_3C$), but gave intractable mixtures with **10b** (R = C_2H_5) and **10c** (R = $(CH_3)_2CH$); aminoacetonitrile and diethyl azodicarboxylate gave *N*,*N*′-dicyanomethylazodicarboxamide. Stannic chloride, and other Lewis acids, catalyzed the dimerization of **2** into an *N*,*N*′-dialkylaminomaleonitrile (**19**), but did not dimerize an *N*-alkylacetimidoyl cyanide (**14**).

Identification of a dimer of hydrogen cyanide as formimidoyl cyanide (**1**) was justified by the kinetic requirement for the combination of a cyanide anion and hydrogen cyanide to be rate determining in tetramerizing the latter at pH 9.2 into diaminomaleonitrile (**3**).[2-4] Formation of a mono-*N*-alkyl derivative **4** of the tetramer **3** from an *N*-alkylformimidoyl cyanide (**2**) and 2 mol of hydrogen cyanide, and the photoisomerization of both **3** and **4** into the corresponding 4-amino-5-cyanoimidazole **5** and **6** confirmed this structural assignment for $(HCN)_2$.[5-7] Addition of hydrogen cyanide transformed **5** into adenine[6] (**7**), but a similar transformation was unavailable to **6**.



Formimidoyl cyanide (**1**) was first obtained from azidoacetonitrile (**8**) by the photoelimination of nitrogen at 77 K. A slow change has been attributed to photoisomerization at 77 K into formimidoyl isocyanide (**9**).[8-11] At room temperature, photolysis of the azide **8** gave hydrogen cyanide (27%), adenine (**7**) in low yield, and **1** as a transient detected by infrared spectroscopy.[8]

$$\mathbf{7} \xleftarrow[25^\circ]{h\nu} \underset{\mathbf{8}}{N_3CH_2CN} \xrightarrow[77\ K]{h\nu} \mathbf{1} \xrightarrow[77\ K]{h\nu} \underset{\mathbf{9}}{HN{=}CHNC}$$

Heretofore, *N*-alkyl derivatives **12** of formimidoyl isocyanide (**9**) were unknown. Photoisomerization of cyanide **2** into isocyanide **12** was reported in error.[8]

Results and Discussion

An *N*-alkylaminoacetonitrile (**10**) and calcium hypochlorite below 25° gave an *N*-chloro-*N*-alkylaminoacetonitrile **11**. Near 40° the *N*-chloro compound (**11**) reacted slowly with calcium hypochlorite to give an α,*N*-dichloro-*N*-alkylaminoacetonitrile. Dehydrochlorination by calcium, lithium, sodium, or barium hydroxide transformed **11** into an *N*-alkylformimidoyl cyanide (**2**) sometimes contaminated with traces of the corresponding *N*-alkylformamide and *N*-alkylchloroformimidoyl cyanide (**13**). Optimum yields of **2** [R = CH_3 (25%), CH_3CH_2 (50%), $(CH_3)_2CH$ (72%), and $(CH_3)_3C$ (76%)] were obtained when the last step occurred under temperatures of 25, 32, 38, and 78°, respectively.

$$\underset{\mathbf{10}}{RNHCH_2CN} \xrightarrow{Ca(OCl)_2} \underset{\mathbf{11}}{RN(Cl)CH_2CN} + [RN(Cl)CH(Cl)CN]$$

$$\mathbf{11} \xrightarrow[-HCl]{Ca(OH)_2} \underset{\mathbf{2}}{RN{=}CHCN} + \underset{\mathbf{12}}{RN{=}CHNC}$$

$$[RN(Cl)CH(Cl)CN] \xrightarrow[-HCl]{Ca(OH)_2} \underset{\mathbf{13}}{RN{=}C(Cl)CN}$$

a, R = CH_3; **b**, R = C_2H_5; **c**, R = *i*-C_3H_7; **d**, R = *t*-C_4H_9

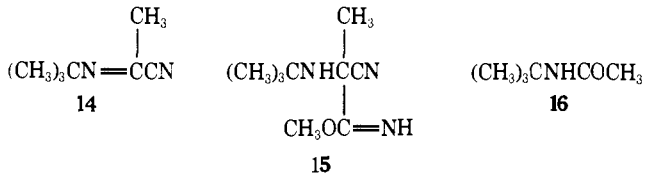
Aminoacetonitrile underwent a similar transformation into the short-lived formimidoyl cyanide (**1**) detected by ir absorption[8] at 3270 (NH), 2960 (CH), 2205 (C≡N), 1605 (>C=N—), 1405, and 1320 cm^{-1}; it rapidly darkened as polymerization occurred.

The *N*-alkylformimidoyl isocyanide **12** was also produced when dehydrochlorination occurred in methylene chloride at 35°, R = CH_3; at 41°, R = C_2H_5 and $(CH_3)_3CH$; and in carbon tetrachloride at 78°, R = $(CH_3)_3C$. Dehydrochlorination of **11** with triethylamine gave cyanide **2** but did not give isocyanide **12**.

When *N*-ethyl- (**11b**) or *N*-isopropyl-*N*-chloroaminoacetonitrile (**11c**) was treated with an excess of calcium hypochlorite in refluxing methylene chloride for 2 weeks, the corresponding *N*-alkylchloroformimidoyl cyanide **13b** or **13c** was the predominant product along with traces of the appropriate cyanide **2b** or **2c**. The similar transformation of **11d** → **13d** was not detected.

With the smaller *N*-alkyl substituents there was a tendency for the cyanide **2** to polymerize; after storage for 1 week at room temperature, an analytical sample of *N*-methylformimidoyl cyanide (**2a**) gave a dark brown partially oxidized oligomer, $(C_3H_4N_2)_7O$.

Dehydrochlorination of α-*N*-chloro-*tert*-butylaminopropionitrile, obtained from α-*N*-*tert*-butylaminopropionitrile[4] and *tert*-butyl hypochlorite, was unsuccessful with triethylamine but with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) gave *N*-*tert*-butylacetimidoyl cyanide (**14**). In contrast with a slow photodissociation of *N*-*tert*-butyliminoacetonitrile into *tert*-butyl isocyanide and hydrogen cyanide, the imine **14** was photostable and quantitatively recovered after ex-



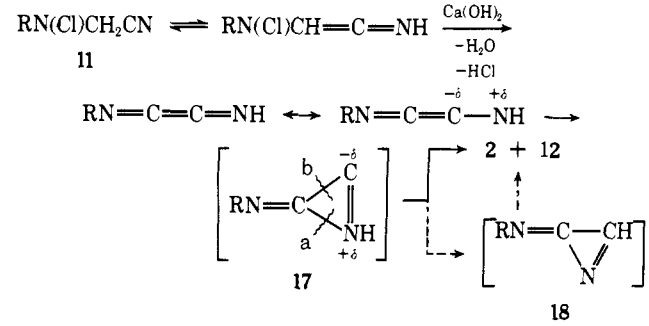
14 **15** **16**

tended irradiation at 254 or 300 nm in cyclohexane. Under conditions whereby Lewis acids caused formimidoyl cyanides **2** to dimerize, the acetimidoyl cyanide **14** remained unaffected. After storage for 3 months in methanol, the imine **14** was transformed into a compound tentatively identified as methyl α-*tert*-butylamino-α-cyanopropionimidate (**15**). On a silica gel column, **15** hydrolyzed, decarboxylated, and lost hydrogen cyanide to give *N*-*tert*-butylacetamide (**16**), which was eluted.

Diethyl azodicarboxylate and *N*-*tert*-butylaminoacetonitrile (**10d**) gave *N*-*tert*-butylformimidoyl cyanide (**2d**) in 72% yield, but neither *N*-ethyl- (**2b**) nor *N*-isopropyl- (**2c**) nor *N*-phenylformimidoyl cyanide was detected after similar treatment of the appropriate amines; *N*,*N*′-dicyanomethylazodicarboxamide was obtained from aminoacetonitrile. Dehydrogenation of **10d** with *o*-chloranil gave **2d** in low yield, but **10b** and **10c** each gave intractable mixtures.

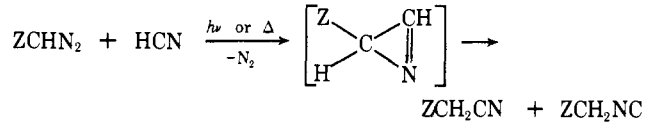
A mixture of **2c**, **12c**, and **13c**, obtained from the aminoacetonitrile (**10c**), was separated by gas chromatography into the (*Z*)-imidoyl cyanide **2c**, the imidoyl chlorocyanide **13c**, and an inseparable mixture of the (*E*)-imidoyl cyanide **2c** and the isomeric (*E*)- and/or (*Z*)-imidoyl isocyanide **12c**. Distinct ir absorption for the isocyanide **12c** at 2120 and for the cyanide **2c** at 2240 cm^{-1}, and their isomeric relationship established by elemental and mass spectrographic analysis of the mixture of **2c** and **12c**, supported their identification. Similar product mixtures were obtained from *N*-ethylaminoacetonitrile (**10b**). Assuming the bulkier group (CN) on the imine carbon is preferably anti to the nitrogen substituent in each formimidoyl cyanide, the assigned stereoisomerism for the imines **2** is supported by thermodynamic data, ultraviolet absorption, refractive index, NMR signal positions, and the magnitude of the coupling constants [^4J(HCNCH)][12] (Tables III and IV).

Interconversion between formimidoyl cyanide **2** and isocyanide **12** was not detected in separate experiments under conditions comparable to their formation, and the isomerization of **12** → **2** at higher temperature was not competitive with polymerization. Although simple 1,2-elimination may transform **11** into **2**, the isomers **2** and **12** can be attributed to the ring-opening of an intermediate zwitterionic azirinonimine **17** with migration of hydrogen to give **2** after cleavage by path a and **12** after cleavage by path b. The intermediacy of the unknown azirinonimine[11] **18** was not detected. The formation of **17** may proceed from an *N*-chloro-*N*-alkylaminoketenimine, in turn produced by the tautomerization of **11** in the presence of hydroxide anion but not triethylamine. Either accompanying or following dehydrochlorination from the tautomer, ring closure with migration of hydrogen from nitrogen to carbon to give **17** would be facilitated by a polarization leading to the development of a zwitterionic nitrenium ion.[13]



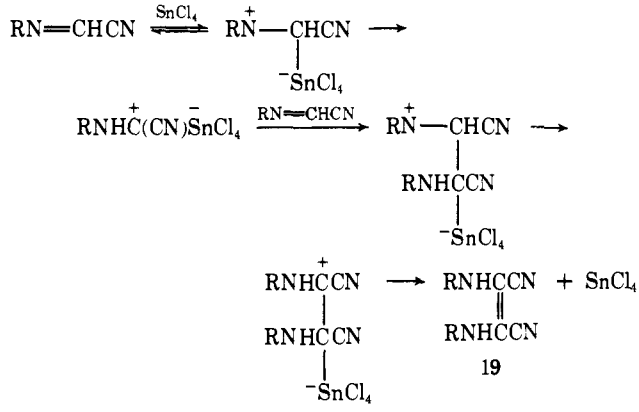
11 **17** **18**

Photoisomerization of an azirine into both a cyanide and an isocyanide has been reported,[14] and the intermediacy of an azirine accounted for the formation of an isocyanide (the cyanide was also produced) in an abnormal Beckmann rearrangement.[15] The formation of an organic cyanide from hydrogen cyanide and a diazoalkane[16] can be explained by



carbene insertion into the C–H bond; however, the simultaneous formation of an isocyanide by carbene insertion into the N–H bond did not occur since hydrogen isocyanide could not be present under the conditions of the reaction.[17] Both products can be accounted for by isomerization of an intermediate azirine produced either directly by the addition of a carbene to the cyano triple bond or indirectly by the extrusion of nitrogen after a 1,3-cycloaddition of hydrogen cyanide to the diazoalkane.

A polarization leading to the development of a zwitterionic nitrenium ion may also facilitate a dimerization, catalyzed by a Lewis acid, of an *N*-alkylformimidoyl cyanide **2** into the corresponding *N*,*N*′-dialkylaminomaleonitrile **19**.



19

The reaction can be attributed to bonding between a Lewis acid and the azomethine carbon and migration of a hydride anion from carbon to nitrogen followed by a similar sequence initiated by the newly generated zwitterion and finally ejection of the Lewis acid catalyst.

Experimental Section

Instruments included Perkin-Elmer grating infrared spectrophotometer Model 237B, Varian A-60 and T-60 NMR spectrometers, Perkin-Elmer 270 mass spectrometer, an AEI Scientific Apparatus Limited MS-30 double beam mass spectrometer, Varian 1800 gas chromatograph with flame ionization detector, and a Varian 20 recorder with disc integrator, and a Varian 700 autoprep for prepar-

Table I. Aminoacetonitriles

RNHCH$_2$CN: *R*; yield %; bp °C (mm); *n*D (°C); ν cm^{-1}; δ

H; 83; 81–82 (6.4);[a] 1.4304 (26); 3390 (NH), 2230 (C≡N);[b] 1.74 (s, 2, NH_2) and 3.59 (s, 2, CH_2)[c]

CH$_3$; 98; 39–40 (2);[d] 1.4195 (23); 3280 (NH), 2230 (C≡N);[e] 1.72 (s, 1, NH), 2.48 (s, 3, CH_3) and 3.53 (s, 2, CH_2)[f]

CH$_3$*CH*$_2$; 52–53 (1.0);[g] 1.4245 (21); 3320 (NH), 2230 (C≡N);[e] 1.11 (t, 3, CH_3CH_2, J = 7 Hz), 1.41 (broad, 1, NH), 2.74 (q, 2, CH_3CH_2, J = 7Hz) and 3.53 (s, 2, CH_2CN)[f]

(*CH*$_3$)$_2$*CH*; 85; 49–50 (1.3);[d] 1.4253 (22); 3340 (NH), 2230 (C≡N);[e] 1.05 (d, 6, $(CH_3)_2CH$, J = 6 Hz), 1.35 (broad, 1, NH), 3.01 (heptet, 1, $(CH_3)_2CH$, J = 6 Hz) and 3.53 (d, 2, CH_2, J = 6 Hz)[f]

(*CH*$_3$)$_3$*C*; 72; 58–60 (7.0);[h] 1.4297 (25); 3320 (NH), 2230 (C≡N);[e] 1.12 (s, 9, $(CH_3)_3C$) and 3.48 (s, 2, CH_2)[f]

C$_6$*H*$_5$; 87; mp 48°;[i] . . .; 3380 (NH), 2250 (C≡N);[e] 3.96 (s, 2, CH_2) and 6.61–7.42 (m, 5, C_6H_5)[c]

[a] A. H. Cook, I. Heilbron, and A. L. Levy, *J. Chem. Soc.*, 201 (1948). [b] CH_2Cl_2 solution. [c] $CDCl_3$ solution. [d] A. H. Cook and S. F. Cox, *J. Chem. Soc.*, 2334 (1949). [e] Neat. [f] CCl_4 solution. [g] E. Knoevenagel and E. Mercklin, *Chem. Ber.*, 37, 4087 (1904). [h] L. J. Exner, L. S. Luskin, and P. L. deBenneville, *J. Am. Chem. Soc.*, 75, 4841 (1953). [i] E. Knoevenagel, *Chem. Ber.*, 37, 4073 (1904).

Table II. *N*-Chloro-*N*-alkylaminoacetonitriles

RN(Cl)CH$_2$CN: *R*; ν cm^{-1}; δ

CH$_3$; 2235 (C≡N); 2.97 (s, 3, CH_3) and 3.89 (s, 2, CH_2)[a]

CH$_3$*CH*$_2$; 2220 (C≡N); 1.16 (t, 3, CH_3CH_2, J = 7 Hz), 3.10 (q, 2, CH_3CH_2, J = 7 Hz) and 3.96 (s, 2, CH_2)[a]

(*CH*$_3$)$_2$*CH*; 2230 (C≡N); 1.22 (d, 6, $(CH_3)_2CH$; J = 6 Hz), 3.27 (heptet, 1, $(CH_3)_2CH$, J = 6 Hz) and 3.93 (s, 2, CH_2)[a]

(*CH*$_3$)$_3$*C*; 2250 (C≡N);[b] 1,28 (s, 9, $(CH_3)_3C$) and 3.92 (s, 2, CH_2)[a]

[a] CCl_4 solution. [b] Neat.

ative gas chromatography. At 70 eV, *m/e* was obtained for the molecular weights of compounds **2b–d, 13b,c, 15b–d, 16,** and for the mixture of isomers **2b** and **12b.** Calcium hypochlorite and all chloramines are potentially explosive compounds.

***N-tert*-Butylaminoacetonitrile.** A mixture of 167 g (1.6 mol) of sodium bisulfite, 200 ml of water, and 48 g (1.6 mol) of formaldehyde (120 ml of formalin) was stirred for 45 min at 70°, treated with 117 g (1.6 mol) of *tert*-butylamine added dropwise, heated 45 min at 60°, cooled, treated in the hood with 104 g (1.6 mol) of potassium cyanide in 250 ml of water, stirred for 1.5 hr, and extracted with ether. The organic layer was washed with water, dried over magnesium sulfate, and concentrated to an oil from which 128.5 g of *N-tert*-butylaminacetonitrile was isolated by distillation. In a similar way, *N*-ethyl-, *N*-isopropyl-, and *N*-phenylaminoacetonitrile were obtained. All are described in Table I.

On replacing formaldehyde with acetaldehyde, 61% of *α-N-tert*-butylaminopropionitrile was obtained: bp 57–58° (30 mm);[18] n^{22}D 1.4253; NMR (CCl_4) δ 1.13 (s, 9, $(CH_3)_3C$), 1.40 (d, 3, CH_3CH, J = 7 Hz), and 3.58 (q, 1, CHCN, J = 6 Hz); ir (neat) 3330 (NH), 2230 cm^{-1} (C≡N).

***N*-Methylaminoacetonitrile.** A mixture of 100.3 g (0.94 mol) of the hydrochloride (commercially available) of *N*-methylaminoacetonitrile and 105.6 g (1.88 mol) of calcium oxide in 400 ml of methylene chloride was stirred under reflux for 4 days. A precipitate was washed with methylene chloride. Distillation of an oil obtained by concentrating the combined methylene chloride solutions gave 60.0 g of colorless *N*-methylaminoacetonitrile after distillation. In a similar way, neutralization of its hydrochloride (commercially available) at 25° gave aminoacetonitrile (Table I).

***N-tert*-Butylformimidoyl Cyanide.** A solution of 29.7 g (0.27 mol) of *N-tert*-butylaminoacetonitrile in 200 ml of methylene chloride was placed in a 500-ml, three-necked, round-bottom flask equipped with a Herschberg stirrer and drying tube, cooled with stirring in an ice bath, and treated with 37.82 g (0.27 mol) of finely ground calcium hypochlorite and about 5 g of anhydrous calcium chloride. As the temperature was held under 25°, the mixture was stirred for 2 days and filtered. Concentration of a few milliliters of the clear filtrate gave *N*-chloro-*N-tert*-butylaminoacetonitrile: bp 45° (0.1 mm); however, bulk quantities were not distilled.

Table III. *N*-Alkylformimidoyl Cyanides, RN=CHCN

R; yield %; *E* ν cm^{-1} (—C≡N, >C=N—), δ;[a] *Z* ν cm^{-1} (—C≡N), >C=N—), δ

CH$_3$;[b] 25; 2230, 1630, 3.54 (d, 3, CH_3, J = 1.7 Hz[c]); 7.39 (q, 1, N=CH, J = 1.7 Hz[c]), 2220, 1615, 3.66 (d, 3, CH_3, J = 2.4 Hz[c]), 7.39 (q, 1, N=CH, J = 2.4 Hz[c])

CH$_3$*CH*$_2$;[d] 50; 2230, 1625, 1.26 (t, 3, CH_3, J = 8 Hz), 3.66 (double q, 2, CH_2, J = 7 Hz, J = 1.25 Hz[c]), 7.34 (t, 1, N=CH, J = 1.5 Hz[c]); 2210, 1610, 1.31 (t, 3, CH_3, J = 8 Hz), 3.69 (double q, 2, CH_2, J = 7 Hz, J = 2.1 Hz[c]), 7.29 (t, 1, N=CH, J = 2.1 Hz[c])

(*CH*$_3$)$_2$*CH*;[d] 72; 2240, 1625, 1.26 (d, 6, $(CH_3)_2CH$, J = 6 Hz), 3.64 (heptet, 1, $(CH_3)_2CH$, J = 6 Hz), 7.44 (s, 1, N=CH); 7.44 (s, 1, N=CH); 2220, 1610, 1.28 (d, 6, $(CH_3)_2CH$), J = 6 Hz), 4.08 (double heptet, 1, $(CH_3)_2CH$, J = 6 Hz, J = 1.6 Hz[c]), 7.32 (d, 1, N=CH, J = 1.6 Hz[c])

(*CH*$_3$)$_3$*C*;[d] 76; 2230, 1620, 1.22 (s, 9, $(CH_3)_3C$), 7.37 (s, 1, N=CH); 2210, 1620, 1.41 (s, 9, $(CH_3)_3C$), 7.48 (s, 1, N=CH)

[a] Ir and NMR from CCl_4 except for neat $(CH_3)_3CN$=CHCN. [b] Anal. Calcd for $C_3H_4N_2$: C, 52.93; H, 5.92; N, 41.15. Found: C, 52.66; H, 6.03; N, 41.18. [c] For ^4J(CH=NCH) 1.6 and 1.7 were assigned to *E*, 2.2 and 2.3 to *Z* isomers (H. J. C. Yeh, H. Ziffer, D. M. Jerina, and D. R. Boyd, *J. Am. Chem. Soc.*, 95, 2741 (1973). [d] References 5 and 6.

The major portion of the filtrate was stirred for 5 days with 39.20 g (0.53 mol) of powdered calcium hydroxide and about 5 g of anhydrous calcium chloride at reflux (40°) until the chloramine was not detected by NMR. The mixture was filtered, concentrated, and distilled to give 22.3 g of colorless *N-tert*-butylformimidoyl cyanide.

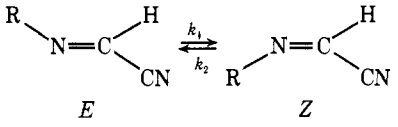
Prepared by this procedure, *N*-chloro-*N*-alkylaminoacetonitriles are described in Table II and *N*-alkylformimidoyl cyanides in Tables III and IV. Optimum transformation into an *N*-alkylformimidoyl cyanide required the temperature during dehydrochlorination to be held under 25, 32, and 38° when the *N*-alkyl substituent was methyl, ethyl, and isopropyl, respectively. Each (*E*)-*N*-alkylformimidoyl cyanide was obtained by distillation (or evaporation) of an *E–Z* mixture at 25–30° (2 mm for **2a,** 1 mm for **2b,** 0.2 mm for **2c,** and 3.0 mm for **2d**). A forerun was enriched in (*Z*)-*N*-methylformimidoyl cyanide, but this pure isomer was not isolated. (*Z*)-*N*-Ethyl- and *N*-isopropylformimidoyl cyanides were obtained from a corresponding *E–Z* mixture by distillation at 45° (90 mm) and at 65° (40 mm), respectively. A mixture of (*E*)- and (*Z*)-*N-tert*-butylformimidoyl cyanide was obtained when the *E* isomer was distilled at 70° (30 mm); on standing at room temperature, the *Z* isomer was converted to the *E* isomer. After 1 week at room temperature, an analytical sample of *N*-methylformimidoyl cyanide polymerized into a brown viscous oil which gave, without purification, an elemental analysis in agreement with the monomer unit ($C_2H_4N_2$) plus 2.8% oxygen (difference).

After separating each *N*-alkylformimidoyl cyanide, further distillation of the pot residue gave small amounts of the corresponding *N*-alkylformamide, HCONHR (R, yield %, bp °C (mm)): CH_3,[19] 7, 46 (0.2); C_2H_5,[19] 3, 62 (0.1); $(CH_3)_2CH$,[19] 2, 60 (0.2). The amount of nondistillable tar increased as the size of the alkyl group decreased.

To obtain product mixtures of *N*-alkylformimidoyl cyanide and isocyanide and *N*-alkylchloroformimidoyl cyanide, the treatment with calcium hydroxide occurred at 35° when the alkyl substituent was methyl, 41° when ethyl or isopropyl. Distillation separated the mixture of formimidoyl cyanides and isocyanides from solvent and from tarry residues.

Each mixture of cyanides and isocyanides was separated into three fractions by gas chromatography using a column of 5% GE-XE-60 on Chromosorb 60–80 AW DMCS in a stainless steel tube 2.4 m × 6.3 mm. Each (*Z*)-*N*-alkylformimidoyl cyanide separated first followed by the *N*-alkylchloroformimidoyl cyanide and finally an inseparable mixture of the (*E*)-*N*-alkylformimidoyl cyanide and the *N*-alkylformimidoyl isocyanide. On a preparative scale, the separation isolated (*Z*)-*N*-isopropylformimidoyl cyanide, *N*-isopropylchloroformimidoyl cyanide (independently prepared, vide infra), and a mixture of (*E*)-*N*-isopropylformimidoyl cyanide and *N*-isopropylimimidoyl isocyanide (flow rate 25 ml of He/min, column at 62°, injection port at 74°, and detector at 90°), for which ^{13}C NMR showed a chemical shift 157.7 ppm downfield from

Table IV. (*E*)- and (*Z*)-*N*-Alkylformimidoyl Cyanides, RN=CHCN (2)[a]



E *Z*

Compd	R	NMR signals	δ *E/Z*	*T*, °C	k_1/k_2, (sec^{-1}) × 10^{-5}	$\Delta G_1^{\ddagger}/\Delta G_2^{\ddagger}$, kJ mol^{-1}	K_{eq} × 10^2	ΔG°, kJ mol^{-1}	Uv_{abs} (ε)[b] *E/Z*	$n^{21}D$ *E/Z*
2a	CH_3			37			62	1.3	276.6 (85)[c]	1.4160[c]
2b	CH_3CH_2	CCH_3	1.34[d]	38	2.5	103.7	36	2.7	277.5 (77)	1.4226
			1.39[d]		7.0	100.7			284.5 (192)	1.4173
2c	$(CH_3)_2CH$	N=CH	7.44	37	10.7	99.5	24	3.7	277.5 (72)	1.4214
			7.32		44.7	95.7			284.0 (209)	1.4148
2d	$(CH_3)_3C$			37			0		283.8 (68)[c]	1.4300[c]

[a] Rate constants were derived from NMR signal integration at time intervals (A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed, Wiley, New York, N.Y., 1961, pp 12–13, 185–186). The free energy of activation, $\Delta G^{\ddagger}$, was given by the Eyring equation: $\Delta G^{\ddagger} = 4.57T(10.32 + \log Tk^{-1})$ and the difference in free energy of the ground states, ΔG°, was $-RT \ln K_{eq}$. Carbon tetrachloride and diglyme solutions of 2 (1.0 *M*) gave identical results. [b] Cyclohexane solutions. [c] For the *E* isomer. [d] This is the furthest downfield peak of the methyl triplet.

Me_4Si for the isocyano carbon[20] (Bruker HFX-90 instrument operating in the Fourier transform mode).

By preparative gas chromatography using a column of 30% SE-30, 45–60 Chromosorb W in an aluminum tube 6.1 m × 9.5 mm, at a flow rate of 75 ml of He/min, column at 90°, injection port at 109°, and detector at 119°, a mixture of isomeric *N*-isopropylformimidoyl cyanide and isocyanide was separated from *N*-isopropylchloroformimidoyl cyanide. Anal. (for the mixture of isomers). Calcd for $C_5H_8N_2$: C, 62.47; H, 8.39; N, 29.14. Found: C, 62.46; H, 8.48; N, 28.93. Ir (CCl_4) 2240 (C≡N) and 2120 cm^{-1} ($^+N{\equiv}^-C$).

***N*-Ethylchloroformimidoyl Cyanide.** A solution of 8.41 g (0.1 mol) of *N*-ethylaminoacetonitrile in 80 ml of methylene chloride was stirred for 2 days with 14.3 g (0.1 mol) of finely ground calcium hypochlorite and 5 g of calcium chloride as the temperature was held under 25°. After separation, the filtrate was treated with 21.4 g (0.15 mol) of calcium hypochlorite and 5 g of calcium chloride and heated at reflux (40°) with stirring for 10 to 14 days or until the chloramine was no longer detected by NMR. The mixture was filtered, concentrated, and distilled to give light yellow *N*-ethylchloroformimidoyl cyanide: bp 38–39° (18 mm);[21] 1.44 g (12%); $n^{23}D$ 1.4403; ir (CCl_4) 2230 (C≡N) and 1645 cm^{-1} (>C=N–); NMR (CCl_4) δ 1.31 (t, 3, CH_3, J = 7 Hz) and 3.72 (q, 2, CH_2, J = 7 Hz).

In a similar way, *N*-isopropylaminoacetonitrile was transformed into *N*-isopropylchloroformimidoyl cyanide: 33% yield; bp 57° (10 mm); $n^{21}D$ 1.4593; ir (CCl_4) 2245 (C≡N) and 1645 cm^{-1} (>C=N); NMR (CCl_4) δ 1.26 (d, 6, CH_3, J = 6 Hz) and 4.08 (heptet, 1, CH, J = 6 Hz). Anal. Calcd for $C_5H_7N_2Cl$: C, 45.99; H, 5.40; N, 21.43. Found: C, 45.99; H, 5.56; N, 21.43.

Dehydrogenation of Aminoacetonitriles. A solution of 10.00 g (89.3 mmol) of *N*-*tert*-butylaminoacetonitrile and 21.80 (125 mmol) of diethyl azodicarboxylate in 100 ml of methylene chloride was stirred for 8 days at 28°. A precipitate of diethyl hydrazodicarboxylate,[22] 17.09 g, mmp 132–133°, gave ir absorption identical with the authentic data. Distillation of the filtrate gave *N*-*tert*-butylformimidoyl cyanide[5] (**2d**): bp 29° (3 mm), 7.08 g, 72%, $n^{28}D$ 1.4267, ir and NMR identical with authentic data.

A mixture of 4.04 g (36.0 mmol) of *N*-*tert*-butylaminoacetonitrile and 10.99 g (44.6 mmol) of *o*-chloranil was stirred for 4 days at 28°. An orange precipitate, triturated with methanol and recrystallized from benzene, gave hexachlorodibenzo-*p*-dioxin-2,3-dione: 3.05 g, mp 305–306° (lit.[23] 296°). Anal. Calcd for $C_{12}O_4Cl_6$: C, 34.24; Cl, 50.53. Found: C, 34.33; Cl, 50.77, *m/e* 418. The hydrochloride of *N*-*tert*-butylaminoacetonitrile (3.08 g, 58%, mp 236–238° dec, NMR ($(CD_3)_2SO$) δ 1.33 (s, 9, $(CH_3)_3C$) and 4.28 (s, 2, CH_2)) was isolated from the methanol solution after concentration. Anal. Calcd for $C_6H_{13}N_2Cl$: C, 48.49; H, 8.82; N, 18.85. Found: C, 48.25; H, 8.84; N, 19.10. On treatment with sodium bicarbonate, the amine **10d** was obtained and was found to be identical with an authentic sample. Distillation of the original filtrate gave *N*-*tert*-butylformimidoyl cyanide (**2d**): bp 29° (3.0 mm), 0.56 g, 14%, with ir and NMR in agreement with authentic data.

***N,N'*-Dicyanomethylazodicarboxamide.** A solution of 1.12 g (20 mmol) of aminoacetonitrile and 3.48 g (20 mmol) of diethyl azodicarboxylate in 10 ml of chloroform was stirred at room temperature for 2 hr. An orange precipitate of *N,N'*-dicyanomethylazodicarboxamide was recrystallized from methanol to give 1.49 g (77%); mp 171–172° dec; ir (KBr) 3290 (NH) and 1725 (>C=O) cm^{-1}; NMR (CD_3SOCD_3) δ 4.43 (d, 4, CH_2, J = 5 Hz) and 9.76 (t, 2, NH, J = 5 Hz). Anal. Calcd for $C_6H_6N_6O_2$: C, 37.12; H, 3.11; N, 43.29. Found: C, 36.89; H, 3.19; N, 43.28.

***α*-*N*-*tert*-Butylacetimidoyl Cyanide.** A mixture of 62.58 g (0.50 mol) of *α*-*N*-*tert*-butylaminopropionitrile in 400 ml of anhydrous ether was cooled in an ice bath and treated dropwise over a period of 30 min with 65.1 g (0.60 mol) of *tert*-butyl hypochlorite. After stirring 2 hr in the dark at 0°, a few milliliters was concentrated to a colorless liquid, *α*-*N*-*tert*-butyl-*N*-chloroaminopropionitrile: ir (CCl_4) 2230 cm^{-1} (C≡N); NMR (CCl_4) δ 1.28 (s, 9, $(CH_3)_3C$), 1.55 (d, 3, CH_3CH, J = 7 Hz), and 4.23 (q, 1, CH_3CH, J = 7 Hz).

To the major portion of the solution at 0°, 107 g (0.70 mol) of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in 50 ml of anhydrous ether was added dropwise. After 5 hr at 0 to 25°, spinning band distillation of the filtrate gave *α*-*N*-*tert*-butylacetimidoyl cyanide: bp 65° (86 mm); 29.8 g (49%); $n^{21}D$ 1.4233; uv (cyclohexane) λ_{max} (ε) 295 nm (116); ir (neat) 2205 (C≡N) and 1660 cm^{-1} (>C=N–); NMR (CCl_4) δ 1.33 (s, 9, $(CH_3)_3C$), and 2.22 (s, 3, CH_3). Anal. Calcd for $C_7H_{12}N_2$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.37; H, 9.78; N, 22.50.

A solution of 3.57 g (28.8 mmol) of *α*-*N*-*tert*-butylacetimidoyl cyanide in 10 ml of methanol was stored for 3 months at 25°. Removal of methanol left a brown viscous oil. Recrystallization from hexane gave methyl *α*-*tert*-butylamino-*α*-cyanopropionimidate as colorless crystals: 1.5 g (30%); mp 103–105°; ir ($CHCl_3$) 3360, 3270 (NH), 2230 (C≡N), and 1670 cm^{-1} (>C=N–); NMR (CCl_4) δ 1.22 (s, 9, $(CH_3)_3C$), 1.32 (broad, 1, –NH–), 1.58 (s, 3, C–CH_3), 3.82 (s, 3, O–CH_3), and 7.97 (broad, 1, C=NH), both NH absorption bands disappeared on exchange with D_2O. Anal. Calcd for $C_9H_{17}N_3O$: C, 58.99; H, 9.35; N, 22.93. Found: C, 58.94; H, 9.47; N, 23.08.

In attempted purification of the product by chromatographic separation from a column of silica gel, chloroform–benzene (1:1) eluted *N*-*tert*-butylacetamide, recrystallized from a mixture of ether and petroleum ether (bp 40°): 0.97 g (29%); mp 93–96°;[24] ir (CCl_4) 3430, 3300 (NH), and 1650 cm^{-1} (>C=O); NMR (CCl_4) δ 1.31 (s, 9, $(CH_3)_3C$), 1.84 (s, 3, CH_3), and 6.90 (broad, 1, NH).

***N,N'*-Di-*tert*-butylaminomaleonitrile.** To 0.31 g (2.8 mmol) of *N*-*tert*-butyliminoacetonitrile in 5 ml of anhydrous benzene, a solution of 0.70 g (3.4 mmol) of stannic chloride in 5 ml of anhydrous benzene was added over a period of 1 hr as the mixture was externally cooled in a water bath at 15°. After the mixture was stirred overnight, 50 ml of water and 100 ml of ether were added.

Table V. *N,N'*-Dialkylaminomaleonitriles

$(RNHC(CN))_2$: *R*; yield %; mp °C; ν cm^{-1}; δ
CH_3CH_2;[a] 35; 62–64; 3360 (NH), 2210 (C≡N), 1605 (C=C);[b] 1.21 (t, 6, CH_3, J = 8 Hz), 3.21 (q, 4, CH_2, J = 7 Hz), and 3.38 (m, 2, NH)[c]
$(CH_3)_2CH$;[d] 74; 89–90; 3330 (NH), 2230 (C≡N), 2190 (C≡N), 1605 (C=C);[e] 1.23 (d, 12, CH_3, J = 6 Hz), 3.50 (heptet, 2, CH, J = 6 Hz), and 3.64 (d, 2, NH, J = 3 Hz)[f]
$(CH_3)_3C$; 96; 78–79;[f] 3350 (NH), 2230 (C≡N), 2190 (C≡N), 1590 (C=C);[f] 1.31 (s, 18, CH_3), and 3.76 (s, 2, NH)[b]

[a] Anal. Calcd for $C_8H_{16}N_4$: C, 58.52; H, 7.37; N, 34.12. Found: C, 58.39; H, 7.56; N, 34.05. [b] CCl_4 solution. [c] $CDCl_3$ solution. [d] Reference 6. [e] $CHCl_3$ solution. [f] H. Dabek, R. Selvarajan, and J. H. Boyer, *J. Chem. Soc., Chem. Commun.*, 244 (1972).

The separated organic layer was washed with aqueous bicarbonate and with water, dried over magnesium sulfate, and concentrated to leave a residue of 0.30 g (96%) of yellow *N,N'*-di-*tert*-butylaminomaleonitrile.[25] Other Lewis acids which were less effective in dimerizing the imine included boron trifluoride etherate, aluminum chloride, aluminum bromide, antimony pentachloride, and ferric chloride. *N,N'*-Diisopropyl- and *N,N*-diethylaminomaleonitrile were also prepared (Table V).

After 1 month, an analytical sample of *N,N'*-diethylaminomaleonitrile became dark brown, but not appreciably more viscous, and gave elemental analysis which had not changed from those obtained above for the freshly purified sample.

Acknowledgment. Financial support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

References and Notes

(1) J. H. Boyer and J. Kooi, "Iminoformyl Cyanides and Isocyanides", Abstracts, 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1974, No. ORGN-64.
(2) J. Oró, *Biochem. Biophys. Res. Commun.*, **2**, 407 (1960).
(3) Th. Völker, *Angew. Chem.*, **69**, 728 (1957).
(4) R. Sanchez, J. P. Ferris, and L. E. Orgel, *Science*, **153**, 72, 3731 (1966); *J. Mol. Biol.*, **30**, 223 (1967).
(5) J. H. Boyer and H. Dabek, *J. Chem. Soc. D*, 1204 (1970).
(6) J. P. Ferris, D. B. Donner, and W. Lotz, *J. Am. Chem. Soc.*, **94**, 6968 (1972).
(7) J. P. Ferris and L. E. Orgel, *J. Am. Chem. Soc.*, **88**, 1074 (1966).
(8) J. H. Boyer and J. Dunn, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, No. ORGN-108.
(9) The free energy difference between a cyanide and an isocyanide is about 15 kcal/mol in favor of the cyanide (National Bureau of Standards, Circular 500, Washington, D.C., 1952; S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); G. W. Van Dine and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 3227 (1968)).
(10) A substance thought to be $(HCN)_2$ was first identified as **1** [J. U. Nef, *Justus Liebigs Ann. Chem.*, **287**, 337 (1895)], later as **9** [A. Michael and H. Hibbert, *Ibid.*, **364**, 70 (1909)], and more recently established as triazine, $C_3H_3N_3$ [C. Grundmann and A. Kreutzberger, *J. Am. Chem. Soc.*, **76**, 5646 (1954)].
(11) Perhaps an oversight accounts for the absence of consideration of **9** in the ranking of the energy contents of candidates for $(HCN)_2$ by quantum chemical calculations: G. H. Loew and S. Chang, *Tetrahedron*, **27**, 2989 (1971), and C. J. Jameson and W. Yang, *J. Theor. Biol.*, **35**, 247 (1972), calculated a greater stability for **1** relative to its carbene isomer, H_2N–C̈–CN, thereby reversing the results of an earlier calculation (J. Serre and F. Schneider, *J. Chim. Phys.*, **61**, 1655 (1964)). More recently W. Yang, R. D. Minard, and C. N. Matthews, *J. Chem. Soc., Chem. Commun.*, 435 (1973), have reported that by calculation azirinonimine is lower in energy than **1** by 46 kcal/mol.
(12) J. B. Bjorgo, D. R. Boyd, C. W. Watson, and W. B. Jennings, *J. Chem. Soc. Perkin Trans. 2*, 757 (1974), and references cited.
(13) T. Fukunaga, *J. Am. Chem. Soc.*, **94**, 3242 (1972), accounts for the formation of an aziridine by the combination of diiminosuccinonitrile in the reactive form of a zwitterionic nitrenium ion and an olefin.
(14) W. Bauer and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, **8**, 772 (1969), reported the photoisomerization of an azirine into both a cyanide and an isocyanide.
(15) E. Miller and B. Narr, *Z. Naturforsch., Teil B*, **16**, 845 (1961).
(16) A. Peratoner and F. C. Palazzo, *Gazz. Chim. Ital.*, **38**, 102 (1908); A. M. van Leusen, G. J. M. Boerma, R. B. Helmholdt, H. Siderius, and J. Strating, *Tetrahedron Lett.*, 2367 (1972).
(17) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **39**, 712 (1963), and **47**, 278 (1967), detected hydrogen isocyanide (HNC) at 14 K and found that it disappeared on warming to 35 K. K. D. Booth and J. N. Murrell, *Mol. Phys.*, **24**, 1117 (1972), predict that hydrogen isocyanide is thermodynamically less stable than hydrogen cyanide by 35.2 kJ/mol, corresponding to an equilibrium constant for the concentration of the isocyanide in the cyanide of approximately 10^{-10} at 300 K.
(18) A. M. Pinchuk, L. N. Markovskii, and I. M. Kosinkaya, *J. Gen. Chem. USSR (Engl. Transl.)*, **38**, 969 (1968).
(19) M. Liler, *J. Chem. Soc. B*, 334 (1971).
(20) R. W. Stephany, M. J. A. de Bie, and W. Drenth, *Org. Magn. Reson.*, **6**, 45 (1974).
(21) J. U. Nef, *Justus Liebigs Ann. Chem.*, **287**, 302 (1895).
(22) O. Diels and E. Fisher, *Chem. Ber.*, **47**, 2043 (1914).
(23) L. Horner and E. Lingnau, *Justus Liebigs Ann. Chem.*, **573**, 30 (1951).
(24) M. V. Lock and B. F. Sagar, *J. Chem. Soc. B*, 690 (1966).
(25) H. Dabek, R. Selvarajan, and J. H. Boyer, *Chem. Commun.*, 244 (1972).