Generation of Cyanonitrene: Study of the Reaction of Sodium Hydrogen Cyanamide, *tert*-Butyl Hypochlorite, and Tertiary Amines[1]

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Reaction of sodium hydrogen cyanamide, *tert*-butyl hypochlorite (BHC), and tertiary amines at low temperatures (<–30 °C) does not yield the anticipated aminimides (R_3N^+–$^-$NCN), but when the reaction mixtures were warmed to approximately 0–10 °C, aminimides are formed in fair to good yields. At 0–10 °C an abrupt and complete precipitation of sodium chloride occurs, and it is concluded that cyanonitrene or a cyanonitrene-like species is formed by α-elimination from the BHC/sodium hydrogen cyanamide reaction product [presumed to be Na–N(Cl)–CN (**5**, eq 4)]. Compound **5** is stable at low temperatures, and reaction with tertiary amines is not observed. If the intercepting nucleophile is omitted, however, and the BHC/sodium hydrogen cyanamide reaction product is allowed to warm up, at 0–10 °C the color of the solution changes from pale yellow to deep orange, concomitant with precipitation of sodium chloride. The workup yields dicyanodiazene (**caution**: explosive when neat), the known dimerization product of cyanonitrene. ^1H and ^{13}C NMR and ESR spectra have been used to monitor the reactions and also to characterize products and intermediates.

In 1972, Swern, Ikeda, and Whitfield[3] proposed a general synthesis of various heteroatom ylides. The synthesis of sulfilimines, for example, consisted of treating thioethers with *tert*-butyl hypochlorite (BHC) at low temperatures (<–30 °C) to generate an ion pair whose structure was postulated as A (eq 1). Subsequent treatment of A, still

$$Me_2S \xrightarrow[<-30\ °C]{BHC} \underset{A}{[Me_2S^+\text{-}Cl]}\ t\text{-}BuO^- \xrightarrow{Na^+\,^-NHTs} \underset{1}{Me_2S^+\text{-}N^-\text{-}Ts} \quad (1)$$

at low temperatures, with sodium sulfonamides gave sulfilimines in good to excellent yields. A typical example is the reaction of dimethyl sulfide with BHC and then sodium toluenesulfonamide to yield *S,S*-dimethyl-*N*-tosylsulfilimine (**1**, eq 1).

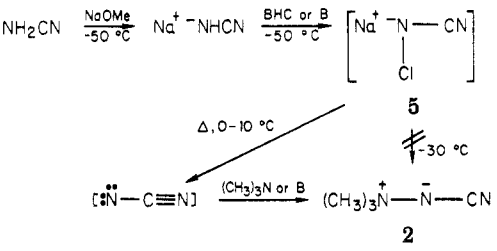
By a similar route, the phosphinimide $(C_6H_5)_3P^+$–$^-$NCN [from $(C_6H_5)_3P$, BHC, and $Na^+\,^-$NHCN] and the aminimide Me_3N^+–$^-$NCN (**2**, from Me_3N, BHC, and $Na^+\,^-$NHCN), were prepared. In the latter instance, no information was provided on the temperature throughout the course of the reaction, and it must now be assumed that the temperature of the reaction mixture had been allowed to reach 0 °C or higher. As will be described later, the temperature of the reaction mixture prior to workup is critically important for successful aminimide syntheses.

These limited results[3] prompted a systematic study of this reaction as a general procedure for the synthesis of aminimides and as a more convenient (and safer) alternative to nitrogen-to-nitrogen coupling methods involving the reaction of sulfonyl or acyl azides with heteroaromatic and tertiary amines.

The initial synthetic goal was the preparation of trimethylamine–*p*-toluenesulfonimide complex (**3**)[4] from BHC and trimethylamine by generation of ion pair intermediate B (analogous to A) which was expected to yield **3** upon treatment with sodium toluenesulfonamide at low temperatures (eq 2). Surprisingly, the major product was

$$Me_3N \xrightarrow[-50\ °C]{BHC} \underset{B}{[Me_3N^+\text{-}Cl]}\ t\text{-}BuO^- \xrightarrow{Na^+\,^-NHTs} \underset{3}{Me_3N^+\text{–}^-NTs} \quad (2)$$

Scheme I



not the aminimide **3** but the corresponding chloramine **4a** (eq 3). Similar results were obtained with sodium 4-

$$B \xrightarrow{Na^+\,^-NHSO_2Ar} Na\text{—}\underset{\displaystyle Cl}{\overset{\displaystyle \cdot\cdot}{N}}\text{—}SO_2Ar + H_2NSO_2Ar \quad (3)$$

4a,b

$R_3N = Me_3N$, pyridine; Ar = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**)

chlorobenzenesulfonamide and either pyridine or trimethylamine. In all cases the major products were the chloramines **4a,b**, containing small amounts of the starting sulfonamides, but no aminimides were detected.

Intermediates A and B are structurally similar, and their reactions with $Na^+\,^-NHSO_2Ar$ would be expected to proceed by analogous pathways, yielding sulfilimines and aminimides, respectively. In the preparation of sulfilimines, however, it does not matter whether A reacts with sodium arylsulfonamides or whether **4a** and **4b** react with dimethyl sulfide (or other thioethers) even at low temperatures; excellent yields are obtained.[5,6] B, in contrast, does not yield aminimides on reaction with sodium arylsulfonamides (eq 3) or sodium *N*-chlorocyanamide (**5**, Scheme I) at low temperatures (<–30 °C); however, if a solution that contains B and **5** is allowed to warm to approximately 0–10 °C, precipitation of sodium chloride occurs abruptly and completely in that temperature range, and the workup gives good yields of **2** (Scheme I). Other tertiary amines such as quinuclidine, *N*-methylmorpholine, and triethylamine also form aminimides in good yields if the reaction temperature is allowed to rise above 0–10 °C.

To obtain information on the proposed pathway shown in Scheme I and to support the conclusion that cyanonitrene is an intermediate derived from **5** by α elimination of sodium chloride, we studied the reaction by ^{13}C NMR

(1) Preliminary communications: (a) Presented at the 181st National Meeting of the American Chemical Society, Las Vegas, NV, Aug 1980. (b) Hutchins, M. G. K.; Swern, D. *Tetrahedron Lett.* **1981**, 4599.
(2) (a) Work done in partial fulfillment of the requirements for the Ph.D., Temple University, 1981. (b) LNP Corp., Malvern, PA 19355.
(3) Swern, D.; Ikeda, I.; Whitfield, G. F. *Tetrahedron Lett.* **1972**, 2635.
(4) Wawzonek, S.; Meyer, D. *J. Am. Chem. Soc.* **1954**, *76*, 2918.
(5) Campbell, M. M.; Johnson, G. *Chem. Rev.* **1977**, *77*, 65.
(6) Gilchrist, T. L.; Moody, C. J. *Chem. Rev.* **1977**, *77*, 409.

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Table I. ^{13}C NMR of the BHC/Na^{+-}NHCN and Related Systems

compd[a]	temp, °C	chemical shift, ppm Me_4Si	CH_3OH	C
$(CH_3)_3N$	−10	0	49.7	47.2
$(CH_3)_3N$/BHC	−10	0	49.7	45.0
Na^{+-}NHCN	−10		49.7	115.3
Na^{+-}NHCN/BHC	−10	0		114.6
NH_2CN	35		49.7	117.5
Na^{+-}NHCN/BHC	35		49.7	117.7

[a] In CH_3OH-CD_3OH solution.

Table II. *tert*-Butoxy Counteranion, ^{13}C NMR

$[Me_3N^+$-Cl]t-BuO^- (B) $Na^{+-}N(Cl)$-CN (5)

temp, °C	reactants	product	chemical shift, ppm $OC(CH_3)_3$	$OC(CH_3)_3$
0	Na^{+-}NHCN/BHC	5	69.2	31.0
35	Na^{+-}NHCN/BHC	NH_2CN	69.2	31.1
0	Me_3N/BHC	B	69.3	31.0
35		*t*-BuOH	68.9	31.2

and by ESR and we are reporting the results in this paper.

There is literature precedent for the proposal that a nitrene is required for aminimide formation by the sequence of Scheme I. It is known that the N–N coupling of nitrenes with tertiary amines occurs readily[7] whereas the reaction of *N*-chloramines with tertiary amines does not.[8]

Results and Discussion

As shown in Table I, $[Me_3N^+$-Cl] t-BuO^- (B) shows an upfield shift in the ^{13}C spectrum of 2.2 ppm relative to trimethylamine. This upfield shift is comparable to that which occurs upon protonation of primary amines (ca. 3-ppm upfield shift).[9] In contrast, conversion of Na^{+-}NHCN to Na^{+-}NClCN (**5**) shifts the nitrile carbon absorption upfield only 0.7 ppm. This is due to the small electronegativity change from H (2.20) to chlorine (2.83). In $[Me_3N^+$–Cl] t-BuO^- (B) the electronegativity of nitrogen is changed from 3.07 to 3.35 upon addition of positive chlorine to Me_3N.[20] As shown in Table II, the ^{13}C NMR signals of the carbons in the *tert*-butoxy group are invariant whether complex B or chloramine **5** is formed. Thus, all changes in the structures involve the carbons attached to nitrogen and not the *tert*-butoxy group; it is probable that *tert*-butyl alcohol rather than *tert*-butoxide is present.

Indirect evidence for a nitrenoid ground-state triplet was obtained in a series of ^{13}C NMR spectra accumulated sequentially from a Na^{+-}NHCN/BHC sample that was allowed to warm in the probe overnight from below 0 °C to ambient temperature. All signals other than solvent signals were transient. This effect of signal transiency is presumed to be due to the unpaired electrons of the ground-state triplet of the nitrenoid.[10]

In addition to the use of ^{13}C NMR as a tool to elucidate the postulated mechanism of *N*-sodio-*N*-chlorocyanamide (chloramine **5**) decomposition to a cyanonitrene-like species (Scheme I), electron spin resonance (ESR) has proved useful to study ground-state triplet nitrenes.[11] A series of measurements were obtained (Table III) in which the temperature and/or the three reactants (BHC, Na^{+-}NHCN, and R_3N) were varied. In all cases, the solvent used was methanol; thus lines are broadened, and some coupling information is lost.[11,12]

The g values for these systems are greater than those for a free electron (2.002 319). The values for most organic radicals with the unpaired electron on carbon are in the range of 2.0022–2.0029.[11,12] Radicals with the electron almost exclusively on oxygen have even larger g values, and there is a trend for the g values to increase with increasing atomic weight of the atom bearing the unpaired electron.[11] As shown in Table III, there are three separate signals with g values of 2.0050, 2.0150 (average), and 2.0229. The first g value, 2.0050, is larger than the value for hydrocarbon radicals; the ESR spectrum shows a splitting pattern (unresolved) of five lines. This is, therefore, assigned to a species that has triplet cyanonitrenoid character. The second g value, 2.0150, is assigned to the radical anion **6**, as this spectrum shows most of the splitting expected for a radical with two pairs of nonidentical nitrogens. The coupling constants, 2.3 and 7.1 (average values), are close to the published values of 2.11 and 7.37 for this radical anion (**6**).[13]

The g value of 2.0229 is assigned to a radical formed during the thermal decomposition of BHC. (The g value of $CH_3CH_2O\cdot$ is 2.026.[14]) This spectrum (run 9) is also readily distinguished by line shape from that of the nitrenoid (runs 4, 10) and the radical anion (runs 5, 6).

The negative results are also of value. For example, there is no signal for BHC/Na^{+-}NHCN until the temperature exceeds 0 °C; at this temperature, the signal assigned to a cyanonitrene-like species (run 4) begins to grow. After some time, this signal changes its shape and g value (run 5) to those of the radical anion **6**. The absence of signals at low temperatures also exists for BHC (run 1) and Na^{+-}NHCN/*N*-methylmorpholine (run 7). This provides additional evidence that the reactions of the BHC/Na^{+-}NHCN/amine system proceed via the chloramine–nitrenoid route at "elevated" temperatures (0–10 °C).

In conclusion, the reaction of BHC with Na^{+-}NHCN below 0 °C leads to *N*-sodio-*N*-chlorocyanamide (**5**) as shown by the change in ^{13}C NMR absorption of the nitrile carbon, while the absorption due to the *tert*-butoxy carbons remains constant. Furthermore, as the sample is allowed to warm, the nitrile carbon signal shifts, consistent with the conclusion that decomposition of **5** via the cya-

(7) Curtius, T. *J. Prakt. Chem.* **1930**, *125* (2), 303. Curtius, T.; Rissom, J. *Ibid.* **1930**, *125* (2), 323. Curtius, T.; Kraemer, G. *Ibid.* **1930** (2), *125*, 340. Curtius, T.; Bottler, H.; Randenbusch, W. *Ibid.* **1930**, *125* (2), 380. Ashley, J. N.; Buchanan, G. L.; Easson, A. P. T. *J. Chem. Soc.* **1947**, 60. Martin, J.; Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2451. Abramovitch, R. A.; Takaya, T. *J. Org. Chem.* **1972**, *37*, 2022. Lindley, J. M.; McRobbie, I. M.; Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans 1* **1980**, 982.

(8) McKillip, W. J.; Sedor, E. A.; Culberton, B. M.; Wawzonek, S. *Chem. Rev.* **1973**, *73*, 255. Wawzonek, S. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 338. Mann, F. G.; Pope, W. J. *J. Chem. Soc.* **1922**, 1052.

(9) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972; pp 51, 52. Gordon, A. J.; Ford, R. A. "The Chemists' Companion"; Wiley-Interscience: New York, 1971; pp 82–86.

(10) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley-Interscience: New York, 1980. Forrester, A. R.; Hay, J. M.; Thomsom, R. H. "Organic Chemistry of Stable Free Radicals"; Academic Press: New York, 1968; p 49.

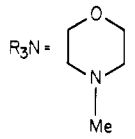
(11) Bersohn, M.; Baird, J. C. "An Introduction to Electron Paramagnetic Resonance"; W. A. Benjamin: New York, 1966; pp 69, 168.

(12) Alger, R. S. "Electron Paramagnetic Resonance Techniques and Applications"; Interscience: New York, 1968; pp 278–80.

(13) Jones, M. T. *J. Am. Chem. Soc.* **1966**, *88*, 227.

(14) Bielski, B. J. J.; Gebricki, J. M. "Atlas of Electron Spin Resonance Spectra"; Academic Press: New York, 1967; p 224.

Table III. ESR Data for the System R_3N/BHC/$Na^{+-}NHCN$



$Na^{+}(N{\equiv}C{-}N{=}N{-}C{\equiv}N)^{\bullet-}$

6

run	temp, °C	BHC	$Na^{+-}NHCN$	R_3N	signal	g	coupling, G
1	−20	+	−	−			
2	−20	−	+	−			
3	−70 to 0	+	+	−			
4	20	+	+	−	:N-CN	2.0050	*a*
5	15 (t = 1 h)	+	+	−	6	2.0140	2.2, 7.0
6	15 (t = 2 h)	+	+	−	6	2.0160	2.4, 7.2
7	−11	+	+	+			
8	0	+	−	+			
9	20	+	−	+		2.0229	9.6
		+	+	+			
10	20	+	+	+	:N-CN	2.0050	*a*

[a] Coupling was observed but could not be measured accurately, due to line broadening.

nonitrenoid intermediate occurs. Evidence for the intermediacy of this nitrene has been deduced from the transient signals from the $Na^{+-}NHCN$/BHC sample in the ^{13}C NMR spectra and from ESR studies.

Chemical evidence for the transient formation of cyanonitrene-like species was obtained by allowing the BHC/sodium hydrogen cyanamide/methanol reaction system to warm to room temperature *without addition of intercepting nucleophiles.* At the anticipated temperature (0–10 °C) sodium chloride precipitated, and the color of the solution changed from pale yellow to deep orange. Low-temperature evaporation of solvent yielded an unstable orange solid residue [mp 50–55 °C (lit.[15] mp 35–37.5 °C)] which exploded on two separate occasions. In two other experiments the orange compound was identified spectrally as dicyanodiazene, N≡C—N=N—C≡N, the dimerization product of cyanonitrene previously prepared only from cyanogen azide.[15,16] No proton resonances were obtained in the ^1H NMR (C_6D_6), and only a single ^{13}C resonance was observed at 118.3 ppm. A strong nitrile absorption at 2200 cm^{-1} was observed in the IR spectrum.

Experimental Section

General Methods. Trimethylamine was obtained from Eastman Kodak Co. as a 25% solution in methanol. Other reagents were obtained from Aldrich Chemical Co. and were used as received. Solvents were stored over a mixture of freshly prepared Linde 3A and 4A molecular sieves. Cyanamide was stored in a desiccator under vacuum. Glassware was dried 12–24 h at 125 °C before use. *tert*-Butyl hypochlorite was prepared according to the procedure of Mintz and Walling.[17]

Melting points were determined on a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. Analytical samples were purified by repeated recrystallization from appropriate solvents until a constant melting point was obtained. Elemental analyses were performed by Micro-Analysis, Wilmington, DE, or by Galbraith Laboratories, Knoxville, TN.

Infrared spectra were obtained on a Pye Unicam SP1000 spectrophotometer, either as films (liquids) or potassium bromide disks (solids). Absorptions are reported in wavenumbers. Absorption intensities are designated as strong (s), medium (m), and weak (w).

Proton magnetic resonance (^1H NMR) spectra were obtained in the designated solvents by using either a Varian XL-100 (100 MHz) or a Perkin-Elmer R-32 (90 Hz) instrument. Chemical shifts are reported in parts per million (δ) downfield relative to tetramethylsilane (Me_4Si) as an internal standard. The spectra are reported as follows: chemical shifts (in order of increasing δ); multiplicity, singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m); integration in proton units; peak assignment.

The ^{13}C NMR spectra were obtained in the designated solvents on a Varian XL-100 (25.16 MHz) instrument equipped with a Nicolet 1180 computer, with chemical shifts being expressed in parts per million relative to internal Me_4Si. Carbon multiplicities were determined in off-resonance spectra and are noted as singlet (s), doublet (d), triplet (t), or quartet (q).

First-derivative ESR spectra were obtained on a Varian 4500-10A X-band spectrometer with a 12-in. rotating magnet, 100-kHz field modulation, variable-temperature insert Dewar, V-4540 controller, and V-4533 cylindrical cavity. Reported temperatures are considered accurate to ±5 °C.

Routine mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6H; high-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2.

Thin-layer chromatography was performed by using 250 μm, 5 × 20 cm, silica gel GF plates (Analtech, Inc.) with UV light for visualization. Solvents are as noted in the appropriate experiment.

Unless otherwise noted, all reactions were begun below and all subsequent additions were to solutions maintained below −50 °C by a dry ice–acetone bath.

Sodium Hydrogen Cyanamide. To a freshly prepared methanol solution (20 mL) containing $Na^{+-}OMe$ (Na, 1.2 g, 0.05 mol) was added NH_2CN (2.1 g, 0.05 mol) in one portion. Stirring was continued for a minimum of 2 h at room temperature. (Use of the solution immediately after addition of NH_2CN leads only to recovery of NH_2CN.) Monitoring of this reaction by thin-layer chromatography (EtOAc/hexane, 1:1) indicated that some NH_2CN was present for at least 1 h after mixing with $Na^{+-}OMe$, and that after 24 h the concentration of $Na^{+-}NHCN$ appeared to decrease.

Reaction of Pyridine, BHC, and $Na^{+-}NHSO_2C_6H_4$-4-Cl. To a stirred methanol solution (30 mL) of pyridine (2.0 g, 0.025 mol) was added a methanol solution (25 mL) of BHC (3.11 g, 90%, 0.025 mol) dropwise while the temperature was maintained below −50 °C. To this was slowly added a methanol solution (30 mL) containing Na (0.57 g, 0.025 mol) and 4-chlorobenzenesulfonamide (4.81 g, 0.025 mol). After addition was complete (~2 h), the solution was allowed to warm to room temperature. Evaporation of the volatiles followed by stirring the residue in absolute EtOH and filtration yielded NaCl (1.29 g, 88%).

Recrystallization of the EtOH-soluble fraction from EtOH yielded *N*-chloro-*N*-sodio-4-chlorobenzenesulfonamide (4-Chlorochloramine-B; 5.49 g, 87%). The mass spectrum and ^{13}C NMR were identical with those of an authentic sample; mp 183 °C, explodes (lit.[18] mp 182 °C, explodes).

(15) F. A. Marsh and M. E. Hermes, *J. Am. Chem. Soc.* **1965**, *87*, 1819.
(16) M. T. Jones, *J. Am. Chem. Soc.* **1966**, *88*, 227. Bak, B.; Jansen, P. *J. Mol. Struct.* **1972**, *12*, 167; **1972**, *11*, 25. Howell, J. M.; Kirschenbaum, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 877.
(17) Mintz, M. J.; Walling, C. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 9.
(18) Baxter, R. R.; Chattaway, F. D. *J. Chem. Soc.* **1916**, 1814.

Reaction of Me_3N, BHC, and $Na^+{}^-NHSO_2C_6H_4$-4-Cl. To a stirred methanol solution (30 mL) of Me_3N/MeOH (10 mL, 25% w/v, 0.09 mol) was added dropwise a methanol solution (25 mL) of BHC (3.81 g, 83%, 0.03 mol) while the temperature was maintained below −50 °C. To this was slowly added a methanol (30 mL) solution containing Na (0.75 g, 0.032 mol) and 4-chlorobenzenesulfonamide (6.96 g, 0.036 mol). After the addition was complete, stirring and cooling (dry ice/acetone bath) were maintained for 3 h. The cooling bath was removed and the stirring continued. A comparison of the R_f values for an authentic sample of 4-Chlorochloramine-B and this solution were made by using the solvent system $CHCl_3$/MeOH [10:1, 1:1, and 1:10 (v/v)]; the values were identical. Evaporation of the solvent yielded 4-Chlorochloramine-B (*4b*): 8.6 g (98%); mp 165 °C, explodes (lit.[18] mp 182 °C, explodes).

Reaction of Me_3N, BHC, and $Na^+{}^-NHTs$. To a stirred methanol solution (25 mL) of Me_3N (8.2 mL, 25% w/v MeOH, 0.035 mol) was added dropwise a methanol solution (25 mL) of BHC (4.24 g, 90%, 0.035 mol) while the temperature was maintained below −50 °C. To this was slowly added a methanol solution (40 mL) containing Na (0.81 g, 0.035 mol) and toluenesulfonamide (6.01 g, 0.035 mol). After addition was complete, cooling was maintained for an additional hour, and the solution was then allowed to warm to room temperature and stirred overnight. The methanol was evaporated, and the residue was refluxed with CH_2Cl_2 (200 mL) and then filtered to give CH_2Cl_2-insoluble material (7.22 g). The CH_2Cl_2 layer contained *p*-toluenesulfonamide (0.9 g, 15% recovery), identified by IR. Recrystallization of the CH_2Cl_2-insoluble material from EtOH yielded Chloramine-T (**4a**): 6.32 g (80%); mp 176 °C, explodes (lit.[19] mp 175–180 °C, explodes).

Low-Temperature NMR and ESR Sample Preparation. In general, NMR samples were taken as ~0.2-mL aliquots from the reaction mixtures as needed and stored until used in 0.5-mm NMR tubes in a dry ice/acetone bath. At that time, while cooling was continued, they were diluted with approximately 0.2 mL of CD_3OD and inserted into the precooled ^{13}C NMR probe. The ESR samples were taken as aliquots from the appropriate reaction mixtures and stored in a dry ice/acetone bath until placed into the sample cell. Both sets of samples were run as taken or mixed as needed and were kept cold until in the instrument probes, which were cooled and/or warmed as listed in Tables I and II (^{13}C NMR) and in Table III (ESR). The ^{13}C NMR samples were diluted 1:1 with CD_3OD. ESR samples were run in CH_3OH only.

Trimethylamine Cyanimide (2).[20] To a stirred methanol solution (25 mL) of BHC (5.4 g, 90%, 0.05 mol) was added dropwise a methanol solution (50 mL) of trimethylamine (11.8 mL, 25% w/v MeOH, 0.05 mol). After about 1 h, a methanol solution (30 mL) of $Na^+{}^-NHCN$ (0.05 mol) was slowly added. After the addition was complete, the cooling bath was removed, and the solution was stirred for a minimum of 3 h after room temperature was reached. The methanol was then evaporated by using minimal heating. To the resulting oily residue was added CH_2Cl_2 (250 mL). This mixture was stirred for 2–3 h, and the mixture was then filtered. Evaporation of the CH_2Cl_2 followed by high-vacuum removal of residual volatiles yielded crude **2**, 3.5 g (63%). Recrystallization of a portion from ethyl acetate yielded an analytical sample: mp 174–176 °C (lit.[20] mp 173.5–176 °C); MS, *m/e* 99 (M^+), 85 (−Me), 69 (−2Me), 59 (−NCN); ^1H NMR ($CDCl_3$) δ 3.3 (s) (lit. δ 3.2); ^{13}C NMR ($CDCl_3$) 75.4, 125.5 ppm; IR 2140 (C≡N, s) cm^{-1}.

***N*-Methylmorpholine Cyanimide.** Similarly, *N*-methylmorpholine (5.1 g, 0.05 mol) yielded the aminimide (4.8 g, 68%). Recrystallization from acetone yielded analytically pure product: 2.2 g (31.2%); mp 92.5 °C; MS, *m/e* 141 (M^+), 126 (−Me), 101 (−NCN), 71 (−NCN and $-CH_4N$ or $-CH_2O$), 43 (C_2H_5N or C_2H_3O); ^1H NMR ($CDCl_3$) 3.20 (s) and 3.27 (dd, 7 H), 3.67 (dt, 2 H), 4.06 (dt, 2 H); ^{13}C NMR ($CDCl_3$) 57.1 (q), 61.4 (t), 125.2 (s) ppm; IR 2140 (C≡N, s) cm^{-1}. Anal. Calcd for $C_6H_{11}N_3O$: C, 51.04; H, 7.85; N, 29.72. Found: C, 50.85; H, 8.00; N, 29.63.

Quinuclidine Cyanimide. Similarly, quinuclidine (11.1 g, 0.1 mol) yielded the aminimide (15.1 g, 100%). Recrystallization from acetonitrile yielded analytically pure product: 13.1 g (87%); mp 270 °C dec; high-resolution MS; calcd for $C_8H_{13}N_3$ (M^+) *m/e* 151.1250, found 151.1107. MS, *m/e* 151 (M^+), 111 (−NCN), 96 ($-C_4H_7$), 84 ($-C_5H_7$), 83 ($-C_4H_6N$), 69 (C_5H_9); ^1H NMR ($CDCl_3$) δ 2.05 (m, 7 H), 3.55 (m, 6 H); ^{13}C NMR ($CDCl_3$) 19.7 (s), 25.6 (t), 59.6 (t), 125.5 (s) ppm. IR 2120 (C≡N, s) cm^{-1}. Anal. Calcd for $C_8H_{13}N_3$: C, 63.54; H, 8.67; N, 27.80; Found: C, 63.31; H, 8.73; N, 27.98.

1,4-Diazabicyclo[2.2.2]octane Monocyanimide. Similarly, 1,4-diazabicyclo[2.2.2]octane (1.12 g, 0.01 mol) yielded the aminimide (0.6 g, 39%). Recrystallization from acetonitrile yielded purified product: 0.4 g (27%); mp 260 °C dec; MS (calcd *m/e* 152), *m/e* 152 (M^+), 126 (−CN), 112 (−NCN); ^1H NMR δ 3.3 (m); ^{13}C NMR 54.2, 57.2, 125.0 ppm; IR 2120 (C≡) cm^{-1}.

Triethylamine Cyanimide.[20] Similarly, triethylamine (5.0 g, 0.05 mol) yielded the aminimide (4.9 g, 70%). A portion was recrystallized from tetrahydrofuran to yield a sample: mp 85–87 °C (lit.[20] mp 87.7–89.4 °C); MS (calcd *m/e* 141), *m/e* 141 (M^+), 112 ($-C_2H_5$), 101 (−NCN), 86 (−NCN, CH_3), 84 ($-C_4H_9$), 70 ($-C_5H_{11}$), 58 (C_3H_8N), 56 (C_3H_6N); ^1H NMR ($CDCl_3$) δ 1.25 (t, 9 H), 3.33 (q, 6 H); ^{13}C NMR ($CDCl_3$) 15.1, 65.7, 125.3 ppm; IR 2120 (C≡N) cm^{-1}.

Dicyanodiazene. A methanol solution (30 mL) of BHC (5.4 g, 90%, 0.05 mol) was added dropwise (exothermic) with stirring to a methanol solution (40 mL) of sodium hydrogen cyanamide (0.05 mol) maintained at 0–10 °C in an ice bath. Evaporation of volatiles from the bright orange solution yielded an occasionally explosive orange solid: mp 50–55 °C dec, explodes (lit.[15] mp 35–37.5 °C); MS, *m/e* 40; ^1H NMR (C_6D_6), no signals; ^{13}C NMR 118.3 ppm (only signal); IR 2200 (C≡N), 1650 (N=N) cm^{-1}.

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Registry No. 2, 35468-56-5; **4a**, 127-65-1; **4b**, 30066-82-1; NaNHCN, 17292-62-5; NaOMe, 124-41-4; NH_2CN, 420-04-2; $NaNHSO_2C_6H_4$-4-Cl, 18522-94-6; Me_3N, 75-50-3; NaNHTs, 18522-92-4; NCN=NCN, 1557-57-9; BHC, 507-40-4; pyridine, 110-86-1; *N*-methylmorpholine cyanimide, 81357-06-4; quinuclidine cyanimide, 81357-05-3; 1,4-diazabicyclo[2.2.2]octane monocyanimide, 83334-43-4; thiethylamine cyanimide, 35468-55-4; *N*-methylmorpholine, 109-02-4; quinuclidine, 100-76-5; 1,4-diazabicyclo[2.2.2]octane, 280-57-9; triethylamine, 121-44-8; cyanonitrene, 1884-64-6.

(19) Chattaway, F. D. *J. Chem. Soc.* **1905**, 145.
(20) Appel, R.; Heinen, H.; Schoellhorn, R. *Chem. Ber.* **1966**, *99*, 3118.