Cyanogen Azide

F. D. MARSH

Contribution No. 1545 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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The preparation of cyanogen azide (1) from sodium azide and cyanogen chloride in anhydrous media is described. In aqueous media these same reagents can also give either sodium 5-azidotetrazole (6) or (diazidomethylene)cyanamide (8). A probable reaction path leading to the various products is proposed.

The brief but rich history of cyanogen azide (N_3CN) (**1**) has already established it as a highly reactive and useful reagent in synthetic and theoretical chemistry. Our preliminary reports of its synthesis[1] and decomposition to cyanonitrene (NCN) (**2**)[2,3] were the bases for two broad areas of research in cyanogen azide and cyanonitrene chemistry. The unique reactivity of **1** with olefins[1,4,5] at 0–35° to give alkylidene cyanamides and *N*-cyanoaziridines had led to a better understanding of azide–olefin reactions[4] and to a convenient method for converting selected olefins to ketones under exceptionally mild conditions.[4] The azide–olefin reaction has been adapted to a new method for contracting rings of steroid ketones.[6] In addition, the azide **1** has broad utility as an intermediate to a number of new heterocyclic systems through reaction with acetylenes,[7] ketones,[8] and nucleophiles,[8] and yields new classes of ylides and substituted cyanamides through reaction with Lewis bases.[8]

The second class of cyanogen azide reactions occurs at *ca.* 50° where **1** loses nitrogen to give cyanonitrene (**2**), a common intermediate in the reactions of cyanogen azide with aliphatic and aromatic hydrocarbons which furnish alkylcyanamides[2] and *N*-cyanoazepines,[9] respectively. Cyanonitrene has also been proposed as an intermediate in selected olefin reactions[10] to give aziridines and is the only known precursor to azodinitrile.[11] The symmetry and ease of preparation of this new first-row triatomic molecule has led to several fundamental studies of its structure and reactivity in the singlet and triplet states.[12]

This paper describes the synthesis and properties of **1** and offers an explanation for the formation of a compound, $(CN_4)_2$, originally reported[13] to be **1**.

Synthesis and Properties of Cyanogen Azide.—Cyanogen azide is obtained in virtually quantitative yield from sodium azide and cyanogen chloride in anhydrous media.

$$NaN_3 + ClCN \longrightarrow \underset{\textbf{1}}{N_3CN} + NaCl$$

The pure azide **1** *is a colorless oil which detonates with great violence when subjected to mild mechanical, thermal, or electrical shock.* Solutions of cyanogen azide, however, can be prepared and handled safely in a number of solvents where most of its properties have been determined.

The pure azide **1** is too sensitive for combustion analysis but it has been characterized both physically and chemically. The infrared spectrum in carbon tetrachloride shows absorptions at 2240 (s), 2199 (vs), 2143 (s), and 2090 cm^{-1} (s) (associated with nitrile and azide stretching vibrations) and at 1245 cm^{-1} (vs) (C–N stretching). In cyclohexane, **1** has two resolved absorptions at 275 mμ (ϵ 103) and 220 (2157). The mass spectrometric cracking pattern of **1** (Table I) shows a peak of 48% relative abundance for the parent ion and is entirely consistent with the formulated structure. The molecular weight (freezing point in benzene) is 69 (calcd, 68). The boiling point and vapor pressure have not been determined, but **1** is estimated to boil at 90° and its vapor pressure at 25° lies between 70 and 100 mm.

TABLE I
MASS SPECTRUM OF N_3CN^a

m/e	Intensity relative to $NCN\cdot^+$	Probable ion
12	94.7	$C\cdot^+$
13	0.9	^{13}C isotope
14	24.2	$N\cdot^+$
26	20.1	CN^+
28	42.4	$N_2\cdot^+$
34	1.2	N_3CN^{2+}
40	100	$NCN\cdot^+$
41	2.0	^{13}C and ^{15}N isotopes
42	3.9	N_3^+
54	0.4	N_3C^+ and/or N_3CN^+
68	48.1^b	$N_3CN\cdot^+$
69	1.4	^{13}C and ^{15}N isotope

[a] Consolidated Electrodynamics Corp. 21-103C mass spectrometer operated with 10.5-μA ionizing current at 70 eV. [b] Parent ion.

For characterization, **1** was reduced to cyanamide in 80% yield and treated with triphenylphosphine and trimethyl phosphite to give, respectively, ylides **3** and **4** nearly quantitatively.

$$N_3CN + H_2S \longrightarrow NH_2CN + S + N_2$$
$$N_3CN + R_3P \longrightarrow R_3P{=}NCN + N_2$$
$$\textbf{3},\ R = C_6H_5$$
$$\textbf{4},\ R = CH_3O$$

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(1) F. D. Marsh and M. E. Hermes, *J. Amer. Chem. Soc.*, **86**, 4506 (1964); F. D. Marsh, U. S. Patent 3,410,658 (1968).

(2) A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *J. Amer. Chem. Soc.*, **87**, 2296 (1965).

(3) A. G. Anastassiou and H. E. Simmons, *ibid.*, **89**, 3177 (1967).

(4) M. E. Hermes and F. D. Marsh, *J. Org. Chem.*, **37**, 2969 (1972).

(5) A. G. Anastassiou, *ibid.*, **31**, 1131 (1966).

(6) R. M. Scribner, *Tetrahedron Lett.*, **No. 47**, 4737 (1967).

(7) M. E. Hermes and F. D. Marsh, *J. Amer. Chem. Soc.*, **89**, 4760 (1967); F. D. Marsh, U. S. Patent 3,322,782 (1967).

(8) F. D. Marsh, in preparation.

(9) F. D. Marsh and H. E. Simmons, *J. Amer. Chem. Soc.*, **87**, 3529 (1965); F. D. Marsh, U. S. Patent 3,268,512 (1966).

(10) (a) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968); (b) R. M. Scribner, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March–April, 1968, Organic Division, paper 144.

(11) F. D. Marsh and M. E. Hermes, *J. Amer. Chem. Soc.*, **87**, 1819 (1965); F. D. Marsh, U. S. Patent 3,278,267 (1968).

(12) Properties of cyanonitrene are discussed by (a) G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, **42**, 3755 (1965); (b) E. Wasserman, L. Barash, and W. A. Yager, *J. Amer. Chem. Soc.*, **87**, 2075 (1965); (c) D. E. Milligan and M. E. Jacox, *J. Phys. Chem.*, **45**, 1387 (1966); (d) M. E. Jacox and D. E. Milligan, *ibid.*, **47**, 1626 (1967); (e) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **89**, 3184 (1967); (f) A. G. Anastassiou and J. N. Shepelevy, *ibid.*, **90**, 492 (1968).

(13) M. G. Darzens, *C. R. Acad. Sci.*, **154**, 1232 (1912).

Cyanogen azide (**1**) is soluble in most organic solvents and water and can be recovered unchanged from aqueous solutions after 24 hr at room temperature. When heated in water, **1** is slowly hydrolyzed to carbamazide in low yield (40°, 54 hr). In 10% sodium hydroxide solution, **1** is slowly converted at room temperature to sodium 5-azidotetrazole (**6**) in 50% yield. The tetrazole presumably arises from initial hydrolysis of **1** to cyanate and azide ions. The azide ion reacts with **1** to give tetrazole **6**, as discussed below.

Solutions of **1** decompose with loss of nitrogen, and the rate depends on temperature and to a lesser degree on the solvent (Table II). The half-life of **1** in acetonitrile (27 wt %) is 15 days at 25°, but solutions in acetonitrile or ethyl acetate have been stored for up to 1 year at 0 to −20° without change. Polar solvents appear to stabilize **1** with respect to thermal decomposition.

TABLE II
THERMAL STABILITY OF CYANOGEN AZIDE IN POLAR AND NONPOLAR SOLVENTS

Solvent	N_3CN, wt %	Temp, °C	N_3CN half-life
Acetonitrile	27	25	15 days
Acetonitrile	27	0 to −20	Indefinite
Acetonitrile	2.8	55	6.5 hr
Benzene	2.2	55	2.1 hr
Cyclohexane	2.8	55	1.6 hr

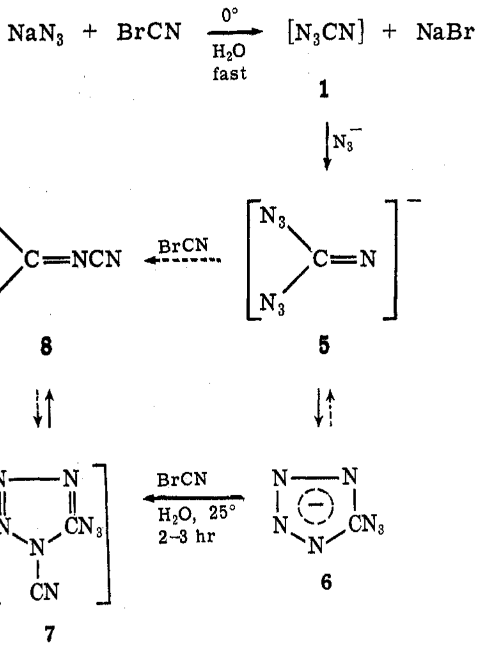
Reaction of Sodium Azide and Cyanogen Bromide in Water.—The older literature[13] describes the synthesis of a compound, $(CN_4)_2$, originally thought to be **1**. We have reinvestigated this work and propose an explanation for the earlier findings.

Darzens[13] added 1 equiv of cyanogen bromide to aqueous sodium azide and obtained a white, crystalline solid, mp 35.5–36°, to which he assigned the structure **1** and the name carbon pernitride. Hart[14] reinvestigated this product and from molecular weight data and chemical studies reported that Darzens' product was a dimer of cyanogen azide, $(CN_4)_2$, having the (diazidomethylene)cyanamide structure **8**. Hantzsch[15] later concluded from spectral data that Darzens' product was **1** and that Hart's findings resulted from an associated dimer of **1** in solution.

Our findings confirm the structure of Darzens' product as **8**. Cyanogen azide has shown no tendency to dimerize as implied by Hart, and we suggest that **8** may arise as shown in Scheme I. When 1 equiv of cyanogen bromide was added to aqueous sodium azide at 0°, an initial rapid reaction consumed all the azide and 0.5 equiv of cyanogen bromide and gave nearly quantitatively a water-soluble, highly explosive CN_7 anion. This product was shown to be sodium 5-azidotetrazole (**6**) by elemental analysis, infrared spectrum, and reduction of the parent acid to the known 5-aminotetrazole.

When the reaction is allowed to continue at 25°, the remaining 0.5 equiv of cyanogen bromide slowly reacts (2–3 hr) and an oil separates, which when crystallized from ether gives the white, explosive solid, mp 42.1–42.9°, first isolated by Darzens. The structure of this solid was confirmed as **8** by elemental analysis, infrared spectrum, and reduction to the known dicyandiamide.

SCHEME I
REACTION OF SODIUM AZIDE AND CYANOGEN BROMIDE IN WATER



The initial fast reaction of sodium azide and cyanogen bromide in water at 0° appears to result from nucleophilic displacement on cyanogen bromide by azide ion and may give **1** as an intermediate. Repeated attempts to isolate or detect **1** in the aqueous reaction mixture or in the organic layer of two-phase reactions failed. Cyanogen azide prepared in acetonitrile, however, reacted rapidly with aqueous sodium azide to give tetrazole **6** in 80% yield. The tetrazole is presumed to form from attack of azide ion on the electron-deficient carbon of **1** to give the hypothetical *gem*-diazide **5**, in a manner similar to the reaction of azide ion with nitriles bearing electron-withdrawing groups.[16] One of the azide groups then closes on the azomethine group in a well-documented reaction[17,18] to give **6**. The second, slower step involves displacement on cyanogen bromide by the tetrazole anion **6** to give **7**, which was not isolated but apparently opens spontaneously to the *gem*-diazide **8** in a reaction characteristic of many tetrazoles.[14,18c]

An equilibrium between **5** and **6** and reaction of the *gem*-diazide **5** with cyanogen bromide as shown by broken arrows in Scheme I can also account for **8**. Other workers have demonstrated that certain tetrazoles, particularly those containing electron-withdrawing substituents, are in equilibrium with the isomeric azide.[18-20]

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[14] C. V. Hart, *J. Amer. Chem. Soc.*, **50**, 1922 (1928).

[15] A. Hantzsch, *Chem. Ber.*, **66B**, 1349 (1933).

[16] H. C. Brown and Robert J. Kassal, *J. Org. Chem.*, **32**, 1871 (1967).

[17] J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 1 (1954).

[18] (a) C. Temple, Jr., C. L. Kussner, and J. A. Montgomery, *J. Org. Chem.*, **31**, 2210 (1966); (b) H. Limpricht, *Chem. Ber.*, **21**, 3409 (1888); (c) F. R. Benson in "Heterocyclic Compounds," 1st ed, Vol. 8, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1967, p 65.

[19] J. H. Boyer and E. J. Miller, Jr., *J. Amer. Chem. Soc.*, **81**, 4671 (1959).

[20] J. H. Boyer and W. H. Hyde, *J. Org. Chem.*, **25**, 458 (1960).

Experimental Section[21]

Synthesis and Handling of Cyanogen Azide.—Synthesis and handling variables depend largely on the choice of the solvent for **1**. Solutions of **1** are usually prepared by adding cyanogen chloride or cyanogen bromide to a well-stirred suspension of sodium azide at 0–12° in anhydrous media. Good yields are obtained in either polar or nonpolar media, including acetonitrile, ethyl acetate, methylene chloride, dibutyl phthalate, cyanogen chloride, toluene, benzene, cyclohexane, or pentane. *Careful consideration must be given to the properties of the solvent used for* **1**, *since in some solutions the azide may separate and detonate if low-boiling solvents evaporate, saturated solutions are cooled, or the solvent is frozen.*

With polar media such as acetonitrile or ethyl acetate the exothermic reaction is complete in less than 1 hr after the reaction mixture is brought to room temperature. The solubility of **1** in polar solvents is good, and solutions containing up tp 30% (wt) of **1** in acetonitrile do not detonate on instantaneous exposure to a 250° hot bar or under a 480 kg-cm drop test (6-kg weight dropped 80 cm) and have been used routinely in our laboratory without event. Cyanogen azide is not readily separated from these solvents in normal laboratory manipulations, since the vapor pressures of **1** and these solvents are nearly the same. These solutions, however, should not be cooled below the freezing point of the solvent. Acetonitrile solutions of **1** are toxic when ingested by rats, producing cyanosis and death at a level of less than 72 mg/kg of body weight, but are absorbed only slowly through unbroken skin of rabbits or by inhalation of solution vapors.

In nonpolar media such as aliphatic and aromatic hydrocarbons, the synthesis of **1** requires up to 24 hr at room temperature and good yields are obtained only with activated[22] sodium azide and a 0.5 to 4 molar excess of cyanogen chloride. Cyanogen azide has a limited solubility in nonpolar solvents, and solutions in aliphatic hydrocarbons containing more than 5% (wt) of **1** are not safe to handle; if cooled, **1** may separate from such solutions and detonate.

Cyanogen azide solutions thus prepared contain sodium chloride, cyanogen chloride, and traces of by-products which can be removed or avoided if desired. Excess cyanogen chloride is removed under vacuum (caution[23]) or avoided by using a small excess of sodium azide. The reaction mixture is filtered (caution[24]) under nitrogen pressure to remove sodium chloride and any unreacted sodium azide. *Dry solvents are important to obtain good yields.* Traces of moisture or excess sodium azide lead to by-products **6** and **8**, which may be isolated in subsequent manipulations as shock-sensitive solids. Solutions of essentially pure **1** are obtained nearly quantitatively when cyanogen chloride is used as the sole reaction media. These solutions are dangerous to handle because the cyanogen chloride (bp 12.7°) may evaporate, leaving pure **1**, but this solvent can be readily exchanged for a higher boiling solvent when the reaction is complete.

Pure cyanogen azide is a lachrymator which has been isolated only *in small quantities* from solutions by gas–liquid chromatography and by evaporating the solvent from cyanogen chloride solutions under reduced pressure.

For many purposes, cyanogen azide can be most conveniently and safely prepared *in situ* where it is frequently consumed as formed. This method of synthesis, for example, is particularly useful in preparing alkylidene cyanamides or *N*-cyanoaziridines from olefins,[4] cyanamides from hydrocarbons,[2] and azepines from aromatic compounds.[9]

Cyanogen azide can also be prepared in high yield from cyanogen bromide or cyanogen fluoride and most ionic azides including lithium, potassium, ammonium, and tetraethylammonium zaides, but sodium azide and cyanogen chloride are used routinely in our laboratory.

Cyanogen Azide–Acetonitrile Solution.—A 1-l. flask equipped with a magnetic stirrer, thermometer, condenser, and gas inlet adapter was flame dried and cooled under nitrogen. Sodium azide (65 g, 1.0 mol) and dry acetonitrile (250 ml) were added and the flask, under a positive nitrogen pressure, was cooled in an ice–salt bath. A coolant at −5 to 0° was circulated through the condenser, and cyanogen chloride (82 g, 1.2 mol) was distilled into the flask above the level of the well-agitated sodium azide–acetonitrile slurry at such a rate as to maintain a temperature between 0 and 12°. When addition was complete, the mixture was stirred for 30 min at 0–12°, then warmed to room temperature over 1 hr and stirred for an additional 1 hr. The system was slowly evacuated (caution[23]) through the cooled condenser (−5 to 0°) to a pressure of 120 mm and a pot temperature of 25° to remove excess cyanogen chloride. The solution was filtered under nitrogen pressure and the filter cake (caution[24]) was washed with two 50-ml portions of dry acetonitrile. The combined filtrates (350–375 ml) were stored at −20° in a bottle fitted with a serum stopper. An aliquot (1–2 ml) of the solution was added to trimethyl phosphite at 0° and the yield (98%) was determined by measuring the nitrogen evolved.

Cyanogen Azide–Toluene Solution.—Cyanogen chloride (120 g, 1.95 mol) was added to activated[22] sodium azide (32.5 g, 0.50 mol) suspended in dry toluene (60 ml) at 0–12° as described above. When addition was complete, the mixture was warmed slowly to room temperature (1 hr) and stirred for 20 hr. Dry toluene (100 ml) was added through the condenser and the mixture was evacuated slowly through the cooled (0°) condenser to 120 mm and a pot temperature of 25° (caution[23]). The mixture was filtered and the filter cake (caution[24]) was washed twice with dry toluene (2 × 25 ml). The combined filtrates (190–220 ml) were analyzed (yield 89–92%) and stored as described above at −20°.

Reduction of Cyanogen Azide.—Cyanogen azide prepared from sodium azide (3.25 g, 0.05 mol) and excess cyanogen chloride was dissolved in ether (50 ml) and treated with hydrogen sulfide at 0° for 1.5 hr and at 25° for 40 min. The solution was filtered and the filtrate was evaporated to dryness. The residue was taken up in water (20 ml), warmed on a steam bath, and filtered to remove sulfur. The filtrate was evaporated to dryness and the solid was sublimed (0.1 mm, 75°) to give analytically pure cyanamide, 1.7 g (80%), mp 46–47°, mmp 46–47° (lit.[25] mp 42°), having an infrared spectrum identical with that of an authentic sample.

***N*-Cyanotriphenylphosphine Imide (3).**—Triphenylphosphine (5.2 g, 0.02 mol) in acetonitrile (40 ml) was added slowly to cyanogen azide (0.02 mol) in acetonitrile (30 ml). When nitrogen evolution was essentially complete, acetone (10 ml) was added and the mixture was heated at 40° for 45 min. The mixture was filtered, and the filtrate was concentrated and cooled to separate **3** (5.3 g, 88%) which was recrystallized from acetonitrile, mp 193–195°, $\lambda_{\max}^{\mathrm{KBr}}$ 4.58 (-C≡N), 6.59 μ (C_6H_5P).

Anal. Calcd for $C_{19}H_{15}N_2P$: C, 75.5; H, 5.0; N, 9.3; P, 10.3. Found: C, 75.7, 75.5; H, 5.4, 5.3; N, 9.6, 9.5; P, 10.1.

Trimethyl *N*-Cyanophosphorimidate (4).—Cyanogen azide (0.10 mol) in acetonitrile (40 ml) was added slowly to trimethyl phosphite (12.4 g, 0.10 mol) in ether (200 ml) with cooling at 15°. When nitrogen evolution was complete, volatiles were removed under reduced pressure and the crystalline residue was washed with cold ether to give the pure ylide (13.1 g, 80%), mp 56.4–56.8°, $\lambda_{\max}^{\mathrm{KBr}}$ 4.42, 4.52 μ (-C≡N).

Anal. Calcd for $C_4H_9N_2O_3P$: C, 29.3; H, 5.5 N, 17.1; P, 18.9. Found: C, 29.3, 29.1; H, 5.7, 5.7; N, 17.2, 17.3; P, 18.4.

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(21) Cyanogen chloride was obtained from the American Cyanamid Co. and was stabilized with trisodium phosphate (~7% wt). Eastman Organic Chemicals practical-grade sodium azide of 97–99% purity was used unless otherwise specified. Melting points were determined in a Mel-Temp apparatus and are not corrected.

(22) Activated sodium azide, necessary to give good yields of **1** in nonpolar media, was prepared as follows. Sodium azide (70 g) was dissolved in distilled water (280 ml) and stirred with hydrazine hydrate (10 ml) for 15 min. The solution was filtered and added dropwise to rapidly stirred dry acetone (3 l.). Excess acetone was decanted and the solid was collected in a pressure funnel and washed with dry acetone (100 ml). The fine powder (40–60 g) was dried under vacuum at 50° for 2 hr. Sodium azide is extremely toxic and the fine powder should be handled with care to avoid breathing the dust.

(23) Traces of cyanogen azide codistil with cyanogen chloride and may detonate if the cyanogen chloride evaporates from the condensate. This step can be avoided when cyanogen chloride does not interfere with the intended use. The volatiles are safely collected in a trap containing an acetone solution of a "deactivating" agent such as ethyl vinyl ether, norbornene, or trimethyl phosphite and cooled at −78°. The vacuum tubes are cut near the trap and both are rinsed into the trap with acetone. The trap is allowed to warm to room temperature and when nitrogen evolution ceases, the solution can be discarded with regard only for the toxic cyanogen chloride.

(24) The filter cake contains absorbed cyanogen azide and may detonate if dried. It is safely deactivated by leaching with excess acetone or by washing with acetone and finally a solution of one of the above "deactivators." The acetone extract is collected in a receiver containing one of the "deactivating" reagents. Washings and filter cake are safely discarded when nitrogen evolution ceases.

(25) W. Traube, F. Kegel, and H. E. P. Schulz, *Z. Angew. Chem.*, **39**, 1465 (1926).

Reduction of (Diazidomethylene)cyanamide (8) to Dicyandiamide.—Compound **8** was prepared according to the procedure of Hart;[16] mp 42.1–42.9° (lit.[16] mp 40.3°); $\lambda_{max}^{CHCl_3}$ 4.30 (w), 4.52 (sh), 4.63 (s), 6.25 (s), 7.56 (s), 8.90, 9.04 (m), 9.40 μ (w).

Compound **8** was reduced with hydrogen sulfide[14] to give dicyandiamide (75%), which was identified by melting point (210°), mixture melting point (210°) (lit.[26] mp 207–290°), and comparison of its infrared spectrum with that of an authentic sample.

Sodium 5-Azidotetrazole (6) from Cyanogen Azide and Sodium Azide.—*Caution: Sodium 5-azidotetrazole is exceptionally shock sensitive. See footnote 27 before attempting this synthesis.*

Cyanogen azide prepared in acetonitrile (20 ml) from sodium azide (3.25 g, 0.05 mol) and cyanogen chloride (12 g, 0.22 mol) was evacuated to 120 mm and a pot temperature of 25° to remove excess cyanogen chloride. The resulting solution was cooled at 5–10° while sodium azide (3.5 g, 0.05 mol) in water (15 ml) was added dropwise and then stirred at room temperature for 1.5 hr. The resulting solution was diluted with water (20 ml) and extracted with ether (3 × 25 ml). Sodium 5-azidotetrazole (2.65 g, 80%) was isolated from one-half of the aqueous layer as described below and identified by comparison of its infrared spectrum with that of an authentic sample.

Sodium 5-Azidotetrazole (6) from Cyanogen Bromide and Sodium Azide.—To a solution of sodium azide (3.8 g, 0.058 mol) in water (10 ml) at 0–5° was added (15 min) finely pulverized cyanogen bromide (6.8 g, 0.064 mol). The mixture was stirred at 0–5° for 30 min, and the cold solution was then extracted with ether (2 × 15 ml). The water layer was evaporated to dryness at 50° (1 mm). (*Caution:* The product may detonate if pressure is changed rapidly when the product is dry.) The resulting salt was extracted with hot acetone (3 × 25 ml). The extract was concentrated to about 35 ml and ether was added to precipitate **6** (2.56 g, 66%), λ_{max}^{KBr} 4.67, 6.84, 7.09, 8.15, 13.57 (s), 8.45, 8.86, 12.56 (m), 7.49, 8.96, 9.52, 9.82 μ (w).

Anal. Calcd for CN_7Na: C, 9.03; N, 73.70; Na, 17.28. Found: N, 73.61, 73.86; Na, 16.6.

5-Azidotetrazole.—*Caution: This compound is shock sensitive. See footnote 27 before attempting synthesis.*

An aqueous solution of **6** prepared as described above from sodium azide (7.6 g, 0.117 mol) and cyanogen bromide (6.2 g, 0.058 mol) was cooled in ice water and acidified with concentrated hydrochloric acid to pH 1. The solution was extracted with ether (3 × 50 ml), and the ether layer was dried and evaporated to dryness at room temperature under nitrogen to give 5-azidotetrazole (4.2 g, 65%) as white needles which were recrystallized once from chloroform, mp 79.6–80.2° (lit.[29] mp 72–73°), λ_{max}^{KBr} 3.25–4 (broad weak multiple bands), 4.67, 6.30, 7.08, 8.34 (s), 9.65, 12.76,13.78, 14.43 μ (m).

Anal. Calcd for CN_7H: N, 88.29. Found: N, 88.16.

Ammonium-5-azidotetrazole.—An aqueous solution of **6** prepared as described above from cyanogen bromide (6.2 g, 0.059 mol) and sodium azide (7.6 g, 0.117 mol) was acidified to pH 1 and extracted with ether (3 × 50 ml). The dried ether extract was saturated with anhydrous ammonia and filtered to separate pure ammonium-5-azidotetrazole[28] (caution[27]) as a white, crystalline solid (15 2 g, 95%), mp 185–186, λ_{max}^{KBr} 4.63, 6.77, 7.14 (s), 3.62, 3.19, 3.35, 7.03, 8.09, 8.74, 13.15 (m), 8.41, 9.52, 12.67 μ (w).

Anal. Calcd for CH_4N_8: N, 87.51. Found: N, 87.42.

Registry No.—**1,** 764-05-6; **3,** 4027-82-1; **4,** 17167-30-5; **6,** 35038-45-0: 5-azidotetrazole, 35038-46-1; ammonium-5-azidotetrazole, 35038-47-2.

Acknowledgment.—The phosphorus ylides were prepared and characterized by Dr. M. E. Hermes.

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[26] E. C. Franklin, *J. Amer. Chem. Soc.*, **44**, 501 (1922).

[27] The explosive properties of sodium 5-azidotetrazole are described by E. Lieber and D. R. Levering, *J. Amer. Chem. Soc.*, **73**, 1313 (1951). The *dry salt is extremely sensitive to friction*, heat, electrical shock, and pressure. For example, a dry sample of **6** at 1-mm pressure will usually detonate if brought rapidly to atmospheric pressure. Great care and adequate protective equipment (shields, leather gloves, and jacket) should be used when preparing even small quanties of the *dry* compound. Samples larger than 0.1 g are best handled remotely. The salt can be prepared and handled safely in aqueous solution or as a free-flowing solid when moistened with water or mixed with an equal weight of mineral oil. We have prepared acetone solutions without event, but Lieber reports that such solutions containing traces of acetic acid may detonate and in this respect our procedure is safer.

Pure dry 5-azidotetrazole is less sensitive than its sodium salt but the same handling precautions apply. Ammonium-5-azidotetrazole is still less sensitive to shock but detonates when heated rapidly to ~190°.

[28] F. D. Marsh and D. W. Thatcher, U. S. Patent 3,374,188 (1968).

N-Cyanoaziridines and 1-Alkylalkylidenecyanamides from Cyanogen Azide and Olefins

M. E. Hermes and F. D. Marsh*

Contribution No. 1546 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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The reaction of molecular cyanogen azide with hydrocarbon olefins at 0–35° gives 1-alkylalkylidenecyanamides and/or 1-cyanoaziridines in high yields. Evidence is presented favoring a 1,3-dipolar concerted addition of the azide followed by opening of the resulting triazoline to a diazonium zwitterion and loss of nitrogen from this labile species to yield products. Linear and simple cyclic olefins generally produce alkylidenecyanamides as the major product, often to the exclusion of *N*-cyanoaziridines. With selected cyclic olefins this reaction is an effective means of forming either ring-enlarged or ring-contracted product. Ring-enlargement products and aziridines are also formed by reacting cyclic alkylidenecyanamides with diazomethane. The 1-alkylalkylidenecyanamides are readily hydrolyzed to ketones; the cyanogen azide reaction thus permits facile, low-temperature conversion of olefins to ketones. More highly substituted olefins often produce *N*-cyanoaziridines, and these compounds are obtained in high yield from polycyclic olefins such as norbornene and dicyclopentadiene. The *N*-cyanoaziridine produced from norbornene, 3-cyano-3-azatricyclo[4.2.1.0^{2,4}]octane, is cleaved with $LiAlH_4$ to the parent aziridine, which is readily converted to 7-aminonorbornane (by hydrolysis and dehalogenation) and *syn*-7-aminonorbornene (by hydrolysis and dehydrochlorination).

Since we reported the synthesis of cyanogen azide (N_3CN) in 1964,[1] two broad areas of chemical reactivity for this highly reactive compound have been defined. We disclosed at that time the facile addition of the molecular azide to olefins accompanied by nitrogen loss and formation of alkylidenecyanamides and *N*-cyanoaziridines. The reaction of cyanogen azide with acetylenes was recently reported[2] to give 1-cyanotriazoles which are in equilibrium with tautomeric α-diazo-*N*-cyanoimines. Other reported reactions of molecular

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[1] F. D. Marsh and M. E. Hermes, *J. Amer. Chem. Soc.*, **86**, 4506 (1964); F. D. Marsh, U. S. Patent 3,410,658 (1968).

[2] M. E. Hermes and F. D. Marsh, *J. Amer. Chem. Soc.*, **89**, 4760 (1967); F. D. Marsh, U. S. Patent 3,322,782 (1967).