1-Cyano-1,2,3-triazole–α-Diazo-N-cyanoimine Tautomers from Cyanogen Azide and Acetylenes

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Abstract: Cyanogen azide reacts with acetylene to form a 1:1 adduct, in 77% yield, which is a ring–chain tautomeric mixture of 1-cyano-1,2,3-triazole and α-diazo-N-cyanoethylidenimine. It has been shown by infrared, ultraviolet, and nmr spectra that the equilibrium is temperature and solvent sensitive and both tautomers have been identified in solution by decomposition with hydrochloric acid to 1,2,3-triazole hydrochloride and nitrogen and chloroacetaldehyde, respectively. Methyl- and dimethylacetylenes give similar tautomeric mixtures with cyanogen azide. The cyanogen azide–ethoxyacetylene adduct is formed in 87% yield and exists exclusively as the open-chain ethyl α-diazo-N-cyanoacetimidate. This diazo compound gives ethyl chloroacetate and nitrogen on treatment with HCl and acts as a 1,3-dipole on addition to norbornene and dimethyl acetylenedicarboxylate to give pyrazoline and pyrazole derivatives. Thermochromic and spectral behavior of 1-cyanobenzotriazole, formed from benzotriazole anion and cyanogen chloride in 67% yield, indicates that some ring opening to a diazo-N-cyanoimine may be occurring.

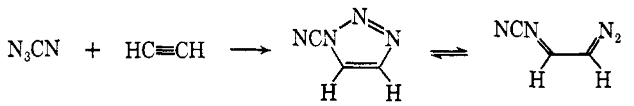
This paper discusses the reaction of acetylenes with cyanogen azide (N_3CN) without loss of nitrogen to form 1-cyano-1,2,3-triazoles which are in equilibrium with α-diazo-N-cyanoimines.

We have reported the preparation of cyanogen azide, its reactions with olefins,[1] and its pyrolysis to form azodicarbonitrile.[2] The reaction of cyanogen azide with cyclooctatetraene[3] and norbornadiene[4] have been described, and the decomposition of the azide to form cyanonitrene which reacts with alkanes[5] and aromatics[6] has been reported.

In general, cyanogen azide reactions carried out above 50° proceed by unimolecular decomposition with loss of nitrogen to an excited singlet cyanonitrene which may or may not form the more stable triplet depending upon reaction conditions,[7,8] followed by attack on the substrate. Below 50°, the azide is usually the reacting species. The acetylene reaction is of this latter type.

Results

Cyanogen azide reacts with acetylene at 45° to give 77% of a 1:1 adduct that is colorless below its melting point (33°) but is yellow in the melt or in solution. The substance (**1**) is a tautomeric composition of 1-cyano-1,2,3-triazole (**1a**) and α-diazo-N-cyanoethylidenimine (**1b**). Evidence for this ring-chain equilibrium is based on infrared and nmr spectral data and chemical transformations.



a b

1

Spectral Evidence for 1a ⇌ 1b. The infrared spectrum of **1** (Table I) is markedly temperature dependent. The spectrum at −10° in KBr has —C≡N absorption at 4.43 μ and only very weak absorption from 4.5 to 7 μ. In contrast, the spectrum at 35° has additional strong absorption at 4.62, 4.70, and 6.40 μ, indicating diazo and >C=N—CN groups are present.[9] The liquid spectrum at 35° resembles the KBr spectrum, and comparison of absorption in the 9–13-μ region of the liquid sample with that region in the spectrum at −10° shows that there is some 1-cyanotriazole present in the liquid state.

Table I. Properties of **1**

Mp, +33°
Infrared (35°, liquid melt): 3.19, 4.43, 4.60, 4.71, 6.40, 7.07, 7.20, 7.65, 7.95, 10.28, 11.10, 12.75 μ
Infrared (35°, KBr wafer): 3.19, 4.43, 4.62, 4.70, 6.40, 7.07, 7.20, 7.63, 7.96, 10.26, 11.10, 12.75 μ
Infrared (−10°, KBr wafer): 3.19, 4.43, 7.04, 7.62, 7.98, 9.54, 10.24, 11.00, 12.45 μ
Ultraviolet: $\lambda_{max}^{CH_2Cl_2}$ . . . 309.5 mμ (ε 1990)
$\lambda_{max}^{CH_3CN}$ 229 mμ (ε 4800); 307 mμ (ε 2280)
$\lambda_{max}^{H_2O}$ 232 mμ (ε 2980); 309 mμ (ε 7120)
Nmr (pure liquid, 35°): τ 1.82 (1 H, doublet, J = 1.7 cps), τ 2.73 (1 H, broad singlet)
Solution, $CDCl_3$: see Figure 1, Table II.

The ultraviolet spectrum of **1** in water, acetonitrile, and dichloromethane (Table I) shows little change in wavelength with solvent variation and the solutions obey Beer's law. However, the extinction coefficient is quite solvent dependent. The shorter wavelength band is less intense in water than in acetonitrile while the long wavelength band becomes more intense from dichlorometh-

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(1) F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).
(2) F. D. Marsh and M. E. Hermes, *ibid.*, **87**, 1948 (1965).
(3) A. G. Anastassiou, *ibid.*, **87**, 5512 (1965).
(4) A. G. Anastassiou, *J. Org. Chem.*, **31**, 1131 (1966).
(5) A. G. Anastassiou, F. D. Marsh, and H. E. Simmons, *J. Am. Chem. Soc.*, **87**, 2296 (1965).
(6) F. D. Marsh and H. E. Simmons, *ibid.*, **87**, 3529 (1965).
(7) G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, **42**, 3755 (1965).
(8) A. G. Anastassiou, *J. Am. Chem. Soc.*, **89**, 3184 (1967).
(9) The 4.43-μ band at the higher temperature does not decrease in intensity, which indicates that this band arises from nitrile in both compounds. Thus, it appears that diazo absorbs as a doublet at 4.62 and 4.70 μ. The 6.4-μ band at 35°, the strongest band in the spectrum, is also characteristic of the C=N bond in alkylidene cyanamides prepared from olefins and N_3CN.

ane to acetonitrile to water presumably as the open-chain form predominates in solution in the more polar solvents.[10]

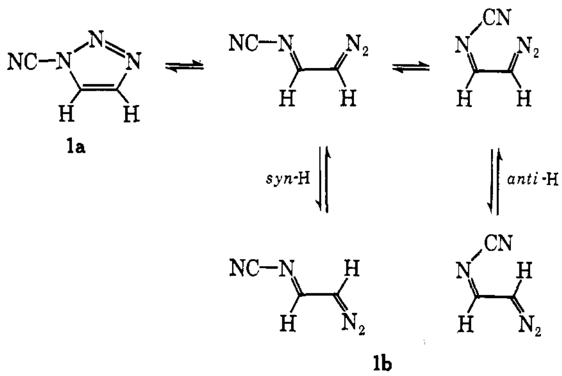
Complex changes in the nmr spectra occur with temperature (Figure 1, Table II). The neat liquid spectrum consists of two areas of absorption each representing one proton. At τ 1.82 a sharp doublet (J = 1.7 cps) and at τ 2.73 a broad single peak are observed. At −60° in $CDCl_3$ two sharp doublets are observed of equal weight with $J = \sim 1.5$ cps at τ 1.60 and 2.02. On warming, the lower field peak becomes somewhat broader, with increasing temperature, but remains a doublet with slightly greater separation (~2.2 cps). The position of this resonance remains essentially constant throughout. The higher field resonance undergoes remarkable changes. On warming of the solution from −60 to +80°, this peak moves upfield with successive broadening, sharpening, and broadening.

Table II. Chemical Shift of Proton Resonance of **1** in $CDCl_3$

Temp, °C	Low field, τ	High field, τ
−60[a]	1.60	2.02
−40	1.47	2.06
−10	1.47	2.08
20	1.44	2.19
50	1.38	2.21
80	1.38	2.36

[a] 5% in $CDCl_3$. All others are 20% in $CDCl_3$.

A possible interpretation of these results involves not only the ring-chain tautomerism **1a** ⇌ **1b** but also the *syn-anti* relationship of the —HC═N—CN group and the *cis-trans* orientation of the diazo and N-cyanoimine group of **1b**.



Since the absorption intensities remain 1:1 throughout the temperature range, it is probably correct to assign each absorption to a specific proton. Thus the low-field absorption is believed to be the C_5–H of the triazole and, coincidently, the —HC═NCN of the open-chain form. The chemical shift of the C_4– and C_5–H's of 12 1-substituted 1,2,3-triazoles has been found to vary between τ 1.8 and 2.8[11] with $J \cong 1$ cps. Thus one may presume that the −60° spectrum fairly represents **1a**.

As the temperature rises, the rate of **1a** ⇌ **1b** increases and, as has been shown by infrared, the proportion of **1b** is also higher. At −10° in solution, we observe broadening and upfield displacement of the higher field peak as averaging of the C_4–H of **1a** and the methine CH of **1b** occurs. A large shift might be expected since Kaplan and Meloy[12] found the methine CH absorption of the *cis* form of diazoacetaldehyde at τ 4.3. It is clear that this resonance of pure **1b** does not approach that value. The broad resonance at this point indicates the rate of **1a** ⇌ **1b** is still slow compared to the chemical shift between the high-field protons of the two forms. Further increase in temperature to +20° sharpens the high-field resonance and moves it to still higher field, indicating that the **1a** ⇌ **1b** rate is fast enough so that the time-averaged resonance line of **1a** and **1b** is approached.

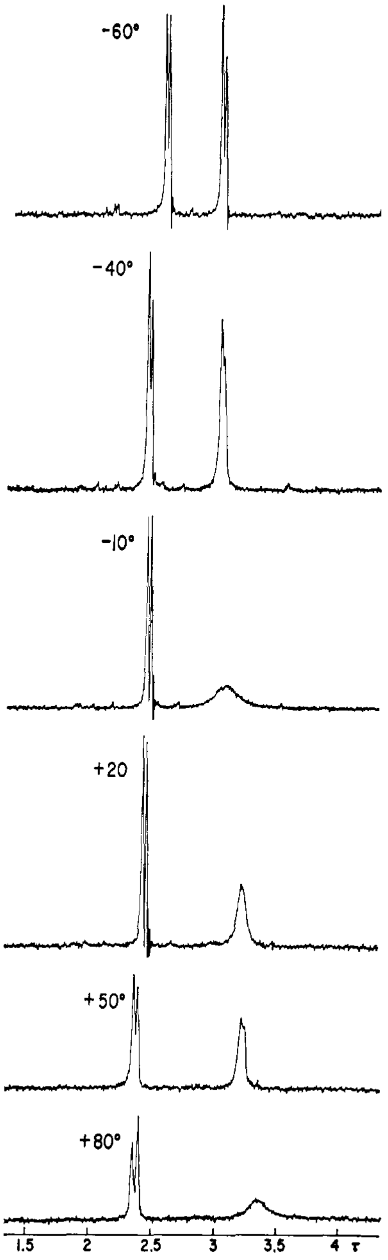


Figure 1. Nmr spectra of the cyanogen azide–acetylene adduct at 60 Mc.

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[10] The ultraviolet spectrum of **1** does not resemble that of α-diazobutyraldehyde, prepared by J. Kučera and Z. Arnold, *Tetrahedron Letters*, 1109 (1966); λ_{max} 249 mμ (ϵ 10,000), 284 mμ (ϵ 6450), and 383 mμ (ϵ 32).

[11] R. A. Clement, personal communication.

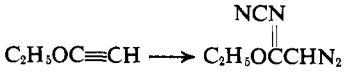
[12] F. Kaplan and G. K. Meloy, *J. Am. Chem. Soc.*, **88**, 950 (1966), discuss the *cis–trans* relationships of α-diazoacetaldehyde and α-diazo ketones.

At this point, let us consider evidence bearing on the possible configurations of **1b**. Isomerization of the cyano group of N-cyanoimines has been observed in isopropylidene cyanamide, prepared from N_3CN and propylene.[13] At 35° the compound has two sharp resonance lines, σ = 0.11 ppm. As the sample, is warmed to 80°, the lines coalesce to a single broad resonance. It is likely that this phenomenon would be observed under the conditions in which **1** was studied. Kaplan and Meloy[12] have shown that α-diazoacetaldehyde and several α-diazo ketones and α-diazo esters exist at equilibrium with carbonyl and diazo groups in both *cis* and *trans* configuration. Rotation in these compounds is somewhat hindered so that at low temperatures the rate is slow enough to permit determination of the isomer ratios by nmr spectroscopy. It was found that diazo ketones prefer the *cis* configuration, the *cis* and *trans* forms of diazoesters are present in nearly equal amounts, and α-diazoacetaldehyde is 70% *cis*, 30% *trans* at these temperatures. The conclusion was drawn that steric interactions between the diazo group and alkyl group attached to carbonyl are important in determining the *cis–trans* ratio.

At +50 and +80°, the high-field resonance line of **1** broadens again and moves upfield. We attribute this shift to an increased rate of **1b** *syn*-H $\rightleftharpoons$ **1b** *anti*-H so that appreciable **1b** *anti*-H is present along with **1a** and **1b** *syn*-H. The equilibrium configuration of **1b** *anti*-H is expected to be primarily *trans* on steric grounds as compared to primarily *cis* for **1b** *syn*-H. This expectation is supported by two observations. The fact that the resonance moves further upfield indicates that the *trans* form is becoming important since Kaplan and Meloy[12] found that the *trans* form of all the α-diazocarbonyl compounds which they studied had methine absorption at 0.2–0.5 ppm higher field than the *cis* form. In addition, the slight change in the low-field resonance, which becomes slightly more broad and has a splitting of 2.2 cps compared to 1.5 cps at lower temperature, indicates the presence of the *trans* form in equilibrium with the *cis*. At all temperatures, if we assume as we have that the low-field resonance is C_5–H with coincident absorption, splitting of the low-field resonance will be a weighted average of the forms present. This splitting remains at 1.5–1.7 cps until, near 80°, it opens to ~2.2 cps. Since the *trans* form of **1b** is expected to have a much larger J_{H-H} than the *cis* form (J_{H-H} *trans* for α-diazoacetaldehyde = 7.5 cps; J_{cis} = 0.3 cps, $J_{av(70°)}$ = 2.2 cps), we expect the average splitting of the hydrogen to increase with *trans* **1b** content.

Other Cyanogen Azide–Acetylene Adducts. The cyanogen azide adducts of propyne-1, butyne-2, and hexyne-1 have been prepared and show similar spectral features that indicate the triazole–α-diazo-N-cyanoimine tautomerism is present.

The reaction of ethoxyacetylene with cyanogen azide gives ethyl α-diazo-N-cyanoacetimidate (**2**) which appears not to be in equilibrium with the triazole.[14] This material has infrared absorption at 4.55, 4.70, and 6.35 μ and nmr absorption in CD_3CN at τ 4.63 for —CH=N₂



$$C_2H_5OC{\equiv}CH \longrightarrow C_2H_5O\overset{\overset{\displaystyle NCN}{\|}}{C}CHN_2$$

2

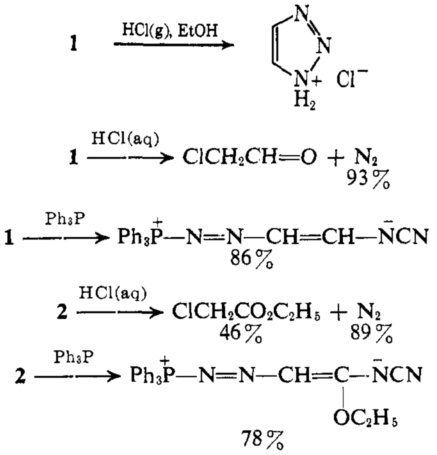
with OC_2H_5 absorption centered at τ 7.63 and 9.00.[15] Neither the infrared nor the nmr spectra are temperature dependent.

The ultraviolet spectrum of **2** resembles that of ethyl diazoacetate: λ_{max} 277 mμ (ϵ 20,300) and 362 mμ (ϵ 55).[16]

Chemistry of the Acetylene Adducts. Perhaps the best evidence for the isomeric structures of **1** and the open-chain compound **2** is provided by hydrolysis experiments. Ethanol solutions of **1** are yellow; however, on passage of HCl gas into the solution, the color is immediately lost and pure 1,2,3-triazole hydrochloride is obtained in 32% yield. It is not known whether this reaction proceeds by rapid ethanolysis of the triazole component or by a rapid shift of **1b** $\rightleftharpoons$ **1a** followed by slow ethanolysis. On addition of **1** to concentrated hydrochloric acid at room temperature, 93% of 1 mole of nitrogen is obtained in 2 hr and chloroacetaldehyde is obtained from the solution.

Reaction of **2** with HCl is more rapid. At room temperature in concentrated HCl after 20 min, 89% of 1 mole of nitrogen is liberated and 46% of ethyl chloroacetate is obtained from the solution.

Both **1** and **2** react with triphenylphosphine without loss of nitrogen to give phosphazine derivatives in high yield.



Cycloaddition reactions of **2** have been demonstrated with bicyclo[2.2.1]heptene and dimethyl acetylenedicarboxylate. For comparison, the cycloadducts of ethyl diazoacetate (**3**) were also prepared with the above dipolarophiles.[17]

Both **2** and **3** react slowly with bicyclo[2.2.1]heptene in tetrahydrofuran at 65°. After 5 days a 41% yield of crystalline **4a** is obtained from **2**. This compound shows NH absorption (3.00 μ) and two sharp C=N absorption bands at 6.26 and 6.60 μ. Coupled with ultraviolet absorption at 342 mμ (ϵ 13,700), the infrared

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(13) M. E. Hermes and F. D. Marsh, *J. Am. Chem. Soc.*, in press.

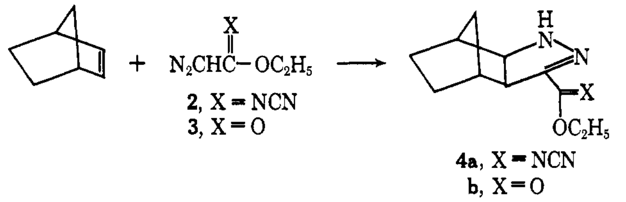
(14) A similar result from ethoxyacetylene and benzenesulfonyl azide was achieved by P. Grünager and P. Vita Finzi, *Tetrahedron Letters*, 1839 (1963), and P. Grünager, P. V. Finzi, and C. Scotti, *Chem. Ber.*, **98**, 623 (1965).

(15) Reference 12 reports the methine proton in ethyl diazoacetate at τ 5.17.

(16) A. E. Gilman and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Ltd., London, 1958, p 63, report λ_{max}^{EtOH} 249 mμ (ϵ 10,050), 377.5 mμ (ϵ 16).

(17) Surprisingly, the uncatalyzed addition of ethyl diazoacetate to dimethyl acetylenedicarboxylate and norbornene has not been reported. R. R. Sauers and P. E. Sonnet, *Tetrahedron Letters*, 1029 (1964), report the CuCN-catalyzed addition to bicyclo[2.2.1]heptene with nitrogen loss.

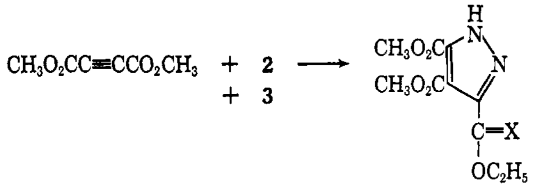
data indicate that **4a** has the conjugated pyrazoline structure shown. Similarly, **3** gives ~50% of **4b**, a high-boiling liquid, after 6 days of reflux in tetrahydrofuran. The infrared spectrum of **4b** shows strong NH absorption at 3.00 μ and C=O and C=N absorptions at 5.90 and 6.22 μ, respectively. Compound **4b** has ultraviolet absorption at 306 mμ (ε 6300).



2, X = NCN
3, X = O

4a, X = NCN
b, X = O

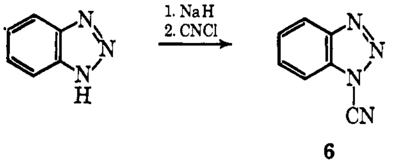
The additions of **2** and **3** to dimethyl acetylenedicarboxylate are somewhat faster than to bicyclo[2.2.1]-heptene. A 76% yield of pyrazole **5a** is formed from **2** in 16 hr at 65° and 75% of **5b** is formed in 1 hr from **3**. Both **5a** and **5b** have broad NH absorption near 3.2 μ and carbonyl stretching at 5.70 and 5.80 μ. The nitrile stretching frequency of **5a** is at 4.50 μ. The C=N frequency of the N-cyanoimine is at 6.10 μ and indicates a lack of conjugation with the pyrazole ring since this band is found at 6.25–6.40 μ in **1b**, **2**, and **4a**. Both **5a** and **5b** show pyrazole C=N absorption as a weak band at 6.35 μ.



5a, X = NCN
5b, X = O

The ultraviolet spectra of **5a** and **5b** confirm the lack of conjugation with the ring; **5b** shows end absorption only while **5a** has $\lambda_{\max}^{\mathrm{EtOH}}$ 215 mμ (ε 22,600) with a shoulder at $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (ε 10,020).

1-Cyanobenzotriazole. The evidence for ring–chain tautomerism of 1-cyano-1,2,3-triazole prompted synthesis of the benzo analog. The reaction of cyanogen azide with benzyne produced from amyl nitrite and anthranilic acid[18] produced very little of the desired triazole; however, 1-cyanobenzotriazole (**6**) was readily prepared by reaction of benzotriazole anion with cyanogen chloride. Triazole **6** is a colorless crystalline material with —C≡N absorption of 4.45 μ. The nmr spectrum shows that **6** is not the symmetrical 2-cyano compound. Ultraviolet absorption is found at $\lambda_{\max}^{\mathrm{EtOH}}$ 253 mμ (ε 6620) and 293 mμ (ε 3300), and there is a weak band at 435 mμ which is not present in cyclohexane solution. In solution in polar solvents or on melting (mp 73–75°), **6** shows reversible thermochromic behavior. Methanol solutions of **6** are light yellow, and the color becomes more intense on heating. The melt of **6** is deep yellow but the color disappears on crystallization.



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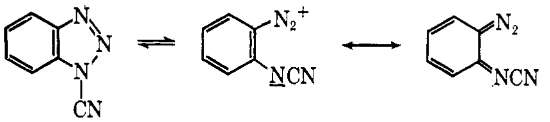
No other spectral or chemical evidence has been obtained to indicate that color formation might be due to ring opening to the diazo-N-cyanoimine. Nevertheless, this remains an intriguing explanation for the observed color changes.



Experimental Section

Warning. Cyanogen azide is a hazardous material. It should be handled only in solution. Concentration of the pure material will lead to violent detonation by heat or shock.

1-Cyanotriazole ⇌ α-Diazo-N-cyanoacetaldehyde Imine (1). An 80-ml Hastelloy pressure tube was charged with 6.5 g (0.10 mole) of sodium azide and 40 ml of acetonitrie. The tube was cooled to −80° and 12 g (0.20 mole) of cyanogen chloride and 10 g (0.40 mole) of acetylene were added. The materials were heated with shaking 12 hr at 45°. The resulting mixture was filtered to remove salts, treated for 10 min at 25° with decolorizing charcoal, and filtered through a bed of Celite. After removal of the acetonitrile at 25° (15 mm) on a rotating evaporator, 7.2 g (77%) of nearly pure **1** remained as a yellow oil. Infrared examination showed only a trace of cyanogen azide (band at 8.0 μ). Sublimation at 20° (0.5 mm) gave pure, crystalline **1**, mp 33°. Spectral data are collected in Table I.

Anal. Calcd for $C_3H_2N_4$: C, 38.3; H, 2.1; N, 59.6. Found: C, 38.4; H, 2.4; N, 59.3.

Methyl-1-cyano-1,2,3-triazole and Isomers. A mixture of 6.5 g (0.10 mole) of sodium azide, 40 ml of acetonitrile, and 12 g (0.30 mole) of propyne was sealed in an 80-ml Hastelloy-lined pressure tube and cooled, and 12 g (0.20 mole) of cyanogen chloride was added. After 20 hr at 45°, the contents were filtered to remove salts, and the solution was treated with decolorizing charcoal and filtered through Celite. Distillation through a short-path molecular-type still gave 6 5 g (60%) of a mixture of 4- and 5-methyl-1-cyano-1,2,3-triazole in equilibrium with open-chain diazo forms, bp 63–72° (pot temperature) (0.5 mm), $n^{25}\mathrm{D}$ 1.5142–1.5260.

Anal. Calcd for $C_4H_4N_4$: C, 44.4; H, 3.7; N, 51.9. Found: C, 45.1; H, 4.1; N, 52.0.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{liquid}}$ 4.45, 4.62, 4.76, and 6.50 μ, nmr (neat) τ 2.08 (four lines, J = 1 cps, 0.27 H), 3.36 (broad, 0.73 H), and 7.86 and 7.96 (J = 1 cps, 3 H). The relative weights of the methine peaks show that the methyl group is located 73% at C_5 and 27% at C_4.

4,5-Dimethyl-1-cyano-1,2,3-triazole and Isomer. To a mixture of 8.8 g (0.135 mole) of sodium azide in 35 ml of acetonitrile in an 80-ml Hastelloy-lined tube was added 16 g (0.25 mole) of cyanogen chloride and 14.5 g (0.27 mole) of 2-butyne. After shaking 20 hr at 45°, the contents were filtered and the solvents and excess cyanogen azide removed *without condensation* on a rotating evaporator at room temperature using water-pump vacuum. The residue was distilled through a short-path still at a pot temperature of 50–65° (0.4 mm). The product crystallized on the −15° condenser. A total of 2.2 g (13%) of 4,5-dimethyl-1-cyano-1,2,3-triazole in equilibrium with 2-diazo-1-methylpropylidene cyanamide was obtained.

Anal. Calcd for $C_5H_6N_4$: C, 49.1; H, 5.0; N, 44.9. Found: C, 48.9; H, 5.3; N, 43.6.

The infrared spectrum showed $\lambda_{\max}^{\mathrm{liquid}}$ 4.46, 4.56, 4.68, 6.18, and 6.26 μ; nmr: τ 7.82 and 7.98.

Ethyl α-Diazo-N-cyanoiminoacetate (2). A solution of 15 g (0.2 mole) of ethoxyacetylene in 20 ml of carbon tetrachloride was added to 0.1 mole of cyanogen azide in 36 ml of carbon tetrachloride. After 2 hr at 40°, no cyanogen azide remained as determined by gas chromatography. On evaporation of the solvent, 12 g (87%) of crude **2** was obtained. Recrystallization from a mixture of 70 ml of carbon tetrachloride and 100 ml of petroleum ether gave 8.6 g (60%) of pure **2**, mp 49.5–52°.

Anal. Calcd for $C_5H_6N_4O$: C, 43.5; H, 4.4; N, 40.6. Found: C, 43.6; H, 4.5; N, 40.6.

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[18] L. Friedman and F. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

Table III. Reaction of **2** and **3** with Norbornene and Dimethyl Acetylenedicarboxylate

Reactants	Reaction time, hr	Yield, %	Mp, °C	Calcd, %			Found, %			Infrared, μ	Nmr, τ	Ultraviolet, mμ (ε)
				C	H	N	C	H	N			
2 + norbornene	120	41	204–207[a]	62.0	6.9	24.1	62.3	6.4	24.0	3.45 4.55 6.25 6.60	1.9 (1 H) NH 5.7 (3 H) 6.7 (1 H) 7.5 (2 H) 1.2 (9 H)	342 (13,700)
3 + norbornene	144	~50	Oil	63.5	7.7	13.4	63.1	7.4	11.7[b]	3.0 5.90 6.46	...	306 (6300)
2 + $CH_3O_2CC{\equiv}CCO_2CH_3$	15	76	172–175[c]	47.1	4.3	20.0	47.0	4.3	19.9	3.3 4.50 5.70 5.77 6.10 6.34	5.6 (1 H) NH 5.7 (2 H) CH_2 6.2 (6 H) CH_3O 8.8 (3 H) CH_3	215 (22,600) 250 (sh) (10,000)
3 + $CH_3O_2CC{\equiv}CCO_2CH_3$	1	75	93–96[d]	47.0	4.7	10.9	46.0	4.8	10.7	3.1 5.70 5.80 6.34	−2.3 (1 H) NH 5.6 (2 H) CH_2 6.1 (1 H) CH_3O 8.6 (3 H) CH_3	End absorption only

[a] Recrystallized 0.5 g from 20 ml of CH_3CN. [b] Contains some unreacted **3**. [c] Recrystallized 2.0 g from 20 ml of CH_3OH. [d] Recrystallized from CCl_4.

Triazole Hydrochloride from 1. Hydrogen chloride was passed into a solution of 1.60 g (0.017 mole) of **1** in ethanol. An immediate reaction gave a colorless solution. Evaporation of the solvent gave 2.1 g of hygroscopic crystals which gave 0.55 g of triazole hydrochloride on crystallization from acetone [32%, mp 142–145° (lit.[19] 142°)].

Anal. Calcd for $C_3H_4N_3Cl$: C, 22.8; H, 3.8; N, 39.8. Found: C, 23.2; H, 4.0; N, 39.2.

Chloroacetaldehyde from 1. To 15 ml of concentrated hydrochloric acid was added 2.0 g (0.021 mole) of **1**. After 2 hr at 25°, 500 ml (93%) of nitrogen had evolved. Continuous extraction of the water solution for 16 hr with ether extracted chloroacetaldehyde with gas chromatography retention time identical with that of an authentic sample. The chloroacetaldehyde gave an impure 2,4-dinitrophenylhydrazone derivative, mp 157.5–160°.

Anal. Calcd for $C_8H_7ClN_4O_4$: C, 37.2; H, 2.7. Found: C, 37.9; H, 3.1.

Ethyl Chloroacetate from 2. Treatment of 1.84 g (0.013 mole) of **2** with 20 ml of 2 *N* hydrochloric acid for 20 min gave 300 ml (89%) of nitrogen and a colorless solution. The solution was extracted twice with ether. The ether was dried and evaporated to give 0.80 g (46%) of ethyl chloroacetate with infrared and nmr spectra and gas chromatographic retention time essentially identical with those of authentic material.

Triphenylphosphine and 1. Mixture of 0.88 g (9.4 mmoles) of **1** and 2.6 g (9.9 mmoles) of triphenylphosphine in 125 ml of ether caused separation of a yellow crystalline adduct without nitrogen evolution. A total of 3.05 g (86%) of [(2-cyanamidovinyl)azo]triphenylphosphonium hydroxide inner salt was obtained, mp 114–115° dec.

Anal. Calcd for $C_{21}H_{17}N_4P$: C, 70.4; H, 4.8; N, 15.7. Found: C, 70.8; H, 5.2; N, 15.4.

The spectra showed λ_{max}^{Nujol} 4.60; $\lambda_{max}^{CH_3CN}$ 260 mμ (ε 6100) and 368 mμ (ε 26,800).

Triphenylphosphine and 2. Reaction of an ether solution of 0.69 g (5 mmoles) of **2** and 1.31 g (5 mmoles) of triphenylphosphine gave 1.55 g (78%) of [(2-cyanamido-2-ethoxyvinyl)azo]triphenylphosphonium hydroxide inner salt, mp 130–132°.

Anal. Calcd for $C_{23}H_{21}N_4OP$: C, 69.2; H, 5.3; N, 14.0. Found: C, 69.1; H, 5.4; N, 13.7.

The ultraviolet spectrum showed $\lambda_{max}^{CH_3CN}$ 268 mμ (ε 5600) and 343 mμ (ε 18,800).

Cycloadducts of 2 and 3 with Norbornene and Dimethyl Acetylenedicarboxylate. Ten millimoles of each reactant were mixed, diluted to 50 ml in tetrahydrofuran, and refluxed, with the results shown in Table III.

1-Cyanobenzo-1,2,3-triazole. A solution of 23.8 g (0.20 mole) of benzotriazole in tetrahydrofuran was added to 9 g of 53.5% sodium hydride in mineral oil (0.2 mole) in 150 ml of tetrahydrofuran. The solution was stirred for 1 hr, then cyanogen chloride (16 g, 0.27 mole) was added over 15 min. The temperature was kept below 40° with cooling.

After 1 hr the solution was filtered and the solvent evaporated to give a partially crystalline oil which was sublimed at 75° (2 μ) to give 19.3 g (67%) of 1-cyanobenzo-1,2,3-triazole, mp 73–75°.

Anal. Calcd for $C_7H_4N_4$: C, 58.3; H, 2.8; N, 38.9. Found: C, 58.4; H, 3.0; N, 39.4.

The ultraviolet spectra showed λ_{max}^{EtOH} 253 mμ (ε 6620), 293 mμ (ε 3300), and 435 mμ (ε 3.5); $\lambda_{max}^{cyclohexane}$ 249 mμ (ε 7450), 258 mμ (ε 5630), and 293 mμ (ε 3570). The nmr spectrum indicates the presence of little or no 2-cyanobenzo-2,1,3-triazole.

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(19) R. Huttel and G. Wetzel, *Ann.*, **593**, 207 (1955).