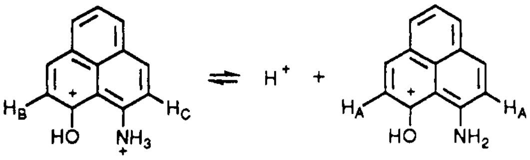
$$k = \frac{\ln 2}{\tau_1} + \frac{\ln 2}{\tau_2} + \frac{\ln 2}{\tau_3} + \ldots \quad (1)$$

But $\tau = k/\ln 2$. Therefore

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + \ldots \quad (2)$$

Appendix 4

For ion **6c**, the question arises as to whether the rates of exchange at H_1 (H_B) and H_9 (H_C) as measured in the nitrogen-protonated dication correspond to the rates of exchange at the same positions in the monocation. The problem arises because H_1 and H_9 (H_A) in the monocation have identical chemical shifts. It follows that the exchange at H_A, H_B, and H_C is governed by the equations



$$H_B = H_{B_0}e^{-k_Bt} \quad (1)$$

$$H_C = H_{C_0}e^{-k_Ct} \quad (2)$$

$$\text{and} \quad H_A = H_B + H_C = H_{B_0}e^{-k_Bt} + H_{C_0}e^{-k_Ct} \quad (3)$$

But $H_{C_0} = H_{B_0}$ and $H_{A_0} = 2\ H_{B_0}$, therefore

$$H_A = \frac{H_{A_0}}{2}\,(e^{-k_Bt} + e^{-k_Ct}) \quad (4)$$

Experiments showed $k_B = \ln 2/6.5d = 0.11d^{-1}$ and $k_C = \ln 2/0.25d = 2.8d^{-1}$. Thus,

$$H_A = \frac{H_{A_0}}{2}\,(e^{-0.11t} + e^{-2.8t}) \quad (5)$$

But $H_A = {}^1/_2H_{A_0}$ when $t = \tau_{1/2}$.

$$\text{Therefore, } \tfrac{1}{2}H_{A_0} = \tfrac{1}{2}H_{A_0}(e^{-0.11\tau_{1/2}} + e^{-2.8\tau_{1/2}}) \quad (6)$$

This equation is true when $\tau_{1/2} = 0.87$ days. This is in reasonable agreement with the experimental value of 1.2 days.

Photochemical Cycloaddition Reactions of Cyanoacetylene and Dicyanoacetylene

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Received January 31, 1990

Photolysis of cyanoacetylene with 185- or 206-nm light yields 1,3,5-tricyanobenzene while 254-nm radiation yields a mixture of tetracyanocyclooctatetraenes, 1,2,4- and 1,3,5-tricyanobenzene. A polymer of cyanoacetylene is the major photoproduct. 1,3,5-Tricarbomethoxybenzene was the only photoproduct identified from the irradiation of methyl propiolate at 254 nm. Mono-, di-, and tricyanobenzenes are formed by irradiation of mixtures of acetylene and cyanoacetylene at 185, 206, and 254 nm along with trace amounts of cyclooctatetraenes. No photoadducts were detected on photolysis of mixtures of cyanoacetylene and CO or HCN. The tetracyanocyclooctatetraene structures were established by UV, MS, and NMR analyses. The ^{1}H NMR of the product mixture exhibited a singlet at δ 7.028 consistent with either **1** or **2** and two singlets at δ 6.85 and 6.91 assigned to **3**. Photolysis of mixtures of dicyanoacetylene and acetylene with either 185- or 206-nm light yielded 1,2-dicyanobenzene and (*E,Z*)-1-buten-3-yne-1,4-dicarbonitrile. These products were also obtained using 254-nm light along with a mixture of tetracyanocyclooctatetraenes. The same three singlets were observed in this product mixture as were observed in the tetracyanocyclooctatetraenes obtained from cyanoacetylene. From this observation it was concluded that the δ 7.02 signal is due to **2** and not **1**. The photolysis of cyanoacetylene and dicyanoacetylene in the presence of ethylene with 185-nm light yields 1-cyanocyclobutene and 1,2-dicyanocyclobutene, respectively. 2-Cyanobutadiene and 2,3-dicyanobutadiene are the photoproducts with 254-nm light. Reaction pathways are proposed to explain these findings.

Cyanoacetylene and dicyanoacetylene have a central role in many cosmochemical processes as indicated by their presence in the interstellar medium,[1] the atmosphere of Titan,[2,3] and the proposed role of cyanoacetylene in the formation of pyrimidines and some amino acids on the primitive Earth.[4-6] Cyanoacetylene and dicyanoacetylene are subjected to ultraviolet radiation in each of these environments, which may result in their conversion to more complex organic compounds. The layer of particulates in the atmosphere of Titan is probably due to the photolysis of aerosols which contain cyanocarbon compounds mixed with hydrocarbons such as acetylene and ethylene.[7,8] Photolysis of these aerosols may yield higher molecular weight compounds and polymers. One of the photochemical reactions of cyanoacetylene is dissociation to radicals with light of 193 nm (eqs 1, 2).[9] Some of these radicals may initiate the reaction of methane on Titan (eqs 3, 4).[10]

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Since there have been very few studies of the photochemistry of cyanoacetylene and dicyanoacetylene, we undertook an investigation of their photolysis as the first step in gaining insight into which light-initiated transformations may be important on Titan and the other environments where they are found in our galaxy.

$$\mathrm{HC{\equiv}CCN} \xrightarrow{h\nu} \mathrm{H^{\bullet}} + {}^{\bullet}\mathrm{C{\equiv}CCN} \tag{1}$$

$$\mathrm{HC{\equiv}CCN} \xrightarrow{h\nu} \mathrm{HC{\equiv}C^{\bullet}} + {}^{\bullet}\mathrm{CN} \tag{2}$$

$${}^{\bullet}\mathrm{CN} + \mathrm{CH_4} \rightarrow \mathrm{HCN} + {}^{\bullet}\mathrm{CH_3} \tag{3}$$

$${}^{\bullet}\mathrm{C{\equiv}CCN} + \mathrm{CH_4} \rightarrow \mathrm{HC{\equiv}CCN} + {}^{\bullet}\mathrm{CH_3} \tag{4}$$

Experimental Section

General. UV spectra were measured on a Varian Cary 219 spectrophotometer, ^{1}H NMR on a Varian XL-200 spectrometer, GC on a Hewlett-Packard 5987A instrument using a 30 m × 0.252 mm fused silica J and W DB-5 capillary column with nitrogen as the carrier gas; MS and GC–MS were performed on a Hewlett-Packard 5987A instrument.

Molecular Mechanics. Calculations on the tetracyanocyclooctatraenes were performed on the PC MODEL program from Serena Software, Bloomington, IN. In every case the skew structure was lower energy, a finding consistent with experimental findings for other substituted cyclooctatetraenes.[11]

Materials. Cyanoacetylene and dicyanoacetylene were prepared by the procedure of Moureu and Bongrand[12] as modified by Miller and Lemmon.[13] Acetylene (Matheson, purified, 99.6%) was separated from acetone by bubbling first through concentrated sodium bisulfite and second through concentrated sodium hydroxide, and then it was dried by passing over anhydrous calcium chloride. It was then distilled at 178 K, condensed at 77 K, and stored on a vacuum line.[14] HCN was prepared by the reaction of aqueous NaCN and H_2SO_4. The HCN was distilled through anhydrous $CaCl_2$ and condensed in an ice–salt bath. Carbon monoxide (Matheson, 99.5‰) was trapped at 77 K and then distilled three times at a bath temperature of 93 K. Gaseous mixtures were prepared on a vacuum line using a Baratron Type 270B signal conditioner and a 370 HA-1000 gauge.

Photochemistry. The photolyses were performed using a low-pressure mercury lamp with principal emissions at 184.9 (185) and 253.7 (254) nm. Light of 254 nm was obtained by use of a Vycor filter to absorb the 185-nm light emitted from the low-pressure mercury lamp. An iodine discharge lamp was used with a water filter to obtain 206.2 (206) nm light.[15] Photolyses were performed in 10 × 2.8 cm cylindrical quartz cells of volume about 50 cm^3. At the end of the photolysis the residue was extracted into CH_2Cl_2 or $CDCl_3$, and the products were analyzed directly by ^{1}H NMR spectroscopy. The limit of detection was a yield of 0.01%. The products of reactions performed using 254-nm light were also fractionally sublimed by heating at 0.1 Torr from 25 to 200 °C in an oil bath. Two rings of sublimate were observed with the upper tricyanobenzene and the lower tetracyanocyclooctatetraene derivatives. The absorption coefficients of each reactant gas at 185, 206, and 254 nm in cm^{-1} atm^{-1} are, respectively: cyanoacetylene, 15, 16, and unknown;[16] acetylene, 11, 0.4, and 0;[17] dicyanoacetylene, 10,[18] 4.6, and 1.6; HCN, 0.5, 0, and 0;[19] carbon monoxide, ~0, 0.03, and 0.[20] Solution-phase photolyses were performed in Supracil tubes in a Rayonet photochemical reactor.

Photolysis of Benzene and Cyanoacetylene. A mixture of 30 Torr of benzene and 30 Torr of cyanoacetylene was photolyzed with 254-nm light for 10 h, and the reaction mixture was dissolved in $CDCl_3$. A broad multiplet was observed at δ 5.8–5.9, characteristic of cyanocyclooctatetraene.[21]

Attempted Photochemical Addition Reactions of Cyanoacetylene and Dicyanoacetylene. A 2-mg sample of 1,3,5-tricyanobenzene was dissolved in 0.5 mL of CH_2Cl_2 and added to a quartz photolysis cell. The CH_2Cl_2 was evaporated from the cell to give a uniform coating of the tricyanobenzene on every side of the cell except the one next to the UV lamp. The cell was then evacuated for 30 min at 0.1 Torr to remove residual CH_2Cl_2. Then 50 Torr of cyanoacetylene was added, and the mixture was photolyzed at 254 nm for 20 h. The reaction products were analyzed by ^{1}H NMR spectroscopy after dissolution in $CDCl_3$. No increase was observed in the peaks ascribed to tetracyanocyclooctatetraene. Similar results were obtained when 1,2,4-tricyanobenzene and 1-butene-3-yne-1,4-dicarbonitrile (**6**) were photolyzed in the presence of cyanoacetylene. The CH_2Cl_2 was evaporated for only 5–10 min when 1-butene-3-yne-1,4-dicarbonitrile was irradiated because of its greater volatility. No new products, other than those formed by photolysis of dicyanoacetylene or cyanoacetylene alone, were observed from the photolyses of dicyanoacetylene with 1,4-dicyanobenzene or cyanoacetylene.

Syntheses of (*E*)-1-Buten-3-yne-1,4-dicarbonitrile (6). To a solution of dimethyl (*E*)-1-buten-3-yne-1,4-dicarboxylate[22] (336 mg, 2 mmol) in 40 mL of dry benzene was added 18 mL (12 mmol) of a 0.67 M solution of the ammonium hydrochloride derived aluminum amide reagent.[23] The mixture was heated at reflux for 5 h under nitrogen, cooled to 5–10 °C, and acidified to pH 3–5 with 1 N HCl. The organic layer was separated, and the aqueous layer was extracted three times with ether. The organic extracts were combined, dried over $MgSO_4$, and concentrated to give 144 mg (60%) of the dinitrile **6**. A purified sample was obtained by sublimation: mp 64 °C; UV$_{max}$ (hexane) 198, 206, 234, 246, 259, and 274 nm (ε 4700, 5200, 2000, 3800, 5900, and 4900, respectively); IR ($CDCl_3$) 3060, 2960, 2255, 2261, 1598, 1260, 1100, 890, and 640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.17 (d, 1, ≡CHC*H*=, *J* = 16.5 Hz), 6.52 (d, 1, NCCH=); ^{13}C NMR δ 71.30 NC*C*≡), 76.64 (C≡*C*CH=C), 104.06 (NCC≡C), 114.89 (N*C*CH=C), 117.86 (≡C*C*H=), 125.71 (NC*C*H=C); mass spectrum, *m*/*e* (relative intensity) 103 (5), 102 (46), 101 (6), 76 (10), 75 (46), 63 (5), 62 (9), 51 (37), 50 (12), 39 (25), 38 (100), 37 (37).

Anal. Calcd for $C_6H_2N_2$: C, 70.59; H, 1.97; N, 27.44. Found: C, 70.62; H, 2.04; N, 27.10.

Photolyses of (*E*)-1-Buten-3-yne-1,4-dicarbonitrile. A solution of 6 mg of **6** was dissolved in 2 mL of CD_3CN and degassed by three freeze–pump–thaw cycles and photolyzed with 254-nm light. The irradiations were performed in 10-min intervals to maintain the temperature below 40 °C. Samples irradiated for 5, 20, and 50 min gave yields of 10, 21, and 31%, respectively, of the corresponding *Z* isomer as identified by ^{1}H NMR ($CDCl_3$) δ 6.12 (d, 1, C=CHC=C, *J* = 11.4 Hz), 6.41 (d, 1, NCCH=C); ^{13}C NMR ($CDCl_3$) δ 71.32 (NC*C*≡C), 76.66 (NCC≡*C*), 104.11 (NCCH=C), 114.89 (N*C*CH=C), 117.01 (C≡C*C*H=C), 124.76 (NCCH=C).

Synthesis of 1,2,3-Tricyanobenzene.[24] 1,2,3-Benzenetricarboxylic acid dihydrate (5 g) was added to PCl_5 (60 g) and heated for 15 min at 90 °C and then for 5 h at 150 °C. The solution was cooled, 20 mL of CH_2Cl_2 was added, and the solid PCl_5 was filtered. Evaporation of the CH_2Cl_2 gave the crude triacid chloride

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of 1,2,3-benzenetricarboxylic acid (3.2 g) (51%). The triacid chloride (1.5 g) was slowly added to 12 mL of concentrated NH_4OH that had been cooled to 0 °C. After 20 min at room temperature, the solution was concentrated to 2 mL, and the product was filtered and crystallized from water to give 1,2,3-benzenetricarboxamide (0.5 g) (43%), mp 320 °C dec. The tricarboxamide (0.5 g) was dissolved in 5 mL of pyridine, 1 mL of $POCl_3$ was added, and the mixture was heated for 2 h under reflux. The reaction mixture was cooled to room temperature, dilute sulfuric acid was added, and the mixture was extracted with chloroform. The extracts were washed with water, dried with magnesium sulfate, and concentrated to dryness. Sublimation of the solid residue at 140–150 °C at 0.1 Torr yielded the impure tricyano derivative, which was crystallized from benzene (0.2 g) (54%): mp 173 °C; ^1H NMR ($CDCl_3$) δ 8.05 (m, 2 H), 7.97 (m, 1 H); mass spectrum, *m/e* (relative intensity) 153 (100), 126 (12), 101 (5), 100 (5), 99 (4), 75 (13).

Photolysis of Ethylene and Dicyanoacetylene. Irradiation of a mixture of 600 Torr of ethylene and 50 Torr of dicyanoacetylene with a low-pressure mercury lamp for 24 h yielded 1,2-dicyanocyclobutene, which was characterized by a peak at 2.944 ppm. GC analysis of the reaction mixture showed a peak with the same retention time as an authentic sample.[25] A trace of 2,3-dicyano-1,3-butadiene was also detected by NMR and GC. Irradiation of a mixture of 200 Torr of ethylene and 50 Torr of dicyanoacetylene with 254-nm light for 3 h resulted in the formation of 2,3-dicyano-1,3-butadiene which was identified by NMR signals at 6.443 and 6.323 ppm.[26] A small yield of 1,2-dicyanocyclobutene was also detected.

Photolysis of Ethylene and Cyanoacetylene. Irradiation of a mixture of 500 Torr of ethylene and 100 Torr of cyanoacetylene for 3 h with a low-pressure mercury lamp resulted in the formation of 1-cyanocyclobutene as identified by NMR peaks at 6.78 (t, J = 0.7 Hz), 2.85 (t, J = 3.1 Hz), and 2.41 (m) ppm.[27] 2-Cyano-1,3-butadiene[28] was obtained when 254-nm light was used.

Photolysis of 2,3-Dicyanobutadiene in Acetonitrile. 2,3-Dicyanoacetylene (20 mg) in 1 g of CD_3CN was degassed by three freeze–pump–thaw cycles and irradiated for 60 h in quartz with 254-nm light. The formation of 1,2-dicyanocyclobutene was established by the presence of an NMR signal at 2.90 (s) ppm.[26]

Results and Discussion

The gas-phase photolysis of pure cyanoacetylene was investigated initially as the first step in understanding its transformations in the presence of other gases. The photolyses were performed with a low-pressure mercury lamp which provided light at 185 and 254 nm or at just 254 nm when a Vycor filter was used and with an iodine lamp with emission at 206 nm.[15]

Black polymeric material is the principal photoproduct obtained on irradiation of 50 Torr of cyanoacetyelene.[29] Since it was not possible to directly measure this material, the relative amounts formed were determined by the increase in absorbance at 300 nm. The yields using 185- and 206-nm irradiation are much greater than those using 254-nm light. This probably reflects the much lower absorbance of cyanoacetylene at 254 nm and hence the lower rate of photolysis, but the possibility that it is due to the different reactivities of the two π, π^* excited-state species cannot be eliminated.[30,31] Polymerization may be initiated by radicals produced by the photochemical dissociation of cyanoacetylene.[9] The extent of polymer formation will be much less in planetary atmospheres or the interstellar medium because of the low partial pressures of cyanoacetylene and the presence of other compounds which will react with these radicals (e.g., eqs 3, 4). The photochemical condensation of cyanoacetylene with acetylene or ethylene is more likely to proceed in the aerosols on Titan because the amounts of these hydrocarbons are greater than that of cyanoacetylene.[2] The properties of this black material were not investigated further in the present research.

Table I.[c] **Yields (%) of Benzene and Tetracyanocyclooctatetraene Derivatives from Photolysis of 50 Torr of Cyanoacetylene**

wavelength, nm	1,3,5-tricyanobenzene	1,2,4-tricyanobenzene	tetracyanocyclooctatetraenes
185 and 254[a]	0.9	0	0
206[a]	0.3	0	0
254[b]	0.03	0.18	0.46

[a] 2-h irradiation. [b] Five reactions were combined after irradiation for 20 h and they were purified by sublimation. [c] In Tables I–V the limit of detection is a yield of 0.01%.

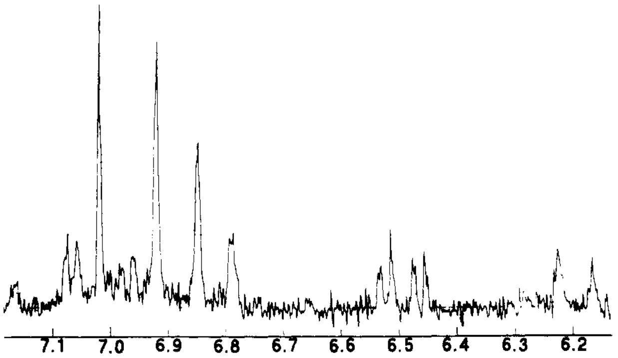

Figure 1. ^1H NMR spectrum of the tetracyanocyclooctatetraene fraction formed by photolysis of cyanoacetylene.

The structures of the lower molecular weight products were determined after separation from the polymeric material by dissolution in deuteriochloroform. This soluble material was characterized directly by ^1H NMR spectroscopy. Alternatively, this fraction was further separated into trimeric and tetrameric derivatives of cyanoacetylene by fractional sublimation at 140 °C and 0.1 Torr.

1,3,5-Tricyanobenzene is a principal trimeric gas-phase photoproduct at 185 and 206 nm (Table I). It is also formed on irradiation in pentane or acetonitrile solution using 206- or 185-nm light. Its structure, and that of the other tricyanobenzene products, was established by comparison of spectral and chromatographic properties with those of authentic synthetic samples.[32-34] Six times as much 1,2,4-tricyanobenzene (0.2%) as 1,3,5-tricyanobenzene is obtained using 254-nm light. By contrast, the 1,2,4-isomer is not formed with 185-nm irradiation and at most a trace amount is formed using a 206-nm light source. No 1,2,3-tricyanobenzene was detected as a photoproduct under any of the photolysis conditions.

Tetracyanocyclooctatetraenes were the principal reaction products when the photolyses were performed at 254 nm (Table I). None of these tetrameric products were detected using 185-nm light, and only traces were observed using

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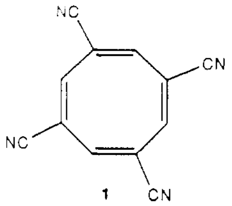
206-nm light. It was demonstrated that the failure to observe these products is not due to their rapid photodegradation by 185-nm light. The tetrameric nature of these adducts was established by the mass spectrum of the sublimed fraction which exhibited a molecular ion at *m/e* 204 and other fragments consistent with the loss of the elements of HCN and cyanoacetylene. The UV spectrum of this fraction (λ_{max} 227 nm, $\lambda_{inflection}$ 302, 316 nm) is consistent with the tetracyanocyclooctatetraene structure. Dicyanocyclooctatetraene has a λ_{max} at 217 (4.47) and 307 (2.86) nm,[35] while the long-wavelength absorption band of 1,2,4,7-tetracarbomethoxycyclooctatetraene is at 310 nm.[36] Insight into the structures of the principal tetrameric adducts were obtained from the ^{1}H NMR spectrum of the sublimed fraction in the δ 6–7.1 region (Figure 1). The sharp signal at δ 7.02 did not change when other signals in the spectrum were irradiated. This finding is consistent with its assigment to either of the symmetrically substituted cyclooctatetraenes **1** or **2** which would be expected to have only one NMR signal. The two slightly broadened singlets at δ 6.85 and 6.91 which did not change upon irradiation of the other signals were assigned to the other symmetrically substituted cyclooctatetraene **3**. The difference in the chemical shift of these two signals of 0.14 ppm is consistent with the difference of 0.18 ppm reported in the corresponding 1,4,5,8-tetracarbomethoxycyclooctatetraene.[37] The signals at δ 7.07, 6.80, 6.52, and 6.20 could not be assigned to other isomeric cyclooctatetraenes with certainty. Structures **4** and **5** are possibilities, but the absence of authentic samples precludes absolute identification. Several approaches to the synthesis of **1–5** were attempted from the corresponding esters[36–39] or by the action of transition-metal catalysts on cyanoacetylene,[37,40] but none were successful.



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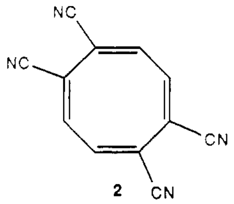

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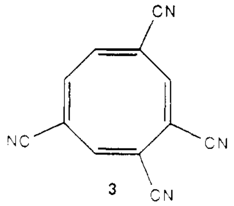

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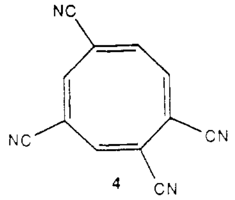

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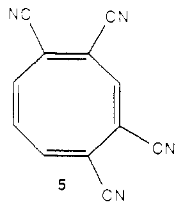

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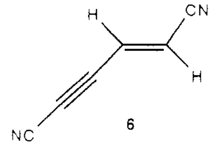

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Table II. Product Yield (%) on Irradiation of Mixtures of Cyanoacetylene and Acetylene at 185 and 254 nm[a]

product	HC_3N:C_2H_2 20:200 Torr[b]	HC_3N:C_2H_2 50:50 Torr[c]	HC_3N:C_2H_2 100:50 Torr[d]
1,3,5-tricyanobenzene	0	0.45	0.6
1,2,4-tricyanobenzene	0	0	0
1,3-dicyanobenzene	0.9	1.0	0.7
1,4-dicyanobenzene	trace	0.07	0.05
benzonitrile	0.8	0.1	0
benzene	0.04	0.03	0.05
tetracyanocyclo-octatetraenes	0	0	0

[a] Yields based on cyanoacetylene except for the yield of benzene. [b] 1.5-h irradiation; ratio of light absorbed 12:88 HC_3N:C_2H_2. [c] 3-h irradiation; ratio of light absorbed 58:42 HC_3N:C_2H_2. [d] 3-h irradiation; ratio of light absorbed 73:27 HC_3N:C_2H_2.

Table III. Product Yield (%) on Irradiation of Mixture of Cyanoacetylene and Acetylene at 206 nm[a]

product	HC_3N:C_2H_2 20:200 Torr[b]	HC_3N:C_2H_2 50:50 Torr[c]	HC_3N:C_2H_2 100:50 Torr[d]
1,3,5-tricyanobenzene	0.04	0.25	0.2
1,2,4-tricyanobenzene	0	0	0
1,3-dicyanobenzene	1.4	0.50	0.2
1,4-dicyanobenzene	0.09	0.07	0.03
benzonitrile	1.3	0	0
benzene	0.05	0.05	0.05
tetracyanocyclo-octatetraenes	trace	trace	trace

[a] Yields are based on cyanoacetylene except for the benzene yield. [b] 4-h irradiation; ratio of light absorbed 29:71 HC_3N:C_2H_2. [c] 3-h irradiation; ratio of light absorbed 97:3 HC_3N:C_2H_2. [d] 3-h irradiation; ratio of light absorbed 99:1 HC_3N:C_2H_2.

Experiments were performed to see if similar cycloadducts were obtained when methyl propiolate was irradiated. Only the 1,3,5-trisubstituted benzene derivative was observed using 254-nm light, and no cyclooctatetraene derivatives were detected. This result is in marked contrast to the 1,2,4-tricyanobenzene and tetracyanocyclooctatetraene products obtained from cyanoacetylene, a result which underlines the difference in the photochemistry of acetylenic nitriles and esters.

Cyanoacetylene forms cycloaddition products with acetylene; the relative amounts of acetylene incorporated into the cycloadduct depends on the composition of the reaction mixture. When 100 Torr of a 1:1 mixture of cyanoacetylene–acetylene is irradiated for 3 h with the 185- and 254-nm light from a low-pressure mercury lamp, 1,3-dicyanobenzene and 1,3,5-tricyanobenzene are the principal products along with smaller amounts of 1,4-dicyanobenzene, benzonitrile, and benzene (Table II). The yield of photoproducts is still increasing after 3-h irradiation so the optimal yields will be higher than those given in Table II. It was not practical to carry out the reactions for long times because the oligomers deposited on the wall of the photolysis cell attenuated the flux of light reaching the gaseous reactants. A comparable suite of cyanobenzene derivatives was obtained when a 206-nm light source was used in place of the low-pressure mercury lamp (Table III). Trace amounts of 1,3,5-tricyanobenzene and 1,3-dicyanobenzene and just detectable amounts of the cyclooctatetraenes are obtained using 254-nm light where cyanoacetylene is the only light-absorbing compound.

The photochemistry of dicyanoacetylene was investigated to gain further insight into the course of the cycloaddition reactions of cyanoacetylene. Photolysis of dicyanoacetylene in the presence of acetylene resulted in the formation of a 1:1 adduct which was identified as an *E,Z* mixture of the isomers of 1-buten-3-yne-1,4-dicarbonitrile (**6**). The variation in the yield of the *E,Z* isomers of **6** with

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Table IV. Product Yield (%) on Irradiation of Mixtures of Dicyanoacetylene–Acetylene

product	C_4N_2:C_2H_2 ratio (Torr)	C_4N_2:C_2H_2 ratio (Torr)	C_4N_2:C_2H_2 ratio (Torr)
A. 185- and 254-nm Light (3 h)			
	10:100[a]	32:32[b]	42:7[c]
1,2-dicyanobenzene	0.4	0.05	trace
(*E*,*Z*)-6	0	0.4	2.5[a,k]
B. 206-nm Light (3 h)			
	30:123[d]	32:32[e]	39:7.5[f]
1,2-dicyanobenzene	0.3	0.07	0
(*E*,*Z*)-6	0.7	0.5	0.7[k]
C. 254-nm Light[g]			
	14:59[h]	32:32[i]	50:10[j]
1,2-dicyanobenzene	0	0	trace
(*E*,*Z*)-6	2.5	1.8	5.8[k]
tetracyanocyclo-octatetraenes	0.4	0.3	1.9[k]

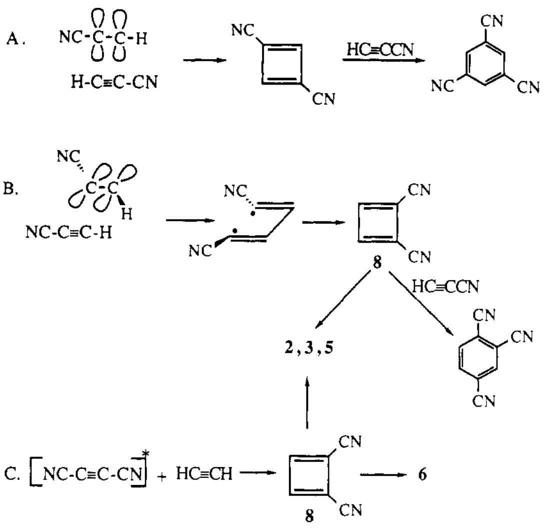
[a] Light absorption: C_4N_2:C_2H_2, 8:92. [b] Light absorption: C_4N_2:C_2H_2, 48:52. [c] Light absorption: C_4N_2:C_2H_2, 85:15. [d] Light absorption: C_4N_2:C_2H_2, 73:27. [e] Light absorption: C_4N_2: C_2H_2, 85:15. [f] Light absorption: C_4H_2:C_2H_2, 98:2. [g] All light absorbed by C_4N_2. [h] 20-h irradiation. [i] 18-h irradiation. [j] 32-h irradiation. [k] Yield based on acetylene; other yields based on C_4N_2.

the percent light absorbed established that it is formed by the addition of ground-state acetylene to the excited state of dicyanoacetylene (Table IV). The yield of dicyanobenzene is dependent on the percent light absorbed by acetylene and so must be formed by an initial addition of ground-state dicyanoacetylene to excited-state acetylene. The structure of 6 was proven by comparison with an authentic sample that was prepared in one step from the corresponding diester.[22] The *E* isomer of 6 was the product of the synthesis,[23] but it was shown to be converted to an *E*,*Z* mixture upon irradiation in acetonitrile with 254-nm light. Thus the formation of an *E*,*Z* mixture of 6 by photolysis of dicyanoacetylene and acetylene, instead of one isomer, has no mechanistic significance.

Tetracyanocyclooctatetraenes were observed by photolysis of dicyanoacetylene in the presence of acetylene only when 254-nm light was used. A similar wavelength dependency was observed with cyanoacetylene photolysis (Table I). The ^1H NMR spectrum of the cyclooctatetraene fraction formed from dicyanoacetylene and acetylene was similar to that obtained from cyanoacetylene alone (Figure 1). The presence of 2 and 3 was established by comparison of the major signals in the ^1H NMR with those found in the mixture of cyclooctatetraenes formed from cyanoacetylene. Since it is highly unlikely that 1 would be formed using dicyanoacetylene as the starting material, compound 2 must be the product of the photolysis of cyanoacetylene unless the proton signals for 1 and 2 have exactly the same chemical shift. Other isomers of tetracyanocyclooctatetraene (e.g., 4, 5) were also formed, but the amounts were much less than those formed from cyanoacetylene. Trace amounts of cyanoacetylene, acetonitrile, and HCN were provisionally detected as reaction products by ^1H NMR in photolyses performed with 254-nm light.[41]

No adducts due to the cycloaddition of cyanoacetylene with either HCN or carbon monoxide were formed when mixtures of these gases were photolyzed. Irradiation of a mixture of 50 Torr of HCN and 50 Torr of cyanoacetylene resulted in the formation of the same products that were observed upon irradiation of cyanoacetylene alone. The only observed effect on irradiation of a mixture containing 50 Torr each of cyanoacetylene and carbon monoxide was a one-third diminution in the yield of 1,3,5-tricyanobenzene. A brown oligomeric fraction was formed in the presence of carbon monoxide, suggesting that a copolymer of cyanoacetylene and carbon monoxide was produced in the presence of carbon monoxide. Polymer formation may proceed preferentially to cycloaddition reactions, thus resulting in lower yields of the cycloadducts.

Scheme I



Photochemical Reaction Pathways. The different reaction pathways observed on excitation of cyanoacetylene with 185- and 206-nm light versus 254-nm light reflect differences in the reactivity of two π, π^* excited states of cyanoacetylene generated at these different wavelengths. Excitation at wavelengths below 230 nm generates a linear singlet excited state resulting from a π, π^* transition.[31] Excitation at wavelengths greater than 230 nm gives a lower energy, bent, π, π^* singlet where the transoid hydrogen and nitrile groups define the plane of the molecule.[30] The $3\pi^*$ antiboding orbitals are also in the plane of excited cyanoacetylene (Scheme I, B). The linear π, π^* singlet excited state undergoes a rapid cycloaddition with ground-state cyanoacetylene to give 1,3-dicyanocyclobutadiene which in turn undergoes a Diels–Alder addition with a second cyanoacetylene to give 1,3,5-tricyanobenzene (Scheme I, A). The observed regiospecificity is a consequence of a dipolar repulsion between the cyano groups in the transition state leading to the 1,3-dicyanocyclobutadiene and the 1,3,5-tricyanobenzene.

Dipolar repulsion of the nitriles will be less in the reaction of the bent $3\pi^*$ excited state of cyanoacetylene with ground state cyanoacetylene (Scheme I, B). Inititial bond formation between the β-carbon atoms of ground- and excited-state cyanoacetylene results in a diradical, where each radical is stabilized by an adjacent nitrile, which cyclizes to 1,2-dicyanocyclobutadiene (8). Diels–Alder addition of cyanoacetylene with 8 yields 1,2,4-tricyanobenzene. Compound 8 also dimerizes to give 1,2,5,6-, 1,2,4,7-, and possibly 1,2,4,5-tetracyanocyclooctatetraene (2, 3, and 5, respectively). The dimerization of 1,2-dicyanocyclobutene to 1,2,5,6-tetracyano-1,5-cyclooctadiene proceeds by a path that is similar to that proposed for conversion of 1,2-dicyanocyclobutadiene to 2.[42] Our failure to observe the formation of cyclooctatetraenes in the

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[41] HCN is formed by photolyses of ammonia in the presence of acetylene. Acetonitrile is an intermediate in this process. Ferris, J. P.; Ishikawa, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4306–4312.

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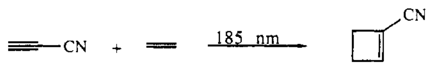
photochemical reactions of tricyanobenzenes with cyanoacetylene establishes that the tetracyanocyclooctatetraenes are not produced from excited tricyanobenzenes.

The photolysis of dicyanoacetylene in the presence of acetylene also yields tetracyanocyclooctatetraenes. It is proposed that the reaction of the excited state of dicyanoacetylene with the ground-state acetylene yields **8** which dimerizes to **2**, **3**, and possibly **5** (Scheme I, C). The other products of this photochemical reaction, the *E*,*Z* isomers of **6**, are formed by the ring opening of **8**. A similar opening of the oxetane formed by cycloaddition of benzaldehyde and 2-butyne has been reported.[43] It is not clear why **8**, when formed by reaction of an excited dicyanoacetylene with acetylene, rearranges to **6** while the same intermediate formed from excited cyanoacetylene does not. One explanation is the faster addition of cyanoacetylene than acetylene to **8**. The rearrangement of **8** to **6** has time to proceed because cycloaddition of **8** with acetylene is a slower reaction. This postulate is consistent with our failure to observe 1,2-dicyanobenzene as a product when dicyanoactylene is irradiated with acetylene with 254-nm light (Table IV) while 1,2,4-tricyanobenzene is a major product of the photolysis of cyanoacetylene with 254-nm light (Table I).

Excitation of cyanoacetylene–acetylene mixtures with 185- or 206-nm light is expected to produce either the singlet excited state of cyanoacetylene[31] or the metastable triplet excited state of acetylene.[44] Either excited state would be expected to undergo cycloadditions with ground-state molecules to yield the observed photoproducts (Tables II and III). The yield of each benzene derivative can be accounted for qualitatively by the extent of light absorbed by each monomer and the relative amounts of each monomer.

The photochemical formation of 1-cyanocyclobutene from ethylene and cyanoacetylene (eq 5) and the formation of 1,2-dicyanocyclobutene from ethylene and dicyanoacetylene (eq 6) with 185-nm light supports the reaction pathways proposed in Scheme I. The cycloadduct formed from ethylene generates a stable adduct while the highly reactive 1,2-dicyanocyclobutadiene excited state species undergoes a further cycloaddition with cyanoacetyene to give 1,3,5-tricyanobenzene. The cycloadducts were observed when 1-cyanocyclobutene was photolyzed in the gas phase by itself or in the presence of cyanoacetylene.[45]



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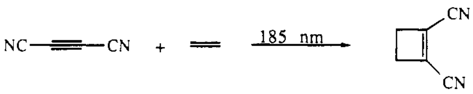

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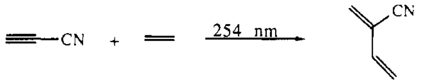

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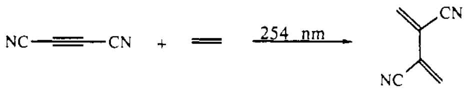

(8)

The formation of 2-cyano-1,3-butadiene by the 254-nm irradiation of mixtures of ethylene and cyanoacetylene (eq 7) and 2,3-dicyano-1,3-butadiene from dicyanoacetylene and ethylene (eq 8) is consistent with the formation of **6** from **8**. No products could be identified in the gas-phase photolysis of 2-cyano-1,3-butadiene. This is a surprising result in view of the facile photochemical cyclization of 2-cyano-1,3-butadiene to 1-cyanocyclobutene and 1-cyanobicyclobutane in acetonitrile.[46] We confirmed that the photolysis of 2,3-dicyano-1,3-butadiene in acetonitrile solution yields 1,2-dicyanocyclobutene.[47]

Acknowledgment. This research was supported by NASA Grant NGR 33-018-148. J.C.G. received a stipend from CNRS of France. We thank Professor Kevin T. Potts for the use of his PC MODEL program and for providing instruction and advice for its use. Professor Robert Strong provided valuable consultation on the spectroscopy of cyanoacetylene.

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(47) **Note Added in Proof.** After this work was submitted for publication we discovered a report of the proposed thermal conversion of cyanoacetylene to 1,2-dicyanocyclobutadiene and the subsequent cycloaddition of the cyclobutadiene to [2,2]paracyclophane. Witulski, B.; Ernst, L.; Jones, P. G.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *29*, 1279.

Oxidative Cleavage of Ethers by Metallic Nitrates Supported on Silica Gel

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Received April 10, 1990

Metallic nitrates supported on silica gel efficiently cleave and oxidize ethers to the corresponding aldehydes or ketones under mild conditions. Silica gel is essential for the efficient oxidation, and $Cu(NO_3)_2$ and $Zn(NO_3)_2$ are suitable for practical use. Overoxidation of the product aldehydes is not observed. In some cases alkyl nitrites are isolated in addition to the carbonyl compounds, and the decomposition of alkyl nitrites to the corresponding carbonyl compounds is promoted by the presence of metallic nitrates supported on silica gel. Mechanistic study suggests nitrogen dioxide is an active species.

Reactions utilizing reagents on insoluble inorganic supports often have the advantages of ease of operation, mild reaction conditions, and increased yields compared with their homogeneous counterparts.[1] In the course of stud-