Regioselectivity of the Photochemical Addition of Ammonia, Phosphine, and Silane to Olefinic and Acetylenic Nitriles

Jean-Claude Guillemin,* Curt M. Breneman, Jeffrey C. Joseph, and James P. Ferris

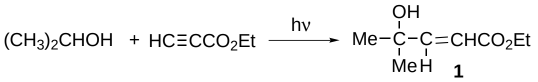
Abstract: An investigation of the regioselectivity and mechanisms of the photochemical addition of NH_3, PH_3, and SiH_4 to olefinic and acetylenic nitriles is described. The photolysis of NH_3 in the presence of acrylonitrile led to the α-addition product 2-aminopropanenitrile (**2**), propanenitrile, and 2,3-dimethylbutanedinitrile (**3**). When NH_3 was photolyzed in the presence of substituted derivatives (crotononitrile, methacrylonitrile, or 1-cyclohexenecarbonitrile), the α-addition products were still obtained. However, under similar reaction conditions, only the β-addition products, **7** and **8**, were obtained from acrylonitrile and PH_3, or acrylonitrile and SiH_4, respectively. On the other hand, the photolysis of 2-butynenitrile and NH_3 gave the β-addition products, (Z)- and (E)-3-aminocrotononitrile (**10**). The photolysis of these acetylenic nitriles with PH_3 or SiH_4 also gave the β-adducts (**12**) and (**13**). The α-addition of NH_3 proceeds by the stepwise addition of $H^\bullet$ and $^\bullet NH_2$, respectively, to the α,β-unsaturated nitriles. The β-addition products are formed by a radical chain mechanism initiated by photochemically generated radicals. The radical chain pathway provides an explanation for a number of previously described photochemical additions to olefins and acetylenes. Photochemical processes similar to the addition of ammonia and phosphine to unsaturated organic compounds may have played a role in the evolution of the atmosphere of the primitive Earth, and may even be currently occurring in the atmospheres of other planets.

Keywords: ab initio calculations · alkenes · alkynes · radical reactions · photochemistry

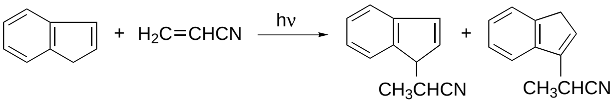
Introduction

Unsaturated nitriles play a key role in many of the pathways proposed for the prebiotic synthesis of biological molecules. These nitriles are formed in electric discharge reactions designed to simulate events on the primitive Earth.[1, 2] They are found on Titan[3, 4] and in the interstellar medium.[5, 6] Michael addition (β-addition) of nucleophiles to acetylenic nitriles is an important step in the prebiotic synthesis of the pyrimidine ring system,[2, 7] while the addition of HCN and NH_3 to propynenitrile results in the formation of the dinitrile of aspartic acid.[1] Aminonitriles are utilized in almost every step in research designed to elucidate the low-energy routes to prebiotic molecules.[8]

Photochemical reactions of unsaturated aminonitriles play an important role in the prebiotic synthesis of purines[9] and imidazole;[2] however, there have been very few studies of the photochemical addition reactions of unsaturated nitriles. The subsequent transformation of these compounds occurs mainly in photochemically driven reactions. It is not possible to infer the regioselectivity of the photochemical addition reactions of unsaturated nitriles, esters, and acids because of the conflicting nature of the limited number of reports available in the literature. Photolysis of ethyl propynoate in the presence of isopropanol resulted in the β-addition of the isopropanol group to the triple bond [Eq. (1)],[10] while α-addition is the principal reaction pathway in the photochemical addition of indene to acrylonitrile [Eq. (2)],[11] in which the ground state of acrylonitrile adds to the excited state of indene. Both α- and β-additions were observed in the photochemical reaction of ammonia to ammonium acrylate [Eq. (3)].[12] β-Addition was the exclusive product at a high photon flux or with UV



$$(CH_3)_2CHOH + HC{\equiv}CCO_2Et \xrightarrow{h\nu} Me{-}\overset{OH}{\underset{Me}{C}}{-}\underset{H}{C}{=}CHCO_2Et \quad \mathbf{1} \qquad (1)$$



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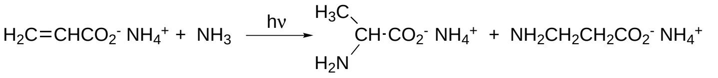

$$H_2C{=}CHCO_2^-\,NH_4^+ + NH_3 \xrightarrow{h\nu} \underset{H_2N}{\overset{H_3C}{}}\!\!\!CH{\cdot}CO_2^-\,NH_4^+ + NH_2CH_2CH_2CO_2^-\,NH_4^+ \qquad (3)$$

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Table 1. Photolysis of acrylonitrile and ammonia.[a]

Irradiation λ [nm]	Pressure [Torr] NH_3	Acrylonitrile	Light absorbed by NH_3 [%]	Products **2**[b] [%]	**3**[b] [%]	Propanenitrile [%]
185, 254	10	50	9[c]	0	0	0
185, 254	50	50	33[c]	0	0	0
185, 254	300	10	94[c]	0.5	1.3	0.4
185, 254	560	3	99[c]	4.5	8.5	3.0
206	10	50	30[d]	0	0	0
206	50	50	68[d]	0	traces	0
206	300	10	98[d]	0.7	3.2	0.5
206	560	3	100[d]	4.5	10	3

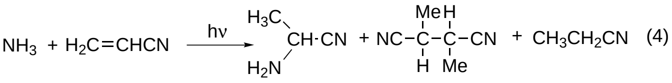
[a] Irradiation time = 3 h. [b] **2**: 2-Aminopropanenitrile; **3**: diastereomers of 2,3-dimethylbutanedinitrile. [c] UV absorbance of acrylonitrile was estimated to be 178 $cm^{-1}atm^{-1}$ at $\lambda = 185$ nm and 22 $cm^{-1}atm^{-1}$ at $\lambda = 206$ nm.[15]

radiation ($\lambda = 140-160$ nm) from a hydrogen lamp. Both α-alanine and β-alanine were observed when a low-intensity laser source ($\lambda = 266$ nm) was used. It should be noted that the identity of the photoproducts rests entirely on their retention times from an ion-exchange column, and therefore requires confirmation.

An investigation of the regioselectivity and possible mechanisms of the photochemical addition of ammonia (NH_3), phosphine (PH_3), and silane (SiH_4) to acetylenic and olefinic nitriles is presented in this report. A comparison of the photoproducts provided insight into the reaction pathway.

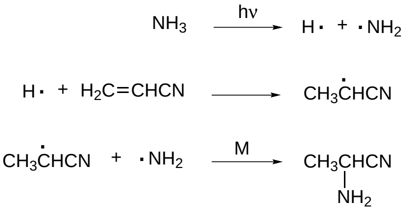
Results and Discussion

Photoaddition to α,β-unsaturated nitriles: The photolysis of NH_3 in the presence of olefinic nitriles resulted in the α-addition of $^{\bullet}NH_2$ [Eq. (4)]. The formation of 2-aminopropanenitrile (alaninenitrile, **2**) was observed when ammonia was photolyzed in the presence of acrylonitrile (Scheme 1, Table 1). Two other products, propanenitrile and the diastereomers of 2,3-dimethylbutanedinitrile (**3**), were also identified. These three products were only observed if NH_3 was present in excess and was the light-absorbing species. No addition products were observed when acrylonitrile was the principal light-absorbing species. Trace amounts of propynenitrile and HCN were detected in a control reaction when acrylonitrile was irradiated by itself in the gas phase but the isomers of **3** were not observed.[13]



$$NH_3 + H_2C{=}CHCN \xrightarrow{h\nu} \underset{\mathbf{2}}{(H_3C)(H_2N)CH{-}CN} + \underset{\mathbf{3}}{NC{-}C(Me)(H){-}C(H)(Me){-}CN} + CH_3CH_2CN \quad (4)$$

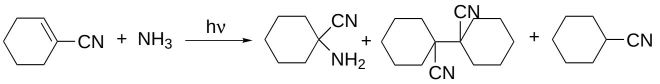
Abstract in French: *La régiosélectivité et le mécanisme de l'addition photochimique de NH_3, PH_3 et SiH_4 sur des nitriles éthyléniques ou acétyléniques sont étudiés. La photolyse de l'ammoniac en présence d'un acrylonitrile conduit à un α-aminonitrile, produit d'α-addition, à un dinitrile et à un alkylnitrile. Dans les mêmes conditions expérimentales, PH_3 et SiH_4 en présence d'un nitrile éthylénique ou acétylénique conduisent aux produits de β-addition de même que NH_3 en présence d'un nitrile acétylénique. Un processus mettant en jeu une réaction radicalaire en chaîne explique la formation des produits de β-addition. Avec NH_3, la formation d'adduits α provient de l'addition, en première étape, d'un radical hydrogène sur l'insaturation; les radicaux formés n'ont pas une énergie suffisante pour arracher un hydrogène à l'ammoniac et débuter une réaction en chaîne. Sous irradiation solaire, des processus photochimiques similaires à ceux de l'addition de l'ammoniac ou de la phosphine sur des composés organiques insaturés peuvent avoir jouer un rôle important dans l'évolution de l'atmosphère primitive terrestre et peuvent actuellement s'effectuer dans les atmosphères d'autres planètes.*



$$NH_3 \xrightarrow{h\nu} H\bullet + \bullet NH_2$$
$$H\bullet + H_2C{=}CHCN \longrightarrow CH_3\dot{C}HCN$$
$$CH_3\dot{C}HCN + \bullet NH_2 \xrightarrow{M} CH_3CH(NH_2)CN$$

Scheme 1. Photolysis of ammonia in the presence of acrylonitrile.

Comparable reaction products were obtained by the photolysis of NH_3 in the presence of crotononitrile, methacrylonitrile, and 1-cyclohexenecarbonitrile (Tables 2 and 3). The low vapor pressure (0.7 Torr at 25 °C) of 1-cyclohexenecarbonitrile precluded photochemical studies where it was present in excess, but the formation of 1-aminocyclohexanecarbonitrile (**4**) was observed in the presence of excess ammonia. The corresponding dicyano compound, the diastereomers of 2,3-dicyclohexylbutanedinitrile (**5**), and the saturated nitrile, cyclohexanecarbonitrile (**6**), were also obtained [Eq. (5)].



4 **5** **6** (5)

$$PH_3 + H_2C{=}CHCN \xrightarrow{h\nu} \underset{\mathbf{7}}{H_2PCH_2CH_2CN} + CH_3CH_2CN \quad (6)$$

$$SiH_4 + H_2C{=}CHCN \xrightarrow{h\nu} \underset{\mathbf{8}}{H_3SiCH_2CH_2CN} + CH_3CH_2CN \quad (7)$$

Table 2. Photochemical addition of NH_3 to crotononitrile.[a]

Irradiation λ [nm]	Pressure [Torr] NH_3	Crotononitrile	Light absorbed by NH_3 [%]	Products **16**[b] [%]	**15**[b] [%]	*n*-Butanenitrile [%]
185, 254	5	25	6[c]	0	0	0
185, 254	25	25	24[c]	0	0	0
185, 254	300	10	94[c]	0.5	1	1.5
185, 254	560	3	98[c]	4.5	2	2
206	5	25	2[d]	0	0	0
206	25	25	8[d]	0	0	0
206	300	10	72[d]	0.7	1.5	1.5
206	560	3	94[d]	4.5	6	6

[a] Irradiation time = 3 h. [b] **16**: 2-Aminobutanenitrile; **15**: diastereomers of 2,3-diethylbutanedinitrile. [c] UV absorbance of crotononitrile was estimated to be 271 $cm^{-1}atm^{-1}$ at $\lambda = 185$ nm. [d] UV absorbance of crotononitrile was estimated to be 140 $cm^{-1}atm^{-1}$ at $\lambda = 206$ nm.

Table 3. Photochemical addition of NH_3 to methacrylonitrile.[a]

Irradiation λ [nm]	Pressure [Torr] NH_3	Acrylonitrile	Light absorbed by NH_3 [%]	Products **17**[b] [%]	**18**[b] [%]	2-Butanenitrile [%]
185, 254	10	50	7[c]	0	+	0
185, 254	50	50	27[c]	+	+	+
185, 254	300	10	92[c]	0.2	0.8	0.2
185, 254	560	3	99[c]	4.9	6.9	3.0
206	10	50	2[d]	+	+	+
206	50	50	11[d]	+	+	+
206	300	10	80[d]	0.5	2.0	0.7
206	560	3	96[d]	5.3	10	3.0
206	560	1	99[d]	8.0	14	3.0

[a] Irradiation time = 3 h; + : detected but < 0.1 % yield. [b] **17**: 2-Amino-2-methylpropanenitrile; **18**: 2,2,3,3-tetramethylbutanedinitrile. [c] UV absorbance of methacrylonitrile was estimated to be 240 $cm^{-1}atm^{-1}$ at $\lambda = 185$ nm. [d] UV absorbance of methacrylonitrile was estimated to be 57 $cm^{-1}atm^{-1}$ at $\lambda = 206$ nm.

On the other hand, when PH_3 was photolyzed in the presence of acrylonitrile, the β-addition product, 3-phosphinopropanenitrile (**7**), was observed [Table 4, Eq. (6)]. Propanenitrile is also formed but **3** was not detected. Photolysis of SiH_4 and acrylonitrile gave 3-silylpropanenitrile (**8**) and propanenitrile [Table 5, Eq. (7)]. However, SiH_4 does not absorb light of $\lambda = 185$ nm;[14] only acrylonitrile is activated by radiation of this wavelength. Products **7** and **8** were only observed when PH_3 or SiH_4 were present in excess, even if they were not the light-absorbing species.

It was initially surprising that α-aminonitriles were obtained by the photoaddition of NH_3 to acrylonitrile while β-addition products were obtained from the photoaddition of PH_3 and SiH_4. The observation of **3** as a photoproduct clearly indicated the formation of the radical $CH_3C^{\bullet}(H)CN$ as a reaction intermediate in the NH_3–acrylonitrile system. This observation suggests that the addition reaction proceeds by a stepwise process in the pathway given in Scheme 1. Here the photochemically generated $H^{\bullet}$ and $^{\bullet}NH_2$ add to acrylonitrile, with the hydrogen atom adding first. The more rapid addition of $H^{\bullet}$ is consistent with the calculation that $H^{\bullet}$ addition to acetylene proceeds 700 times more rapidly than $^{\bullet}NH_2$ addition.[17] Hydrogen atom addition to acrylonitrile proceeds at the β-carbon because the radical formed is stabilized by delocalization of its *p* orbital by the π-bond of the nitrile group. Ab initio calculations at several levels of theory show that hydrogen atom addition to the β-carbon of acrylonitrile gives a more stable radical than if the addition was at the α-carbon or the nitrile group (Table 6). The same addition

Table 5. Photochemical reaction of SiH_4 and acrylonitrile.[a]

Irradiation λ [nm]	Pressure [Torr] SiH_4	H_3C_3N[b]	Products[c, d] **8** [%]	Propanenitrile [%]
185, 254	70	2	3.0	traces
185, 254	75	8	1.6	2.7
185, 254	60	8	0.6	1.0
185, 254	40	40	traces	0
185, 254	8	75	0	0

[a] Irradiation time = 1 h. [b] 100 % light absorbed at $\lambda = 185$ nm by acrylonitrile. [c] **8**: 3-Silylpropanenitrile. [d] Traces of unidentified products have been observed but the α-adduct $MeCH(CN)SiH_3$ was never detected.

Table 4. Photochemical addition of PH_3 to acrylonitrile.[a]

Irradiation λ [nm]	Pressure [Torr] PH_3	Acrylonitrile	Light absorbed at 185 nm by PH_3[b] [%]	Products[c] **7**[d] [%]	Propanenitrile [%]	P_2H_4 [%]
185, 254	70	2	95	2.4	1.4	0.2
185, 254	70	4	91	2.4	7.0	0.4
185, 254	60	6	85	1.9	6.3	traces
185, 254	40	40	36	0.3	2.1	traces
185, 254	6	60	5	0	traces	0

[a] Irradiation time = 1 h. [b] UV absorbance of acrylonitrile was estimated to be 178 $cm^{-1}atm^{-1}$ at $\lambda = 185$ nm,[15] UV absorbance of PH_3 was estimated to be 100 $cm^{-1}atm^{-1}$ at $\lambda = 185$ nm.[16] [c] The α-adduct $MeCH(CN)PH_2$ was never detected. [d] **7**: 3-Phosphinopropanenitrile.

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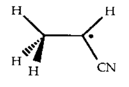
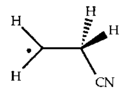
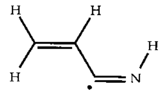
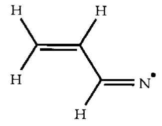
Table 6. Calculated energies of H$^\bullet$ addition products of acrylonitrile.

	ROHF/6-31G**	ROHF/6-31G**/UHF/6-31G*	UHF/6-31G*(S^2, S^2A)
C=C Addition:			
	-170.3414	-170.3399	**-170.3469** (0.917, 0.767)
	-170.3312	-170.3311	-170.3286(0.762, 0.750)
C=N Addition:			
	-170.2922	-170.2827	-170.2953(1.044, 0.792)
	-170.3136	-170.3083	-170.3249(1.454, 1.030)

mechanism accounts for the regioselectivity of the photochemical addition of NH_3 to crotononitrile, methacrylonitrile, and 1-cyclohexenecarbonitrile.

It should be noted that ab initio calculations involving molecules with unpaired electrons are often more difficult to interpret than those of closed-shell molecules. The reason for this difficulty stems from the potential for spin contamination of the final wavefunction resulting from the admixture of states of higher multiplicity with the desired state. This can lead to distorted geometries if optimization is attempted, or to artificially low energies in single-point calculations. Several options are available to minimize these effects. First, it is possible to specify that the spatial part of the wavefunctions for α- and β-electrons be identical. This type of calculation uses an ROHF (restricted open-shell Hartree–Fock) Hamiltonian which cannot result in spin contamination, but it can also incorrectly represent the spin density and the underlying electron density of the system. UHF (unrestricted Hartree–Fock) calculations use separate spatial descriptions for each of the electrons, but can lead to the spin-contamination problems described above. For comparative purposes, all of the ab initio calculations in this paper were performed with several levels of theory for both geometry optimization of the radical species as well as for the calculation of the final energies of each species. The most reliable method used in this work to remove spin contamination and to account for electron correlation is PMP2/6-31G+, a method in which the Møller–Plesset second-order perturbation method is used to give a spin-projected, correlated wavefunction.

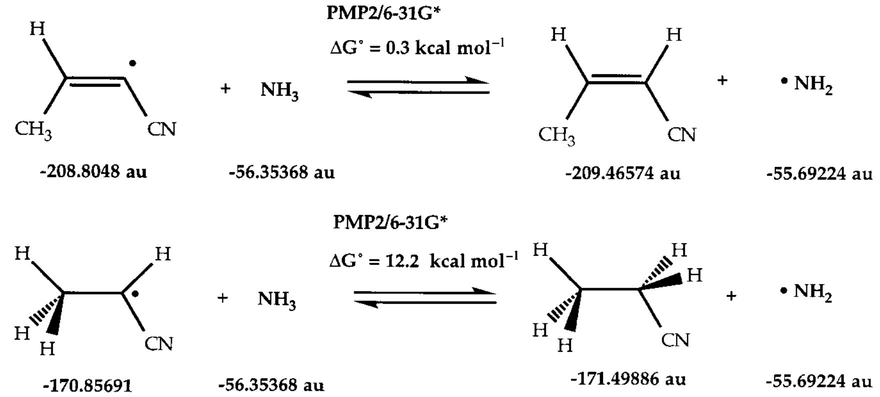
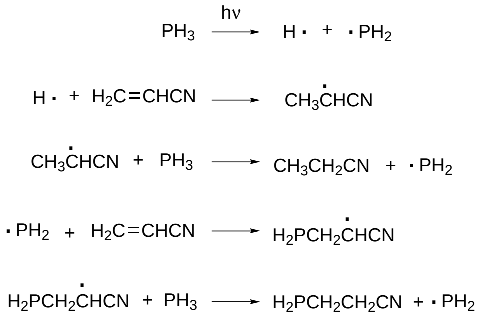


Figure 1. Energetics of hydrogen abstraction from NH_3.

The formation of β-substituted products in the photoaddition of PH_3 and SiH_4 to acrylonitrile indicated that $CH_3C^\bullet(H)CN$ was not a reaction intermediate. The major difference between NH_3 addition and the addition of PH_3 and SiH_4 is the much higher NH bond energy of NH_3 (107.4 kcal)[18] versus that of PH in PH_3 (78 kcal),[19] and SiH in SiH_4 (90.3 kcal).[18] Spin-projected MP2/6-31G+ ab initio calculations (Figure 1) suggest that the abstraction of H$^\bullet$ from NH_3 by $CH_3C^\bullet(H)CN$ is not energetically favored, while the much lower bond energies of PH_3 and SiH_4 suggest that abstraction occurs to generate $^\bullet PH_2$ and $^\bullet SiH_3$, respectively. The β-adduct of NH_3 with acrylonitrile is observed because H$^\bullet$ addition generates a stabilized α-cyano radical (Scheme 2). Hydrogen abstraction from PH_3 and SiH_4 is fast because of the high partial pressures of PH_3 or SiH_4 in the reaction cell. Consequently, dimerization of the radical intermediates is not observed with PH_3 and SiH_4, while dimer **3** is observed in the NH_3 addition reaction.



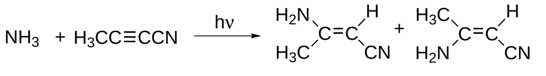
Scheme 2. Photolysis of phosphine in the presence of acrylonitrile.

The mechanism of the addition of PH_3 and SiH_4 differ from that of the addition of NH_3 in that PH_3 and SiH_4 add by a radical chain process initiated by any radical species that can abstract hydrogen from these gases. The resulting radical chain process then generates the $^\bullet PH_2$ or $^\bullet SiH_3$ radicals which perpetuate the chain. The equivalent of the radical chain addition of PH_3[20] or silylphosphines[21] to olefins has been proposed. In the case of NH_3 the radicals which add are generated by NH_3 photolysis. In the case of PH_3 the radicals which initiate the chain reaction are formed by dissociation of PH_3 to $^\bullet PH_2$ and H$^\bullet$,[22] but in the case of SiH_4 the radicals are generated by photolysis of the acrylonitrile since SiH_4 does not absorb light at wavelengths equal to or greater than 185 nm.[14]

The greater ease of hydrogen abstraction from PH_3 and SiH_4 versus NH_3 also explains the formation of propanenitrile if PH_3 or SiH_4 are irradiated in the presence of acrylonitrile. The radical formed by the β-addition of a hydrogen atom to acrylonitrile can abstract a hydrogen atom from PH_3 or SiH_4 to form propanenitrile (Scheme 2). The same radical, formed by the photolysis of NH_3 in the presence of acrylonitrile (Scheme 1), cannot abstract a hydrogen from NH_3 so no propanenitrile is formed by this route. The relatively low proportion of propanenitrile, as compared with the reaction of acrylonitrile with PH_3 and SiH_4, must be formed by the combination of a hydrogen atom with $CH_3C^{\bullet}(H)CN$.

Photoaddition to α,β-unsaturated acetylenic nitriles: Photolysis of mixtures of NH_3 and propynenitrile resulted in β-addition to the triple bond with the formation of the *E* and *Z* isomers of 3-amino-2-propenenitrile (**9**). The structure of this compound was determined by ^1H and ^{13}C NMR spectroscopy.[23] Control reactions established that the thermal β-addition of NH_3 to propynenitrile proceeds almost as rapidly as the photoinitiated reaction. Consequently, it is not certain that the observed β-addition products are actually the consequence of photochemical initiation. Subsequent studies were performed with 2-butynenitrile: the thermal addition reaction proceeds much more slowly than the photochemically initiated process.

Photolysis of 40:2.5 Torr mixtures of NH_3 and 2-butynenitrile, respectively, in which NH_3 absorbed >95% of the light, resulted in the β-addition of $^{\bullet}NH_2$ to the triple bond and the formation of the *E* and *Z* isomers of 3-aminocrotononitrile (**10**) [Table 7, Eq. (8)]. Conversions of 1–3% were determined by ^1H NMR after irradiation times of 0.25–1 h. The yield did not increase if the irradiation time was extended because a polymer formed on the inside of the cell which absorbed the UV light. The yield was not changed by the addition of ethane (150 Torr) or N_2 (600 Torr) to the reaction mixture.[24] 2-Aminocrotononitrile[8] was not detected in the NMR spectra of the product mixture. Traces of crotononitrile were observed after a short irradiation time, but disappeared on longer irradiation.



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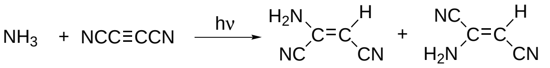
(*E*)-**10** (*Z*)-**10**

An investigation of the photolysis of a mixture of NH_3 (400 Torr) and 2-butynenitrile (100 Torr) at $\lambda = 254$ nm for 24 h at 4 °C was not successful. 2-Butynenitrile has a weak absorption at $\lambda = 254$ nm,[25] while NH_3 does not absorb at all.[26] The only observed products were the *E* and *Z* isomers of 3-aminocrotononitrile (**10**), however, comparable yields of this isomer mixture were formed in a nonirradiated control so it could not be determined if these were photoproducts.

It was not possible to study the gas-phase photochemical addition of NH_3 to butynedinitrile because the thermal process proceeded almost immediately at room temperature upon mixing the gases. A mixture of butynedinitrile (14 Torr) and NH_3 (59 Torr) resulted in a 57% yield of 2-amino-2-butenedinitrile (**11**), which consists of 92% *Z* and 8% *E* isomers [Eq. (9)].[27] Compounds (*E*)-**11** and (*Z*)-**11** were identified by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry (HRMS). No hydrazine (N_2H_4) was detected as a photoproduct when NH_3 was photolyzed. This is because N_2H_4 is rapidly decomposed to N_2 and H_2 by the hydrogen atoms produced during NH_3 photolysis.[28]



(9)

(*E*)-**11** (*Z*)-**11**

The photolysis of a mixture of propynenitrile and PH_3 or SiH_4 yielded 3-phosphinoacrylonitrile [**12**, Eq. (10)] and 3-silylacrylonitrile [**13**, Eq. (11)] respectively, along with acrylonitrile (Tables 8 and 9). The (*Z*) and (*E*) phosphines **12** were obtained in 85:15 ratio and characterized by ^1H and ^{31}P NMR spectroscopy and high-resolution mass spectrometry (HRMS). For each isomer, three signals were observed in the ^1H NMR spectrum. For the *Z* isomer, the signal at $\delta = 3.85$, with a coupling constant $J = 215$ Hz, is typical of the hydrogens attached to a phosphorus atom. The signals of the vinylic protons were observed at $\delta = 5.87$ and 7.04 with a coupling constant $^3J(H,H)_{cis} = 12.6$ Hz and the expected multiplicity. The observation of the molecular ion by HRMS (calcd for C_3H_4NP: 85.0081, found: 85.0079) confirms the structure. The (*Z*)- and (*E*)-3-silylacrylonitriles (**13**) were

$$PH_3 + HC{\equiv}CCN \xrightarrow{h\nu} H_2PCH{=}CHCN \qquad (10)$$

12

$$SiH_4 + HC{\equiv}CCN \xrightarrow{h\nu} H_3SiCH{=}CHCN \qquad (11)$$

13

Table 7. Photochemical addition of ammonia to 2-butynenitrile.

Irradiation λ [nm]	Pressure [Torr] NH_3[a]	2-Butynenitrile	N_2	Ethane	Light absorbed by NH_3[b] [%]	Irradiation time [min] (Temperature [°C])	(*Z*)-**10**[c] [%]	(*E*)-**10**[c] [%]
185, 254	40.0	2.5	0.0	0.0	>95	15 (25)	0.47	1.02
185, 254	40.0	2.5	600.0	0.0	>95	5 (25)	0.61	1.07
185, 254	40.0	2.5	0.0	150.0	>95	10 (25)	0.70	1.34
185, 254	40.0	2.5	0.0	0.0	>95	30 (−8)	0.37	0.76

[a] The extinction coefficient of NH_3 at $\lambda = 185$ nm was taken to be 87.0 $cm^{-1}\,atm^{-1}$. [b] The extinction coefficient of 2-butynenitrile at $\lambda = 185$ nm was taken to be 13.5 $cm^{-1}\,atm^{-1}$.[25] [c] **10**: (*Z*)- and (*E*)-aminocrotononitrile.

Table 8. Photochemical reaction of PH_3 and propynenitrile.[a]

Irradiation[a] λ [nm]	Pressure [Torr] PH_3	HC_3N	Light absorbed by PH_3[b] [%]	**12**[d] [%]	Products[c] Acrylonitrile [%]	P_2H_4 [%]
185, 254	75	8	98	0.4	1.3	0.06
185, 254	40	40	87	0.36	0.45	0
185, 254	8	74	42	0.03	0.1	0
254	75	8	0	2.0	2.9	0
254	40	40	0	0.45	0.63	0
254	8	75	0	≈0.3	1.3	0

[a] Irradiation time = 1 h at λ = 185 and 254 nm or 3 h irradiation at λ = 254 nm. A medium-pressure mercury lamp Philips TUV6W was used for these experiments. [b] Percent light absorbed at λ = 185 nm; UV absorbance of PH_3 was estimated to be 100 $cm^{-1}atm^{-1}$ at λ = 185 nm.[16] [c] Products formed from the photolysis of HC_3N alone[32] were never observed. [d] **12**: 3-Phosphinoacrylonitrile.

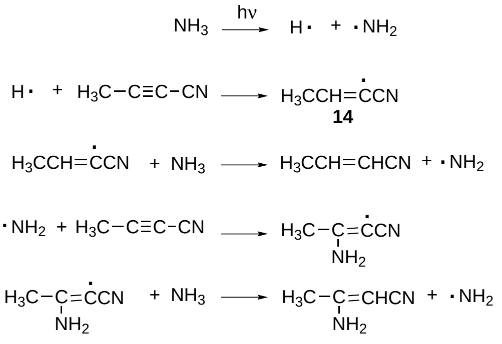
Table 9. Photochemical reaction of SiH_4 and propynenitrile.[a]

Irradiation λ [nm]	Pressure [Torr] SiH_4	HC_3N[b]	Products[c] **13**[d] [%]	Acrylonitrile[d] [%]	$Ph(CN)_3$[e] [%]	COT[e] [%]
185, 254	140	40	0.4	0.25	0.2	0
185, 254	40	40	0.26	0.09	0.41	0
185, 254	7	100	nd	nd	0.55	0
254	100	30	0.58	0.34	traces	traces
254	40	40	0.12	0.10	0.3	0
254	8	75	0	0	0.5	0

[a] Irradiation time = 1 h at λ = 185 and 254 nm or 3 h at λ = 254 nm. A medium-pressure mercury lamp Philips TUV6W was used for these experiments. [b] 100% light absorbed by propynenitrile. [c] Traces of unidentified silanes have also been observed. [d] **13**: 3-Silylacrylonitrile. [e] Products formed in the photolysis of HC_3N by itself.[32]

characterized by ^1H NMR spectroscopy. The Z:E ratio (87:13) was determined by integration of the SiH_3 signals at $\delta = 4.01$ and 3.92, respectively. The signals of the vinylic protons of the Z isomer were observed at $\delta = 6.25$ and 6.85. Control reactions established that neither PH_3 nor SiH_4 added to propynenitrile under these conditions in the absence of UV irradiation. Diphosphine (P_2H_4), a product of PH_3 photolysis,[29] was also detected as a product when PH_3 was irradiated in the presence of propynenitrile. Attempts to detect disilane (Si_2H_6)[30] when propynenitrile was irradiated in the presence of SiH_4 were unsuccessful.

The photochemical β-addition of NH_3 to 2-butynenitrile stands in marked contrast to the α-addition of ammonia to acrylonitrile, but is consistent with the mechanistic principles derived from the above studies of the photoaddition reactions of α,β- unsaturated nitriles (Scheme 3). The reaction is initiated by the α-cyano radicals formed by H$^\bullet$ addition to the β-carbon of 2-butynenitrile, to generate a cyanovinyl radical (**14**), the most stable of all the possibilities (Tables 10 and 11). This abstracts hydrogen from NH_3 to generate $^\bullet NH_2$. The formation of $^\bullet NH_2$ initiates the chain reaction process leading to the β-substitution products. Spin-projected open-shell ab initio calculations performed at a reliable level of theory which includes the effects of electron correlation (PMP2/6-31G+) suggests that the abstraction of a hydrogen atom from NH_3 by this radical is nearly thermoneutral (0.3 kcal mol^{-1}, Figure 1), a value so close to zero that, in the absence of an unusually large ΔS° of reaction, the only conclusion that can be drawn is that the reaction is highly probable. The same calculation gives an enthalpy of abstraction of hydrogen from



$$NH_3 \xrightarrow{h\nu} H^\bullet + {}^\bullet NH_2$$
$$H^\bullet + H_3C{-}C{\equiv}C{-}CN \longrightarrow \underset{\mathbf{14}}{H_3CCH{=}\dot{C}CN}$$
$$H_3CCH{=}\dot{C}CN + NH_3 \longrightarrow H_3CCH{=}CHCN + {}^\bullet NH_2$$
$${}^\bullet NH_2 + H_3C{-}C{\equiv}C{-}CN \longrightarrow H_3C{-}\underset{NH_2}{C}{=}\dot{C}CN$$
$$H_3C{-}\underset{NH_2}{C}{=}\dot{C}CN + NH_3 \longrightarrow H_3C{-}\underset{NH_2}{C}{=}CHCN + {}^\bullet NH_2$$

Scheme 3. Photolysis of ammonia in the presence of 2-butynenitrile.

Table 10. Propynenitrile H$^\bullet$ addition series.

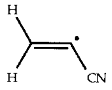
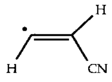
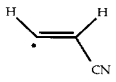
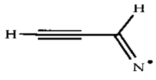
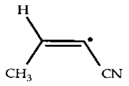
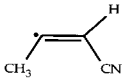
	ROHF/6-31G**	ROHF/6-31G**/UHF/6-31G*	UHF/6-31G*(S^2, S^2A)
C≡C Addition:			
	-169.1214	-169.1129	-169.1378(1.480, 1.197) -169.1878 (PUHF) **-169.6340 (PMP2)**
	-169.1186	-169.1167	-169.1264(1.197, 0.837) -169.1500 (PUHF) -169.6188 (PMP2)
	-169.1183	-169.1164	-169.1263(1.206, 0.846)
C≡N Addition:			
	-169.0963	-169.0933	-169.1074(1.305, 0.943)
-169.0710	-169.0644	-169.0788	(1.386, 1.100)

Table 11. 2-Butynenitrile H$^\bullet$ addition series.

	ROHF/6-31G**	ROHF/6-31G**/UHF/6-31G*	UHF/6-31G*(S^2, S^2A)
	-208.1593	-208.1517	-208.1780 (1.4440, 1.1517) -208.2257 (PUHF) **-208.8048 (PMP2)**
	-208.1629	-208.1618	-208.1727 (1.1231, 0.8126) -208.1933 (PUHF) -208.7971 (PMP2)

NH_3 by the α-cyanoethyl radical of $+12.2\,kcal\,mol^{-1}$, which clearly shows that the reaction will probably not occur in the absence of the same special entropy considerations (Figure 1). Observation of the β-substituted product of 2-butynenitrile demonstrates that hydrogen abstraction does indeed take place with the formation of $^{\bullet}NH_2$, which then undergoes β-addition to the ground state 2-butynenitrile (Scheme 3). This reaction proceeds by the radical chain pathway proposed previously for the addition of PH_3 and SiH_4 to acrylonitrile. SiH_4 and PH_3 also undergo radical chain addition to propynenitrile to give the β-substituted acrylonitrile products.

The photochemical addition of silane must be initiated by the radicals formed by irradiation of propynenitrile,[31] because SiH_4 does not absorb light at $\lambda = 185$ nm.[14] The observation of benzene-1,3,5-tricarbonitrile, a known photoproduct of propynenitrile, establishes that propynenitrile is absorbing the UV light.[32]

The photoaddition mechanisms derived from the present study provide mechanistic interpretations for previously reported photochemical addition reactions. It is now clear that the photochemical β-addition of isopropanol to methyl propynoate[10] [Eq. (1)] proceeds by the radical chain process observed in the photochemical addition of ammonia to 2-butynenitrile. The photochemical addition of PH_3 to fluoro or simple olefins[33] is now understandable on the basis of the radical chain mechanistic pathway developed in the present study. When PH_3 is principal absorbing species, then the main reaction products can be explained by the radical chain mechanism. Addition to propene yields *n*-propanephosphine and, in a lower yield, *iso*-propanephosphine [Eq. (12), Scheme 4]. The *n*-propanephosphine is the product expected from the radical chain process. The *iso*-propanephosphine is probably also formed by this pathway, but the process is less regioselective for a simple olefin. Irradiation of PH_3 in the presence of 1-propyne yields the (*Z*)- and (*E*)-1-propenephosphines[34] expected by the radical chain mechanism [Eq. (13)]. Similarly, the addition of H_2S[35, 36] and GeH_4[36] to propyne yields the corresponding (*Z*)- and (*E*)-propenethiols and -germanes.

$$\cdot PH_2 + H_3CCH{=}CH_2 \longrightarrow CH_3\dot{C}HCH_2PH_2$$

$$CH_3\dot{C}HCH_2PH_2 + PH_3 \longrightarrow CH_3CH_2CH_2PH_2 + \cdot PH_2$$

Scheme 4. Radical chain mechanism for the photoaddition of phosphine to propene.

$$PH_3 + H_3CCH{=}CH_2 \xrightarrow{h\nu} CH_3CH_2CH_2PH_2 + (CH_3)_2CH(PH_2) \qquad (12)$$

$$PH_3 + H_3CC{\equiv}CH \xrightarrow{h\nu} H_3CCH{=}CHPH_2 + (H_3C)H_2PC{=}CH_2 \qquad (13)$$

Conclusions

These investigations have determined the reaction pathway for the photochemical addition of inorganic compounds [HX] to simple and activated olefins and acetylenes. In most cases, the reaction proceeds by a radical chain pathway which can be explained by the initial addition of the radical $X^{\bullet}$ to the unsaturated bond to give the most stable radical. The organic radical formed then abstracts a hydrogen atom from HX to give the addition product and another $X^{\bullet}$ to propagate the reaction. In the addition of NH_3 to olefins, the radical formed was not sufficiently energetic to abstract a hydrogen atom from NH_3. Thus, it was necessary to generate the radicals required for the addition reaction by photolysis of NH_3. If the inorganic component does not absorb all the light, then the product mixture will be complicated by the addition of HX to hydrocarbons formed by photolysis of the starting olefin. If the inorganic component used does not absorb the UV light used, the radical chain pathway will still occur if the radicals formed by irradiation of the hydrocarbon are sufficiently energetic to abstract a hydrogen from the inorganic gas.

Solar UV was the most abundant energy source on the primitive Earth[37] and this radiation is still the most prevalent energy source in our solar system. Consequently, the disequilibrium species present in the atmospheres of the planets and their moons in our solar system are formed by solar UV light. Unsaturated hydrocarbons and unsaturated nitriles are produced in processes initiated by these photons and the compounds formed undergo the light-initiated addition reactions described in this report. Of particular interest is the α-addition of NH_3 to acrylonitrile to form an α-aminonitrile, which in turn can be hydrolyzed to the amino acid alanine. A wide array of aminonitriles, and hence amino acids, may have been formed by the addition of NH_3 to substituted acrylonitriles in a reducing atmosphere on the primitive Earth. These same NH_3 addition reactions could have occurred on Titan before all its atmospheric ammonia was photolyzed to molecular nitrogen and hydrogen. The α-aminonitriles formed would have precipitated on the cold surface of this moon. Photochemically generated adducts of NH_3 with the unsaturated hydrocarbons present on Jupiter are a likely source of the nitrogen-containing organics found there.[38] The P-containing adducts are probably formed in much smaller amounts because the partial pressures of PH_3 are much lower than those of NH_3 on Jupiter.[39] The structures of these adducts and of those formed with SiH_4 follow directly from the regiochemistries of the addition processes delineated in these investigations.

Experimental Section

Caution: Phosphines and silanes are pyrophoric compounds and must be used with great care in oxygen-free atmospheres.

General: UV spectra were determined on a Cary 219 spectrophotometer; ^1H, ^{31}P, and ^{13}C NMR spectra on a Varian XL-200, a Varian Unity 500, and a Bruker ARX400; GC/MS was performed on a Hewlett Packard 5987A spectrometer; GC analyses were performed on a Hewlett Packard 5890 with a J and W DB-5 capillary column (30 m × 0.2 mm id). Propynenitrile, 2-butynenitrile, and butynedinitrile were prepared by the procedure of Moureu and Bongrand[40] as modified by Miller and Lemmon.[41] 1-Cyclohexenecarbonitrile,[42] 2,3-dicyclohexylbutanedinitrile (**5**),[43] and 2,2,3,3-tetramethylbutanedinitrile (**18**)[44] were prepared by literature procedures. The diastereomers of 2,3-dimethylbutanedinitrile (**3**) and 2,3-diethylbutanedinitrile (**15**) were prepared by the procedure of Whiteley and Marianelli; [45] 2-aminopropanenitrile (**2**), 2-aminobutanenitrile (**16**), and 2-amino-2-methylpropanenitrile (**17**) by the procedure of Bold et al.[8] Cyclohexanecarbonitrile (**19**)[46] was prepared by dehydration of the corresponding amide with P_4O_{10} in sea sand. 3-Phosphinopropanenitrile (**7**)[47] and 3-silylpropanenitrile (**8**)[48] were prepared as previously reported. Commercial samples of acrylonitrile, crotononitrile, methacrylonitrile, 3-aminocrotononitrile ((*E*)-**10** and (*Z*)-**10**), butanenitrile, and isobutanenitrile were purified by distillation or sublimation before use.

Photochemistry: Photolyses were performed in cylindrical quartz cells (10 cm × 2.8 cm). The gas mixtures were prepared on a Hg-free vacuum line equipped with a Baratron Type 270 B signal conditioner and a 370 HA-1000 vacuum gauge. The light sources were a low-pressure mercury lamp with principal emissions at $\lambda = 184.9$ and 253.7 nm, a iodine discharge lamp with principal emission at $\lambda = 206.2$ nm,[49] and a Philips lamp TUV 6W with principal emission at $\lambda = 253.7$ nm. The light from the iodine lamp was filtered through 1 cm of distilled water to remove shorter wavelengths.[50] Controls were always performed to establish that there were indeed photochemical reactions: the gas mixtures were allowed to stand at room temperature in the absence of light for the same period of time that the corresponding samples were irradiated. The products of photochemical reactions and controls were analyzed by NMR. In the calculation of the percent light absorbed by NH_3 the absorption coefficients of NH_3 were estimated to be 87 and 47 $cm^{-1}\,atm^{-1}$ at $\lambda = 185$ and 206 nm, respectively.[51] The absorption coefficient of PH_3 at $\lambda = 185$ nm were estimated to be 100 $cm^{-1}\,atm^{-1}$.[16] The absorption coefficient of propynenitrile at $\lambda = 185$ and 206 nm were estimated to be 15 and 16,[32] respectively.

Photochemical addition of NH_3 to α,β-unsaturated nitriles: In a typical experiment, ammonia (50 Torr) was added to propynenitrile (50 Torr) in a quartz photolysis cell and the mixture was immediately irradiated. A brown solid, presumably oligomeric products, formed in the cell within 5 min. After irradiation for 1 h, the cell was quickly rinsed with either CH_2Cl_2 or $CDCl_3$ and immediately analyzed. The polymeric product was insoluble in these solvents. The spectral analysis of the extract proved the presence of 3-amino-2-propenenitrile (**9**).[23] UV (CH_2Cl_2): $\lambda_{max} = 247$ nm; *Z isomer*: ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 3.97$ (1 H, dt, $^3J(H,H)_{cis} = 8.3$ Hz, $^4J(H,H) = 0.8$ Hz, H2), 4.80 (2 H, broad, NH_2), 6.77 (1 H, dt, $^3J(H,H)_{cis} = 8.3$ Hz, $^3J(H,H) = 10.6$ Hz, H3); ^{13}C NMR ($CDCl_3$, 25 °C, TMS): $\delta = 62.5$ (ddt, $^1J(CH) = 178.9$ Hz, $^2J(CH) \approx {}^2J(CH) = 6.2$ Hz), 118.8 (d, $^2J(CH) = 13.8$ Hz), 150.3 (d, $^1J(CH) = 169.4$ Hz); *E* isomer: ^1H NMR ($CDCl_3$, 25 °C, TMS) $\delta = 4.29$ (1 H, dt, $^3J(H,H)_{trans} = 13.9$ Hz, $^4J(H,H) < 0.4$ Hz, H2), 4.55 (2 H, broad, NH_2), 7.00 (1 H, dt, $^3J(H,H)_{trans} = 13.9$ Hz, $^3J(H,H) = 10.7$ Hz, H3); ^{13}C NMR ($CDCl_3$, 25 °C, TMS): $\delta = 64.9$ (dt, $^1J(CH) = 168.6$ Hz, $^2J(CH) = 6.8$ Hz), 121.8 (d, $^2J(CH) = 5.4$ Hz), 151.6 (ddt, $^1J(CH) = 166.7$ Hz, $^2J(CH) \approx {}^3J(CH) = 4.2$ Hz); MS (70 eV): *m*/*z* (%) = 69 (3) [M^+], 68 (100) [$M^+ - H$], 67 (47) [$M^+ - 2H$], 66 (23) [$M^+ - 3H$], 52 (17) [$M^+ - NH_2 - H$], 41 (83) [$M^+ - HCN$]. The product yield was determined by a comparison of the area of the ^1H NMR spectrum with that of an internal standard of $CHCl_3$. It was not possible to detect the presence of 2-amino-2-propenenitrile or 2-aziridinecarbonitrile.[8]

The slow thermal addition of NH_3 to propynenitrile is complete within 12 h to form a mixture of (*E*,*Z*)-3-amino-2-propenenitrile (**9**). The rate of this addition appears to increase with time and a yield of < 0.5 % was observed after 1 h.

The same procedure was used in the investigation of the photochemical addition of ammonia to the other unsaturated nitriles used in this study, with the exception that a photolysis time of 3 h was used for the olefinic nitriles. The photolyses of acrylonitrile alone yielded a polymeric material and < 0.5 % of HCN and propynenitrile. The vapor pressure of 1-cyclohexenenitrile is 0.7 Torr at room temperature, therefore, it was only possible to study the reaction of 0.7 Torr of this unsaturated nitrile with excess (440 Torr) NH_3. The addition of ammonia to 2-butynenitrile gave the *E* and *Z* isomers of 3-aminocrotononitrile (**10**).[52]

2-Amino-2-butenedinitrile (11):[27] Butynedinitrile (50 Torr) and ammonia (50 Torr) were introduced into a photolysis cell; a brown solid formed in ≈ 1 min. The walls of the cell were then washed with either CH_2Cl_2 or $CDCl_3$. Evaporation of the solvent in vacuo led to the crude product (Yield: 21 %). The two isomers were obtained in a 8:1 ratio. *Major isomer*: ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 4.50$ (s, 1 H), 6.70 (br d, 2 H); ^{13}C NMR ($CDCl_3$, 25 °C, TMS): $\delta = 74.3$ (d, $^1J(CH) = 184.1$ Hz), 114.1 (d, $^2J(CH) = 6.3$ Hz), 115.7, 133.4; *Minor isomer*: ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 4.75$ (s, 1 H), 6.70 (br d, 2 H); ^{13}C NMR ($CDCl_3$, 25 °C, TMS): $\delta = 77.6$ (d, $^1J(CH) = 180$ Hz), 112.8, 116.8, 133.8; IR ($CHCl_3$) ($E + Z$) : $\tilde{\nu} = 3501$ (s, NH), 3398 (s, NH), 3020 (vs, NH), 2240 (w, CN), 2205 (m, CN), 1624 (s, C=C) cm^{-1}.

Photochemical addition of PH_3 or SiH_4 to α,β-unsaturated nitriles: In a typical experiment, phosphine (40 Torr) was added to propynenitrile (40 Torr) in a quartz photolysis cell, and the mixture was immediately irradiated. A pale yellow solid, presumably oligomeric products, formed in the cell within 5 min. The cell was irradiated for 1 h, then it was evacuated on a vacuum line and the volatile products were condensed onto a cold finger (77 K). A solvent ($CDCl_3$) was added at this step. The cold finger was disconnected from the vacuum line and dry nitrogen was added until the pressure had risen by 1 atm. The liquid nitrogen was removed and the products and solvent were collected in a NMR tube fitted to the bottom of the finger.

3-Phosphinopropanenitrile (7):[47] ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = -137.4$ (ttt, $^1J(P,H) = 195.5$ Hz, $^2J(P,H) = 10.5$ Hz, $^3J(P,H) = 5.7$ Hz); ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 1.85$ (dtm, 2 H, $^2J(P,H) = 10.5$ Hz, $^3J(H,H) = 7.2$ Hz), 2.56 (tm, 2 H, $^3J(H,H) = 7.2$ Hz, $^3J(P,H) = 5.7$ Hz), 2.83 (dm, 2 H, $^1J(P,H) = 195.5$ Hz).

3-Silylpropanenitrile (8):[48] ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 1.14$ (tq, 2 H, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 3.8$ Hz), 2.45 (t, 2 H, $^3J(H,H) = 8.0$ Hz), 3.58 (t, 3 H, $^3J(H,H) = 3.8$ Hz).

3-Phosphinoacrylonitrile (12) (*Z*:*E* = 85:15): *Z* isomer: ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = -136.0$ (tdd, $^1J(P,H) = 215$ Hz, $^2J(P,H) = 19.2$ Hz, $^3J(P,H) = 10.6$ Hz); ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 3.85$ (ddd, 2 H, $^1J(P,H) = 215$ Hz, $^3J(H,H) = 7.2$ Hz, $^4J(H,H) = 1.7$ Hz; PH_2), 5.87 (ddt, 1 H, $^3J(H,H)_{cis} = 12.6$ Hz, $^3J(P,H) = 10.6$ Hz, $^4J(H,H) = 1.7$ Hz; CHCN), 7.04 (ddt, 1 H, $^2J(P,H) = 19.2$ Hz, $^3J(H,H)_{cis} = 12.6$ Hz, $^3J(H,H) = 7.2$ Hz; CHP). *E* isomer: ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = -132.8$ (tdd, $^1J(P,H) = 209$ Hz, $^2J(P,H) = 17.9$ Hz, $^3J(P,H) = 5.6$ Hz); ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 3.70$ (ddd, 2 H, $^1J(P,H) = 209$ Hz, $^3J(H,H) = 6.7$ Hz, $^4J(H,H) = 1.9$ Hz; PH_2), 5.81 (ddt, 1 H, $^3J(H,H)_{Htrans} = 17.9$ Hz, $^3J(P,H) = 5.6$ Hz, $^4J(H,H) = 1.9$ Hz; CHCN), 7.18 (ddt, 1 H, $^2J(P,H) = {}^3J(H,H)_{trans} = 17.9$ Hz, $^3J(H,H) = 6.7$ Hz; CHP); HRMS: calcd. for C_3H_4NP: 85.00814, found: 85.0079; MS: *m*/*z* (%) = 86 (3.7) [M^+], 85 (86.7) [$M^+ - H$], 83 (22.8) [$M^+ - 3H$], 82 (24.2) [$M^+ - 4H$], 59 (19.6) [$M^+ - CN$], 58 (61.9) [$M^+ - HCN$], 57 (100) [$M^+ - H_2CN$].

3-Silylacrylonitrile (13) (*Z*:*E* = 83:17): *Z isomer*: ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 4.01$ (d, 3 H, $^3J(H,H) = 3.5$ Hz; SiH_3), 6.25 (d, 1 H, $^3J(H,H)_{cis} = 15.0$ Hz; CHCN), 6.85 (dq, 1 H, $^3J(H,H)_{cis} = 15.0$ Hz, $^3J(H,H) = 3.5$ Hz; CHSi). *E isomer*: ^1H NMR ($CDCl_3$, 25 °C, TMS): $\delta = 3.92$ (dd, 3 H, $^3J(H,H) = 3.3$ Hz, $^4J(H,H) = 0.6$ Hz; SiH_3), 6.03 (dd, 1 H, $^3J(H,H)_{trans} = 19.5$ Hz, $^4J(H,H) = 0.6$ Hz; CHCN), 7.00 (dq, 1 H, $^3J(H,H)_{Htrans} = 19.5$ Hz, $^3J(H,H) = 3.3$ Hz, CHSi). This data is in good agreement with that reported for the trimethylsilyl derivatives.[53]

Computational methods: All ab initio calculations were performed on a Silicon Graphics Indigo II workstation and Gaussian 94, Rev B. The computational data reported in Tables 6, 10, and 11 and Figure 1 are presented in the accepted format of the Theoretical Model/Basis Set. In cases where different levels of theory were used in the geometry optimization and energy determination portions of the calculation, the Model/Basis reported first refers to the energy calculation and the second Model/Basis refers to the theoretical model used in the geometry optimization. When only one Model/Basis data designation is given, both the geometry optimization and energy calculations were performed with the same method. In most cases, multiple theoretical models were used and their results reported to facilitate comparisons between the methods. Bold results indicate the lowest energy isomers of a given series. Since the calculations were performed on open-shell doublet species, several methods of handling the unpaired electron were tested. ROHF optimized energies were compared to UHF energies with the ROHF geometries. The full UHF geometry-optimized results are presented with S^2 values before and after spin annihilation (S^2, S^2_A). Where electron correlation was expected to contribute significantly to an energy comparison result, projected MP2 open-shell calculations were used at the 6-31G+ level of theory.

Acknowledgments: We thank Dr. Yoji Ishikawa and Dr. R. R. Jacobson for performing some of the initial photolyses of ammonia and propynenitrile. Financial support was provided by NASA grant NAG5-4557. J.-C.G.

thanks the Programme National de Planétologie (INSU-CNRS, France) for financial support.

Received: September 24, 1997 [F833]

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