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Synthesis and Characterization of 2,4-Pentadiynenitrile—A Key Compound in Space Science**

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Many molecules have been detected in the interstellar medium, around the stars, in comets, and in the atmospheres of the planets or satellites of the solar system.[1,2] Several of these molecules were probably also present on primitive Earth. Among the satellites, Titan, the largest moon of Saturn, is considered as a frozen model of early Earth. Many compounds were observed in the atmosphere of Titan, and assessments by astrobiologists have revealed that it could have similar atmospheric components and pressure conditions as Earth had four billion years ago. It is generally believed that the first chemical steps that led to life might have taken place in the atmosphere of Titan, and that the products were kept by freezing.[3]

The family of compounds that associates one or several C–C triple bonds and only one carbonitrile substituent ($H{-}(C{\equiv}C)_n{-}C{\equiv}N$) plays an important role in astrobiology.[4] As an example, the largest molecule detected in the interstellar medium is $HC_{11}N$ ($n=5$). The first member of this family, cyanoacetylene ($HC{\equiv}C{-}C{\equiv}N$ (**1**)), has been observed in the atmosphere of Titan,[3] in the interstellar medium,[1] in comets,[2] and in numerous laboratory simulations of planetary atmospheres.[5] It was often proposed as a key compound because it reacts readily with many nucleophiles,[6,7] and that could be the starting point of a rich organic chemistry in these media and particularly on primitive Earth.[8] Cyanobutadiyne (2,4-pentadiynenitrile, $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$ (**2**)) is the second member of this family. It has been detected in the interstellar medium,[1] in comets,[2] and appears in numerous laboratory simulations of Titan's atmosphere.[5]

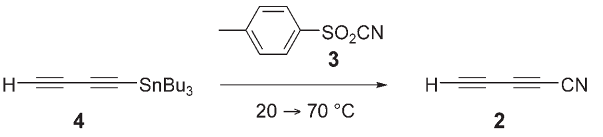
To confirm (or to disprove) models that foresee the presence of cyanobutadiyne on Titan, it is essential to have this molecule at hand. An infrared spectrum of the pure product would allow an estimation of the partial pressure of this molecule on Titan, provided it is detected there. The reaction of this compound with many reagents is of great interest in itself and by comparison with cyanoacetylene and cyanopropyne.[6,7] Moreover, the synthesis of pure cyanopolyynes with the formula $H{-}(C{\equiv}C)_n{-}C{\equiv}N$ is the key to a better knowledge of this family of compounds.

However, although the preparation of cyanoacetylene was reported long ago,[9] cyanobutadiyne has never been prepared in a pure form. The most important approaches are the desilylation of the corresponding trimethylsilylcyanobutadiyne[10] and a direct-current discharge in a mixture of cyanoacetylene and acetylene.[11] The recent detection of HC_5N in the pyrolysis of pyridine at 1200 °C in the presence of PCl_3[12] shows, once again, how challenging the preparation of this species is. In these approaches, the analysis was performed in the gas phase by microwave or infrared spectroscopy, but cyanobutadiyne has never been characterized in the condensed phase (by NMR spectroscopy, for example).

We now report the first isolation of cyanobutadiyne, its characterization by ^1H and ^{13}C NMR spectroscopy and by HRMS. We also described photochemical studies to propose syntheses of this compound in the interstellar medium or on planetary atmospheres, and some chemical reactions (the addition of Me_2NH, NH_3, and *t*BuSH) to study its reactivity with nucleophiles.

In 1993, Knochel and co-workers reported the synthesis of cyanooctyne by the reaction of commercially available *para*-toluenesulfonyl cyanide (**3**) with an octynylzinc derivative.[13] Some other organometallic compounds have also been used in such cyanation reactions.[14] Most of these compounds were prepared in low-boiling-point solvents (mainly ethers) and were not easily isolated in pure form. Hence, even if the reaction of alkynyl metal compounds with **3** could give the expected product, the extraction of a kinetically unstable product from the reaction mixture and its purification would be a very difficult problem. Other heterocompounds, such as silicon derivatives, can only be obtained by heating the reaction mixture for long periods of time, and these methods cannot be used to prepare kinetically unstable compounds in a facile manner.[15] However, tin derivatives with various functional groups are easily prepared, can be isolated in pure form, and are often reasonably reactive. For instance, 1,3-butadiynyltributylstannane (**4**), a potential precursor for cyanobutadiyne, has already been synthesized.[16] Thus, we sought an approach starting from **4** that would allow the continuous extraction of cyanobutadiyne from the reaction mixture as it is formed.[17]

The reaction of **4** with excess cyanide **3** led to the cyanobutadiyne **2**, which was selectively trapped at −80 °C to remove low-boiling-point impurities [Eq. (1)]. The high-boiling-point impurities were removed in the first trap cooled at −30 °C. The compound was obtained in pure form but in only 15 % yield. About 300 mg of cyanobutadiyne (**2**) has been prepared in one experiment through this approach. The



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Supporting information for this article (synthesis of **8**–**10** and photochemical studies) is available on the WWW under http://www.angewandte.org or from the author.

dilution of the reagents in a solvent (DMSO, dichlorobenzene, tetraethyleneglycol dimethyl ether, BMI-PF6 (an ionic liquid)) gave the product in similar or lower yields. The ^{1}H NMR signal was observed at $\delta = 2.41$ ppm, slightly upfield of the chemical shift for cyanoacetylene ($\delta = 2.51$ ppm). In the ^{13}C NMR spectra, the five signals for H-C5≡C4-C3≡C2-C1≡N were easily assigned by the decrease in the coupling constants between 5-H and the five carbon atoms. The molecular ion was detected by HRMS. Pure cyanobutadiyne can be kept indefinitely in dry ice, but decomposes slowly at −40 °C in pure form or at room temperature in $CDCl_3$.

This reaction between an unsaturated stannane and **3** can be extended to the preparation of cyanopropyne (85 % yield) or cyanoacetylene (37 % yield). Crotylstannane and allenylstannane reacted with a partial allylic transposition (crotyl/1-methallyl cyanide = 3:2, 43 % yield; allenyl/propargyl cyanide = 2:3, 72 % yield respectively).

The formation of cyanobutadiyne in the interstellar medium or in planetary atmospheres could occur photochemically.[18] Our synthesis of **2** allows traces of this molecule to be detected easily by ^{1}H NMR spectroscopy in various mixtures of compounds. Its presence can be confirmed by the addition of small amounts of an authentic sample to the NMR sample solutions and the observation of only one signal at $\delta_H = 2.41$ ppm. Thus we tried to determine which mixtures of gases would allow the photochemical formation of cyanobutadiyne. We irradiated gas mixtures with a mercury lamp ($\lambda =$ 185 and 254 nm or $\lambda = 254$ nm) with mercury UV lamps. We studied the photolysis of cyanoacetylene by itself, of cyanoacetylene with acetylene or butadiyne (**5**), and of dicyanoacetylene (**6**) with acetylene or butadiyne. All these compounds have been observed in the interstellar medium and the atmosphere of Titan. Several compounds were formed during the irradiations,[19] but we only discuss cyanobutadiyne.

We did not detect cyanobutadiyne in the photolysis of cyanoacetylene (50 mbar) by itself at 254 nm or at 185 and 254 nm. However, traces were detected in the photolysis of cyanoacetylene (50 mbar) with acetylene (50 mbar) at 185 and 254 nm. The best results were obtained when cyanoacetylene (3 equiv) absorbed most of the light (80 %).[19] Cyanobutadiyne was not observed in the same experiment with the 254-nm lamp. These results allow us to propose a reaction pathway that accounts for the fact that the breaking of the H−C bond of cyanoacetylene [Eq. (2)] and acetylene [Eq. (3)]

$$\mathrm{HC{\equiv}C{-}C{\equiv}N}\ (\mathbf{1}) \xrightarrow{h\nu} \mathrm{H}^{\cdot} + {}^{\cdot}\mathrm{C{\equiv}C{-}CN} \qquad (2)$$

$$\mathrm{H{-}C{\equiv}C{-}H} \xrightarrow{h\nu} {}^{\cdot}\mathrm{C{\equiv}C{-}H} + \mathrm{H}^{\cdot} \qquad (3)$$

does not occur at 254 nm irradiation.[20,21] A radical recombination of ethynyl and cyanoethynyl radicals could lead to the formation of **2** on a third body [Eq. (4)]. However, the

$${}^{\cdot}\mathrm{C{\equiv}C{-}H} + {}^{\cdot}\mathrm{C{\equiv}C{-}CN} \xrightarrow{\mathrm{M}} \mathbf{2} \qquad (4)$$

amounts of both radicals are probably too low to allow them to come close enough to each other to react. Consequently, the addition of the cyanoethynyl radical to acetylene [Eq. (5)]

$${}^{\cdot}\mathrm{C{\equiv}C{-}CN} + \mathrm{H{-}C{\equiv}C{-}H} \rightarrow \mathbf{2} + \mathrm{H}^{\cdot} \qquad (5)$$

or of the ethynyl radical to **1** [Eq. (6)] with concomitant

$${}^{\cdot}\mathrm{C{\equiv}C{-}H} + \mathbf{1} \rightarrow \mathbf{2} + \mathrm{H}^{\cdot} \qquad (6)$$

elimination of a hydrogen radical is a more likely reaction pathway. On the basis of previous studies[18,22] and by comparison with the addition of cyanide to acetylene,[23] the reaction pathway corresponding to Equations (2) and (5) seems to be the most favourable.

A mixture of **1** (50 mbar) and **5** (50 mbar) was irradiated at 254 or at 185 and 254 nm. In both cases, cyanobutadiyne (**2**) was not detected. A mixture of dicyanoacetylene (**6**) (50 mbar) and acetylene (50 mbar) was also irradiated. Traces of **2** were detected in the sample irradiated at 254 or at 185 and 254 nm. In this case, the absorption coefficients of each reactant gas are quite similar at 185 nm but only **6** absorbs light at 254 nm.[19] Compound **2** could possibly be formed by the breaking of an NC−C bond of **6** [Eq. (7)] and

$$\mathrm{NC{-}C{\equiv}C{-}CN}\ (\mathbf{6}) \xrightarrow{h\nu} \mathrm{N{\equiv}C}^{\cdot} + {}^{\cdot}\mathrm{C{\equiv}C{-}CN} \qquad (7)$$

then by addition of cyanoethynyl radical to acetylene [Eq. (5)]. On the other hand the formation of cyanoacetylene (**1**) in these reactions can be attributed to the addition of the cyanide radical to acetylene.[23]

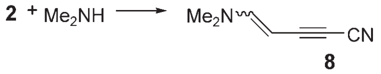
Under irradiation at 254 or at 185 and 254 nm, the photolysis of mixtures of **5** (50 mbar) and **6** (50 mbar) led to small amounts of **2**. The addition of the cyanide radical to **5** [Eq. (8)] gives a simple explanation of these results.[24]

$$\mathrm{N{\equiv}C}^{\cdot} + \mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}H}\ (\mathbf{5}) \rightarrow \mathbf{2} + \mathrm{H}^{\cdot} \qquad (8)$$

It also seems possible that cyanohexatriyne (HC≡C−C≡C−C≡C−C≡N (**7**)) is formed by the addition of the cyanoethynyl radical to butadiyne. Similarly, **7** might be formed in the photolysis of mixtures of **1** and **5** reported above. In both cases, without an authentic sample of **7**, we were not able to confirm its presence on the sole basis of the signal observed at $\delta_H = 2.38$ ppm. For the moment we have demonstrated that cyanobutadiyne (**2**) is easily formed in the photolysis of several mixtures of gases. More sophisticated experiments will be necessary to quantify its formation.

Cyanoacetylene reacts readily with nucleophiles such as ammonia, primary or secondary amines, and thiols to give the corresponding adduct.[6,7,25,26] In the same way, we investigated the reactivity of cyanobutadiyne, particularly with nucleophiles, and determined the products formed. Cyanobutadiyne can potentially undergo 1,4- or 1,6-addition. In this preliminary study, we carried out the addition to cyanobutadiyne in a solvent of Me_2NH, NH_3, and *t*BuSH.

N,*N*-Dimethylamine reacts with cyanobutadiyne (**2**) to give the corresponding 1,6-adduct. The 5-(dimethylamino)-4-penten-2-ynenitrile (**8**) was analyzed by HRMS and by ^{1}H and ^{13}C NMR spectroscopy [Eq. (9)]. Compound **8** decomposes upon standing at room temperature. Similarly, ammonia



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(9)

reacts with cyanobutadiyne to give 5-amino-4-penten-2-ynenitrile (**9**), which is kinetically unstable at room temperature, even when diluted in CDCl$_3$ ($\tau_{1/2} = 1$ h) [Eq. (10)]. A stable adduct, 5-[(1,1-dimethylethyl)thio]-4-penten-2-ynenitrile (**10**) was obtained by the addition of *t*BuSH to **2** in the presence of a catalytic amount of triethylamine [Eq. (11)]. In all cases, only the product corresponding to the 1,6-addition reaction was observed.

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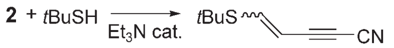

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In conclusion, cyanobutadiyne (**2**) was synthesized in pure form by the reaction of the 1,3-butadiynyltributylstannane with *p*-toluenesulfonyl cyanide. This approach paves the way to the synthesis of other cyanopolyynes and the corresponding isotopomers. According to our study, cyanobutadiyne can possibly be formed on Titan or in the interstellar medium by photolysis of mixtures of acetylene and cyanoacetylene or dicyanoacetylene or mixtures of dicyanoacetylene and butadiyne. Compound **2** only undergoes 1,6-addition with nucleophiles. The measurement of the gas-phase IR spectrum of a pure sample of **2**, the study of its photochemistry, and the extension of this approach to other cyanopolyynes are currently underway in our laboratory.

Experimental Section

2: Two traps equipped with stopcocks were attached to a vacuum line. 1,3-Butadiynyltri-*n*-butylstannane (**4**; 0.54 g, 1.6 mmol) and *p*-toluenesulfonyl cyanide (**3**; 0.90 g, 5.0 mmol) were introduced into a flask equipped with a stirrer bar and the flask was attached to the vacuum line. The flask was immersed in a bath and slowly warmed to 70 °C over 1 h. The cyanobutadiyne (**2**) formed was continuously removed by distillation in vacuo from the reaction mixture. The first trap, cooled at −30 °C, selectively removed the less-volatile products, and **2** (18 mg, 0.24 mmol, 15 %) was selectively condensed in the second trap cooled at −80 °C. IR (gas phase): $\tilde{\nu} = 642, 1272, 2190$ ($\nu_{C\equiv C}$), 2253 ($\nu_{C\equiv N}$), 3328 cm^{-1} ($\nu_{C\text{-}H}$); ^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): $\delta = 2.41$ ppm; ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): $\delta = 48.9$ ($^{4}J_{C,H} < 1$ Hz; C2), 66.0 ($^{2}J_{C,H} = 52.2$ Hz; C4), 66.9 ($^{3}J_{C,H} = 6.4$ Hz; C3), 71.7 ($^{1}J_{C,H} = 265.0$ Hz; C5), 104.8 ppm (C1); HRMS: calcd for HC$_5$N: 75.01090; found: 75.0109; MS: *m/z* (%): 76 (3.6), 75 (100), 74 (11.2), 50 (3.4), 49 (6.8).

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