salts in solution ranging from all anti to all syn eliminations, including cases where one stereoisomer is formed by anti and the other by syn elimination.[2,21]

The present study provides direct information on the intrinsic regio- and stereospecificity of a model base-induced 1,2-elimination reaction in the dilute gas state, where interference from solvation and ion pairing is completely excluded. The relevant results point to a regiospecific attack of NMe_3 on the onium intermediates I, yielding preferentially the Hoffman olefin over the Saytzeff one, via a mechanism involving a transition state (i.e. IV*) with an anti configuration, in partial agreement with analogous solvolytic processes. No stereoelectronic control is, instead, exerted in the gas-phase base-induced ring opening of cyclic onium ions, such as II (path c of Scheme II), a process which is still unknown in solution chemistry.

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(21) Bartsch, R. A.; Zavada, J. *Chem. Rev.* **1980**, *80*, 453.

Thioformyl Cyanide. Gas-Phase Synthesis and Millimeter Wave Spectrum

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Abstract: The elusive monomeric thioformyl cyanide HCSCN, a possibly cosmic species, has been generated in the gas phase, either by flash-thermolytic retroene reaction of allylcyanomethyl sulfide or by vacuum gas–solid dehydrochlorination of cyanomethylsulfenyl chloride over potassium carbonate. An investigation by millimeter wave spectroscopy led to unambiguous identification, molecular constants, and lifetime of HCSCN.

The elusive molecule thioformyl cyanide, HCSCN (**1**), has been until now only indirectly detected. [$4\pi + 2\pi$] adducts deriving from thioaldehyde **1** were obtained when the reaction of dibromoacetonitrile with potassium ethylxanthate[1] or the photolysis of cyanomethylphenacyl sulfide[2] was performed in the presence of 2-ethoxybutadiene. The regioselectivity observed in these cycloadditions of **1** was explained on the grounds of molecular orbital calculations.[3] Adducts between **1** and cyclopentadiene or 2,3-dimethylbutadiene were also obtained by dehydrosulfonation of the corresponding Bunte salt using triethylamine in the presence of these dienes and calcium chloride.[4] A kinetic study of the gas-phase flow thermolysis of allyl cyanomethyl sulfide (**2**), leading only to propene and trimers of **1**, led to the conclusion of a nonconcerted process for the involved retroene reaction.[5]

Several small organosulfur compounds, closely related to **1**, have already been generated by flash vacuum thermolysis (FVT) and investigated, inter alia, by millimeter wave spectroscopy.[6] As a part of our work concerning reactive molecules, possibly involved as interstellar species owing to their simplicity and the cosmic abundance of their constituting functions ($C\equiv N$, $C=O$, $C=S$; see ref 7 for some reviews on the interstellar chemistry) we reported recently the retroene synthesis and millimeter wave spectrum of formyl cyanide, HCOCN;[8] such spectra, when compared with radiotelescopic signals, are of utmost interest for an unambiguous identification of interstellar molecules.[9] We describe now two independent gas-phase syntheses of thioformyl cyanide **1** (Scheme I) as well as, for the first time, the experimental identification and molecular constants of monomeric **1**, by millimeter wave spectroscopy.

The reaction of chloroacetonitrile (**3**) with sodium allylmercaptide led to allyl cyanomethyl sulfide (**2**),[5] obtained in 70% yield after distillation on a spinning-band column (Scheme I, path A). The flash vacuum thermolysis (FVT) of **2** (10^{-5} mbar, 800 °C) led exclusively, via a retroene reaction, to propene (yield 90%, determined by NMR spectroscopy) and solid 1,3,5-trithiane **4**, as already observed in the flow thermolysis of **2**;[5] the NMR spectrum of this solid, when compared with those of *s*-trithiane-2,4,6-trithiols,[10] was in agreement with the mixture trans/cis **4** (ratio 85/15). The monomeric **1** was characterized by on-line millimeter wave spectroscopy (see hereafter); however, attempts at direct observation of **1**, either by mass or low-temperature (−196 °C) IR spectroscopy, remained negative (the identification of

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(1) Vedejs, E.; Arnost, M. J.; Dolphin, J. M.; Eustache, J. *J. Org. Chem.* **1980**, *45*, 2601–2604.

(2) Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445–1447.

(3) Vedejs, E.; Perry, D. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1983**, *105*, 6999–7001.

(4) Kirby, G. W.; Lochead, A. W.; Sheldrake, G. N. *J. Chem. Soc., Chem. Commun.* **1984**, 922–923.

(5) Martin, G.; Martinez, H.; Suhr, H.; Suhr, U. *Int. J. Chem. Kinet.* **1986**, *18*, 355–362.

(6) See, e.g.: Block, E.; Penn, R. E.; Olsen, R. J.; Sherwin, P. E. *J. Am. Chem. Soc.* **1976**, *98*, 1264–1265. Penn, R. E.; Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 3622–3623. Block, E.; Penn, R. E.; Ennis, M. D.; Owens, T. A.; Yu, S.-L. *J. Am. Chem. Soc.* **1978**, *100*, 7436–7437. Block, E.; Penn, R. E.; Revelle, L. K. *J. Am. Chem. Soc.* **1979**, *101*, 2200–2201. Georgiou, K.; Kroto, H. W. *J. Mol. Spectrosc.* **1980**, *83*, 94–104. Block, E.; Corey, E. R.; Penn, R. E.; Renken, T. L.; Sherwin, P. E.; Bock, H.; Hirabayashi, T.; Mohmand, S.; Solouki, B. *J. Am. Chem. Soc.* **1982**, *104*, 3119–3130.

(7) Huntress, W. T., Jr. *Chem. Soc. Rev.* **1977**, *6*, 295–323. Mann, A. P. C.; Williams, D. A. *Nature* **1980**, *283*, 721–725. Turner, B. E. *J. Mol. Evol.* **1980**, *15*, 79–101. Green, S. *Annu. Rev. Phys. Chem.* **1981**, *32*, 103–138. Kroto, H. W. *Chem. Soc. Rev.* **1982**, *11*, 435–491. Duley, W. W.; Williams, D. A. *Interstellar Chemistry*; Academic Press: New York, 1984.

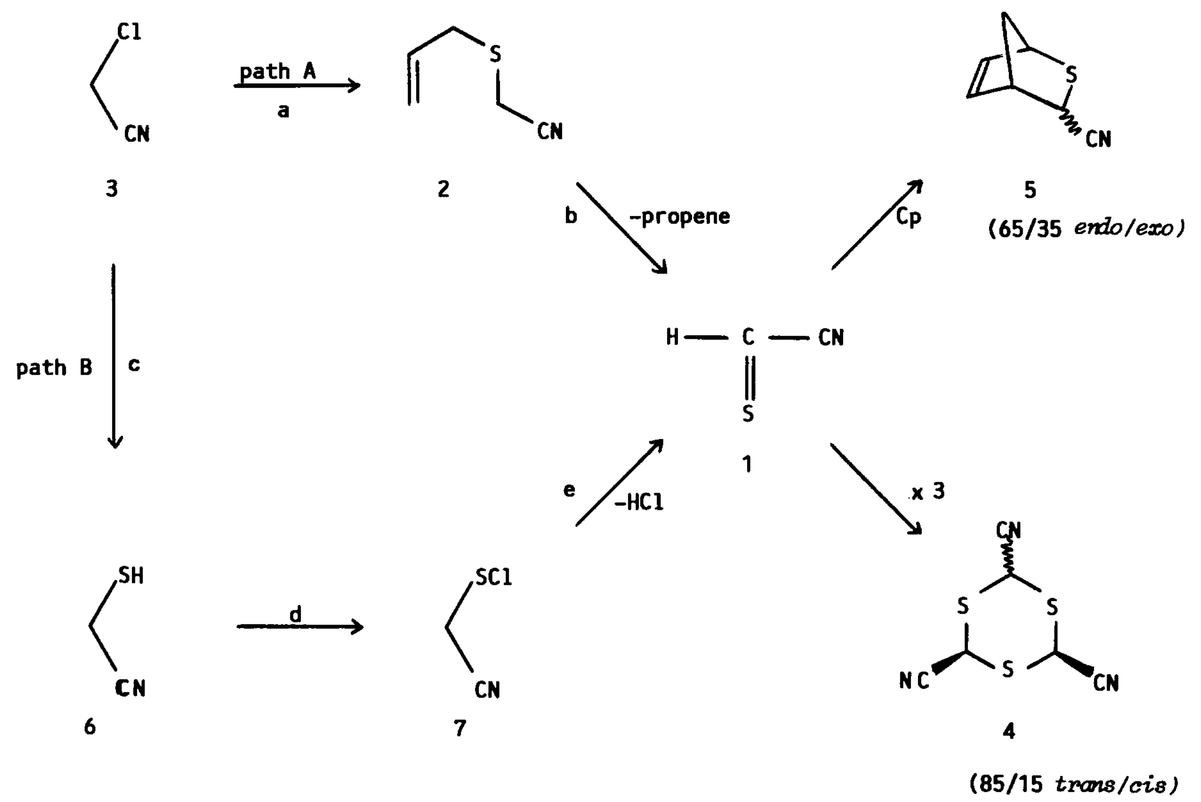
(8) Bogey, M.; Destombes, J. L.; Vallée, Yo.; Ripoll, J. L. *Chem. Phys. Lett.* **1988**, *146*, 227–229.

(9) Winnewisser, M. *Chem. Unserer Zeit* **1984**, *18*, 1–61.

(10) Akerström, L.; Olsson, K. *Chem. Scr.* **1980**, *16*, 130–133.

0002-7863/89/1511-7399$01.50/0

Scheme I



[a] Allylmercaptan, NaOH, MeOH, 0 °C. [b] FVT, 700–800 °C, 10^{-5} mbar. [c] Aq NaSH, 0 °C. [d] NCS, $CHCl_3$, 0 °C. [e] VGSR, K_2CO_3, 220 °C, or Et_3N, benzene, −30 °C.

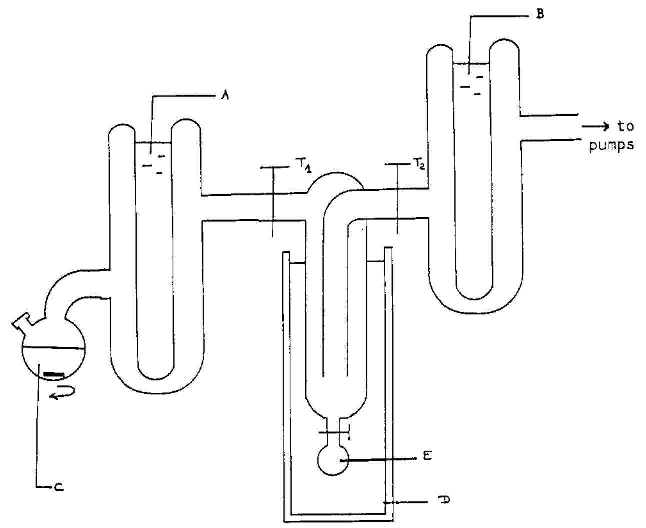


Figure 1. Apparatus used for purification of sulfenyl chloride (**7**): A, B, cold fingers (liquid nitrogen); C, flask with reaction mixture; D, cold trap (−40 °C); E, receiving flask; T_1 and T_2, O-ring taps.

formyl cyanide using this last technique has been, by contrast, successful[8]). In the FVT of **2**, the admission of gaseous cyclopentadiene at the oven exit, followed by cotrapping of the products at −196 °C, led to the expected cycloadduct **5**, identical with that already reported,[4] in 42% yield.

Treatment of **3** with aqueous sodium hydrosulfide gave the thiocyanohydrin (**6**),[11] which afforded, after chlorination by N-chlorosuccinimide (NCS), the sulfenyl chloride **7** (Scheme I, path B). Purification of the thermally labile **7** was performed by trap-to-trap distillation (see Experimental Section and Figure 1). The vacuum gas–solid reaction (VGSR)[12] of **7** with potassium carbonate at 220 °C led to thioformyl cyanide **1**, directly analyzed by millimeter wave spectroscopy. The dehydrochlorination of **7** by triethylamine in benzene solution, performed at −30 °C in the presence of cyclopentadiene, afforded the cycloadduct **5** in ca. 50% yield.

Figure 2. Part of the HCSCN spectrum showing a characteristic pattern with different K_a components of the J:33←32 transition (together with some lines belonging to an unidentified byproduct); frequency scan 204.2–204.3 GHz.

Millimeter Wave Spectroscopy of Thioformyl Cyanide (1). To our knowledge, no theoretical ab initio structure of **1** has been determined. Therefore, the molecular geometry and the dipole moment of this molecule are unknown. However, estimated values of the rotational and centrifugal distortion constants have been deduced from those of propynethial,[13] which is isoelectronic to **1**: these constants were scaled with the same factors as those relating the experimental parameters of the two isoelectronic molecules formyl cyanide[8] and propynal.[14]

These values were used to predict the millimeter wave absorption spectrum and a characteristic pattern for the transition J:34←33 was searched for in the 210-GHz region. Many lines were observed when allylcyanomethyl sulfide (**2**, Scheme I, path

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(11) Mathias, E.; Shimanski, M. *J. Chem. Soc., Chem. Commun.* **1981**, 569–570.

(12) For the description of this apparatus and some other synthetic applications, see, for example: Guillemin, J. C.; Denis, J. M. *Tetrahedron* **1988**, *44*, 4431–4446.

(13) Brown, R. D.; Godfrey, P. D.; Champion, R.; Woodruff, M. *Aust. J. Chem.* **1982**, *35*, 1747–1753.

(14) Winnewisser, G. *J. Mol. Spectrosc.* **1973**, *46*, 16–24.

Table I. Rotational and Centrifugal Distortion Constants of HCSCN

	this work	estd from comparison with HCSCCH[a]
A, MHz	43 314.0052 (34)	42 314.40
B, MHz	3205.67686 (24)	3227.87
C, MHz	2975.32470 (23)	2995.29
D_J, kHz	1.26557 (17)	1.33
D_{JK}, kHz	−102.0177 (24)	−101.0
D_K, kHz	3756.07 (32)	4170
d_1, kHz	−0.228 786 (42)	−0.235
d_2, kHz	−0.008 266 (20)	−0.005
H_J, Hz	0.002 753 (41)	
H_{JK}, Hz	−0.137 27 (41)	
H_{KJ}, Hz	−19.310 (38)	
H_K, Hz	977.9 (86)	
h_1, Hz	0.000 919 (11)	
h_2, Hz	0.000 040 0 (99)	
h_3, Hz	0.000 018 2 (15)	
L_{KJ}, Hz	−0.006 34 (19)	
S_{KJ}, Hz	−0.000 002 01 (27)	

[a] See text.

A) was thermolyzed inside the cell, and the experimental conditions were checked by observing a millimeter wave transition of propene. The identification of the lines belonging to thioformyl cyanide **1** was confirmed by generating this compound using the vacuum gas–solid reaction of sulfenyl chloride **7** over potassium carbonate at 220 °C (Scheme I, path B). Both methods led to a common pattern of lines (Figure 2) which were definitely ascribed to **1** and identified. The best absorption signal was obtained, by using path A, with a pressure in the cell of 10^{-2} mbar and a thermolysis temperature of ca. 700 °C.

The first identifications led to an improvement of the predictions via a least-squares analysis of the data. Successive iterations of this process allowed the measurement of 152 lines belonging to the a- and b-type spectra in the frequency range 130–280 GHz. They are characterized by $2 < J < 57$ and $K_a < 20$. A complete list of the measurements is available as supplementary material (see the paragraph at the end of the paper).

As for formyl cyanide,[15] some lines were split by quadrupolar hyperfine interaction induced by the ^{14}N nucleus; this definitely confirmed the attribution of the measured spectrum to thioformyl cyanide. However, owing to the weakness of these lines and to the overlapping of some of the components by transitions belonging to unidentified byproducts, a careful analysis of this interaction was not possible.

All the measurements were fitted to Watson's S-reduced Hamiltonian in the I^r axis representation,[16] and the deduced molecular constants are given in Table I. Owing to the high values of J and K_a of some observed transitions, two higher order centrifugal distortion terms, L_{KJ} (octic) and S_{KJ} (dectic) were included in the Hamiltonian. The transition frequencies are believed to be accurate to 30–50 kHz, and the standard deviation of the fit is 28.8 kHz, consistent with this accuracy. It is noteworthy that these molecular constants agree quite well with those empirically deduced from the isoelectronic molecule propynethial (see Table I). Note that the determination of the geometrical structure will need the study of all the isotopically monosubstituted species.

In order to measure the lifetime of thioformyl cyanide **1**, we have used an external oven connected to the cell via a glass stopcock. We then measured a $1/e$ lifetime of 4.5 s at 10^{-2} mbar, much shorter than that of formyl cyanide (29 min in similar conditions).[8]

Experimental Section

General Procedures. All reactions were carried out under nitrogen. Solvents and starting materials were redistilled prior to use. NCS and K_2CO_3 used in VGSR[12] were dried for 15 h at 150 °C under vacuum. IR spectra were obtained by using Perkin-Elmer 1420 or 1756 spectrometers. NMR spectra were recorded on Bruker WP 80 CW or AM 300 with chemical shifts δ (ppm) relative to internal $SiMe_4$. The millimeter wave spectrometer used in this work has been described previously.[17]

Allyl Cyanomethyl Sulfide (2). To a solution, stirred at 0 °C under nitrogen, of sodium hydroxide (7.2 g, 0.18 mol) in methanol (70 ml), freshly distilled allyl mercaptan (13.3 g, 0.18 mol) and, after 1 h, chloroacetonitrile (13.6 g, 0.18 mol) were added slowly. After 20 h, the reaction mixture was filtered, ether added, and the mixture washed with brine. After drying of the organic layer over sodium sulfate and evaporation of solvents, the product was quickly distilled under 12 mbar and redistilled on a spinning-band column to give 14.2 g of sulfide **2** (bp_{12} = 76–77 °C, yield 70%); ^{1}H NMR ($CDCl_3$) δ 3.23 (s, 2 H), 3.48 (d, 2 H), 4.85–6.16 ppm (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 15.5, 34.9, 116.3, 119.3, 131.9 ppm; IR (film) 2978, 2245, 1632, 1430, 1402, 992, 928 cm^{-1}.

FVT of Sulfide 2. Sulfide **2** (100 mg, 0.88 mmol) was evaporated in ca. 5 min through an empty quartz tube (l = 10 cm, i.d. = 1.6 cm) heated at 800 °C ($p = 10^{-5}$ mbar). For NMR experiments, the products were collected at −196 °C over solid $CFCl_3$. After separation of an insoluble solid, the solution, analyzed by ^{1}H NMR, showed only the presence of propene (0.79 mmol, 90% yield by comparison with an internal standard of benzene). The solid residue (45 mg, 72%), fairly soluble in methanol and DMSO, was shown, by comparison with the previously reported results,[5] to be trimeric thioformyl cyanide (**4**): ^{1}H NMR (DMSO) δ 5.03 (15%, cis isomer), 6.3–6.7 ppm (85%, trans isomer); ν_{CN} (KBr) 2245 cm^{-1}.

The thermolysis of sulfide **2** was repeated in the above conditions, unless 0.2 mL of cyclopentadiene were evaporated during the thermolysis from a flask placed at the oven exit. The products trapped at −196 °C were allowed to warm to room temperature, and the propene and excess of cyclopentadiene removed under vacuum. The residual material (51 mg), dissolved in $CDCl_3$ and analyzed by NMR, was shown to be a ca. 65/35 mixture of *endo–exo*-2-thiabicyclo[2.2.1]hept-5-ene-3-carbonitrile (**5**) in accordance with the reported values[4] (yield 42%).

Cyanomethanesulfenyl Chloride (7). In a 25-mL round-bottomed flask C (Figure 1) was placed a solution of NCS (0.43 g, 3.22 mmol) in 2.5 mL of freshly distilled chloroform. After this was cooled to 0 °C, a solution of thiocyanohydrin (**6**, 0.2 g, 2.74 mmol, prepared according to the literature[11] by treatment of chloroacetonitrile (**3**) with aqueous sodium hydrosulfide) in chloroform (0.8 mL) was added dropwise with stirring during 90 min. The temperature was maintained for 5 min, and then the flask was fitted on the vacuum line. Due to the instability of sulfenyl chloride **7**, the apparatus described in Figure 1 was used. Volatile compounds ($CHCl_3$ and sulfenyl chloride **7**) were distilled at room temperature and collected on the liquid nitrogen cold finger A. Then, sulfenyl chloride **7** was purified by warming after cooling B to −196 °C and the trap D to −40 °C, this last temperature allowing only the condensation of **7**. The two O-ring taps T_1 and T_2 were then turned off, and the product **7** was collected in the flask E by cooling this flask to −196 °C; purity >95% (NMR); 50% yield; ^{1}H NMR ($CDCl_3$) δ 3.98 ppm (s); ^{13}C NMR ($CDCl_3$) δ 26.7 (t, ^1J = 149 Hz), 114.8 ppm (t, ^2J = 7.9 Hz); ν_{CN} (CCl_4) 2250 cm^{-1}. Formation of cyanomethyl disulfide [^{1}H NMR ($CDCl_3$) δ 3.76 ppm (s)] occurred if the rate of addition was too fast. The temperature used in the reaction $\mathbf{6} \rightarrow \mathbf{7}$ has to be carefully controlled owing to the rapid thermal decomposition of **7** (half-life ca. 5 min at 20 °C).

2-Thiabicyclo[2.2.1]hept-5-ene-3-carbonitrile (5). A solution of freshly distilled cyclopentadiene (0.11 g, 1.66 mmol) in benzene (2.5 mL) was added with stirring to sulfenyl chloride **7** purified as above (0.10 g, 0.93 mmol). After this was cooled to −30 °C, a solution of Et_3N (0.19 g, 1.88 mmol) in methanol (2.5 mL) was added dropwise during 15 min. The temperature was maintained for 30 min, and then the reaction flask was allowed to warm to room temperature. After 60 min, benzene and methanol were removed, and the reaction mixture was shown by ^{1}H NMR to consist mainly of the cycloadduct **5** obtained in ca. 50% yield (same isomeric ratio as above).

Thioformyl Cyanide (1): Analysis by Millimeter Wave Spectroscopy. The observation cell (l = 175 cm) mainly consisted of a Pyrex tube (i.d. = 10 cm) terminated by a sphere (i.d. = 35 cm) containing a quartz FVT oven (l = 10 cm, i.d. = 1.6 cm),[18] this configuration reducing the wall recombination of reactive species. An external cooling of the sphere was maintained by flowing water from an annular shower. Allylcyanomethyl sulfide (**2**) was slowly vaporized through the oven under 10^{-2}–10^{-3} mbar, and the gaseous flow directly analyzed when passing through the cell.

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(15) Bogey, M.; Destombes, J. L.; Vallée, Yo.; Ripoll, J. L., to be published.

(16) Watson, J. K. G. *Vibrational Spectra and Structure*; Durig, J. R., Ed; Elsevier: Amsterdam, 1977; Vol. 6, pp 1–89.

(17) Bogey, M.; Demuynck, C.; Destombes, J. L.; Lapauw, J. M. *J. Phys. E: Sci. Instrum.* **1986**, *19*, 520–525.

(18) Bogey, M.; Destombes, J. L.; Denis, J. M.; Guillemin, J. C. *J. Mol. Spectrosc.* **1986**, *115*, 1–14.

For VGSR generation of thioformyl cyanide (**1**) the precursor **7** was vaporized through an external reactor (l = 20 cm, i.d. = 2.5 cm, half-filled with dried K_2CO_3) fitted to the sphere and heated to 220 °C (p = 10^{-2} mbar). The lifetime of **1** in the gas phase (25 °C, 10^{-2} mbar) was obtained by thermolysis of the precursor **2** in an external FVT oven; the observation cell was then isolated by stopcocks from oven and vacuum pumps, and the decay of the absorption recorded.

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Supplementary Material Available: Millimeter wave spectrum of thioformyl cyanide in the ground vibrational state between 130 and 280 GHz (measured and calculated frequencies) (3 pages). Ordering information is given on any current masthead page.

Vinylation of Aromatic Substrates by Free Unsolvated Vinyl Cation in the Gaseous and Liquid Phase

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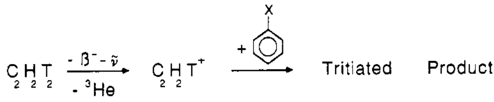
Abstract: The nuclear-decay technique has been employed to generate free, unsolvated vinyl cation, $C_2H_2T^+$, and to investigate its reactivity and selectivity toward substituted arenes both in the gas phase and in the liquid phase. The differences between the reactivity pattern of unsubstituted vinyl cation in the two environments are rationalized in terms of the much greater efficiency of collisional stabilization in the condensed phase, allowing a larger fraction of the excited arenium ions, from the highly exothermic ($-\Delta H° > 73$ kcal mol^{-1}) attack of the vinyl cation on the selected aromatics, to survive dissociation. An additional difference arises from a change of the nature of the vinylating reactant, when additives, such as Ar or CO, are introduced into the gaseous mixtures. The mechanisms of the two major competitive processes promoted by $C_2H_2T^+$ attack on substituted arenes, i.e. vinylation and tritonation, as well as the isomerization pathways of the ensuing adducts as a function of the experimental conditions, are discussed and compared with related results. The present study allows the first experimental evaluation of the substrate and positional selectivity of a very elusive species, such as $C_2H_3^+$, which is compared with that of other reactive gaseous electrophiles and of more conventional vinylating reagents produced under solvolytic conditions.

Substituted vinyl cations are now recognized organic intermediates,[1] some of them stable enough to be directly observable by ^1H and ^{13}C NMR spectroscopy under non-nucleophilic conditions.[2] However, very little is known as to the actual occurrence and the reactivity of the unsubstituted vinyl cation. In fact, generation of $C_2H_3^+$ in solution is an interesting challenge that was first undertaken by Berthelot as long ago as 1862.[3] His studies, and those of others over the following 20 years, established that acetylene is converted, in H_2SO_4, first into acetaldehyde and then into crotonaldehyde. More recently, Olah et al.[4] showed that the reaction of acetylene with FSO_3H at low temperatures gives vinyl fluorosulfate, which, however, decomposed above −15 °C. Then, Tidwell et al.[5] carried out a quantitative study of the reactions taking place in C_2H_2/90–95% H_2SO_4 mixtures at 25 °C in an attempt to determine spectroscopically whether $C_2H_3^+$ is involved.

In the gas phase, $C_2H_3^+$ ions can easily be produced by mass spectrometry and their heat of formation evaluated.[6] A number of mass spectrometric investigations have been carried out to determine the reactivity pattern of $C_2H_3^+$ ions with simple hydrocarbons and to measure the rate constants for the formation of the charged products.[7] In these approaches, a major difficulty is found in the largely variable energy content of the encounter complex between the vinyl cation and the substrate molecule, which makes kinetic measurements[8] and product distribution[9] appreciably dependent upon the method adopted and, in any event, hardly comparable with those from the same processes occurring between thermally equilibrated species in the condensed phase.

This difficulty has been recently overcome by resorting to the nuclear-decay technique,[10] which allowed us to obtain electronically ground-state vinyl cations by spontaneous β-decay in bitritiated ethylene in both gaseous and liquid phase (eq 1).[11] By



(1)

(I)

X = H, Me, F, Cl, Br, OMe

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(1) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979.

(2) Koch, E. W.; Siehl, H. U.; Hanack, M. *Tetrahedron Lett.* **1985**, *26*, 1493, and references cited herein.

(3) Berthelot, M. *C.R. Hebd. Seances Acad. Sci.* **1862**, *50*, 805.

(4) Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1845.

(5) Quoted as ref 35 in: Tidwell, T. T. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 20.

(6) (a) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357. (b) Lossing, F. P. *Ibid.* **1972**, *50*, 3973. (c) Field, F. H.; Lampe, F. W. *J. Am. Chem. Soc.* **1958**, *80*, 5587. (d) Smith, R. D.; Futrell, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *20*, 71.

(7) (a) Adams, N. G.; Smith, D. *Chem. Phys. Lett.* **1977**, *47*, 383. (b) Buttrill, S. E., Jr.; Kim, J. K.; Huntress, W. T., Jr.; LeBreton, P.; Williamson, A. *J. Chem. Phys.* **1974**, *61*, 2122. (c) Senzer, S. N.; Lim, K. P.; Lampe, F. W. *J. Phys. Chem.* **1984**, *88*, 5314. (d) Kim, J. K.; Anicich, V. G.; Huntress, W. T., Jr. *Ibid.* **1977**, *81*, 1798. (e) Batey, J. H.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1263.

(8) (a) Fornarini, S.; Gabrielli, R.; Speranza, M. *Int. J. Mass Spectrom. Ion Proc.* **1986**, *72*, 137. (b) Fornarini, S.; Speranza, M. *J. Chem. Phys.* **1987**, *91*, 2154.

(9) (a) Morrison, J. D.; Stanney, K.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 838. (b) Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1985**, *107*, 5358.

(10) Cacace, F.; Speranza, M. In *Techniques for the Study of Ion Molecules Reactions*; Farrar, J. M., Saunders, W., Jr., Eds.; Wiley: New York, 1988.

(11) Fornarini, S.; Speranza, M. *Tetrahedron Lett.* **1984**, *25*, 869.