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Gas-Phase Base-Induced Elimination Reactions in Onium Intermediates. 2.[1] Stereochemistry and Orientation in Alkene Formation from Gaseous Halonium Ions

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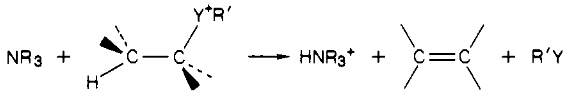
Abstract: The stereochemistry and the orientation in gas-phase NMe_3-induced elimination reactions on a number of halonium ions were investigated under different experimental conditions. The halonium ion intermediates were generated in the gas phase at 760 Torr by attack of radiolytically formed $C_nH_5^+$ (n = 1,2) acids on selected 2,3-dihalobutanes. Isolation and identification of the neutral haloalkenes formed allowed us to demonstrate that, under the used experimental conditions, 3-halo-1-butene is preferentially formed over isomeric 2-halo-2-butenes. In addition, gas-phase base-induced elimination reactions occur predominantly via a transition state with an anti configuration. The elimination pathway takes place in competition with an intramolecular nucleophilic displacement within protonated 2,3-dihalobutene yielding the inverted 2,3-butanediylhalonium ion, which further rearranges slowly to the 2-halo-2-butyl cation. No stereoelectronic control is exerted in the NMe_3-induced ring opening of 2,3-butanediylhalonium ions, whereas 2-halo-2-butyl cation generates preferentially *trans*-2-halo-2-butene (ca. 70%). Kinetic treatment of the experimental results enabled us to provide a quantitative estimate of the relative extent of bimolecular elimination reactions and unimolecular displacement and rearrangement processes within protonated 2,3-dihalobutanes. Furthermore, the influence of the nature and the configuration of the substrate upon the relative extent of these processes could be evaluated. A mechanistic model is proposed for gas-phase base-induced eliminations in onium ions at relatively high pressures, which is contrasted with those from related low-pressure ion cyclotron resonance mass spectrometry and solution-chemistry studies.

Important questions regarding ionic E2 elimination reactions concern the orientation control exerted by the substrate on the incoming base and the stereochemistry of the ensuing transition state. In fact, the specific behavior responds to intrinsic electronic and conformational requirements in the substrate and to the properties of the attacking base, factors which can be dramatically perturbed in solution by specific solvation phenomena.[2] Kinetic investigation of ionic elimination reactions in the gas phase, where interference from solvent and counterion is excluded, would appear as a straightforward answer to such questions. Accordingly, ion cyclotron resonance and FT-ICR mass spectrometry[3] as well as the flowing afterglow technique[4] proved to be very useful for the study of gas-phase E2 elimination reactions induced by the attack of negative ions on neutral substrates. FT-ICR has also been applied by one of us to gain first insight into another class of gas-phase E2 elimination reactions, namely, the promoted by the interaction of a neutral base with an onium intermediate (eq 1).[1]



(1)

R, R′ = H or alkyl groups; Y = halogen

The relevant results, discussed in the preceding paper,[1a] indicate that, under FT-ICR conditions, several elimination mechanisms are operative, whose relative extent is dependent on the energy content of the electrostatically bound encounters between the onium ion and the amine base.[1b] It follows that an accurate investigation of the stereochemistry and orientation in gas-phase E2 elimination process (eq 1) and its comparison with relevant reactions in solution call for a methodology that allows an efficient thermal equilibration of the reactants involved and of their electrostatically bound encounters before reacting. This essential condition can be achieved by resorting to the high-pressure radiolytic method, which, unlike most conventional mass spectrometric techniques, allows the actual isolation of the neutral elimination products from eq 1 and the determination of their isomeric composition.[5] In this way, direct information on the orienting properties of the onium ion toward NR_3 and the geometry of the relevant transition state can be readily achieved from the isomeric composition of the alkenes resulting from the reaction visualized in eq 1.

The radiolytic technique uses a steady-state concentration of gaseous acids, i.e. $C_nH_5^+$ (n = 1,2), obtained in known yields by γ-radiolysis of CH_4[6] and their attack on n-type electrons of selected isomeric 2,3-dihalobutanes in the presence of variable concentrations of an external base (NMe_3). Attack of $C_nH_5^+$ ions on the halogen atoms of 2,3-dihalobutanes is expected to generate the corresponding onium intermediate (I) (eq 2), wherein the potential leaving group, HY, can be easily eliminated by interaction of (I) with B = NMe_3 (eq 2a). The choice of the isomeric 2,3-dihalobutanes of eq 2 as precursors of the onium intermediates (I) undergoing elimination was dictated by the fact that the same model compounds were employed in previous radiolytic investigations aimed at quantitatively evaluating the extent and the stereochemical features of acid-induced nucleophilic displacements

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[1] (a) Part I: Occhiucci, G.; Speranza, M.; de Koning, L. J.; Nibbering, N. M. M., preceding paper of this issue. (b) A similar dependence of the elimination mechanism on the energy level of the encounter complex, under FT-ICR conditions, has been observed in the attack of amines on diethylhalonium ions: Occhiucci, G.; Speranza, M.; de Koning, L. J.; Nibbering, N. M. M., to be submitted for publication.

[2] (a) Saunders, W. H., Jr.; Cockerill, A. F. *Mechanism of Elimination Reactions*; Wiley-Interscience: New York, 1973; Chapter III. (b) Cockerill, A. F.; *Comprehensive Chemical Kinetics*; Elsevier: Amsterdam, The Netherlands, 1973; Vol. 9.

[3] (a) Beauchamp, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 5925. (b) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160. (c) van Berkel, W. W.; de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 7602.

[4] (a) De Puy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034. (b) Bierbaum, V. M.; Filley, J.; De Puy, C. H.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2818.

[5] (a) Ausloos, P. *Annu. Rev. Phys. Chem.* **1966**, *17*, 205. (b) Ausloos, P. *Prog. React. Kinet.* **1969**, *5*, 113. (c) Ausloos, P.; Lias, S. G. *Ion-Molecule Reactions*; Plenum: New York, 1975. (d) Cacace, F. *Kinetics of Ion-Molecule Reactions*; Plenum: New York, 1979. (e) Speranza, M. *Gazz. Chim. Ital.* **1983**, *113*, 37. (f) Laguzzi, G.; Speranza, M. *J. Am. Chem. Soc.* **1988**, *110*, 30.

[6] Ausloos, P.; Lias, S. G.; Scala, A. A. *Adv. Chem. Ser.* **1966**, *58*, 264.

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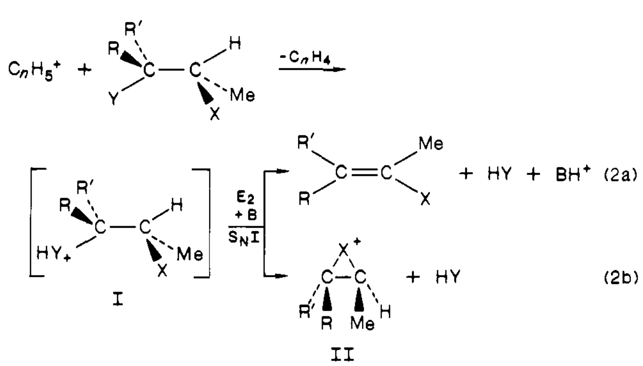

X,Y = F, Cl(1); Cl, Cl(2); Cl, Br(3); Br, Br(4).
R, R′ = H, Me(erythro or meso form); Me, H(threo or *dl* form).

(eq 2b), which are expected to compete with the elimination processes 2a.[7]

Experimental Section

Materials. Methane, oxygen, and trimethylamine were high-purity gases from Matheson Co., used without further purification. Isomeric 2-chloro-2-butenes and 2-bromo-2-butenes as well as 3-chloro-1-butene, 3-bromo-1-butene, 2-chloro-1-butene, and 2-bromo-1-butene, used as standards in chromatographic analyses and, in some cases, as substrates in radiolytic experiments, were research-grade chemicals from ICN Biomedicals, Inc., Pfaltz & Bauer, Inc., and Aldrich Chemie, GmbH.

The preparation purification, and NMR analysis, of *meso-* and *dl-*2,3-dichloro- and 2,3-dibromobutanes, *erythro-* and *threo-*2-chloro-2-fluoro- and 2-bromo-3-chlorobutanes, used as substrates in the radiolytic experiments, has been described elsewhere.[7c]

Procedure. The preparation and irradiation of the gaseous samples were carried out according to experimental techniques described in detail elsewhere.[7] The typical composition of the gaseous mixtures was the following: 2,3-dihalobutane **1–4**, 1–2 Torr; O_2, 4 Torr; NMe_3, 0–20 Torr; CH_4, 760 Torr. The gaseous mixtures were irradiated with ^{60}Co γ-rays in a 220 Gammacell (Nuclear Canada Ltd.) at 37.5 °C, at a dose rate of 10^4 Gy h^{-1} to a total dose of 3×10^4 Gy, as determined by a neopentane dosimeter. Analyses of the irradiated samples were accomplished by injecting measured portions of the homogeneous reaction mixture into a Perkin-Elmer Model Sigma 1 gas chromatograph, equipped with a FID detector, and the product yields determined from the areas of the corresponding eluted peaks, using individual calibration factors. The following columns were employed for the gas chromatographic analyses: (i) a 50-m long 0.2-mm-i.d. UCON LB 550X stainless steel capillary column, operated at $T = 65$ °C; (ii) a 50-m long 0.32-mm-i.d. CP Sil 8 CB quartz capillary column, operated at temperatures ranging from 40 to 100 °C (20 deg min^{-1}).

Results

Gas-phase attack of radiolytic $C_nH_5^+$ (n = 1,2) ions on the isomeric 2,3-dihalobutanes **1–4** gives rise to a neutral product distribution, which is strongly dependent on the presence and the concentration of the added base NMe_3. In fact, in the absence of NMe_3, the major product is butanone (relative yield 41–85%), accompanied by minor amounts of *trans-* and *cis-*2-halo-2-butene as well as 3-halo-1-butene (overall relative yield 8–55%). Also, limited quantities of 2-halo-1-butene, isomeric 1-halo-1-butenes, and allyl halide (overall relative yield 0–28%) were recovered under these conditions. In the presence of variable concentrations of NMe_3 (2–20 Torr), instead, the product pattern changes significantly. Thus, isomeric 2-halo-2-butenes and 3-halo-1-butene become predominant (overall relative yield 55–100%) over butanone and the other haloalkenes, whose individual relative yields never exceed 10%.

The absolute yields of the neutral products, expressed as the percent ratio of their G_M values (i.e. the number of molecules M produced per 100 eV of energy absorbed by the gaseous mixture) to the known $G_{CH_5^+}$ and $G_{C_2H_5^+}$ values of the ionic reactants from the γ-radiolysis of CH_4, are themselves markedly dependent on the experimental conditions.[8] In general, the overall absolute yield of products reaches a maximum value of 35–61% at 760 and 2–5 torr of NMe_3. At higher NMe_3 concentrations (10–20 Torr) the overall absolute yield of products drops by a factor of 2–3.

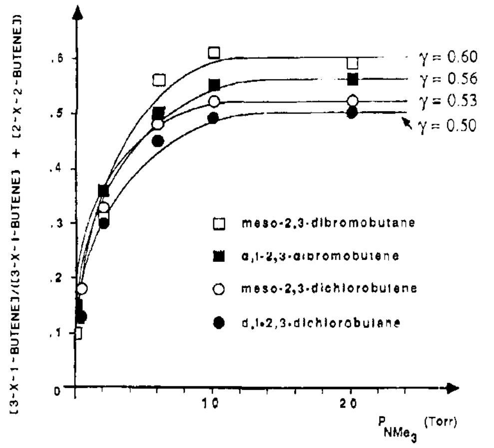

Figure 1. Dependence of the [3-halo-1-butene]/([3-halo-1-butene] + [2-halo-2-butenes]) ratio from *meso-* (○) and *dl-*2,3-dichlorobutane (●) and *meso-* (□) and *dl-*2,3-dibromobutane (■) as a function of the partial pressure of added NMe_3 at 760 Torr. The [3-halo-1-butene]/([3-halo-1-butene] + [2-halo-2-butenes]) ratios reach the limiting values γ (0.53, ○; 0.50, ●; 0.60, □; 0.56, ■) at the highest NMe_3 partial pressures (10–20 Torr). For sake of clarity, similar trends concerning *erythro-* (γ(X) = 0.57 (Cl)) and *threo-*2-chloro-3-fluorobutane (γ(X) = 0.50 (Cl)) and *erythro-* (γ(X) = 0.61 (Cl); 0.52 (Br)) and *threo-*2-bromo-3-chlorobutane (γ(X) = 0.62 (Cl); 0.51 (Br)) are omitted.

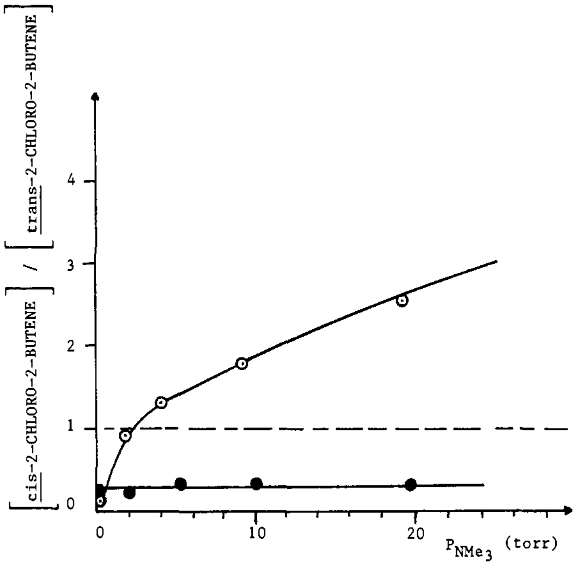

Figure 2. Dependence of the [*cis-*2-chloro-2-butene]/[*trans-*2-chloro-2-butene] ratio from *erythro-* (⊙) and *threo-*2-chloro-3-fluorobutane (●) as a function of the partial pressure of added NMe_3 at 700 Torr.

Concerning the relative distribution of isomeric 2-halo-2-butenes and 3-halo-1-butene, Figure 1 illustrates the dependence of the [3-halo-1-butene]/([3-halo-1-butene] + [2-halo-2-butenes]) ratios at 760 Torr as a function of the NMe_3 concentration. For all substrates, a drastic increase of the 3-halo-1-butene fraction with the NMe_3 concentration is observed, which tends to reach the limiting value γ ($0.50 \leq \gamma \leq 0.62$) at the highest NMe_3 partial pressure (Figure 1).

Direct information on the isomeric distribution of the 2-halo-2-butenes from **1–4** under different experimental conditions is given in Figures 2–6, reporting the cis/trans isomer yield ratios at P_{CH_4} = 760 Torr in the presence of variable concentrations of NMe_3. Inspection of Figures 2–6 reveals that, while *threo-* or *dl-***1–4** invariably produce predominant yields of *trans-*2-halo-2-butene (from ca. 75 to over 90%), *erythro-* or *meso-***1–4** give rise to both cis and trans isomers, with the cis one prevailing at high NMe_3 partial pressures.

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[7] (a) Angelini, G.; Speranza, M. *J. Chem. Soc., Chem. Commun.* **1978**, 213. (b) Speranza, M.; Angelini, G. *J. Am. Chem. Soc.* **1980**, *102*, 3115. (c) Angelini, G.; Speranza, M. *J. Am. Chem. Soc.* **1981**, *103*, 3792, 3800.

[8] Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341.

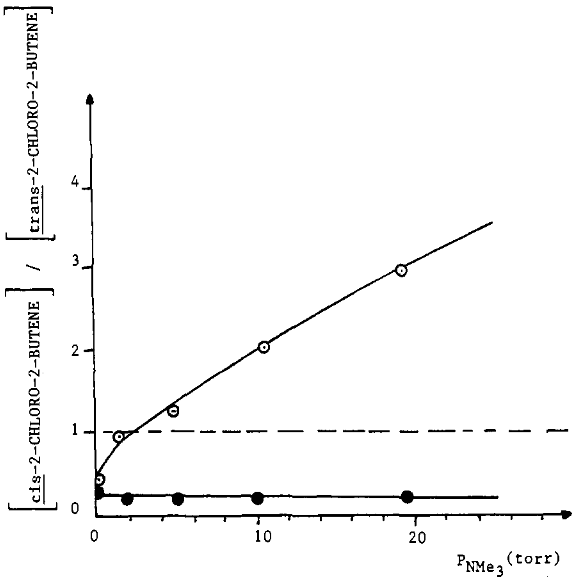


Figure 3. Dependence of the [*cis*-2-chloro-2-butene]/[*trans*-2-chloro-2-butene] ratio from *meso*- (⊙) and *dl*-2,3-dichlorobutane (●) as a function of the partial pressure of added NMe_3 at 760 Torr.

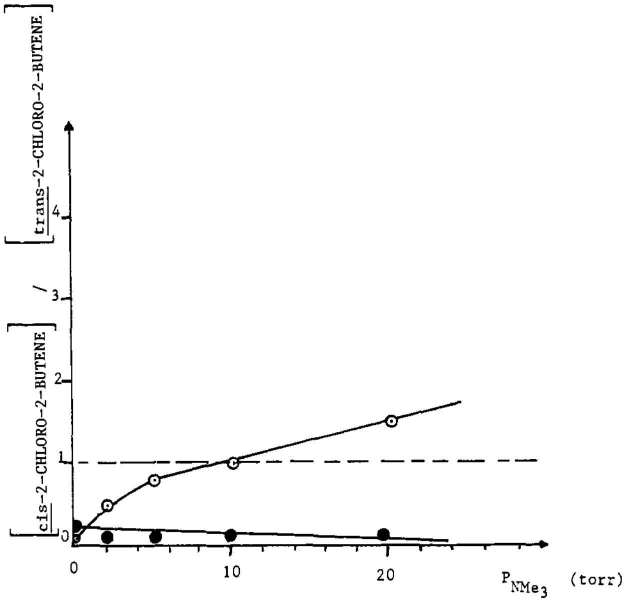


Figure 4. Dependence of the [*cis*-2-chloro-2-butene]/[*trans*-2-chloro-2-butene] ratio from *erythro*- (⊙) and *threo*-2-bromo-3-chlorobutane (●) as a function of the partial pressure of added NMe_3 at 760 Torr.

Independent information on the isomeric distribution of 2-halo-2-butenes by proton loss from 2-halo-2-butyl cation to a basic acceptor was obtained by preparing the cation by $C_nH_5^+$ protonation of 2-halo-1-butene at 760 Torr in the presence of variable concentrations of NMe_3. The relevant cis/trans ratios are reported in Figure 7, which indicates that, irrespective of the specific 2-halo-2-butyl cation involved, the limiting 70% trans–30% cis distribution is obtained, at the highest NMe_3 concentrations. It should be noted that no measurable amounts of 3-halo-1-butene could be recovered among the products from $C_nH_5^+$ attack on 2-halo-1-butene under all conditions.

Discussion

Nature of the Elimination Processes. As discussed in related papers,[7] the conditions typical of the present experiments, in particular the low concentration of the 2,3-dihalobutane diluted in a large excess of CH_4, rule out direct radiolysis of the halogenated substrate as a significant route to the elimination products, i.e. the isomeric halobutenes. In addition, the presence of an efficient thermal radical scavenger (O_2) in the gaseous mixtures minimizes conceivable free-radical reactions in favor of the competing ionic elimination pattern, whose role is demonstrated by the sharp decrease of the overall absolute yield of products by addition of sufficient concentrations (1–2 mol %) of a powerful ion interceptor, such as NMe_3. Finally, the limited concentrations of NMe_3 (<2 mol %) with respect to the bulk gas, i.e. CH_4, ensures that protonated 2,3-dihalobutanes (I) from eq 2 are thermally equilibrated by many unreactive collisions with the CH_4 molecules before interacting with the bases present in the irradiated mixtures. The exceedingly high collision frequency (over 10^{10} s^{-1}) typical of the present high-pressure (760 Torr) experiments ensures removal of the energy excess developed in the attractive electrostatic interactions in the encounter complex between the ionic intermediate (I) from eq 2 and NMe_3.[5f] The gas-phase data obtained under such conditions allow, therefore, an adequate comparison with related elimination processes occurring in solution.[2]

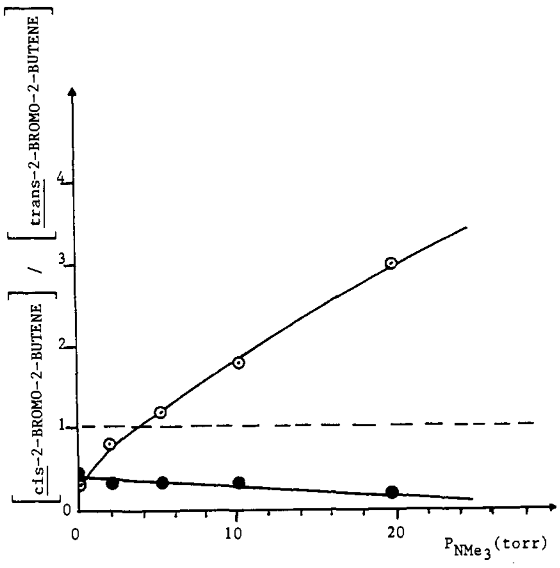


Figure 5. Dependence of the [*cis*-2-bromo-2-butene]/[*trans*-2-bromo-2-butene] ratio from *erythro*- (⊙) and *threo*-2-bromo-3-chlorobutane (●) as a function of the partial pressure of added NMe_3 at 760 Torr.

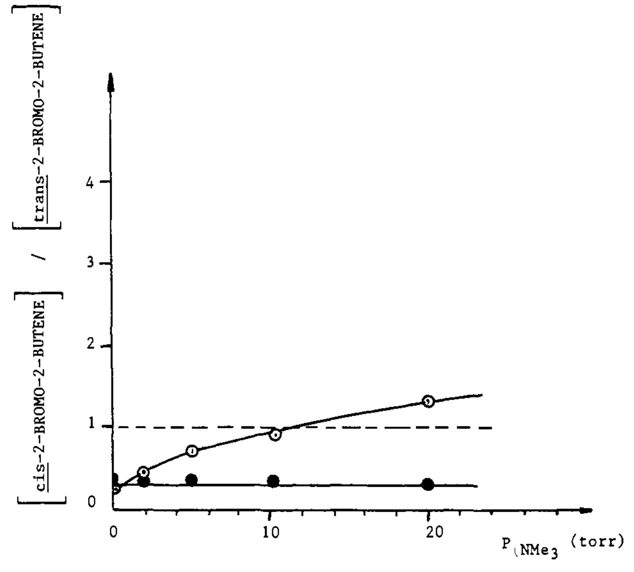


Figure 6. Dependence of the [*cis*-2-bromo-2-butene]/[*trans*-2-bromo-2-butene] ratio from *meso*- (⊙) and *dl*-2,3-dibromobutane (●) as a function of the partial pressure of added NMe_3 at 760 Torr.

Reaction Pattern. According to the general conclusions reached in previous papers for the same systems,[7] exothermic $C_nH_5^+$ (n = 1,2) attack on 2,3-dihalobutanes **1**–**4** induces the reaction network outlined in Scheme I.[9] The nature and the distribution

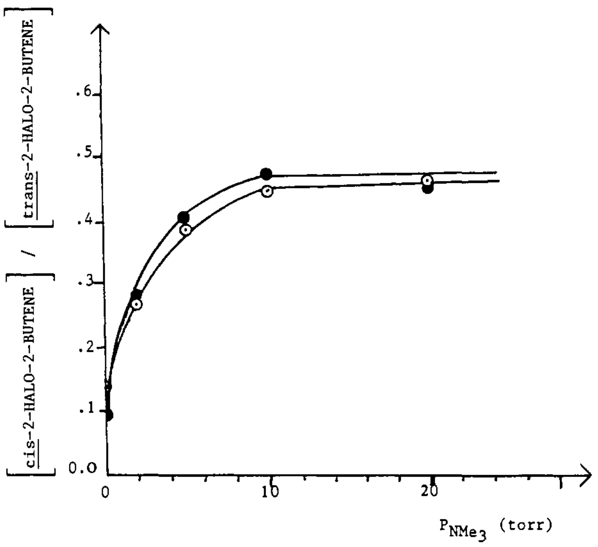
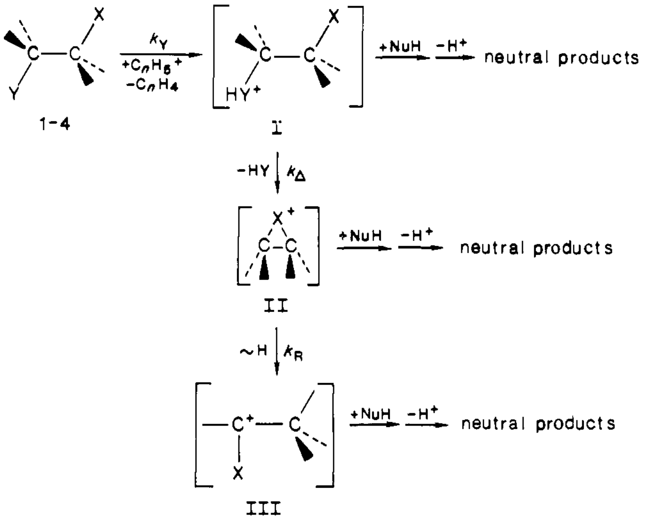
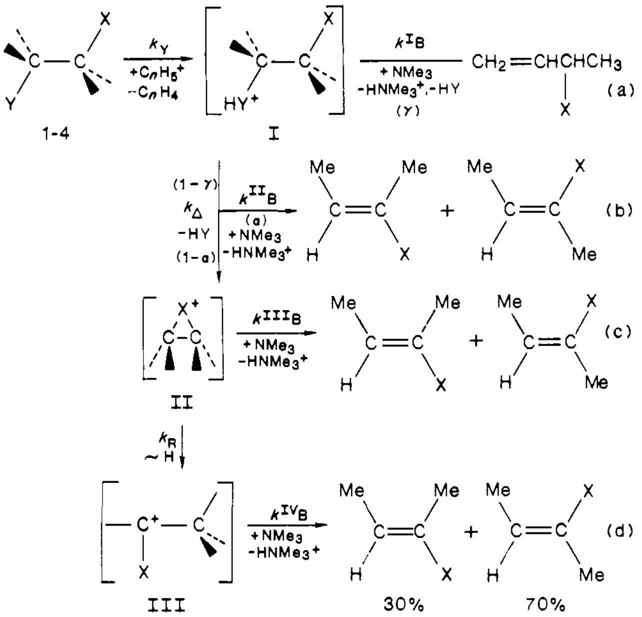


Figure 7. Dependence of the [*cis*-2-halo-2-butene]/[*trans*-2-halo-2-butene] ratio from 2-chloro- (⊙) and 2-bromo-2-butyl cation (●) as a function of the partial pressure of added NMe_3 at 760 Torr. No detectable amounts of 3-halo-1-butene are formed under all conditions.

Scheme I



Scheme II



γ = fraction of I yielding 3-halo-1-butene (path a)
1−γ = fraction of I yielding isomeric 2-halo-2-butenes, either directly (path b) or via II (path c) or III (path d)
α = fraction of isomeric 2-halo-2-butenes formed directly from I (path b)
1−α = fraction of isomeric 2-halo-2 butenes formed directly from II (path c) and III (path d)

of the neutral products of Scheme I depend on many factors, including the nature and the concentration of the nucleophiles NuH present in the irradiated mixtures. Thus, previous investigations indicated that, when NuH = H_2O, intermediates I and II undergo nucleophilic substitution by H_2O, producing the inverted and the retained 3-X-butan-2-ols, respectively, whereas intermediate III yields butanone.[7] In the present experiments, instead, the nucleophile NuH is mostly represented by NMe_3, a very powerful base (PA = 225.1 kcal mol^{-1}),[10] which efficiently competes for I–III, with the traces of H_2O invariably present or radiolytically formed in the samples. Trimethylamine is able to abstract a proton from all ionic intermediates I–III of Scheme I, yielding *cis*- and *trans*-2-halo-2-butene and -3-halo-1-butene, which are the predominant products recovered in the irradiated samples containing NMe_3.[11] However, Figure 7 shows that NMe_3 attacks 2-halo-2-butyl cations, yielding invariably 30% *cis*-2-halo-2-butene and 70% *trans*-2-halo-2-butene, without any detectable formation of 3-halo-1-butene. No similar direct evidence is available as regards to the X-butenes distribution from amine attack on cyclic halonium ions II. Nevertheless, some hint is provided by previous results on the elimination product distribution arising from the attack of NH_3 on O-phenylated 2-methyloxiranium ions.[12] The lack of allyl phenyl ether among the elimination products suggests that abstraction of one of the primary hydrogens of II by the amine base to yield 3-halo-1-butene is negligible with respect to other competing processes, such as proton transfer from the ring carbons to NMe_3, giving isomeric 2-halo-2-butenes. Accordingly, it is concluded that 3-halo-1-butene is essentially generated from attack of NMe_3 on the fraction γ of intermediates I. The remaining portion 1− γ of I undergoes attack by NMe_3, producing 2-halo-2-butenes. Analysis of the [*cis*-2-halo-2-butene]/[*trans*-2-halo-2-butene] trends of Figures 2–6 suggests that, of the fraction 1 − γ of I yielding 2-halo-2-butenes, a portion α is stable enough to give them directly by deprotonation by the NMe_3, whereas the other part 1 − α is unstable and rapidly undergoes intramolecular substitution to II and eventually III, before interaction with the base.

The reaction pattern reported in Scheme II summarizes the above evidence. Thus, $C_nH_5^+$ protonation of **1–4** leads to excited intermediates I, a fraction of which is able to cyclize to II. Cyclic onium ions II interact with NMe_3, yielding both *trans*- and *cis*-2-halo-2-butenes (path c). The same products are generated from III to 70% trans–30% cis proportions (path d). The remaining portion of I is, instead, relatively stable. It has no tendency to

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(9) Protonation by CH_5^+ (ΔH_f = 221 kcal mol^{-1}: Chupka, W. A.; Berkowitz, J. A. *J. Chem. Phys.* **1971**, *54*, 4256. Jelus, B. L.; Murray, R. K., Jr.; Munson, B. *J. Am. Chem. Soc.* **1975**, *97*, 2362) and $C_2H_5^+$ (ΔH_f = 215 kcal mol^{-1}: Baer, T. *J. Am. Chem. Soc.* **1980**, *102*, 2482) on the halogen atom(s) of the selected compounds is calculated to release 45–60 and 15–30 kcal mol^{-1}, respectively. Condensation by $C_2H_5^+$ is exothermic for ca. 25–40 kcal mol^{-1}.[10,11]

(10) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1983**, *13*, 695.

(11) NMe_3-induced elimination in I to yield $HNMe_3^+$, HY, and a X-butene (paths a and b of Scheme II) is estimated to be from ca. 20 to ca. 40 kcal mol^{-1} exothermic, depending on the nature of the halogens X and Y and the structure of the X-butene. Ring opening of II promoted by proton abstraction by NMe_3 to form HNR_3^+ and X-butene (path c of Scheme II) is calculated to be ca. 35 kcal mol^{-1} exothermic as well as deprotonation of III by NMe_3 (path d of Scheme II), which is estimated to release over 35 kcal mol^{-1}. Approximate enthalpy values are calculated from ref 10 by using the group additivity rules: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. The heats of formation of neutrals were taken from: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

(12) Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1988**, *66*, 2506.

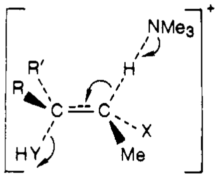
Table I. Kinetic Parameters for the Formation of Isomeric 2-Halo-2-butenes from NMe_3 Attack on I–III

substrate	X	k_Δ, $\times 10^{-9}$ s^{-1}	k_R, $\times 10^{-9}$ s^{-1}	α	β	γ	$\gamma + \alpha(1 - \gamma)$	$(1 - \gamma)(1 - \alpha)$	δ^a	$\frac{\delta}{1 + \delta}$	$\frac{\gamma(1 + \delta)}{\delta(1 - \gamma)}$
erythro-**1**	Cl	3.7	0.4	0.3	0.4	0.57	0.70	0.30	0.05	0.05	26
meso-**2**	Cl	1.7	0.4	0.2	0.4	0.53	0.62	0.38	0.07	0.06	17
erythro-**3**	Cl	3.7	0.4	0.0	0.4	0.61	0.61	0.39	0	0	∞
erythro-**3**	Br	1.7	0.2	0.1	0.5	0.52	0.57	0.43	0.03	0.03	39
meso-**4**	Br	2.7	0.2	0.0	0.5	0.60	0.60	0.40	0	0	∞
threo-**1**	Cl	2.6	0.7	0.4	0.5	0.50	0.70	0.30	0.12	0.11	9
dl-**2**	Cl	2.1	0.4	0.5	0.5	0.50	0.75	0.25	0.22	0.18	5
threo-**3**	Cl	2.5	0.5	0.8	0.5	0.62	0.92	0.08	0.71	0.41	4
threo-**3**	Br	0.7	0.3	0.3	0.6	0.51	0.66	0.34	0.27	0.21	5
dl-**4**	Br	2.2	0.2	0.5	0.6	0.56	0.78	0.22	0.20	0.16	8

[a] $\delta = \alpha K_B{}^{11}[NMe_3]/(1 - \alpha)k_\Delta$; $[NMe_3] = 6.4 \times 10^{17}$ molecule/cm^3 (P_{NMe_3} = 20 Torr).

cyclize to II, but rather it is able to interact with NMe_3, producing either isomeric 2-halo-2-butenes (path b) or 3-halo-1-butene (path a).

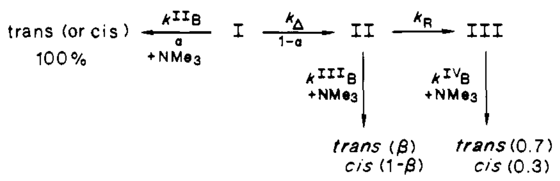
Stereochemistry and Orientation of Base-Induced Elimination Reactions. Direct information on the stereochemistry of the NMe_3-induced elimination reaction in I can arise from the stereoisomeric distribution of 2-halo-2-butenes, measured at the highest NMe_3 concentration (P_{NMe_3} = 20 Torr; Figures 2–6), i.e. at the shortest ion lifetime (ca. 10^{-9} s).[13] Under these conditions, in fact, cyclization of the unstable fraction of I to II and, therefore, formation of 2-halo-2-butenes from paths c and d of Scheme II are expected to be minimized. The relevant 2-halo-2-butenes distribution indicates that the base-induced elimination path b of Scheme II on the primary intermediates I essentially proceeds through the transition state IV*, characterized by an anti configuration.



IV*

Indeed, threo or *dl* forms of **1–4** give rise predominantly to *trans*-2-halo-2-butene (from 77 to 91%) and their erythro or meso forms produce preferentially the cis isomer (from 56 to 76%) (Figures 2–6). These distributions represent only the lower limits of the stereospecificity of the NMe_3-induced E2 elimination in I, owing to the possible partial cyclization of I to II even at the highest NMe_3 concentration used (vide infra). At lower NMe_3 partial pressures, i.e. at longer ion lifetimes (ca. 10^{-8} s),[13] cyclization of the unstable fraction of I to II competes favorably with the NMe_3-induced E2 elimination path b on I. As pointed out in previous studies,[7] cyclization takes place via an intramolecular nucleophilic displacement of the leaving HY molecule by the adjacent X moiety, involving inversion of the configuration of the carbon center. Thus, *erythro*- or *meso*-I yields predominantly *trans*-II, while *threo*- or *dl*-I produces essentially *cis*-II.[7] These, in turn, may eventually isomerize to the open-chain structure III,[7] if not neutralized by proton loss to NMe_3. Therefore, the 2-halo-2-butene distribution measured in the present investigation at low NMe_3 partial pressures would reflect a complicate interplay among the individual stationary concentrations of I–III at any given delay time from $C_nH_5{}^+$ attack on **1–4** and the stereochemical features of the relevant NMe_3-induced elimination pathways. A quantitative evaluation of these factors requires a detailed kinetic analysis of the reaction pattern of Scheme II.

Scheme III



For our purposes, kinetic analysis can be restricted to the competing paths b–d of Scheme II. The relevant kinetic network, given in Scheme III, is used, with the only very reasonable condition of a completely stereospecific base-induced anti elimination in I and rapid NMe_3-induced deprotonation steps for I–III. Making use of the known II/III concentration ratios at 2.4×10^{-9} s from $C_nH_5{}^+$ attack on **1–4**, given by the retained 3-X-butan-2-ol/butanone yield ratios, measured in previous experiments,[7,14] the theoretical cis/trans ratios of 2-halo-2-butenes, arising from kinetic treatment of Scheme III, could be evaluated and compared with the experimental ones of Figures 2–6.

Satisfactory coincidence between the two sets of data (within 30% uncertainty) was attained, when, the k_Δ, k_R, β, and α parameters of Scheme III reach the values reported in Table I.

The best fit results of Table I are found to be highly sensitive to the stereospecificity level of the base-induced ring opening in II (related to the β values of Table I), yielding in some cases meaningless negative or exceptionally high values for α, k_Δ, and k_R, as the β parameter deviates appreciably from those of Table I.

The β parameters ranging invariably around 0.5 for both *erythro*- or *meso*- and *threo*- or *dl*-**1–4** exclude any significant stereoelectronic control in the base-induced ring opening in the corresponding *trans*- and *cis*-II. Inspection of the calculated k_Δ and k_R values of Table I reveals that intramolecular nucleophilic displacement within unstable I to yield the corresponding II (eq 2b) is a relatively fast process competing efficiently with the base-induced elimination channels a and b of Scheme II even at the highest NMe_3 concentrations. The relevant k_Δ values appear to be a complex function of the leaving HY group ability, the participating properties of the vicinal X moiety, and the proton distribution between the *n* centers of the 2,3-dihalobutane substrates. In general, however, the configuration of the starting substrate plays a distinct role in determining the tendency of the unstable fraction of the corresponding I to undergo the intramolecular displacement 2b, as shown by the higher k_Δ values of the *erythro*- or *meso*-**1–4** with respect to those of the corresponding threo or *dl* forms. The presence of two eclipsed methyl groups in the transition state involved in the conversion of *threo*- or *dl*-I to *cis*-II may be responsible for the relatively low k_Δ value of the corresponding S_Ni processes 2b.[7b]

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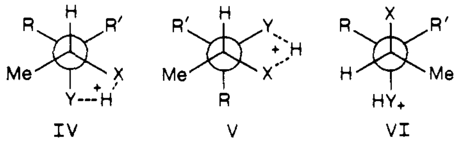
[13] Estimated from ADO calculations (Bowers, M. T.; Su, T. In *Interactions between Ions and Molecules*; Ausloos, P., Ed.; Plenum: New York, 1975) of the collision rates of I–III with NMe_3, within the reasonable assumption that any collision between I–III and NMe_3 involves neutralization of the ion by proton transfer to the base.

[14] Within the same assumptions introduced in the text, the II/III concentration ratio after 2.4×10^{-9} s from $C_nH_5{}^+$ attack on **1–4** is given by the retained 3-X-butan-2-ol/butanone yield ratio measured from ref 7c in systems containing ca. 2 Torr of H_2O. The 2.4×10^{-9} s delay time in 2 Torr H_2O systems is estimated from ADO calculations of the collision rates of II and III with H_2O.[13]

The cyclic halonium ions II are, instead, relatively stable species, slowly rearranging to the open-chain isomers III under the used experimental conditions.[7c] The relevant k_R values, in fact, are invariably lower than the corresponding k_Δ ones by a factor ranging from ca. 2 to ca. 13. As evident from Table I, the k_R values and, thus, the relative stability of the corresponding cyclic halonium ions II appear to be poorly sensitive of the nature of their precursor, being mostly dependent upon the nature of the halogen X involved ($k_R(\mathrm{Cl})/k_R(\mathrm{Br}) = 2.0$–$3.5$) and the configuration of the cyclic intermediate II (k_R(erythro or meso)/k_R(threo or *dl*) = 0.6–1.0). Configurational effects, related to the presence of two eclipsed methyl groups in *cis*-II, are responsible for the relatively higher k_R values estimated for the threo or *dl* systems.[7c] The 2,3-butanediylchloronium ion (II; X = Cl) < 2,3-butanediylbromonium ion (II; X = Br) stability order is consistent with previous gas-phase evidence[7c] and with similar trends observed in low-nucleophilicity solvent systems[15] and predicted on theoretical grounds.[16]

As pointed out before, the α values of Table I provide an estimate of the fraction of stable intermediate I, which generates directly the relevant 2-halo-2-butene by NMe_3-induced anti elimination via IV* (path b of Scheme II). The $1 - \alpha$ values represent, instead, the fraction of unstable I producing isomeric 2-halo-2-butenes indirectly via deprotonation of the daughter ions II (path c) and III (path d) by NMe_3 (Scheme II). Since 3-halo-1-butene is formed exclusively from I (path a of Scheme II), namely from the stable fraction γ of I amounting to ca. 0.5–0.6 of the total (Figure 7), a rough estimate of the overall fraction of stable I is provided by the $\gamma + \alpha(1 - \gamma)$ terms of Table I. Of course, the complementary $(1 - \alpha)(1 - \gamma)$ terms of Table I refer instead to the fraction of unstable I able to produce II and, eventually, III.

Inspection of Table I reveals that the configuration of the starting substrate and the nature of the X and Y halogens play a role in determining the $\gamma + \alpha(1 - \gamma)$ values. In fact, they appear to be significantly higher in the threo or *dl* forms of **1–4** with respect to the erythro or meso ones. Furthermore, the $\gamma + \alpha(1 - \gamma)$ values slightly increase in the X, Y order: Br, Br < Br, Cl < Cl, Cl < Cl, F, namely with ability of the X, Y pair to establish an intense hydrogen bond between them. On these grounds, it is tempting to identify the stable fraction of I with structures IV and V characterized by extensive internal proton-bonding between the X and Y centers. This particularly stabilizing interaction is absent in the unstable portion of I, namely in structure **VI**, wherein, on the contrary, the trans–anti relationship necessary for a fast X-to-HY nucleophilic displacement to yield II is present.[17]



IV V VI

R, R'=H,Me(threo or *dl* forms); Me,H (erythro or meso forms)

The regiospecificity of the attack of NMe_3 on the protonated intermediates I could, in principle, be estimated from the relative distribution of 3-halo-1-butene (path a of Scheme II) and the relevant 2-halo-2-butene isomer (path b of Scheme II), obtained at $P_{NMe_3} = 20$ Torr. Under these conditions, in fact, rapid proton transfer from I to NMe_3 minimizes extensive interconversion among conformers IV–VI and cyclization of VI to the corresponding intermediate II. However, partial occurrence of the latter process may still take place even at $P_{NMe_3} = 20$ Torr, as shown by the $\delta = \alpha K_B{}^{11}[NMe_3]/(1 - \alpha)k_\Delta$ branching ratios of path b vs paths c and d of Scheme II calculated at $P_{NMe_3} = 20$ Torr ($[NMe_3] = 6.4 \times 10^{17}$ molecule/cm^3; Table I).

The relevant values (δ in Table I) allow us to evaluate the fraction of 2-halo-2-butenes directly arising from path b of Scheme II, at $P_{NMe_3} = 20$ Torr ($\delta/(1 + \delta)$ in Table I). From this, the actual 3-halo-1-butene/2-halo-2-butene yield ratios from NMe_3 attack on stable I are calculated, whose values, related to the regiospecificity of reaction 2a, are given in the last column of Table I. Even considering the uncertainty associated to the relevant kinetic parameters of Table I, the calculated regiospecificity factors are found to significantly exceed the statistical value of 3, expected from indiscriminate attack of NMe_3 on all hydrogens adjacent to C–YH$^+$ in I. On these grounds, it is concluded that NMe_3 predominantly attacks the primary hydrogens of the methyl group rather than the tertiary H adjacent to the leaving HY moiety of stable I to yield preferentially the Hoffmann olefin, i.e. 3-halo-1-butene, over the Saytzeff one, i.e. the corresponding 2-halo-2-butene.

Comparison with Related Gas-Phase and Solution Chemistry Studies. The present gas-phase results find a unique gas-phase counterpart in related low-pressure ICR investigation on acid-induced dehydration of alcohols.[3a,19] Here, however, the elimination is induced on the protonated alcohol by attack of the conjugate base of the acid catalyst. As a consequence, a cis 1,2-elimination exclusively takes place within the intermediate complex of the acid catalyst and the alcohol, involving a nonstereoselective transition state. In fact, the authors claimed to have obtained equal amounts of *cis*- and *trans*-2-butene from acid-induced dehydration of specifically deuterated butan-2-ols, based on the indirect evidence of the H/D label distribution in the ionic products, an estimate that is confused by the simultaneous operation of H/D label scrambling within the substrate, unknown primary and secondary kinetic isotope effects, and competition of the dehydration with other undesired processes. In the light of the conclusions of the preceding paper,[1a] a further source of confusion may arise from the superposition of several mechanisms of elimination triggered by the excitation energy of the electrostatically bound encounter between the acid catalyst and the neutral alcohol. The present high-pressure radiolytic study demonstrates from direct analysis of the neutral products that gas-phase 1,2-elimination within thermally equilibrated encounters between an onium intermediate, such as I, and an external powerful base, i.e. NMe_3, takes place essentially via the transition state IV*, characterized by an anti configuration.

The proposed gas-phase base-induced elimination model on onium substrates finds interesting analogies in solution chemistry, in particular in solvolytic base-induced elimination in alkylammonium salts.[2] Here, however, intrinsic steric and electronic effects in the onium substrate and the properties of the base and of the leaving group, factors mediated in solution by specific solvation phenomena,[2] profoundly influence the stereochemistry of the bimolecular elimination reaction.[20] As a consequence, a complex pattern arises from attack of bases on alkylammonium

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(17) Occurrence of 57–92% of stable intermediates I by $C_nH_5{}^+$ attack on **1–4** appears at first glance inconsistent with the very low proportions of inverted 3-X-butan-2-ols obtained when the reaction is carried out in the presence of H_2O, as the nucleophile (2 Torr).[7] In this case, however, direct proton abstraction form I to H_2O is energetically prevented, owing to the relatively low proton affinity of H_2O (PA = 166.5 kcal mol^{-1}).[10] As a consequence, the internal hydrogen bonding in IV and V can be readily destroyed by interaction of the proton with H_2O to form an entropically favored proton-bound cluster between I and H_2O.[7b,18] Within this cluster, free rotation around the C(2)–C(3) bond is fully restored so that a H_2O-solvated structure VI is obtained, which is able to rapidly cyclize to inverted II before collision with a further molecule of H_2O.

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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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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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