refluxed for 25 h. The acetic acid was then removed by distillation at reduced pressure, and the precipitate that formed was separated by filtration and dissolved in 70 mL of boiling $CHCl_3$. The $CHCl_3$ was concentrated to 10 mL, and the precipitate that deposited from the ice-cooled solution was separated by filtration and recrystallized twice from $CHCl_3$ to give 0.552 g (85%) of white plates, mp 341–343 °C, the ^1H NMR, ^{13}C NMR, and mass spectra of which were identical with those of the sample prepared from *p-tert*-butylphenol and paraformaldehyde in the one-step procedure, as described above. A mixture of the materials from these two sources showed no depression in melting point.

Miscellaneous Experiments. Base-Induced Reaction of 2,6-Bis(hydroxymethyl)-4-*tert*-butylphenol (16) via Munch Conditions. A 2.5-g sample of 2,6-bis(hydroxymethyl)-4-*tert*-butylphenol [mp 64–65 °C after several recrystallizations; shows single spot on TLC (lit.[51] mp 74–75 °C)] and 0.04 mL of 10 N KOH were added to 12.5 mL of xylene, and the mixture was heated at reflux for 4 h in an inert atmosphere. From the cooled reaction mixture, 1.4 g (73%) of a solid separated which TLC analysis indicated to contain cyclic octamer, hexamer, tetramer, and bishomo compound, with the cyclic octamer being the major constituent. Crystallization from $CHCl_3$ yielded 0.75 g (39%) of pure cyclic octamer, mp 409–411 °C. The filtrate from the crystallization was combined with the xylene-soluble fraction, and the solvent was removed by evaporation to leave 1.1 g (57%) of material which was indicated by ^1H NMR inspection of the resonances at δ 4.4 and 3.8 to contain ~60% of the bishomo compound along with the cyclic octamer, hexamer, and tetramer. Trituration and recrystallization from various solvents yielded an additional 0.75 g (4%) of cyclic octamer, 0.035 g (2%) of cyclic tetramer, 0.145 g (7.5%) of bishomo compound, and 0.110 g (6%) of a mixture along with 0.6 g (31%) of a solid residue.

Base-Induced Reaction of 2,6-Bis(hydroxymethyl)-4-*tert*-butylphenol (16) via Cornforth Conditions. A 5.0-g sample of 2,6-bis(hydroxymethyl)-4-*tert*-butylphenol[51] was mixed with 0.1 mL of 10 N KOH and heated at 110–120 °C. The mixture quickly melted and after 1 h began to resolidify and foam. A TLC analysis at this stage indicated that a small amount of cyclization to cyclic octamer, hexamer, tetramer, and bishomo compound had already occured, and a ^1H NMR analysis showed that the number of CH_2OCH_2 linkages was equal to the number of $ArCH_2Ar$ linkages. The solid material was dissolved in 35 g of Dowtherm and heated to 200–220 °C for 2 h in an atmosphere of N_2. The cooled residue was then treated with 80 mL of ethyl acetate, and the resulting precipitate was separated by filtration and washed with 30 mL of methanol to yield 1 g of a solid which was indicated by TLC to be a mixture of hexamer and tetramer. Trituration with hot toluene left 0.225 g (6%) of cyclic hexamer undissolved, and upon cooling the toluene 0.56 g (14.5%) of cyclic tetramer, mp 340–342 °C, was deposited. From the Dowtherm-soluble fraction there was obtained, by a series of triturations and crystallizations, an additional 0.5 g (13%) of cyclic hexamer, mp 372–374 °C, and 0.21 g (5.5%) of cyclic tetramer.

Action of Base on *tert*-Butylcalix[4]arene (4). A 100-mg sample of cyclic tetramer (4) and 0.04 mL of 10 N KOH were added to 4 mL of xylene, and the mixture was heated at reflux for 4 h. The reaction mixture was assayed by TLC and shown to contain only trace amounts of substances other than the starting material. A $CHCl_3$ solution of the product was washed with 5 mL of 1 N HCl, and the $CHCl_3$ was evaporated and the residue recrystallized from toluene to give 70 mg (70%) of colorless solid, mp 342–344 °C, which showed no depression in melting point when admixed with starting material.

Action of Base on *tert*-Butylcalix[6]arene (3). A 100-mg sample of cyclic hexamer (3) was treated in the manner described above for the cyclic tetramer and gave similar results. The recoverd material, after recrystallization from $CHCl_3$/methanol, consisted of 78 mg (78%) of colorless solid, mp 373–375 °C, identical with starting material.

Thermolysis of *tert*-Butylbishomooxacalix[4]arene (14). A 110-mg sample of bishomo compound (14) was added to 1 g of Dowtherm, and the mixture was heated at 210–220 °C for 2 h in an atmosphere of N_2. To the cooled mixture 5 mL of ethyl acetate was added, causing the precipitation of a small amount of material which was indicated by TLC analysis to contain trace amounts of cyclic octamer, hexamer, and tetramer and large amounts of a substance which remained at the origin. TLC analysis of the ethyl acetate-soluble fraction indicated it to contain cyclic octamer, hexamer, tetramer, unreacted starting material, linear oligomers (probably), and a significant fraction which remained at the origin. A comparable experiment in which xylene instead of Dowtherm was used yielded unreacted starting material as the major product. However, when xylene along with a small amount of KOH was used (i.e., Munch conditions), a small amount of conversion of 14 to cyclic octamer, hexamer, and tetramer was noted.

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Gas-Phase Acid-Induced Nucleophilic Displacement Reactions. 4. A Stereochemical Probe for the Existence and the Relative Stability of Cyclic Halonium Ions in the Gas Phase[1]

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Abstract: A comprehensive investigation on the existence and the relative stability of gaseous three-membered cyclic butene halonium ions was carried out by establishing the stereochemistry of the acid-induced displacement by nucleophiles such as H_2O, H_2S, etc., on a number of positively charged intermediates. The latter were obtained in the gas phase from the reaction of radiolytic formed Brønsted (CH_5^+ and $C_2H_5^+$) and Lewis ($C_2H_5^+$ and $CH_3FCH_3^+$) acids with 2,3-dihalobutanes. The stereoisomeric distribution of the neutral 3-halobutan-2-ols (or thiols) formed in these processes strongly implies the intermediacy of cyclic 2,3-butene halonium ions, whose stability in the gas phase depends on the nature of the halogen involved, increasing in passing from Cl to Br. No evidence for the occurrence of stable cyclic 2,3-butene fluoronium ions was obtained by the same procedure. Other factors, namely the strength of the radiolytic gaseous acid "catalysts" and the configuration of the starting dihalobutane, were found to play a role in determining the stereochemistry of the substitution processes investigated. A close correspondence does exist between the present results and those from strictly related mass spectrometric and condensed phase investigation.

Since their first recognition as elusive intermediates in the trans addition of halogens to alkenes,[2] three-membered cyclic alkenehalonium ions [I] excited considerable interest,[3] especially in relation to the study of adjacent group participation in solvolytic

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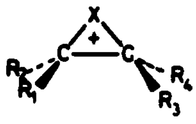


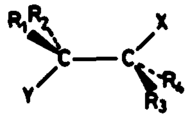
X = halogen

[I]

reactions.[4] However, the precise characterization of such transient species, and of their role in either electrophilic halogen–alkene additions[5] or anchimerically assisted solvolytic processes,[6] encountered serious obstacles from the presence of the solvent and of the counterion which invariably affect the structure and the reactivity of the charged intermediates and, consequently, the kinetics of the nucleophilic steps of these processes. It should be noted, in fact, that stable cyclic halonium ions could be directly observed and their features determined only following the introduction of low-nucleophilicity solvent systems, such as the superacidic media.[3,7] The evaluation of the structural parameters and the relative energetics of the cyclic ions [I] and their isomers has been the subject of extensive theoretical investigation[8] as well which concluded, in agreement with experimental evidence,[9] that the relative stability of these isomeric species is markedly dependent on several factors, including the nature of the X and R_1–R_4 groups and the extent of ion solvation.[10] Unfortunately, in some instances, different theoretical approaches led to contradictory results as to the relative stability of cyclic halonium ions [I] and of their open-chain isomers.[8]

From the above considerations, a detailed investigation on the existence and the reactivity of the ions [I] in the gas phase appears of special interest, because it would allow evaluation of the intrinsic features of these species under conditions excluding the solvent and the counterion interference, which invariably complicates solvolytic studies. In fact, many attempts to give experimental evidence of the occurrence of the cyclic halonium ions [I] in the gas phase by a variety of techniques, including photoionization (PIMS),[11] ion cyclotron resonance (ICR),[11,12] and conventional mass spectrometry,[13] have been recently reported. Some of them seem to point to the formation of the gaseous halonium ions [I] by electron impact on appropriate precursors, without of course providing any conclusive evidence on their actual structure, but rather discriminating the hypothetical cyclic ions [I] from their structural isomers on the grounds of different reaction patterns toward neutral substrates.[11,12] As pointed out elsewhere,[14] the validity of such methodology for ion-structure analysis remains open to question, since the observed reactivity patterns may just reflect different internal energy levels of a single isomer, due to its particular formation process from diverse precursors.

In view of the present situation, we decided to undertake a detailed investigation on the occurrence of gaseous cyclic alkenehalonium ion [I] and their relative stability as a function of the halogen X by a radiolytic technique that, unlike the ordinary mass spectrometric approaches, is specifically designed to allow the actual isolation of the neutral end products and the determination of their isomeric composition.[15] Such technique uses a steady-state concentration of gaseous acids ($GA^+ = CH_5^+$, $C_2H_5^+$, and $CH_3FCH_3^+$) obtained by the γ-radiolysis of the appropriate neutral precursor (CH_4 or CH_3F), and their attack on the nucleophilic sites of the following 2,3-dihalobutanes (**1**–**6**), in the presence of an external nucleophile (:NuH). Attack of GA^+ ions on the halogen atoms of the bifunctional compounds (**1**–**6**) is expected to generate the corresponding protonated ($GA^+ = CH_5^+$ and $C_2H_5^+$), ethylated ($GA^+ = C_2H_5^+$), or methylated ($GA^+ = CH_3FCH_3^+$) derivatives (e.g., [II]), wherein the potential leaving group, e.g., YA, can be easily displaced by the present nucleophiles, with inversion of the configuration of the reaction center[1b] (eq 1). Previous papers of this series[1a,b] pointed to the high stereospecificity of the acid-induced nucleophilic displacement (eq 1), in gases at atmospheric pressure, and the predominance of retained product over the inverted one, when efficient neighboring group effects are involved in the displacement on bifunctional intermediates [II]. In this case, in fact, two consecutive substitution events take place with a double inversion and, therefore, retention of the configuration of the reaction site(s) occurs (eq 2). If a



$R_1 = R_4 = CH_3$; $R_2 = R_3 = H$ meso or erythro forms
$R_1 = R_3 = CH_3$; $R_2 = R_4 = H$ *d*,*l* or threo forms

1, X = Y = F
2, X = F; Y = Cl
3, X = F; Y = Br
4, X = Y = Cl
5, X = Cl; Y = Br
6, X = Y = Br

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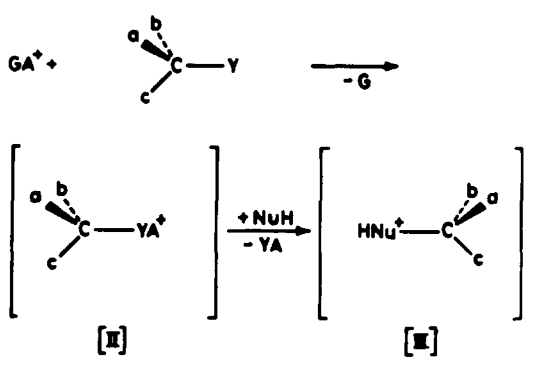

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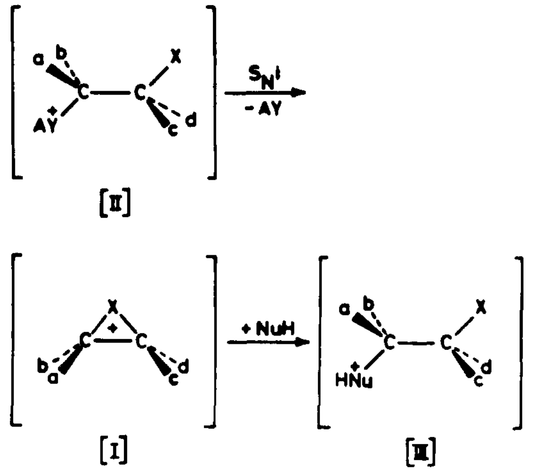

(2)

similar participation takes place when the neighboring group is a halogen (X = F, Cl, and Br), it must involve the intermediacy of the cyclic halonium ion [I] (eq 2), whose occurrence and lifetime in the gas phase determine the stereochemical distribution of the final products from the competing substitutions 1 and 2.

The present paper is aimed at determining the stereochemistry of gas-phase acid-induced nucleophilic displacements on 2,3-dihalobutanes (**1**–**6**), in the presence of suitable nucleophiles, as a function of the nature of the acid GA^+ and of the halogen atoms of the selected bifunctional substrates, in order to gather insight into the existence and the stability order of the corresponding cyclic intermediates [I] in highly diluted gaseous solutions, in the absence of solvation, ion pairing, and other complicating factors.

Experimental Section

Materials. Methane, methyl fluoride, oxygen, hydrogen sulfide, and ammonia were high-purity gases from Matheson Co., used without further purification. The preparation of the 3-halobutan-2-ol isomers (erythro and threo forms), used as standards for the identification of the irradiation products, has been described elsewhere.[1b] *meso*- and *d,l*-2,3-dichloro- and 2,3-dibromobutanes were prepared in good yields by halogen addition to the appropriate isomeric 2-butenes.[16] *erythro*- and *threo*-2-chloro- and 2-bromo-2-fluorobutanes were obtained by F-to-Cl and, respectively, F-to-Br displacement by the action of anhydrous HF/HgO (red) on the corresponding 2,3-dihalobutanes at −20 °C.[17] The isomeric mixture of the ditosylate of the 2,3-butanediols,[18] treated at 150 °C with anhydrous KF, afforded *meso*- and *d,l*-2,3-difluorobutanes.[19] Isomeric 3-halobutane-2-thiols were synthesized by the action of thiourea on the proper 2,3-dihalobutane. *erythro*- and *threo*-2-bromo-3-chlorobutanes were a kind gift from G. Stöcklin, KFA, Jülich, West Germany. Each pair of the starting dihalobutane isomers (*erythro*- and *threo*-**2**, -**3**, and -**5**; *meso*- and *d,l*-**1**, -**4**, and -**6**) was resolved and purified by preparative GLC (5-m 20% diisodecylphthalate on Chromosorb W 60–80 mesh; T_c 45 °C (**1**), 70 °C (**2** and **3**); 4-m 20% tricresylphosphate on Chromosorb W 60–80 mesh; T_c 70 °C (**4**), 100 °C (**5** and **6**)), and their identity checked by NMR analysis. All the starting compounds were repeatedly purified and their purity checked by GLC, using flame ionization detection (FID).

Procedure. The preparation and irradiation of the gaseous samples were carried out according to experimental techniques described in detail elsewhere.[1a,b] 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 0.35 Mrad h^{-1} to a total dose ranging from 1 to 10 Mrad, as determined by a Fricke dosimeter. Analyses of the irradiated samples were accomplished by injecting known aliquots of the homogeneous gaseous system into a Hewlett-Packard Model 5700 A gas chromatograph, equipped with a FID unit, and the product yields determined from the areas of the corresponding eluted peaks, using individual calibration factors.

Results

Table I gives the absolute yields and the isomeric distribution of the products from the gas-phase $C_nH_5^+$ (n = 1, 2) ions attack on the selected 2,3-dihalobutanes (**1**–**6**) in the presence of H_2O as the external nucleophile (:NuH). The results concerning the irradiation of the same systems in CH_3F, as the batch gas, are reported in Table II.

It should be noted that only isomeric 3-halobutan-2-ols were listed as products, omitting other major species not directly relevant to the present study, such as butanone, whose formation mechanism and implication in the quantitative estimate of the gas-phase acid-induced neighboring group participation in bifunctional compounds are discussed in the following paper. The tables give the $G_{(M)}$ values, expressed as the number of molecules of M produced per 100 eV of energy absorbed by the gaseous mixture, at 37.5 °C and 760 torr, to a total dose of 4.8 Mrad (dose rate = 0.35 Mrad h^{-1}). The listed figures represent the mean $G_{(M)}$ values obtained from several separate irradiations, carried out under the same conditions, whose reproducibility is expressed by the standard deviations quoted. Serial irradiations carried out at doses ranging from 1 to 10 Mrad showed an essential constancy of both the absolute $G_{(M)}$ values and the relative distribution of the products. Table I summarizes also the absolute yields of the isomeric 3-halobutan-2-ol, expressed by the ratio of their $G_{(M)}$ values to the known $G_{(CH_5^+)}$ and $G_{(C_2H_5^+)}$ values of the ionic reactants from the γ-radiolysis of CH_4 at 480 torr.[20] The results of these calculations, while largely approximate,[21] represent nevertheless an estimate of the relative efficiency order of the substitution processes.

The ionic character of these reactions is demonstrated by the sharp decrease of the overall product yields (ranging from 68 to 85%) caused by addition to the gaseous mixtures of 2 mol % of NH_3, an efficient Brønsted acid interceptor.

Inspection of the $G_{(M)}$ values in the tables reveals that dichlorobutanes **4** give the highest observed halohydrin yields in both CH_4 and CH_3F mixtures. Progressive replacement of their chlorine atoms with either F or Br reduces the total yields of the corresponding halohydrins. A similar halohydrin yield trend, in fact, arises in both CH_4 (**4** > **2** > **5** ≃ **3** > **6** ≃ **1**) and CH_3F (**4** > **5** > **2** > **3** > **6** > **1**). The nature of the gaseous acid "catalyst" plays a role in determining the halohydrins yields, as well. In particular, while small amounts of fluorohydrins were recovered from the irradiation of CH_3F mixtures containing traces of H_2O and **1**, their formation from the same reagents could not be observed at all in CH_4.

More readily, high yields of butanone were formed in both systems. Comparison of the 3-Y- *vs.* 3-X-butan-2-ol yield ratios from every single starting dihalobutane gives the apparent leaving-group ability order F > Br > Cl in CH_4, whereas it appears to be Br > Cl > F in CH_3F experiments.

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[21] There are considerable uncertainties as to the radiation dose actually absorbed by the gas, as to the pressure dependence of the $G_{(CH_5^+)}$ and $G_{(C_2H_5^+)}$ values, and therefore as to their precise values at 760 torr. In addition, there are several reaction channels available for $C_nH_5^+$ (n = 1, 2) following their attack on 2,3-dihalobutanes that represent only one of the nucleophiles present in the system.

Table I. Product Yields from the Gas-Phase Attack of $C_nH_5^+$ (n = 1,2) Ions on 2,3-Dihalobutanes

system composition[a]			$G_{(M)} \times 10^2$ values of products[b]								total absolute yields,[c] %
			$CH_3CHXCHOHCH_3$				$CH_3CHOHCHYCH_3$				
substrate, RX $\mathrm{CH_3\underset{X}{CH}-\underset{Y}{CH}CH_3}$	torr of RX	torr of H_2O	X	% threo	% erythro	ret/inv ratio	Y	% threo	% erythro	ret/inv ratio	
meso-1	1.0	2.1	F	n.d.[d]	n.d.						
d,l-1	0.7	1.2	F	n.d.	n.d.						
erythro-2	1.0	2.2	F	1.9 (6)	0.9 (3)	0.5	Cl	3.3 (10)	26.6 (81)	8.1	12
threo-2	1.1	2.3	F	1.7 (5)	2.0 (6)	0.8	Cl	24.7 (73)	5.4 (16)	4.6	15
erythro-3	0.8	1.6	F	3.4 (59)	2.4 (41)	0.7	Br	n.d.	n.d.		2
threo-3	0.7	1.3	F	1.6 (31)	3.5 (69)	0.5	Br	n.d.	n.d.		2
meso-4	0.8	2.1	Cl	5.0 (8)	56.3 (92)	11.3					22
d,l-4	0.9	2.0	Cl	51.1 (90)	5.7 (10)	9.0					20
erythro-5	0.4	1.3	Cl	3.5 (17)	16.8 (80)	4.8	Br	0.3 (1.4)	0.4 (1.9)	1.3	8
threo-5	0.4	0.5	Cl	3.8 (70)	1.6 (30)	2.4	Br	n.d.	n.d.		2
meso-6	0.2	1.5	Br	n.d.	n.d.						
d,l-6	0.1	0.7	Br	n.d.	n.d.						

[a] CH_4, 760 torr; O_2, 4 torr. Radiation dose, 4.8 Mrad (dose rate, 0.35 Mrad h^{-1}). [b] $G_{(M)}$ values as the number of molecules M produced per 100 eV of absorbed energy. Standard deviation of data ca. 10%. [c] Total absolute yields estimated by using $G_{(CH_5^+)} = 1.9 \pm 0.2$ and $G_{(C_2H_5^+)} = 0.9 \pm 0.2$ (ref 20). [d] n.d. = below detection limit ($G_{(M)} < 1 \times 10^{-4}$).

Table II. Product Yields from the Gas-Phase Attack of $CH_3FCH_3^+$ Ions on 2,3-Dihalobutanes

system composition[a]			$G_{(M)} \times 10^2$ values of products[b]								total product yields ($G_{(M)} \times 10^2$)
			$CH_3CHXCHOHCH_3$				$CH_3CHOHCHYCH_3$				
substrate, RX $\mathrm{CH_3\underset{X}{CH}-\underset{Y}{CH}CH_3}$	torr of RX	torr of H_2O	X	% threo	% erythro	ret/inv ratio	Y	% threo	% erythro	ret/inv ratio	
meso-1	1.2	2.3	F	0.2 (>95)	n.d.[c] (<5)	<0.05					0.2
d,l-1	1.2	2.4	F	n.d. (<9)	0.1 (>91)	<0.1					0.1
erythro-2	1.8	3.8	F	5.1 (50)	3.5 (34)	0.7	Cl	0.7 (6)	1.0 (10)	1.4	10.3
threo-2	1.7	3.6	F	0.4 (14)	1.6 (55)	0.2	Cl	0.7 (24)	0.2 (7)	3.5	2.9
erythro-3	0.7	1.4	F	2.7 (73)	1.0 (27)	0.4	Br	n.d.	n.d.		3.7
threo-3	0.7	1.6	F	0.3 (12)	2.2 (88)	0.1	Br	n.d.	n.d.		2.5
meso-4	0.6	1.4	Cl	2.7 (21)	10.1 (79)	3.7					12.8
d,l-4	0.8	2.2	Cl	15.2 (90)	1.7 (10)	8.9					16.9
erythro-5	0.6	1.1	Cl	3.1 (26)	8.7 (73)	2.8	Br	0.0_7 (1)	0.0_9 (1)	1.3	12.0
threo-5	0.2	0.5	Cl	3.8 (83)	0.6 (12)	6.3	Br	0.2 (4)	0.0_8 (1)	2.5	4.7
meso-6	0.2	1.4	Br	0.2 (40)	0.3 (60)	1.5					0.5
d,l-6	0.3	1.3	Br	1.0 (56)	0.8 (44)	1.2					1.8

[a] CH_3F, 760 torr; O_2, 4 torr. Radiation dose, 4.8 Mrad (dose rate, 0.35 Mrad h^{-1}). [b] See footnote *b* of Table I. [c] See footnote *d* of Table I.

More direct information on the stereochemistry of the processes occurring in the radiolytic systems is reported in Figure 1, whose inspection reveals that mostly *retained* chloro- and bromohydrins are formed from chlorinated (**2**, **4**, and **5**) and, respectively, brominated (**5** and **6**) starting compounds, whereas predominantly *inverted* fluorohydrins are obtained from the fluorine-containing substrates **1**, **2**, and **3**.

The stereospecificity of the substitution processes is found to depend on many factors, including the nature of the bulk component of the irradiated gas and, to a lesser extent, the configuration of the starting dihalobutane. In general, when occurring in CH_3F, the fluorohydrin formation from **2** and **3** is more stereospecific than that taking place in CH_4. For instance, *threo*-**2** gives rise to 80% *inverted* fluorohydrin in CH_3F, while its relative yield in CH_4 amounts to only 54%. The reverse picture arises from the chlorohydrin formation process from **2**, **4**, and **5**, since its apparent stereospecificity in CH_4 is in general higher than that observed in CH_3F mixtures. This trend is evident from the pertinent histograms of Figure 1 that show the marked stereospecificity (89% *retention*) of the chlorohydrin formation from *erythro*-**2** in CH_4, whereas the corresponding process occurring in CH_3F is characterized by extensive "racemization" (59% *retention*, 41% *inversion*). Finally, irradiation of CH_4 mixtures containing the erythro or meso forms of a given substrate gives more stereospecific substitution processes, when compared to those involving the threo or d,l isomers, an opposite trend from that being observed in CH_3F experiments.

Discussion

Nature of the Substitution Processes. As discussed in related papers,[1a,b] the conditions typical of the present experiments, in particular the low concentrations of the substrate diluted in a large excess of CH_4 (or CH_3F), rule out direct radiolysis of the halogenated compound as a significant route to the substituted products. Further support to this conclusion is provided by the extremely low overall product yields from the systems containing brominated substrates which are known to be particularly prone to radiolytic decomposition. 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 substitution pattern, whose role is demonstrated by the sharp decrease of substituted product yields by addition of fair concentrations of a powerful ion interceptor (NH_3). The role of the stable ions from γ-radiolysis of CH_4[15c,22] (or CH_3F)[23] as gaseous Brønsted (CH_5^+ and $C_2H_5^+$) and Lewis ($C_2H_5^+$ and $CH_3FCH_3^+$) acids toward halogenated compounds has been amply demonstrated by ion cyclotron resonance (ICR)[12c,24] and chemical ionization (CIMS)[25] mass spectrometry, and by independent radiolytic studies.[1a,b,22,23,26] The CH_5^+ ion (ΔH°_f = 221 kcal

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(22) (a) Ausloos, P.; Lias, S. G.; Scala, A. A. *Adv. Chem. Ser.* **1966**, *58*, 264. (b) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1964**, *40*, 1854-1860.

(23) (a) Speranza, M.; Pepe, N.; Cipollini, R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1179-1186. (b) Colosimo, M.; Bucci, R. *J. Phys. Chem.* **1979**, *83*, 1952-1957.

(24) Beauchamp, J. L.; Holtz, D.; Woodgate, S. D.; Patt, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 2798-2807.

(25) (a) Jardine, I.; Fenselau, C. *J. Am. Chem. Soc.* **1976**, *98*, 5086-5089. (b) Luczynski, Z.; Herman, J. A. *J. Phys. Chem.* **1978**, *82*, 1679-1682. (c) Sen Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* **1978**, *100*, 5826-5830. (d) Richter, W. J.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 424-439.

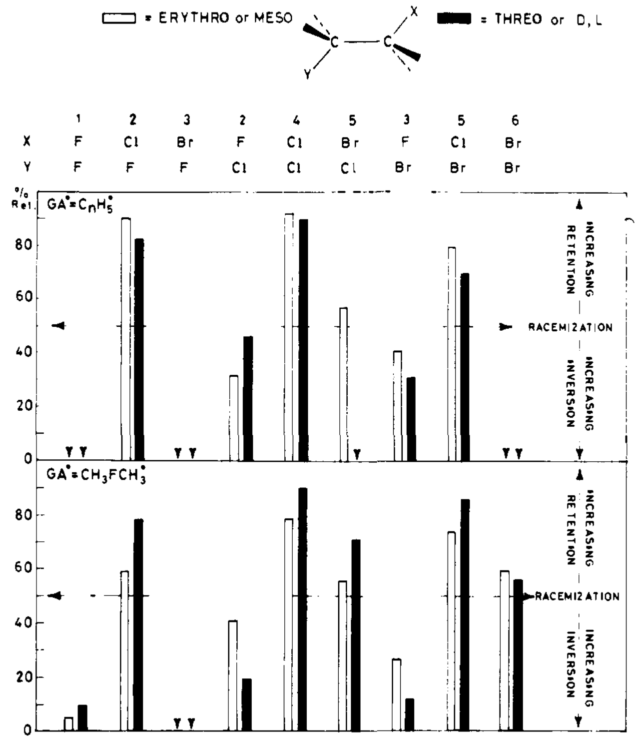
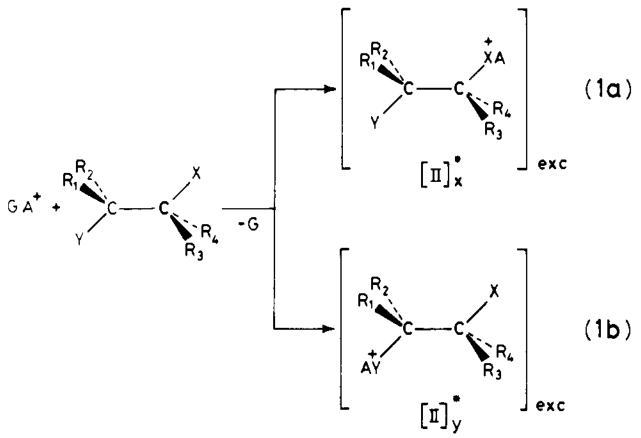


Figure 1. Stereoisomeric distribution of 3-X-butan-2-ols from 3-X-2-Y-butanes (X = participating group, Y = leaving halogen, ▼ = product yield below detection limit).

mol^{-1})[27] reacts essentially as a strong protonating agent (proton affinity (PA) of CH_4 = 127 kcal mol^{-1}), attacking predominantly the n center(s) of the selected substrates,[28] whereas the accompanying $C_2H_5^+$ ion (ΔH°_f = 215 kcal mol^{-1})[29] is a milder Brønsted acid (PA(C_2H_4) = 161 kcal mol^{-1}) that, in addition to protonation, may react as a typical Lewis acid, leading to condensation intermediates.[30] On the other hand, the $CH_3FCH_3^+$ ion (ΔH°_f = 161 ± 8 kcal mol^{-1}),[31] from γ-radiolysis of CH_3F, behaves exclusively as a pure gaseous Lewis acid, methylating the halogen atom(s) of the substrate via processes that are substantially less exothermic than the corresponding protonation by CH_5^+.[32]

Attack of the GA⁺ Acids on 2,3-Dihalobutanes. As discussed in details in the following paper, the radiolytic GA^+ acids, thermalized by many unreactive collisions with their parent molecules (CH_4 or CH_3F), eventually attack the n centers (Y or X) of the substrates **1**–**6** (eq 1a,b) inducing a complex reaction pattern that involves isomerization, unimolecular dissociation of the intermediates formed, and backside bimolecular displacement of their leaving group (AX or AY) by nucleophiles (NuH) present in the gas. Among the factors determining the relative extent of such competing processes, the excitation energy of [II]*, and, hence, the exothermicity of its formation process assume particular importance. The highly exothermic $C_nH_5^+$ ion attack on **1**, in fact, induces complete isomerization and fragmentation of the corresponding excited intermediate [II]*, while the less exothermic[32] methylation of **1** by $CH_3FCH_3^+$ ions allows partial



collisional stabilization of the methylated [II]* before attack of the external nucleophile (H_2O), eventually leading to the corresponding fluorohydrin. The occurrence of several competing channels following process 1a,b, coupled with the presence of relatively high concentrations of the external nucleophile (from 1.2 to 7.5 times that of 2,3-dihalobutane) competing with the substrate for the GA^+ acid(s), accounts for the apparently low yields of halohydrins (from less than 1 to ca. 20%). Evaluation of the halohydrin yields in the light of these considerations reveals that the halohydrin formation from **2** and **4** can be regarded as a major reaction pathway occurring in the irradiated samples. At first glance, other substrates seem to behave differently. While the poor yields of fluorohydrins from **1**, largely counterbalanced by high yields of isomerization products (i.e., butanone), can be actually traced to extensive displacement processes (see the following paper), the apparently low total yields of product from brominated substrates (**3**, **5**, and **6**) can be accounted for by the lack of bromohydrin formation, due to the high stability of cyclic bromonium-ion precursors (vide infra).

The nature of the halogen atoms in asymmetric 2,3-dihalobutanes **2**, **3**, and **5** determines the Y- vs. X-hydrin distribution as well. Thus, a F > Cl leaving-group ability order can be deduced for the attack of $C_nH_5^+$ ions on **2**, whereas the reverse trend (Cl > F) is observed in CH_3F systems. This behavior can be satisfactorily rationalized by extending Pearson's HSAB concept[33] to the competitive electrophilic attack of GA^+ acids on the halogen atoms of the substrate, regarded as nucleophilic sites with different hardness (F > Cl > Br). Taking into account that the hardness of the selected gaseous GA^+ acids increases with the order $CH_3FCH_3^+ < C_2H_5^+ < CH_5^+$,[34] a preferential $C_nH_5^+$ attack on the F atom of **2**, with predominant formation of chlorohydrins, is expected, and is actually observed (~90%, Table I). Similarly, a more extensive methyl transfer from the "soft" $CH_3FCH_3^+$ ion to the chlorine atom of **2** takes place, inducing predominant formation of fluorohydrins (~70–80%, Table II). The failure to determine a similar trend from the other asymmetric dihalobutanes (**3** and **5**) arises from the negligible yields of bromohydrins, which prevent meaningful measurement of the relative leaving-group ability of AF and ACl with respect to that of ABr.

For the specific purposes of the present study, our attention will now be focussed on the stereochemistry of nucleophilic displacements following formation of [II]* intermediates, disregarding for the moment the collateral processes which invariably accompany them, and that will be the subject of the following paper.

Nucleophilic Displacements on the [II] Intermediates. The stereoisomeric distribution of the halohydrins formed by attack of GA^+ acids on the selected 2,3-dihalobutanes in the presence of H_2O indicates that, when X = Cl or Br, the H_2O-to-AY (Y

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(26) (a) Cacace, F.; Speranza, M. *J. Am. Chem. Soc.* **1972**, *94*, 4447–4450. (b) Speranza, M.; Cacace, F. *Ibid.* **1977**, *99*, 3051–3055.

(27) (a) Chupka, W. A.; Berkowitz, J. A. *J. Chem. Phys.* **1971**, *54*, 4256–4259. (b) Jelus, B. L.; Murray, R. K., Jr.; Munson, B. *J. Am. Chem. Soc.* **1975**, *97*, 2362–2365.

(28) (a) Field, F. H.; Munson, M. S. B.; Becker, D. A. *Adv. Chem. Ser.* **1966**, *58*, 167. (b) Field, F. H. "Ion-Molecule Reactions"; Franklin, J. L., Ed.; Butterworths: London, 1972.

(29) Quoted in ref 11.

(30) Cacace, F.; Cipollini, R.; Giacomello, P.; Possagno, E. *Gazz. Chim. Ital.* **1974**, *104*, 977–989.

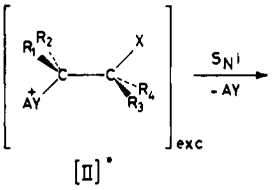
(31) Quoted in ref 24.

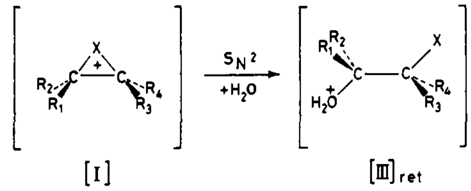
(32) Protonation by CH_5^+ and $C_2H_5^+$ on the halogen atom(s) of the selected compounds is computed to release 45–60 kcal mol^{-1} and 15–30 kcal mol^{-1}, respectively. Condensation by $C_2H_5^+$ is exothermic for ca. 25–40 kcal mol^{-1}. The exothermicity of the $CH_3FCH_3^+$ ion attack on the halogenated substrates is calculated to range from 15 to 35 kcal mol^{-1}.

(33) Pearson, R. G. "Hard and Soft Acids and Bases"; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1973.

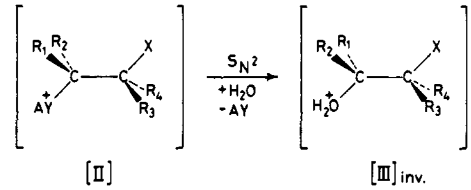
(34) The reported order is based on the hardness scale $CH_3^+ < C_2H_5^+ < H^+$ and on the consideration that CH_5^+ and $CH_3FCH_3^+$ can be regarded in the first approximation as CH_4- and CH_3F-solvated H^+ (ref 26) and, respectively, CH_3^+ (ref 23) ions.

henceforth identified as the leaving halogen) nucleophilic displacement involves preliminary cyclization to the corresponding butenehalonium ion [I] (eq 2a). These findings are consistent with the general tendency, outlined in previous studies,[1a,b] of nucleophilic vicinal groups for fast participation in gas-phase acid-induced nucleophilic displacements, causing two successive inversions of the configuration of the reaction center(s) and consequently yielding the retained substituted intermediates ($[\text{III}]_{\text{ret}}$).[35] A different mechanism must operate for X = F since, in this case, relatively high yields of the *inverted* fluorohydrins are invariably formed. Their predominance (from 54 to 95%) over the retained isomers denotes the failure of the F atom to effectively participate via the energetically allowed mechanism 2a to the substitution process,[36] ruling out therefore intervention of the fluorinated ions [I]. Rather, a simple direct H_2O-to-AY bimolecular mechanism must be operative in this case, involving inversion of the configuration of the reaction site (eq 2b).



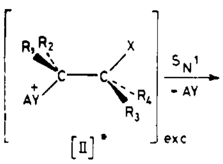


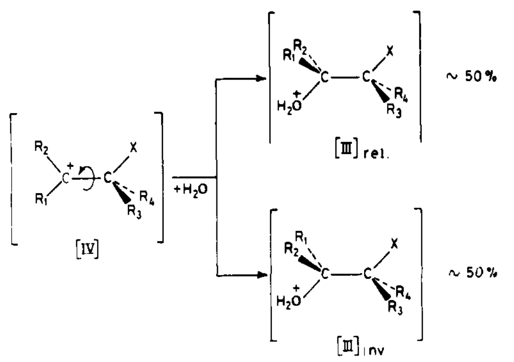
(2a)



(2b)

The high stereospecificity characterizing the majority of these halohydrin formation processes underlines the relatively small tendency of the intermediates [II]*, even when excited by the exothermicity of their formation processes,[32] to undergo unimolecular dissociation to AY and the residual carbocation [IV] (eq 2c) in gases at atmospheric pressure. Occurrence of a fast process (eq 2c) would, in fact, lead to the formation of an almost equimolar mixture of *inverted* and *retained* ("racemized") halohydrins, rather than the observed predominance of a single isomer.[37] However, when vicinal group participation is negligible, increasing exothermicity of the GA^+ acid ($C_nH_5^+$ vs. $CH_3FCH_3^+$) attack on the 2,3-Y,X-butane (Y = Cl, Br; X = F) leads to an increasing racemization of the resulting fluorohydrins (see Figure 1). On the other hand, when extensive neighboring group participation takes place (e.g., Y = F, Cl, Br; X = Cl), the higher the energy content of [II]*, the faster is its cyclization to [I] precursor of the corresponding $[\text{III}]_{\text{ret}}$ (eq 2a). As a consequence high retained vs. inverted chlorohydrin ratios are measured in CH_4 systems, whereas a certain tendency toward "racemization" characterizes the chlorohydrins recovered in the CH_3F samples.





(2c)

However, several other factors play a role in determining the stereospecificity of the substitution processes, including the configuration of the starting dihalobutane and the nature of the leaving halogen Y, which may somewhat influence the rate of the reaction leading to [I][38] and, hence, the extent of vicinal halogen participation to the displacement process.

In conclusion, the large predominance of retained chlorohydrins from **2**, **4**, and **5** in both CH_4 and CH_3F systems provides strong evidence in favor of the fast formation of the chlorinated [I] ions in the diluted gaseous state. On the contrary, the prevailing formation of *inverted* fluorohydrins from **1**, **2**, and **3** confirms in all instances the stereochemical course of a single-acid-induced nucleophilic displacement step, invariably taking place with predominant *inversion of configuration* of the reaction center[1a,b] and, therefore, demonstrates the reluctance of their ionic precursors to cyclize to fluorinated [I] ions.

Formation and Reactivity of Gaseous Cyclic Bromonium Ions [I]. As previously pointed out, the presence of bromine atom in the dihalogenated substrate appreciably limits the total yields of the substituted products, since only negligible amounts of bromohydrins are formed in both CH_4 and CH_3F systems (Tables I and II). The failure to observe appreciable bromohydrin yields from the pertinent substrates (**3**, **5**, and **6**) cannot be traced to exclusive attack of the GA^+ acids on the bromine atom of the substrate,[39] owing to the limited selectivity of such electrophiles toward different n centers, demonstrated by independent radiolytic[1a,b,26] and mass-spectrometric[12c,24,25a] investigation. Furthermore, even postulating a GA^+ attack exclusively on the Br atom, it is still hard to explain the lack of bromohydrin formation from **6**. The high activation barrier for formation of the brominated ions [I] from **3**, **5**, and **6** could provide another argument for rationalizing the absence of bromohydrins in such systems. In this case, however, appreciable amounts of *inverted* bromohydrins should be formed, on account of the relative leaving-halogen (AY) ability in intermediates [II] from **3**, **5**, and **6**. A plausible explanation for the extremely low bromohydrin yield can rather be found in a fast cyclization of the brominated [II]*'s to the bromonium ion [I], whose stability, under our experimental conditions, makes its reaction with water a slow process. This hypothesis is supported by the appreciable yields of *retained* derivatives from **5** and **6** from systems containing more powerful external nucleophiles, such as H_2S, 1,4-dihydroxybutane, ... (Table III). The preferred retention of the configuration indicates the fast formation of cyclic bromonium ions [I], which can yield $[\text{III}]_{\text{ret}}$ only by attack of nucleophiles more reactive than H_2O.[11] However, the relatively small amounts of thiols produced in the samples

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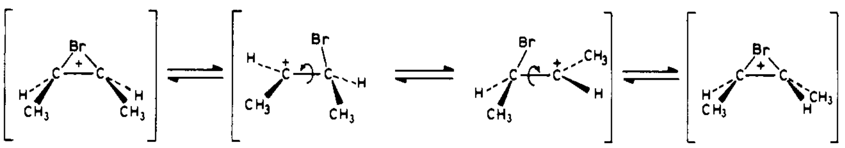
[35] The substituted intermediates [III] eventually undergo neutralization by losing their exceeding proton to a suitable base, either deliberately added to the system (H_2O, H_2S, NH_3, etc.) or formed from its radiolysis. The basic centers of the glass walls of the bulb can behave as a good proton acceptor too.

[36] Rough calculations carried out with the use of an estimated heat of formation of 172 ± 5 kcal mol^{-1} for fluorinated [I]'s indicate that cyclization process 1a → 2a is approximately thermoneutral only when $GA^+ = CH_5^+$. For the other selected acids, the same process is from 15 to 30 kcal mol^{-1} endothermic.

[37] As a matter of fact, the present data cannot rule out a fast exothermic ($\Delta H^\circ \simeq -15$ kcal mol^{-1}) [IV] → [I] isomerization taking place at rates higher than of a single C–C bond rotation in [IV].

[38] An approximate measure of the configurational effects on the stabilities of [II] and [I] ions can be drawn from: (a) Kollman, P. A.; Kenyon, G. L. *J. Am. Chem. Soc.* **1977**, *99*, 1892–1895. (b) Reference 8b.

[39] As pointed out in the text, hard gaseous acids, such as CH_5^+, should rather prefer to attack fluorine instead of bromine atoms.



[VII] [IX] [VIII]

(3)

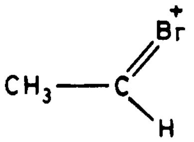
containing H_2S suggest that the H_2S-to-HBr displacement in [I] is a rather slow process, probably involving appreciable activation energy. On the other hand, when the neighboring group participation process within the bifunctional nucleophiles 1,4-dibromo- and 1,4-dihydroxybutane partially meets the electronic demand of its nucleophilic moiety (Br or OH) during the transfer to brominated [I], the relative yields of the corresponding substituted products increase appreciably. Any attempt to further improve these yields by using very powerful nucleophiles, such as NH_3, was frustrated by the drastic overall decrease of the recovered products and by the almost exclusive formation of elimination derivatives (olefins).

The high stability of the brominated ion [I] accounts as well for the marked difference in the overall products yields from the $C_nH_5^+$-induced H_2O-to-YA displacements on **2** and **3** (Table I). It should be noted that this difference is mostly due to the lack of any bromohydrin formation from **3**, while the fluorohydrin yield from both substrates is comparable. These findings are consistent with the preferential attack of $C_nH_5^+$ ions on the F atom of both substrates, leading to mostly *retained* chlorohydrins from **2** (via the corresponding chlorinated [I]), whereas the same path is precluded to brominated intermediates [I] on account of their exceedingly high stability. On the other hand, when the $C_nH_5^+$ acids attack the other halogen (Cl or Br) of **2** and **3**, it can promote only direct intermolecular displacement by the external nucleophile with formation of comparable yields of *inverted* fluorohydrins. This result suggests a similar gas-phase reactivity toward H_2O of open-chain chloronium and bromonium ions [II], but substantially higher than that displayed by cyclic bromonium ion [I]. The same arguments apply for the dependence of both the total and individual halohydrin $G_{(M)}$ values upon the nature of the substrate, if the comparison is extended to **4**, **5**, and **6**, in CH_4/H_2O mixtures.

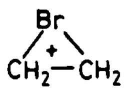
As to the CH_3F/H_2O systems (Table II), the softness of the $CH_3FCH_3^+$ acid directs methylation on the halogen atoms of 2,3-dihalobutane, with the preference order F < Cl < Br. As a consequence, formation of high stable cyclic bromonium ion [I] is less extensive than in the $GA^+ = C_nH_5^+$ case, and, therefore, the overall total $G_{(M)}$ value of products is less affected by the nature of the halogen atoms of the precursor.

In conclusion, the relative stability of gaseous [I] ions, inferred by the relative yield and the stereoisomeric distribution of the substituted products from the acid-induced displacement reactions on the 2,3-dihalobutanes (**1**–**6**), appears to be Cl < Br, while no evidence is obtained in favor of the existence of gaseous fluorinated [I]. Such findings are in full agreement with the qualitative trend observed in low-nucleophilicity solvent systems[7] and with theoretical predictions.[8,40]

Comparison with Related Experimental and Theoretical Data. Recent developments of sophisticated mass-spectrometric instrumentation (PIMS, ICR, CA, etc.) allowed the gathering of indirect evidence in favor of the existence of relatively stable ethylene halonium ions in the gas phase.[11,13] In their detailed PIMS and ICR investigation, Berman et al.[11] proposed the formation of two distinct noninterconverting $C_2H_4X^+$ (X = Cl, Br) structural isomers from several dihaloethane precursors, although, owing to the uncertainties in the thermochemistry of the neutral precursors involved, the small differences in the calculated heats of formation of the $C_2H_4X^+$ isomers did not allow a firm conclusion for the existence of unique and distinguishable isomers of $C_2H_4X^+$. Despite such uncertainty, a reactivity and stability scale of the $C_2H_4X^+$ isomers has been proposed on the grounds of the reaction pattern of $C_2H_4X^+$ species from several different neutrals toward a few substrates, although the validity of such methodology has been recently questioned.[14] The method of preparation of a certain ionic species from different precursors can impair the value of its reactivity pattern as a diagnostic tool for ion structure analysis, as demonstrated by the diverging conclusions as to the occurrence and the relative stability of the isomeric $C_2H_4Br^+$ ions [V] and [VI] generated in an ICR source.



[V]



[VI]

In Caserio's exhaustive investigation on ion–molecule reactions on substituted alcohols,[12c] arguments were brought to bear against the intervention of ion [VI] from β-bromoethanol by noting that the reactivity pattern of the fragment $C_2H_4Br^+$ is rather consistent with species [V], arising from the alcohol either directly or via a fast [VI] → [V] rearrangement. In Beauchamp's view, instead, electron impact on 1,2-dihaloethanes gives rise to two distinguishable, noninterconverting sets of $C_2H_4Br^+$ ions, [V] and [VI], the latter being the most stable.[11,12b]

Extension of such investigation to dihalobutanes revealed that the presence of methyl groups in bridged and open-chain haloalkyl cation isomers causes a gradual increase of the stability of structure [V] over the [VI] cyclic isomer, although, once formed, the cyclic isomer retains its structural integrity and does not rearrange to the more stable open structure within the ICR time scale.[12b]

From a general standpoint, the presence of isomerization products (i.e., butanone), invariably accompanying, in the present high-pressure experiments, the formation of mostly retained halohydrins, is consistent with fast vicinal halogen participation to the displacement process, followed by a slow isomerization of the resulting cyclic intermediate to the open-chain isomer, in substantial agreement with the mass-spectrometric evidence. On the other hand, the distinct sensitivity of the cyclization process 2a to a variety of factors, including the strength of the GA^+ acid, the leaving-group ability of AY, and the configuration of the starting substrate, is indicative of the influence of the specific preparation method in the stereodistribution of the resulting ionic species. This accounts for some gross discrepancies plaguing mass spectrometric investigations involving different starting reagents.[11,12]

This view finds counterpart in solution chemistry, where treatment of vicinal dihaloethanes with SbF_5 in low-nucleophilicity solvent systems (e.g., SO_2ClF) leads to a mixture of non-interconverting cyclic and open-chain halonium ions, the cyclic isomer being predominant at temperatures below −88 °C, i.e., *under kinetically controlled conditions.*[7l,41] Furthermore, methyl-substituted cyclic halonium ions are not stable even at relatively low temperatures (e.g., −40 °C) and slowly rearrange to the thermodynamically more stable open structure[7b,c] in qualitative agreement with gas-phase evidence. However, closer inspection on the features of cyclic halonium ions under stable-ion conditions revealed that, even at low temperatures, the same isomeric dimethylbromonium-ion distribution (30% [VII]; 70% [VIII]) is

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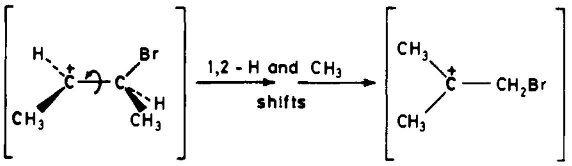
(41) Olah, G. A.; Mo, Y. K.; Halpern, Y. *J. Org. Chem.* **1972**, *37*, 1169–1174.

Table III. Effects of Different External Nucleophiles on the Product Yields from $C_nH_5^+$ (n = 1, 2) Ion Attack on Brominated Substrates

system composition[a]		$G_{(M)} \times 10^2$ values of products[b] $CH_3CHXCHNuCH_3$					
substrate (torr) $CH_3CH(X)CH(Br)CH_3$	nucleophile NuH (torr)	X	Nu	% threo	% erythro	ret/inv ratio	total absolute yields,[c] %
erythro-5 (0.4)	H_2O (1.3)	Cl	OH	3.5 (17)	16.8 (80)	4.8	8
		Br	OH	0.3 (1.4)	0.4 (1.9)	1.3	
threo-5 (0.4)	H_2O (0.5)	Cl	OH	3.8 (70)	1.6 (30)	2.4	2
		Br	OH	n.d.[d]	n.d.		
erythro-5 (0.5)	1,4-Br_2-C_4H_8 (0.7)	Br	Br	1.0 (10)	9.1 (90)	9.1	4
threo-5 (0.8)	1,4-Br_2-C_4H_8 (0.7)	Br	Br	10.4 (96)	0.4 (4)	26.0	4
erythro-5 (0.5)	1,4-$(OH)_2$-C_4H_8 (0.5)	Cl	OH	8.5 (16)	35.5 (67)	4.2	19
		Br	OH	1.4 (3)	7.8 (15)	5.6	
threo-5 (1.0)	1,4-$(OH)_2$-C_4H_8 (0.6)	Cl	OH	13.5 (68)	2.0 (10)	6.7	7
		Br	OH	3.3 (17)	1.0 (5)	3.3	
meso-6 (0.2)	H_2O (1.5)	Br	OH	n.d.	n.d.		
d,l-6 (0.1)	H_2O (0.7)	Br	OH	n.d.	n.d.		
meso-6 (0.4)	H_2S (2.0)	Br	SH	0.5 (25)	1.6 (75)	3.2	0.8
d,l-6 (0.4)	H_2S (2.0)	Br	SH	0.3 (72)	0.1 (28)	2.6	0.2
meso-6 (1.0)	1,4-$(OH)_2$-C_4H_8 (0.7)	Br	OH	0.3 (14)	1.9 (86)	6.3	0.8
d,l-6 (1.0)	1,4-$(OH)_2$-C_4H_8 (0.7)	Br	OH	2.1 (62)	1.3 (38)	1.6	1.2

[a] See footnote *a* of Table I. [b] See footnote *b* of Table I. [c] See footnote *c* of Table I. [d] See footnote *d* of Table I.

obtained regardless of whether *meso*- or *d,l*-2,3-dibromobutane is used as the precursor. These results are thought to arise from the occurrence of "non-static" (or rapidly interconverting) carbenium ion [IX], in equilibrium with the cyclic bromonium ions [VII] and [VIII] (eq 3), responsible for the rapid rearrangement to open-chain bromocarbenium isomer [X] at higher temperatures (eq 4).[7m] This picture is even more dramatic for the chloro



(4)

[IX] [X]

analogues of [VII]–[VIII] ions, in that neither "static" nor rapidly interconverting cyclic dimethylchloronium ions but only the open-chain isomer could be observed to date. At first sight, such results seem inconsistent with the high stereospecificity accompanying bromo- and chlorohydrin formation in the gas phase which, on the contrary, indicates the intermediacy of "static" cyclic ions [I]. This apparent inconsistency finds a plausible explanation in the absence of any solvation energy contribution to the stabilization of ionic species in the gas phase. Thus, as recently proposed[9,10,42] and verified by the present investigation, any n center (e.g., halogen) in a gaseous ion serves as a donor in internally solvating and, therefore, delocalizing the positive charge to some extent. Such an effect is overwhelmed even in low nucleophilicity solvents, where the presence of the solvent itself coupled with the rather unpredictable role of the specific counterion involved in stabilizing equilibrating isomeric ions[43] supplies enough stabilization energy to the open carbocation to make it easily interconvertible with the bridged from or, in the less favorable cases (e.g., X = Cl), the only observable isomer.

Conclusions

A radiolytic approach to the characterization of cyclic halonium ions in the gas phase is illustrated in the present study. Occurrence of gaseous cyclic 2,3-butene chloronium and bromonium ions is demonstrated by the stereochemistry of acid-induced nucleophilic displacements on suited substrates. No evidence for the formation of stable 2,3-butene fluoronium ions has been obtained in agreement with theoretical predictions. The present results consolidate the knowledge about gaseous cyclic halonium ions, providing reasonably firm grounds for evaluating the effects of the solvent and of the counterion on the occurrence and stability of cyclic halonium ions.

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[43] Cathcart, R. C.; Bovenkamp, J. W.; Moir, R. Y.; Bannard, R. A. B.; Casselman, A. A. *Can. J. Chem.* **1977**, *55*, 3774–3785.