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(10 Calculational methods are described in ref 5.

(11) Using perturbation expression 1, one finds:

$$\text{stabilization} \propto \frac{[(0.72)(0.86) - 2(0.46)(0.32)]^2}{\Delta E_{2\text{-}3}} = \frac{0.11}{\Delta E_{2\text{-}3}}$$

This is to be compared with the stabilization of nortricyclyl which can be thought of as simply the interaction of methyl cation LUMO with cyclopropane HOMO

$$= \frac{[(1.00)(0.72)]^2}{\Delta E_{1\text{-}2}} = \frac{0.52}{\Delta E_{1\text{-}2}}$$

Thus the stabilization energy due to the second cyclopropane in quadricyclyl should be no greater than 0.11/0.52 = 0.21 of the initial stabilization in nortricyclyl. This fraction is reduced still further since $|\Delta E_{1\text{-}2}| < |\Delta E_{2\text{-}3}|$ (i.e., the methyl cation LUMO is lower than the cyclopropyl carbinyl LUMO). This simple perturbation theory result is to be compared with the experimental relative rates

$$\frac{\log\left(\frac{k_3}{k_2'}\right)}{\log\left(\frac{k_2}{k_1}\right)} = \frac{1.2}{8.8} = 0.14$$

(12) This species is stabilized yet further, of course, because of relief of angle strain at the cationic center. It is the intention of this paper to focus on only electronic effects, however.

(13) Using the procedure of ref 11, $(H_{L\text{-}H})^2 \propto 0.47$ for the interaction of cyclopropane with the already strongly stabilized cyclopropyl allyl cation; this represents 90% of the stabilization due to interaction of cyclopropane with methyl cation.

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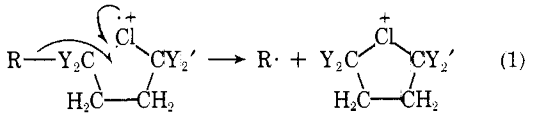
The Gaseous Tetramethylenechloronium Ion[1]

Sir:

The formation of chloronium and bromonium ions in the gas phase was postulated[2] to explain the dominant peaks in the mass spectra of higher 1-haloalkanes (eq 1). Despite the apparent general acceptance of this rationalization,[3] and the postulation of similar cyclization-displacement reactions involving anchimeric assistance to explain[3] unusual peaks in the spectra of *n*-alkyl amines, thiols, nitriles, and ketones,[4] no direct evidence for such ion structures has yet been presented. Cyclic halonium ions have been identified in SbF_5-SO_2 solution by Olah, Peterson, and their coworkers,[5] supporting previous postulates of 1,2- and 1,4-halonium ion participation in solvolysis. However, although relatively high stabilities are found for tetramethylenehalonium (Cl, Br, I) and ethylenehalonium ions in solution,[5] mass spectral examples in which high ion abundance indicates such special stabilization have been found only for $C_4H_8Cl^+$ and $C_4H_8Br^+$ ions and not for gaseous ions such as $C_4H_8I^+$, $C_2H_4Cl^+$, or $C_2H_4Br^+$. Recent ion-molecule reaction studies[6] indicate that $C_4H_8Br^+$ ions are substantially more stable than $C_2H_4Br^+$ ions. Theoretical studies[7] utilizing ab initio calculations, which neglect solvent effects, also predict the ethylenehalonium ions to be stable. Thus we felt that unequivocal evidence for the structure of the parent tetramethylenechloronium ion **1** in the gas phase was necessary before further comparisons of gas and solution phase behavior of these ions was warranted.



1, R = C_2H_5; Y = Y′ = H
1a, R = C_2H_5; Y = H; Y′ = D
1b, R = C_2H_5; Y = D; Y′ = H

2

Table I. Partial Mass Spectra of Labeled 1-Chlorohexanes

	Relative abundance					
Compound *m/e*	90	91	92	93	94	95
1-Chlorohexane	0.3	72.	3.6	23.	1.3	
1-Chlorohexane-*1,1*-d_2		0.2	1.9	70.	3.8	23
1-Chlorohexane-*4,4*-d_2		0.5	1.6	71.	3.8	22

Table II. Collisional Activation Spectra of $C_4H_8{}^{35}Cl^+$ and $C_4H_6D_2{}^{35}Cl^+$ Ions[13]

m/e	1-Chloroheptane[a]	1-Chlorohexane[a]	1-Chlorohexane, 18 eV[a]	1-Chlorohexane-*1,1*-d_2[b]	1-Chlorohexane-*4,4*-d_2
27	16	15	16	8.0	7.4
28	4	4	4	8.5	8.0
29	9.2	10	9.1	5.4	5.5
30				5.6	5.0
31				3.4	3.3
39	14	15	14	7.5	7.1
40	2	2.	2	7.2	7.1
41	9.6	9.5	8.3	5.9	5.7
42				3.7	3.6
43				4.0	4.0
47	1.1	1.2	1.5	1.0	1.0
48	0.5	0.5	0.5	0.5	0.5
49	12	12	10	5.7	5.2
50	1.	1.	1.	2.6	2.7
51	3.4	3.3	3.6	5.5	5.2
52	0.5	0.5	0.5	1.5	2.0
53	7.2	6.5	6.7	1.7	1.5
54	<2	<2	<3	3.0	3.0
(55)	(140)	(180)	(110)	3.5	3.5
61	4.3	4.3	4.1	2.	2.
(62)	(15)	(16)	(13)	(7)	(7)
(63)	(19)	(21)	(16)	(8)	(8)
73	1.	1.0	1.1	0.4	0.4
74		0.1	0.1	0.4	0.3
75	4.	3.5	4.3	1.0	0.9
76		0.5	1.	1.3	1.3
77				1.2	1.2
78				0.2	0.2
90	10	11	12	0.2	0.3
91				0.7	1.1
92				5.5	7.6

[a] Abundances are relative to the total ion abundance = 100, excluding *m/e* 55, 62, and 63 which arise in part from metastable ion decompositions. [b] Abundances are relative to the total = 100 for the ions used in footnote *a* and their deuteriated derivatives; contribution of such ions to *m/e* 62 and 63 is assumed to be 3/100.

The base peak in the spectrum of 1-chlorohexane, **1**, has the composition $C_4H_8Cl^+$. In the mass spectra of both 1-

chlorohexane-*1,1*-d_2 (**1a**)[8] and -*4,4*-d_2 (**1b**)[9] (Table I) this ion retains both deuterium atoms, consistent with the specific loss of the terminal C_2H_5 group as required by eq 1.

The collisional activation (CA) spectrum[12] of the $C_4H_8{}^{35}Cl^+$ ions from 1-chlorohexane (Table II) is not affected by lowering the electron energy, indicating that a single ion structure is formed. The same CA spectrum is observed for these ions from 1-chloroheptane, consistent with a common mechanism of formation.

A unique feature of the chloronium ion **2** in comparison to $ClCH_2CH_2CH_2CH_2{}^+$ or most alternative structures is its axis of symmetry. Thus the $C_4H_6D_2Cl^+$ ion produced from **1a** should be identical with that from **1b**, while open chain ion products would differ in their position of deuterium substitution. The CA spectra of the $C_4H_6D_2{}^{35}Cl^+$ ions from **1a** and **1b** are virtually identical. Of course this would be true for even an open chain $C_4H_8Cl^+$ structure if complete H/D scrambling occurred before decomposition; the spectra indicate that H/D scrambling, although extensive, is not complete. Fortunately, there is a relatively small degree of scrambling in the $CH_2{}^{35}Cl^+$ ions (*m/e* 49 for d_0) formed by loss of C_3H_6.[15] If **1a** and **1b** gave the open chain ions $ClCD_2CH_2CH_2CH_2{}^+$ and $ClCH_2CH_2CH_2CD_2{}^+$, respectively, the *m/e* 49 peak of **1** should appear largely at *m/e* 51 and 49 in **1a** and **1b**, respectively. However, in the CA spectra of the $C_4H_8{}^{35}Cl^+$ ions from both **1** and **1b**, the amounts of CH_2Cl^+ and CD_2Cl^+ formed are *equivalent*, and double that of $CHDCl^+$. This must result from decomposition of $C_4H_8Cl^+$ ions in which carbons 1 and 4 have become equivalent to each other but not to carbons 2 and 3, completely consistent with the chloronium ion structure **2**.[16]

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(9) Phenyl propionate was reduced with $LiAlD_4$ in triethylene glycol dimethyl ether.[10] Treatment of the resulting $C_2H_5CD_2OH$ with PBr_3 yields $C_2H_5CD_2Br$ which was converted to $C_2H_5CD_2C_3H_6OH$ by treating its Grignard with trimethylene oxide.[11] This was converted to $C_2H_5CD_2C_3H_6Cl$ with $SOCl_2$ and purified by GC (2% d_1, 98% d_2).
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(15) Decomposition of completely H/D scrambled $C_4H_6D_2Cl^+$ ions would give $[CH_2Cl^+]$:$[CHDCl^+]$:$[CD_2Cl^+]$ of 15:12:1.
(16) It is possible that the $CHDCl^+$ ions in the CA spectrum are due to the formation of an additional $C_4H_8Cl^+$ isomer, not just to scrambling accompanying the decomposition of **2**. Such a $C_4H_8Cl^+$ isomer would be expected to give abundant CH_2Cl^+ ions in its CA spectrum also, however, so that the proportion present should be small in comparison to that for **2**.
(17) Postdoctoral Fellow, 1974; on leave from the NFWO, Belgium.

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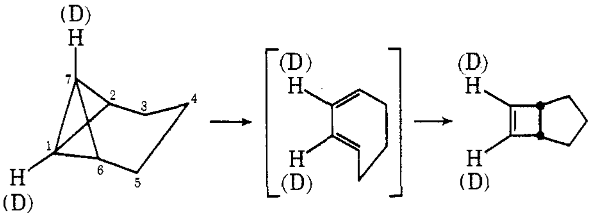
Thermal Rearrangement of Some Endo-Endo′-Bridged Bicyclo[1.1.0]butanes

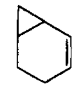
Sir:

The thermal rearrangement of bicyclo[1.1.0]butane to butadiene is considered to be a concerted $[_\sigma 2_s + {}_\sigma 2_a]$ type reaction.[1,2] Recently Dewar and Kirschner[3] on the basis of MINDO/3 calculations concluded, that a two-step mechanism with a diradical intermediate is more favorable and not in contradiction with the allowed and stereoselective[1,2] formation of the products. Wiberg and Szeimies[4] obtained bicyclo[3.2.0]hept-6-ene (**3**) on gas phase pyrolysis of tricyclo[4.1.0.0^{2,7}]heptane (**1**). Since the direct conversion **1** → **3** is forbidden,[1] the authors proposed *cis,trans*-cyclohepta-1,3-diene (**2**) as intermediate, which on conrotatory ring closure forms the cis substituted cyclobutene (**3**). As expected **1a** is transformed to **3a.**[5]



1 (**1a**) **2** (**2a**) **3** (**3a**)

We wish to report the results of a study, in which **1**, tricyclo[4.1.0.0^{2,7}]hept-3-ene (**5**), tricyclo[3.1.0.0^{2,6}]hexane (**9**), and tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane (**12**) were rearranged in solution. Since in toluene-d_8 thermolysis of **1** produces only a small amount of **3** and mainly 2-norcarene (**4**), the



4

formation of which is probably acid catalyzed,[6] we used tetramethylethylenediamine (TMEDA) as solvent and obtained after heating to 200° for 24 hr 40% **3** and 60% **4**.

Recently the preparation of (**5**) and its thermolysis to bicyclo[3.2.0]hepta-2.6-diene (**8**) were reported.[7] The by-product cycloheptatriene does not appear, if the reaction is carried out in the presence of TMEDA. At 135° the half-life was determined to be 1 hr, the yield more than 90%. An overall pathway analogous to the **1** thermolysis is indicated by the reaction product **8**. Being less symmetric than **1, 5**