in the nmr spectrum of the ester with the probe temperature maintained at 28°. When not actually recording the spectrum, the sample was maintained at 28° in a constant-temperature bath. The region of the nmr spectrum used in determining the solvolysis rate was that of the allylic methyl resonances. By measuring the decrease in peak height or area of the *downfield* half of the allylic methyl doublet of the ester and the corresponding increase in the *upfield* half of the allylic methyl doublet of the ether product at appropriate time intervals, the pseudo-first-order solvolysis rate data summarized in Table II and Figure 2 were obtained.

Acknowledgment. The authors wish to acknowledge gratefully the support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society (PRF-2357-A1,4).

Stable Carbonium Ions. XCVI.[1a] Propadienylhalonium Ions and 2-Haloallyl Cations[1b]

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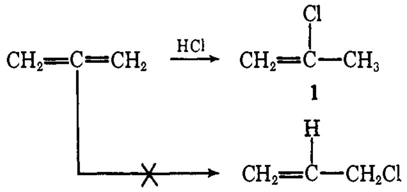
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 2, 1969*

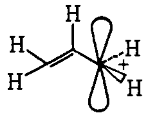
Abstract: 2,3-Dihalopropenes in SbF_5–SO_2 solution form propadienylhalonium ions which were studied by nmr spectroscopy. These intermediates have recently been postulated to be responsible for the direction of halogen additions to allene and substituted allenes. We have also prepared and studied by nmr spectroscopy a series of 2-halopolymethylallyl cations which exist as nearly planar allyl cations. In some of these ions we have been able to measure free energies of activation for rotation.

Polar additions of hydrogen halides to allene yield 2-halopropenes (**1**) rather than 3-halopropenes (**2**).[2] The reason usually given for this result is that addition of a proton to the central carbon of allene does not give a resonance-stabilized allyl cation but rather one in which the p orbital of the carbonium ion carbon is orthogonal to the p orbital of the double bond (**3**). Apparently this ion is less stable than the vinyl cation (**4**).



$$CH_2{=}C{=}CH_2 \xrightarrow{HCl} CH_2{=}C(Cl){-}CH_3 \quad \mathbf{1}$$

$$CH_2{=}C{=}CH_2 \not\longrightarrow CH_2{=}C(H){-}CH_2Cl \quad \mathbf{2}$$



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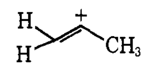

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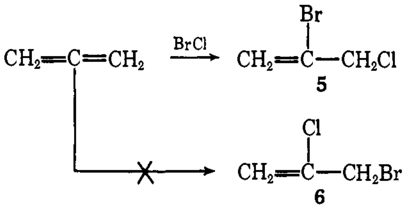
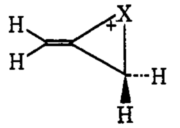
A note by Peer,[3] however, reported the addition of bromine chloride to allene to give 2-bromo-3-chloropropene (**5**) rather than the isomeric material (**6**) expected if the addition followed the same orientation as that of the hydrogen halide additions. This behavior is explicable if one postulates bridging by halogen (**7**) as a means of stabilizing the intermediate twisted allyl cation. Addition of the nucleophile to **7** could take place in either conjugate or normal fashion (S_N2) shown in Schemes I and II, respectively.



$$CH_2{=}C{=}CH_2 \xrightarrow{BrCl} CH_2{=}C(Br){-}CH_2Cl \quad \mathbf{5}$$

$$CH_2{=}C{=}CH_2 \not\longrightarrow CH_2{=}C(Cl){-}CH_2Br \quad \mathbf{6}$$



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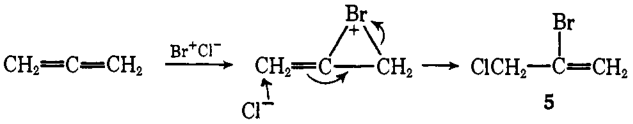
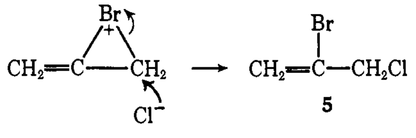
Scheme I



$$CH_2{=}C{=}CH_2 \xrightarrow{Br^+Cl^-} \longrightarrow ClCH_2{-}C(Br){=}CH_2 \quad \mathbf{5}$$

Scheme II



$$\longrightarrow CH_2{=}C(Br){-}CH_2Cl \quad \mathbf{5}$$

Peer proposed that 2,3-dichloropropene (**8**) and propargyl chloride (**9**) obtained by chlorination of allene in CH_2Cl_2, $CHCl_3$, and *sym*-$C_2H_4Cl_2$ arise from a "propadiene-Cl^+ complex" (**10**). This complex could lead directly to **8**. A "four-center elimination reaction" involving **11** was suggested for the formation of **9**.

Waters and Kiefer[4] have investigated the methoxymercuration of allenes. The reaction of allene with methanolic mercuric acetate produced only one product,

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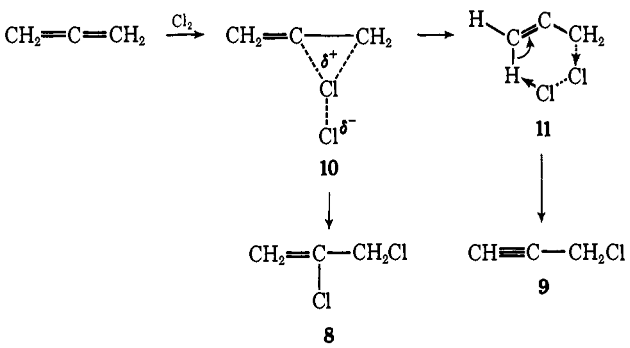
[1] (a) Part XCV: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 6883 (1969); (b) presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; (c) undergraduate research participant.

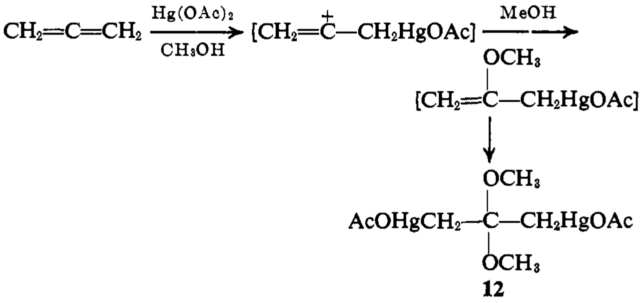
[2] D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

[3] H. G. Peer, *Rec. Trav. Chim. Pays-Bas*, **81**, 113 (1962).

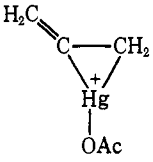
[4] W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967).



1,3-bis(acetoxymercury)2,2-dimethoxypropane (**12**). These authors conclude that their results on methyl-substituted allenes provide strong support for the existence of bridged mercurinium ions as stable intermediates in these reactions. Their result on allene itself

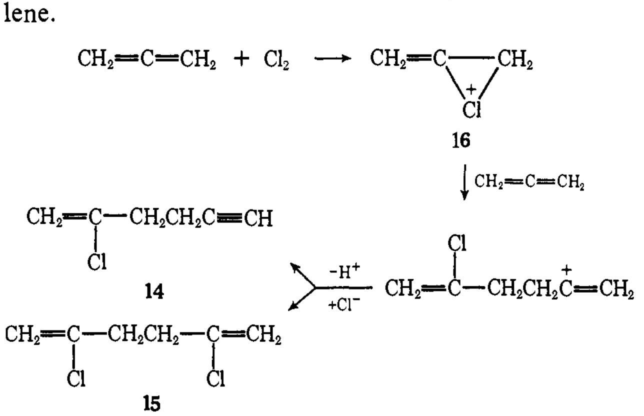


does not necessarily support an unsubstituted mercurinium ion (**13**).



13

More recently, Poustma[5] has reported the formation of a number of other products in addition to 2,3-dichloropropene and propargyl chloride on chlorination of neat allene at −30°. The four isolated products were **8** (23%), **9** (20%), 2-chloro-1-hexen-5-yne (**14**) (4.3%), and 2,5-dichloro-1,5-hexadiene (**15**) (1.5%). Dimeric species **14** and **15** were postulated to have arisen by attack of an "(allene–Cl^+)" species (**16**) on allene.

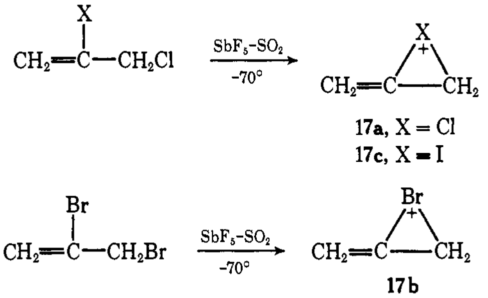


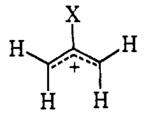
Osborn[6] has reported nmr evidence for Pt^{II} and Rh^{III} complexes of allene in which the metal is viewed as bonding *via* two σ bonds to the carbon atoms analogously to the mercurinium ions. Perhaps the best evidence for the intervention of bridged intermediates in the halogenation of allene is the recent work of Waters, Linn, and Caserio[7] who reported stereospecific *trans* addition of halogen and oxymercury species to 1,3-dimethylallene. Also, Wedegaertner and Millam[8] have reported *trans* addition of bromine to 1,2-cyclononadiene.

We wish now to report observations of halonium ions of allene (**17**) in SbF_5–SO_2 solution at low temperature. For purposes of comparing and contrasting the behavior of these ions, we have also prepared a series of 2-chloro- and 2-bromopolymethylallyl cations and their nonhalogenated analogs in strong acid media.

Results

When 2,3-dichloropropene is dissolved in SbF_5–SO_2 solution at −78°, a deep red solution results on slight warming of the solution. The nmr spectrum of this species is shown in Figure 1. The fact that three groups of absorptions with peak area ratios 2:1:1 (from high field to low field) are observed is clearly inconsistent with the formation of an allylic cation, but is completely consistent with the bridged ion **17a**. Figures 2 and 3 illustrate the spectra obtained for ions **17b** and **17c**, respectively. It is apparent that absorptions due to another species are also present. We have not been able to determine what these other species are. They appear to have three different types of protons which rule out allylic cations such as **18**.





18

Quenching ions **17a–c** in sodium methoxide–methanol gave less than 20% yields of the expected 2-halo-3-methoxypropenes (identified by their nmr spectra). We have not been able to find any quenching conditions under which recovery of material could be improved.[9] Possibly the main reaction on quenching is loss of a proton, yielding a propargyl halide which undergoes further reaction in the basic methanol. Indeed when we added propargyl chloride (bromide) to a sodium methoxide–methanol solution, no material could be recovered using our usual technique of work-up.

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(5) M. L. Poutsma, *J. Org. Chem.*, 33, 4080 (1968).

(6) J. A. Osborn, *Chem. Commun.*, 1231 (1968).

(7) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968).

(8) D. K. Wedegaertner and M. J. Millam, *J. Org. Chem.*, 33, 3943 (1968).

(9) We have also tried quenching these ions in a potassium carbonate suspension in methanol and by adding the SO_2 solutions of these ions to a suspension of potassium bromide in SO_2. In the latter case, small quantities of the dibromide could be isolated from **17b**.

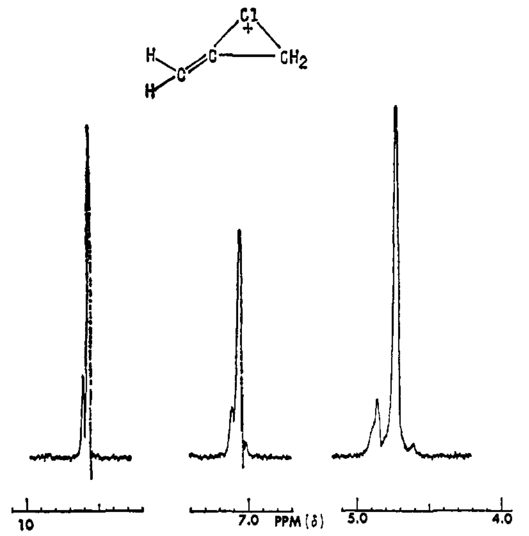
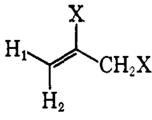
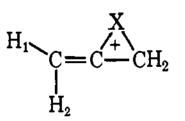


Figure 1. Pmr spectrum of the propadienylchloronium ion (**17a**) in SbF_5–SO_2 solution at −80°.

Another explanation for low yields of methanolysis products is that the ions have reacted with SO_2, leading to products which are water soluble. If this were so, our identification of the species formed in SO_2–SbF_5 would be incorrect. The possibility of reaction with SO_2 was excluded at least in one case by preparation of the ion in the absence of SO_2.[10] Pmr data of propadienylhalonium ions and their dihalide precursors are summarized in Table I.

Table I. Pmr Data of 2,3-Dihalopropenes and Their Propadienylhalonium Ions[a]

								
Halogen			Dihalide[c]			Ion **17a–c**		
X	X′	H_1	H_2	CH_2	H_1	H_2	CH_2	
Cl	Cl[b]	5.58	5.40	4.11	9.58	7.07	4.72	
Br	Br[b]	6.03	5.63	4.17	9.55	7.60	4.77	
I	Cl	6.47	5.89	4.21	9.50	7.28	5.02	
Cl	I	5.60	5.31	4.09				
I	I	6.40	5.74	4.26				

[a] Chemical shifts for these ions are δ in parts per million from external TMS. They were measured in SbF_5–SO_2 at −80°. Chemical shifts for the dihalides were measured at room temperature in CCl_4 and are δ in parts per million from internal TMS. [b] These shifts agree with those reported by N. S. Bhacca, L. F. Johnson, and J. N. Shoolery ("High Resolution Nmr Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962), with the proton *cis* to the halogen assigned to the lowest field vinyl resonance. [c] In all cases the lower field proton was more strongly coupled to the halomethylene group, with the coupling between the upfield vinyl proton and the halomethylene group being immeasurably small for all but 2-iodo-3-chloropropene.

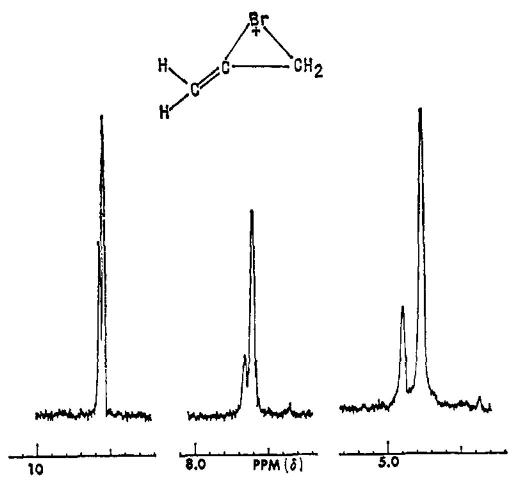


Figure 2. Pmr spectrum of the propadienylbromonium ion (**17b**) in SbF_5–SO_2 solution at −80°.

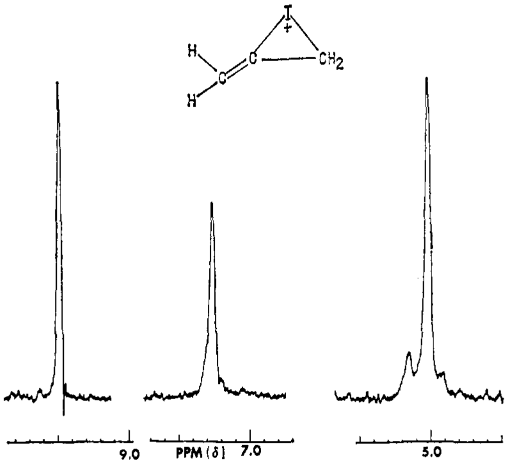
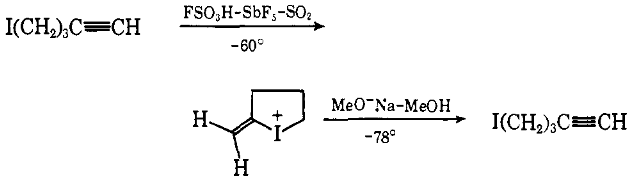


Figure 3. Pmr spectrum of the propadienyliodonium ion (**17c**) in SbF_5–SO_2 solution at −80°.

As inferred, proton loss from ions **17a–c** on quenching is reasonable since Peer has shown that a substantial amount of propargyl chloride is produced by chorination of allene in inert solvents. Furthermore, we previously reported[11] what we thought to be an abnormal result obtained on quenching cation **19** (which was prepared by protonation of 5-iodopentyne-1) to give back the starting iodopentyne. We have investigated this system and find that a species of undetermined structure is initially formed which is slowly converted at −60° to the five-membered ring halonium ion **19**. Starting material, 5-iodopentyne-1, was obtained from both of these species on quenching.



19

A further area of interest to us was the preparation of 2-halopolymethylallyl cations. It was expected

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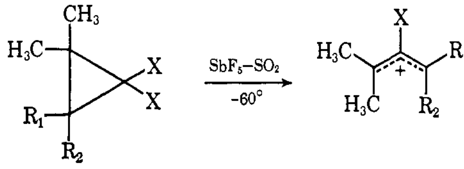
[10] We have attempted to prepare ions **17a–c** in SO_2ClF–SbF_4 solution at −117°. From 2,3-dichloropropene we obtained the same ion, **17a**, which we had previously prepared in SbF_5–SO_2 solution although some broad high-field absorptions were also present. This suggests that reaction with SO_2 has not occurred. We were unable to obtain well-resolved spectra of ions **17b** and **17c** from the related 2,3-dihalopropenes in SO_2ClF–SbF_5. The same halonium ions should be produced by protonation of the appropriate acetylenes. Unfortunately these halonium ions are unstable in HSO_3F–SbF_5–SO_2 solution. However, electrophilic addition reactions of propargyl halides are being examined for halogen participation.

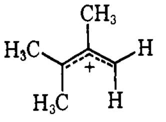
[11] G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 6988 (1968).

that the methyl groups in the pmr spectra of these ions should be nonequivalent if these species are nearly planar but that the rotational barriers might be lower than those of some previously reported allyl cations[12,13] because of stabilization of the transition state (presumed to be a twisted allyl cation) by halogen participation.[14] We have now succeeded in preparing a series of 2-halomethylallyl cations by ionization of the appropriately substituted cyclopropanes.



20–22 a, X = Cl **23–25**
b, X = Br
20a,b and **23a,b**, $R_1 = R_2 = H$
21a,b and **24a,b**, $R_1 = H$; $R_2 = CH_3$
22a,b and **25a,b**, $R_1 = R_2 = CH_3$

The 2-chloro-1,1-dimethylallyl cation **23a** exists as a nearly planar species and showed nonequivalent methyl groups separated by about 4.9 Hz at 100 MHz at −70°. These methyl resonances coalesced to a single broad line near −39°. At −7° rotation is rapid and the methyl resonances appear as a sharp triplet due to coupling (J = 1.2 Hz) with the vinylic protons.[15] Calculation of $\Delta G^{\ddagger 12}$ at the coalescence temperature (T_c) gave a value of 12.5 kcal/mol. Comparison of this value with that obtained for the 1,1,2-trimethylallyl cation **26** (11.7 kcal/mol) determined in the same way suggests no significant participation in the exchange process.

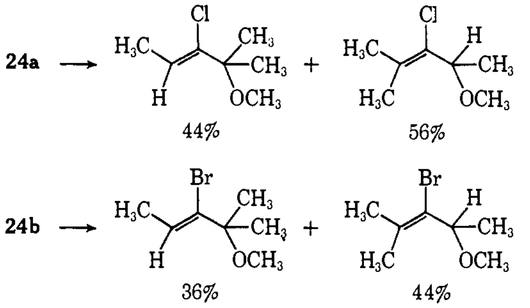


26

The 2-bromo-1,1-dimethylallyl cation **23b** (which could only be prepared in SbF_5–SO_2ClF solution) exhibited a single broad line for its methyl groups at temperatures down to −110°. This single line may be due to accidental equivalence of the methyl groups or to rapid rotation around the partial double bond. If the ion were rapidly rotating at all temperatures, the methyl resonance should appear as a triplet.[15] The failure to observe this multiplicity below −60° may be the result of lower resolution at these temperatures or of some nonequivalence of the methyl groups with the broadening due to long-range coupling. When **23a** was prepared in SbF_5–SO_2ClF solution, resolution was decreased so that a separation could not be measured either, and so we tend to favor the latter explanation. We do not have an explanation for the extreme instability of **23b** in SbF_5–SO_2. We also examined the ionization of the *gem*-difluorocyclopropane in this series but we were unable to deduce definitely the structure of the resulting ion although it appears to be the expected 2-fluoro-1,1-dimethylallyl cation.

Ion **24a** at 100 MHz showed nonequivalent methyl groups separated by *ca.* 5.6 Hz. The coalescence temperature was determined to be near −8° for these signals which gave a $\Delta G^{\ddagger}$ for rotation of about 14.2 kcal/mol.[16] In **24b** definite separation of the *gem*-dimethyl signals could not be determined positively, although the total line width suggested that there was in fact some separation. The spectra of both these ions are quite complicated since the nonequivalent methyls are coupled to each other, to the third methyl group, and to the vinylic proton.

Solutions of **24a** and **b** were quenched smoothly in sodium methoxide–methanol at −78° to give 70–75% yields of the expected ethers. Interestingly, these ethers were formed in nearly equal amounts, although in quenching other stable ions, we have always seen a great predominance of the more highly substituted ether. The stereochemistry of the minor products in each case was not rigorously established but is likely as shown, based on the structure of the cation.[17]



Ions **25a** and **25b** both showed a single sharp line for their methyl resonances at temperatures as low as −110°. At still lower temperatures resolution had decreased to where one would not be able to observe a small separation between nonequivalent methyl resonances. This equivalence could be accidental or it could be indicative of rapid rotation. We favor the latter explanation. This suggests halogen participation, although some of the barrier lowering could arise from increased ground-state steric effects. We have also ionized the related *gem*-difluorocyclopropane and *gem*-diiodocyclopropane, but have not been able to establish with certainty the ions produced. Quenching **25a** and **25b** in sodium methoxide–methanol at −78° gave mixtures of the corresponding ethers and butadienes in overall yields of 75–80%.[18]

We prepared ions **28a** and **28b** by ionization of the *cis*-dimethyldihalocyclopropanes **27a** and **27b** in SbF_5–SO_2ClF, SbF_5–SO_2, or in 1:1 HSO_3F–SbF_5–SO_2 at temperatures ranging from −60 to −117°. Ions **30a** and **30b** were prepared by ionization of the *trans*-di-

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[12] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 6082 (1968).

[13] P. von R. Schleyer, T. Su, M. Saunders, and J. Rosenfeld, *ibid.*, **91**, 5174 (1969).

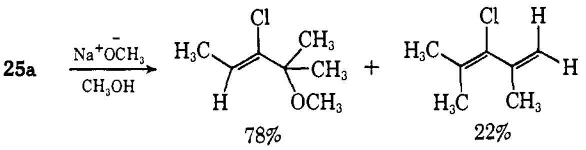
[14] G. A. Olah, *et al.*, *ibid.*, **89**, 4744 (1967); **90**, 947, 2587, 4675, 6989 (1968).

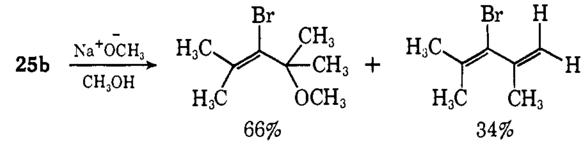
[15] Identical behavior was noted earlier for the 1,1,2-trimethylallyl cation reported in ref 12. For this ion and **23a**, decoupling experiments demonstrated unequivocally that the triplet nature of the absorption at high temperatures was caused by coupling to the vinylic protons. Ion **23b** also showed a triplet at temperatures above −50°, but near −15° decomposition took place.

[16] Exact separations were difficult to determine. An error of ±2 Hz for a separation of 6 Hz would cause an error of about ±0.4 kcal/mol. The separations were somewhat temperature dependent, decreasing by as much as 0.5 Hz before exchange began in some cases. Similarly, the coalescence temperature was difficult to estimate. An error of ±5° could cause an error of about 0.6 kcal/mol, making the total error in free energy about ±1 kcal/mol.

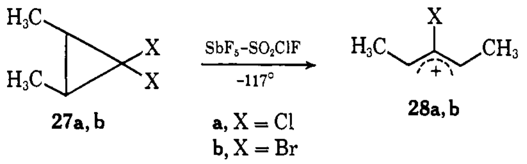
[17] S. R. Sandler, *J. Org. Chem.*, **32**, 3876 (1967).

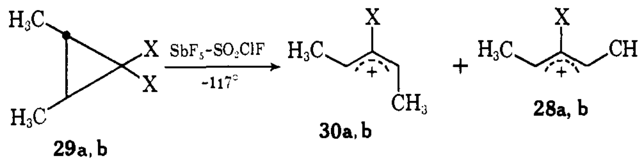
[18] G. C. Robinson, *ibid.*, **33**, 607 (1968), and S. R. Sandler, *ibid.*, **33**, 4537 (1968), have published preparative procedures involving reactions of certain methyl-substituted *gem*-dichloro- and dibromocyclopropanes to yield products similar to these.



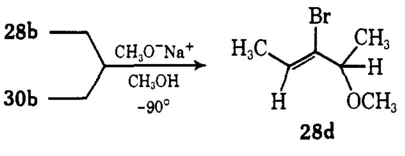


methyldihalocyclopropanes **29a,b** at ethanol slush temperatures (*ca.* −117°). If ionization of **29a,b** was conducted at higher temperatures, even that of methanol slush (*ca.* −95°), only traces of **30a,b** could be observed with **28a,b** predominating. In fact, at −117°, the ionization was still not completely stereospecific, *i.e.*, **29a** gave 77–99% **30a** and **29b** gave 48–76% **30b**. The rearrangement of ions **30a,b** must have taken place during their preparation since both ions were not detectably further isomerized after 48 hr at −78°. The most probable reason for this lack of stereospecificity is the presence of a competing pathway for generation of the allylic cation. Protolytic ring opening (possibly to a halonium ion) followed by hydrogen halide loss is a likely path since we had previously observed this route to allyl cations.[12] Protonation of **29a,b** in 1:1 HSO_3F–SbF_5–SO_2ClF does in fact yield the allylic ions **28a,b** but also some **30a,b** even at −78°. The use of SO_2 with the 1:1 HSO_3F–SbF_5 allows the formation of only **28a,b** under all conditions we have tried. At present we are unable to account for these results. However, we were able to measure the rate of isomerization of **30a,b** to **28a,b**. These reactions could be conveniently followed by integration of the separate signals of the vinyl proton resonances near −20°.[19] The rate constants obtained in this way were not of high reproducibility, probably because accurate integration is not feasible with the relatively low ion concentrations[20] with which we are dealing.

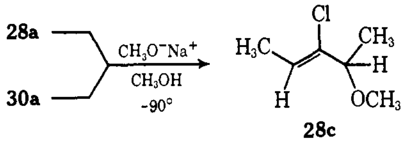




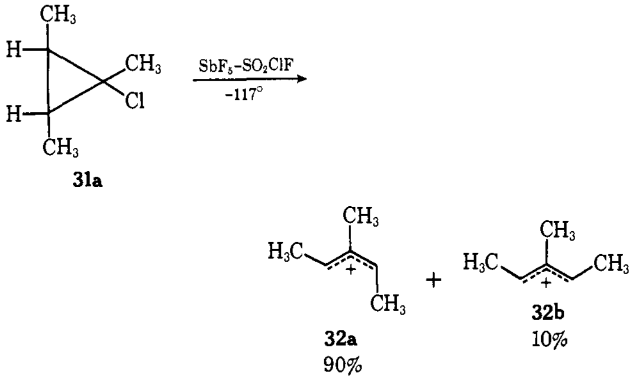
Quenching either **28b** or **30b** in a suspension of sodium methoxide in methanol at −90° gave **28d** as the only detectable product (by nmr). This compound has been reported previously by Waters, *et al.*,[7] and our identification was made on the basis of the nmr data presented by these authors. Sandler[17,18] has reported products related to **28d** as the sole products arising from thermal reactions of either **27b** or **29b**. These results were explained as arising from either a preferential attack at one end of **30b** or from isomerization prior to product analysis. Parham and coworkers[21] have reported a similar observation in the silver ion assisted solvolysis of *cis*- and *trans*-3,3-dichloro-1,2-di-*n*-propylcyclopropane and attributed this to preferential attack of solvent on one end of the allylic cation.

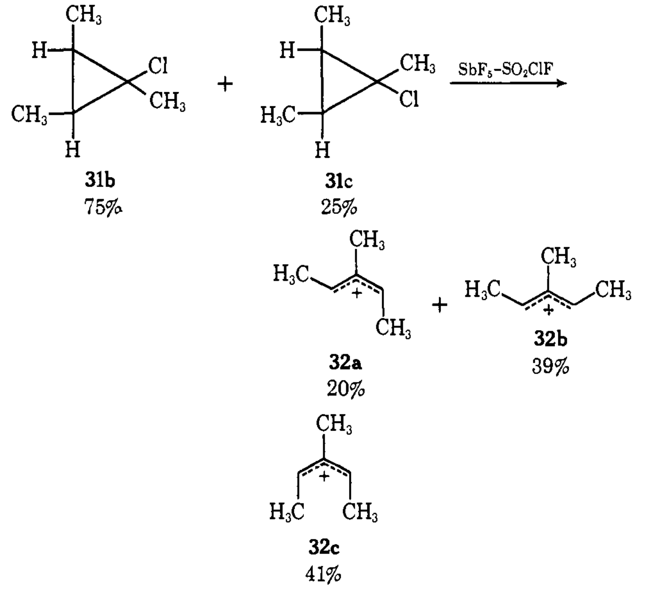


We also obtained only one product on quenching **28a** or **30a**. We assume that the single product is **28c**.



For further investigation of the rotational process in allylic cations we also prepared ions **32a–c** by ionization of **31a–c**.





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(19) The methyl signals for both pairs of ions were coincident. This observation is not surprising in view of the report by L. M. Jackman and R. H. Wiley (*J. Chem. Soc.*, 2881 (1960)) that halogens have the same effect on *cis*- and *trans*-methyl groups on olefins.

(20) This lack of reproducibility was not caused by concentration effects within small variations which occur when we make up the samples. This was tested by adding differing amounts of dihalide to the same quantity of SbF_5–SO_2ClF for comparison at the same temperature. Because of the low accuracy involved, we did not try to calculate all of the activation parameters. A plot of log k_{av} against $1/T$ yielded a value of 11 for log A. This is reasonably close to the value reported by Schleyer, Saunders, *et al.*,[13] and nearly double that reported previously by us.[12]

(21) W. E. Parham and K. S. Yong, *J. Org. Chem.*, **33**, 3947 (1968), and references therein; W. E. Parham and R. J. Sperley, *ibid.*, **32**, 924 (1967).

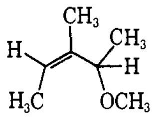
Table II. Pmr Data of Allylic Cations[a]

Allyl cation	C_1–CH_3 (H)	C_2–CH_3 (H)	C_2–CH_3 (H)
1,1,2-Trimethyl (**26**)[b]	3.53, 3.41 (m)	2.38 (d)	8.27, 7.72 (m)
cis,cis-1,2,3-Trimethyl (**32c**)	3.37 (d)	2.69 (s)	9.73 (q)
trans,trans-1,2,3-Trimethyl (**32b**)	3.26 (d)	2.49 (s)	9.73 (q)
cis,trans-1,2,3-Trimethyl (**32a**)	3.26 (d), 9.73 (q)	2.59 (s)	3.26 (d), 10.46 (q)
trans,trans-2-Chloro-1,3-dimethyl (**28a**)	3.67 (d)		10.22 (q)
cis,trans-2-Chloro-1,3-dimethyl (**30a**)	3.67 (d), 10.22 (q)		3.67 (d), 10.88 (q)
trans,trans-2-Bromo-1,3-dimethyl (**28b**)	3.69 (d)		10.38 (q)
cis,trans-2-Bromo-1,3-dimethyl (**30b**)	3.69 (d), 10.38 (q)		3.69 (d), 10.95 (q)
1,1,2,3-Tetramethyl (**35**)[b]	3.31, 3.22 (m)	2.37 (s)	2.97 (m)
Pentamethyl (**36**)	3.10, 2.94 (m)	2.30 (br, s)	
2-Chloro-1,1-dimethyl (**23a**)[c]	3.68, 3.63 (m)		8.61, 8.00 (m)
2-Bromo-1,1-dimethyl (**23b**)	3.88 (br, s)		9.20, 8.53 (m)
2-Chloro-1,1,3-trimethyl (**24a**)[c]	3.40 3.34 (m)		2.95, 9.89 (m)
2-Bromo-1,1,3-trimethyl (**24b**)	3.40 (m)		2.98, 9.96 (m)
2-Chlorotetramethyl (**25a**)	3.46 (s)		
2-Bromotetramethyl (**25b**)	3.46 (s)		
cis,cis-1,3-Dimethyl (**37a**)[d]	3.58 (d), 10.00 (m)	8.30 (t)[e]	3.58 (d), 10.00 (m)
cis,trans-1,3-Dimethyl (**37b**)[d]	3.46 (d), 9.97 (m)	8.31 (m)[e]	3.46 (d), 10.61 (m)
trans,trans-1,3-Dimethyl (**37c**)	3.38 (d), 9.88 (m)	8.24 (t)[e]	3.38 (d), 9.88 (m)

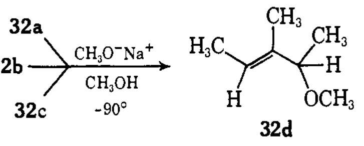
[a] At −60° in SbF_5–SO_2ClF; chemical shifts are in parts per million (δ) from external TMS. Abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. The doublets had coupling constants between 5.4 and 5.7 Hz. [b] The solvent was 1:1 HSO_3F–SbF_5 in SO_2 made by mixing approximately equal volumes of a 1:1 *M* solution of HSO_3F–SbF_5 and SO_2. [c] The solvent was SbF_5–SO_2. [d] Data taken from ref 13. [e] The magnitudes of the coupling constants of these protons were useful for assigning the stereochemistry.

As with ionization of **29a,b** we experienced the same difficulty here with stereospecificity, and a temperature of −117° was required to obtain high concentrations of **32a**. $\Delta G^{\ddagger}$ for isomerization of **32a** to **32b** (23.6 kcal/mol) was considerably higher, *cf.* isomerizations of **30a** to **28a** (18.5 kcal/mol) and **30b** to **28a** (18.2 kcal/mol), and a temperature of 44° or higher was required to make isomerization of **32a** occur at a convenient rate. The rates of isomerization of **32c** to **32a** and **32a** to **32b** were very reproducible since we were able to measure concentrations by integration of the methyl resonances. E_a for conversion of **32c** to **32a** was measured as 16.6 ± 1.0 kcal/mol with a value for log *A* of 11.5 ± 0.9. For isomerization **32a** → **32b**, the measured value of E_a is 21.9 ± 1.2 kcal/mol with log *A* of 11.6 ± 1.0.[22]

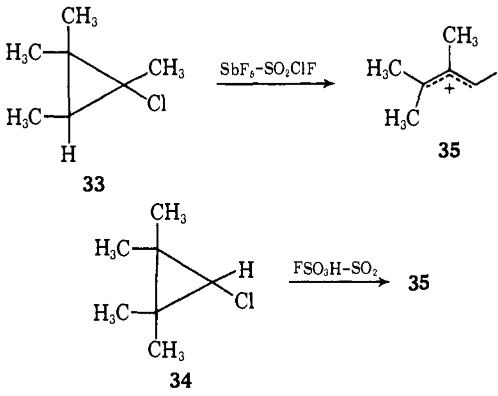
Our quenching results are inconclusive since mixtures of ions containing 41% **32c** which ought to give some **32e** gave only a single product which we assume is **32d**. Thus isomerization has occurred.



32e



Another ion which we had reported previously[12] as giving a spectrum which was difficult to intepret has now been prepared under conditions of high resolution. Now the spectrum is easily interpreted as that of the 1,1,2,3-tetramethylallyl cation **35**. It could be prepared from **33** in SbF_5–SO_2ClF or alternatively from **34** in HSO_3F–SO_2.[23]



For the rotational process whereby the *gem*-dimethyl groups in **35** become equivalent, $\Delta G^{\ddagger}$ is 15.8 kcal/mol, 4 kcal/mol more than that of the 1,1,2-trimethylallyl cation **26**.

Nmr spectra of these allylic cations are summarized in Table II.

In Table III are listed the free energies of activation for rotation in allylic cations.

Discussion

Our previously reported[12] activation parameters for rotation in allylic cations appear to be in error. The measured frequency factors were less than half that expected for a first-order reaction.[13] Part of our error probably arose from a decrease in chemical shift with temperature which occurred before any rotation had actually begun.[24] Nevertheless, we believe that the coalescence of signals is caused by a kinetic process which is most probably rotation about the partial double bond. We have determined that the apparent coalescence temperature is not measurably changed (side-by-side comparison) by a twofold increase in chloride ion concentration for those ions generated from chlorine-

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(22) Errors are root-mean-square errors.

(23) We were surprised at this rearrangement since we have previously observed[12] that protonation of **33** gave the symmetrical 1,1,3,3-tetramethylallyl cation. We will report on this rearrangement in greater detail in subsequent publications.

(24) This tended to flatten out the curves making the slope smaller than it should have been. We also neglected the effects of overlap. [See A. P. Downing, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., B*, 111 (1969), and references therein for a discussion of error in measurements of this type.]

Table III. Free Energies of Activation for Rotation in Allylic Cations

Allyl cation	$\Delta G^{\ddagger}$, kcal/mol[a]	Temp, °C	$\Delta\nu$, Hz[b]
1,1,2-Trimethyl (**26**)	11.7 ± 1	−49	8.4
1,1,2,3-Tetramethyl (**35**)	15.8 ± 1	+22	6.2
Pentamethyl (**36**)	13.8 ± 1	−11	8.0
2-Chloro-1,1-dimethyl (**23a**)	12.5 ± 1	−39	4.9[c]
2-Bromo-1,1-dimethyl (**23b**)			0.0
2-Chloro-1,3-dimethyl (**30a**)	18.5 ± 1.2[d,e]	−16[d]	
2-Bromo-1,3-dimethyl (**30b**)	18.2 ± 1.2[d,e]	−22[d]	
2-Chloro-1,1,3-trimethyl (**24a**)[f]	14.2 ± 1	−8	5.6[c]
2-Bromo-1,1,3-trimethyl (**24b**)[f]			0.0
2-Chloro-1,1,3,3-tetramethyl (**25a**)			0.0
2-Bromo-1,1,3,3-tetramethyl (**25b**)			0.0
cis,cis-1,2,3-Trimethyl (**32c**)	18.1[g,h]	−21[h]	
cis,trans-1,2,3-Trimethyl (**32a**)	23.6[g,i]	+44[i]	
cis,cis-1,3-Dimethyl (**37a**)	18.7[j,k]	+35[j]	
cis,trans-1,3-Dimethyl (**37b**)	22.3[l,m]	−10[l]	

[a] Errors were estimated to be about 1.0 kcal/mol for those $\Delta G^{\ddagger}$ values determined by peak coalescence. See ref 24. [b] Peak separation measured at 60 MHz unless otherwise noted. Values other than 0.0 Hz were measured under conditions of no exchange. [c] Measured at 100 MHz. [d] This value is for the conversion of the *cis,trans* isomer (**30**) to the *trans,trans* isomer (**28**). At the temperature listed, the half-life was about 10 min. [e] The error was calculated from the spread of the rate constants from three determinations at the temperature listed. [f] Spectra of these ions are extremely complex due to coupling, making it difficult to determine the separation of the signals and the coalescence temperature. [g] See text for errors in measurement of E_a and log A from which $\Delta G^{\ddagger}$ was calculated. [h] For the conversion of **32c** to **32a**. [i] For the conversion of **32a** to **32b**. [j] This value is for the process *cis,cis* isomer (**37a**) → *cis,trans* isomer (**37b**). [k] For calculation of $\Delta G^{\ddagger}$, values of E_a and log A of 17.5 ± 1.0 kcal/mol and 11.8 ± 0.8, respectively[13] were used. [l] This value is for the conversion *cis,trans* isomer (**37b**) → *trans,trans* isomer (**37c**). [m] Values of E_a and log A of 24.0 ± 1.0 kcal/mol and 14.0 ± 1.0, respectively,[13] were used for calculation of $\Delta G^{\ddagger}$.

containing precursors. Because of the uncertainties involved in obtaining rate constants at different temperatures for these ions, we are reporting only $\Delta G^{\ddagger}$ values determined from the coalescence temperature and peak separation under conditions of no exchange. These values should be proportional to the E_a values for rotation which should be useful for comparisons within the series of allyl cations.

In order to rationalize the relative magnitudes of these rotational barriers, the effect of methyl substitution on the relative energies of the ground states and transition states must be assessed. Conrow has pointed out that a methyl group in the 1 or 3 position of an allylic cation stabilizes the ion by at least 5.3 kcal/mol.[25] This value was arrived at by comparison of solvolysis rates of allyl cations. Conrow reports a stabilization of 3.7 kcal/mol for methyl on a tropylium cation. He has also calculated that a p-CH_3 group in a trityl cation stabilizes it by 1.40 kcal/mol in H_2SO_4 and somewhat less in other media. From partial rate factors for *para* substitution in toluene by certain electrophilic agents, 3.9–4.6 kcal/mol stabilization of the intermediate by the methyl group is indicated. Work of Deno and associates[26] shows that the difference in $pK_R{}^+$ between the 1,5,5-trimethylcyclohexenyl cation and the 1,3,5,5-tetramethylcyclohexenyl cation in H_2SO_4 is −3.6, corresponding to a 4.9 kcal/mol lowering of ΔG (at 298 °K) for the latter ion. Downing and coworkers[24] find an effect of 2.9 kcal/mol for a methyl substitution in a rotational process presumed to involve formation of a carbonium ion center in the transition state. This value is relatively small because the carbon atom onto which the methyl substitution was made also bore a dimethylamino group which undoubtedly carries most of the charge.

Conrow[25] has suggested that the amount of stabilization of a cation by a methyl group depends upon the amount of charge localized on the carbon atom to which the methyl is attached. Therefore, we would expect 1- or 3-methyl substitution for hydrogen to have a larger lowering effect on the transition-state energy than on the ground-state energy since the assumed transition state, the twisted allyl cation, has no delocalization of charge to the π system. Comparison of the 1,1,2-trimethylallyl cation (**26**) with the 1,1,2,3-tetramethylallyl cation (**35**) shows the expected result of the lowering of the ground-state energy by methyl substitution. The 4 kcal/mol elevation of $\Delta G^{\ddagger}$ for rotation in **35** is slightly less than anticipated which suggests some stabilization of the transition state. This is expected to be 1–2 kcal/mol, less any increased steric effects. Therefore the 4 kcal/mol increase in $\Delta G^{\ddagger}$ for rotation in **35**, *cf.* that in **26**, is reasonable. On going from **35** to the pentamethylallyl cation **36**, we would predict the same increase in $\Delta G^{\ddagger}$ for rotation of 4 kcal/mol, reduced by the difference between a 1,3-CH_3,H interaction and a 1,3-CH_3,CH_3 interaction estimated as 6.0 kcal/mol.[27,28] The net effect predicted is a 2.0 kcal/mol reduction in $\Delta G^{\ddagger}$ for rotation in **36** *cf.* **35**, in good agreement with observation.

Comparing rotation in an unsymmetrically substituted ion, *e.g.*, the 1,1,2-trimethylallyl cation, with that in a symmetrically substituted ion, *e.g.*, the 1,2,3-trimethylallyl cation **32a** or **c**, we expect the difference in $\Delta G^{\ddagger}$ to be due primarily to a difference between transi-

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(25) K. Conrow, *J. Amer. Chem. Soc.*, 83, 2343 (1961).

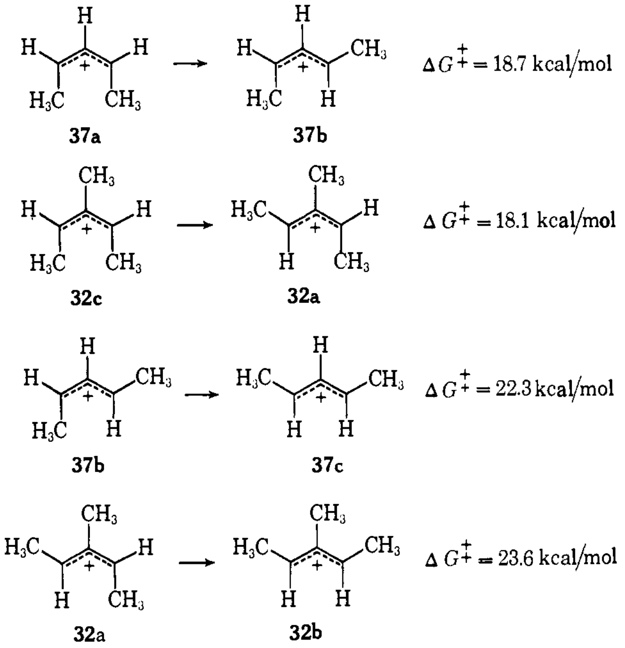
(26) N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Hauser, *ibid.*, **85**, 2998 (1963).

(27) P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, 88, 2868 (1966), and references therein.

(28) Resonance energy is assumed to vary inversely with the cos² of the angle of twist of two π systems (L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 482). We do not know how rapidly steric interactions will be reduced with the angle of twist in allylic cations such as these. The results reported in ref 13 where a 6.5 kcal/mol difference in E_a is observed and a 6.0 kcal/mol difference is predicted between isomeric 1,3-dimethyl cations suggest that steric strain energy and resonance energy vary with the same magnitude (but opposite sign) as the angle of twist from planarity is varied. The $pK_R{}^+$ data of Deno, *et al.*,[26] support this conclusion. The difference in $pK_R{}^+$ between the 1,1,3,3-tetramethylallyl cation and the 1,3-dimethylcyclopentenyl cation is −4.0 corresponding to a 5.5 kcal/mol lowering of ΔG (at 298 °K) for the latter ion.

tion-state energies since comparison is between a tertiary ion and a secondary ion. An estimate of this effect can be made from the data of Saunders and Hagen[29] which suggest that the difference in enthalpy between a tertiary and a secondary carbonium ion in this medium (from a rate process in the *t*-amyl cation) is 11–15 kcal/mol. The prediction then is 11–15 kcal/mol elevation in the transition-state energies for rotation in **32a,c**, *cf.* **26**. Presumably the ground-state energy of **26** is the same as that of **32a**,[30] and the observed 12 kcal/mol increase in $\Delta G^{\ddagger}$ for **32a**, *cf.* **26**, is in good agreement with expectation. The difference in $\Delta G^{\ddagger}$ between **32a** and **32c** ($\delta\,\Delta G^{\ddagger} = 5.5$ kcal/mol) can be ascribed to a 1,3-CH_3,CH_3 interaction, expected to decrease $\Delta G^{\ddagger}$ for **32c** by about 6 kcal/mol.[27]

The similarity of the barriers for the isomerizations **37a** → **37b** and **32c** → **32a** and for **37b** → **37c** and **32a** → **32b** suggests that the effect of 2-methyl substitution is to stabilize equally both ground states and transition states.



As a check on the above estimates, we can predict $\Delta G^{\ddagger}$ for **32a** → **32b** based on the measured rotational barrier for **35**. The difference between transition-state energies for rotation in **32a**, *cf.* **35**, is expected to increase $\Delta G^{\ddagger}$ for **32a** by 9–12 kcal/mol; however, the ground-state energy of **32a** should be about 4 kcal/mol higher than **35** since **32a** has one less methyl group than does **35**. Our prediction for $\Delta G^{\ddagger}$ (21–24 kcal/mol) for **32a** → **32b** is in agreement with observation (23.6 kcal/mol).

Halogen Participation. It should be clear from our observations that methyl-substituted haloallylic ions do not remain as static, halogen-bridged species under long-lived ion conditions. In contrast, the related ions without methyl groups appear to be static bridged halonium ions, and it is likely that the haloallyl form of these ions is unstable relative to the bridged species. Some previously reported chemical reactions of methyl-substituted allene indicate that bridged or open ions can be formed depending on conditions.[2,3,7] Our results suggest some halogen participation in **30a** and **b**. For these ions $\Delta G^{\ddagger}$ for rotation is lowered by about 4 kcal/mol compared with **32a** or **37b**. It is somewhat surprising that so little difference exists between the effect of chlorine and bromine which may be suggestive of some ground-state destabilization. The effect of the halogen substitution in the other ions was not clear in that we could not distinguish between accidental equivalence and rapid rotation, *i.e.*, **25a,b**, **23b**, and **24b**. Comparing **24a** with **35** suggests some participation in the former; however, this is not consistent with the result obtained for **23a** where no participation is indicated, *cf.* **26**.

Thus, although there is indication of halogen participation in the transition state for rotations in haloallyl cations, the results are not unequivocal.

Experimental Section

The preparation of ions and the measurement of their spectra were performed as reported previously,[11,12,14] with the important exception that those ions with *cis,trans* stereochemistry were prepared in an nmr tube at −117° (ethanol slush bath). The precursor was dissolved in a minimum volume of SO_2ClF, cooled to −117°, and added with stirring to the SbF_5–SO_2ClF solution also at −117°. This procedure also worked very well for other ions in this series, giving only slightly colored solutions with very few extraneous absorptions of low intensity. Quenching was carried out as described previously.[11,14]

2-Iodo-3-chloropropene was prepared by the addition of iodine monochloride (Eastman, practical grade) to allene (Matheson) in carbon tetrachloride at −20°. Iodine monochloride (16.2 g, 0.1 mol) was dissolved in 100 ml of reagent grade CCl_4. The solution was cooled to −20°. Gaseous allene was bubbled through the mixture until the CCl_4 solution was saturated with allene. The reaction mixture still retained the color of iodine, but this disappeared when the reaction was allowed to come to room temperature. The crude product was analyzed by vpc and nmr spectroscopy, showing that the reaction products were nearly equal amounts of 2-iodo-3-chloropropene and 2,3-diiodopropene with traces of what is probably 3-iodo-2-chloropropene. There was isolated from this reaction mixture 4.6 g of 2-iodo-3-chloropropene (which rapidly turned violet); bp 35–40° (8 mm). The 2,3-diiodopropene decomposed on heating.

3-Iodo-2-chloropropene[31] was prepared by treating 2,3-dichloropropene with sodium iodide in acetone; bp 45–48° (15 mm).

2,3-Dichloropropene and **2,3-dibromopropene** were Eastman white-label reagents, distilled once before use.

All of the *gem*-**dichloro**-[32] and *gem*-**dibromocyclopropanes**[33] were prepared by standard literature procedures.

1,2,2,3-Tetramethyl-1-chlorocyclopropane was prepared as described in ref 12.

1,2,3-Trimethylchloropropane was prepared in 20% yield (3.6 g) from 20 g of ethylidene chloride (Matheson Coleman and Bell) and 13 ml of *trans*-2-butene (J. T. Baker, C.P.) in 50 ml of dry ether to which was added 100 ml of 1.6 *M* *n*-butyllithium in hexane (Foote) over a half-hour period while the temperature was maintained at about −30°. The product distilled at 48–51° (85 mm). The nmr spectrum,[34] which showed absorptions at δ 0.44 (m), 1.10 (distorted d), 1.24 (d, J = 6 Hz), and 1.52 (s), unambiguously confirmed the structure.

cis-**2-Butene** was treated in an identical manner, and 2.7 g (13% yield) of the product was obtained: bp 51–53° (84 mm). This

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(29) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968). Also see D. M. Brouwer, *Rec. Trav. Chim. Pays-Bas*, **87**, 210 (1968).

(30) We are assuming that delocalization energy in ground states of these systems is a property of the π system and for a given degree of substitution is the same, irrespective of symmetrical or unsymmetrical substitution.

(31) R. K. Freǐdlina and F. K. Velichko, *Chem. Abstr.*, **55**, 18565c (1961).

(32) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

(33) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(34) Nmr spectra were obtained on CCl_4 solutions. Chemical shifts are in parts per million (δ), referred to internal TMS as a standard. Abbreviations are: s, singlet; d, doublet; m, multiplet.

product was composed of 25% *cis,cis,cis*-1,2,3-trimethylchlorocyclopropane and 75% *trans,cis,cis*-1,2,3-trimethylchlorocyclopropane as determined by integration of the nmr spectrum of the mixture and as inferred from the relative amounts of allylic cations produced. The nmr spectrum of *cis,cis,cis*-1,2,3-trimethylchlorocyclopropane had absorptions at δ 0.98 (m), from about 0.98 to 1.40 (m), and 1.57 (s). The nmr of *trans,cis,cis*-1,2,3-trimethylchlorocyclopropane had absorptions at δ 0.98 (m), from about 0.98 to 1.40 (m), and 1.40 (s).

1,1-Difluoro-2,2-dimethylcyclopropane was prepared by the method of Tarrant, *et al.*[35]

1,1-Difluorotetramethylcyclopropane[36] was prepared in an autoclave by the method of Knox, *et al.*[37] We experienced difficulty in separating the difluoride from unreacted tetramethylethylene. The desired product (of about 90% purity) was obtained by low-temperature bromination of the undiluted mixture of the two compounds followed by vacuum distillation. The yield of material was 24% from 0.3 mol of olefin and 0.3 mol of sodium chlorofluoroacetate.

Kinetic Studies. Plots of log of the ratios of the integrated intensities of the decreasing absorption over the sum of the decreasing absorption plus the increasing absorption $[\log (I_d)/(I_d + I_i))]$ against time were linear after temperature stability had been reached.

Rate constants were determined from the slopes of these lines. For ions **28a** and **b** only the vinyl resonances could be used and reproducibility was good only to about a factor of ten. For ion **32a** separate methyl resonances were observed and these could be used to determine the rate constants at different temperatures, from which the activation parameters could be determined. Temperatures were measured with a calibrated thermometer which fit into an nmr tube.

Acknowledgment. Support of the work by the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged.

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(35) P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 77, 2783 (1955).

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Electrostatic Catalysis by Ionic Aggregates. II. The Reversible Elimination of HCl from *t*-Butyl Chloride and the Rearrangement of 1-Phenylallyl Chloride in Lithium Perchlorate–Diethyl Ether Solutions[1,2]

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Abstract: In lithium perchlorate–diethyl ether solutions (LPDE), the reaction of *t*-butyl chloride with either pyridine or lithium azide has the characteristics of a unimolecular elimination process, E1. Similarly, the dilution of radiochloride tracer during the reaction of *t*-butyl chloride with saline radiochloride is due, almost entirely, to an E1 process with little or no substitution accompanying it. The first-order rate constant, k_t, for the ionization of *t*-butyl chloride in LPDE solutions increases a millionfold on going from pure ether ($k_t^0 = 4.2 \times 10^{-11}$ sec^{-1}) to 5.5 *M* lithium perchlorate ($k_t = 4.8 \times 10^{-5}$ sec^{-1}). The rate of addition of HCl to isobutylene is proportional to $[\mathrm{HCl}]^2$ in pure ether but is only first order in acid in LPDE solutions. The striking effect of LPDE solutions manifests itself in the addition reaction as well, thereby leaving the ratio $k_t/k_r = 5.3 \pm 0.2 \times 10^{-5}$ *M* essentially unaffected. Powerful electrostatic catalysis was also documented for the rearrangement of 1-phenylallyl chloride (**1**) to cinnamyl chloride (**2**): first-order rate constants were determined in pure ether ($k_i^0 = 2.5 \times 10^{-7}$ sec^{-1}) and in solutions containing up to 2.83 *M* lithium perchlorate ($k_i = 7.84 \times 10^{-3}$ sec^{-1}).

In part I[1] we showed that lithium perchlorate–diethyl ether solutions (LPDE) were media in which extremely powerful catalysis was operative with respect to the ionization of triphenylmethyl chloride and hydrogen chloride. This catalysis was essentially electrostatic in nature and was shown to arise from the capacity of $[\mathrm{Li^+(OEt_2)}_m, \mathrm{ClO_4^-}]_n$ ion pair aggregates to promote the ionization process.

In the present paper, the striking catalytic efficiency of LPDE solutions is further delineated, this time with respect to the elimination of HCl from *t*-butyl chloride in the presence of pyridine and lithium azide. We also report on the rates of radiochloride exchange between *t*-butyl chloride and lithium radiochloride as well as on the rates of olefin formation. Our data indicate that an electrostatically assisted E1 mechanism is under observation. We have further demonstrated that the addition of HCl to isobutylene is powerfully catalyzed by LPDE solutions but that the ratio, k_t/k_r, is independent of the lithium perchlorate concentration. The present paper also includes a report on the allylic rearrangement of 1-phenylallyl chloride (**1**) to cinnamyl chloride (**2**) in LPDE solutions.[5] Our results, taken as a whole, clearly illustrate both the magnitude and the usefulness of the electrostatic catalysis associated with

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(4) Taken in part from the Ph.D. Thesis of Richard F. Buchholz, University of Washington, 1969.

(5) Only the rate of rearrangement of **1** is discussed here in view of the nature of this paper. A more complete investigation of **1** is under way in these laboratories.