ion, and a better leaving group, which is understandable if the solvation effects are important in controlling nucleophilicity but have less effect on leaving group ability, so that the lower Lewis basicity of the azide ion dictates leaving group ability.

Nature of the Carbonium Ions. There is extensive evidence that discrete ion pairs are intermediates in SN1 solvolyses, particularly in weakly ionizing solvents, and these ion pairs either dissociate or react chemically.[8,15,16] In discussing the stabilization of tri-*p*-anisylmethyl carbonium ions or carbonium ion-like transition states by bulky anions such as perchlorate, we suggest that interionic attractions are in part responsible, although we cannot distinguish between discrete ion pairs and very transient ionic aggregates which could be present in solutions of relatively high ionic strength. It has been noted that ion pairs formed in solvolysis may have some covalent character, and this could also be so in our systems, for example, alkyl perchlorates are generated in acidic media in which perchlorate ion acts as a nucleophile.[43]

(43) D. M. Hoffman, *J. Org. Chem.*, **36**, 1716 (1971).

Stable Carbocations. CXXVII.[1] Cyclohexenyl and Cyclopentenyl Cations and Their Methylated Derivatives

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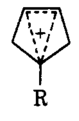
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received July 28, 1971*

Abstract: The nuclear magnetic resonance spectroscopic study of the 2-cyclohexenyl (**3a**), 1-methyl-2-cyclohexenyl (**3b**), 1,5-dimethyl-2-cyclohexenyl (**3c**), 1,3-dimethyl-2-cyclohexenyl (**3d**), 1,3,5-trimethyl-2-cyclohexenyl (**3e**), 2-cyclopentenyl (**4a**), and 1-methyl-2-cyclopentenyl (**4b**) cations is reported. Ring contraction reactions of cyclohexenyl cations to methyl-substituted cyclopentenyl cations are described. No significant 1,3-orbital interaction is observed in cyclopentenyl cations, as is revealed by carbon-13 nmr studies. Under stable ion conditions, *cis*-3-bicyclo[3.1.0]hexanol forms ion **4b** with no indication of the trishomocyclopropenyl cation.

With the discovery that many substituted allylic cations are stable in aqueous mineral acids,[2–6] in fluorosulfuric acid,[7–10] or in antimony pentafluoride based superacids,[11,12] the possibility was provided for the direct observation of allyl cations by spectroscopic methods (particularly by nmr) and the study of their rearrangements. In the reported stable cyclic alkenyl cations, the terminal positions of the allylic system were partially or completely alkylated (or arylated). Even though an estimate of the stability of cyclohexenyl and cyclopentenyl cations can be obtained from solvolysis studies,[13–16] there was until now no direct observation of the unsubstituted parent cycloalkenyl cations.[7]

Bartlett and Rice[13] have found the absence of the anchimeric assistance by the double bond in the acetolysis of Δ^3-cyclopentene bromide. However, results of product studies and interpretation of rate data in some recent works[17–19] do support the presence of such an effect. In view of these data and the chemical stability of carbocations in superacid systems,[20] we have attempted to observe cycloalkenyl cations, bishomocyclopropenyl (**1**), and trishomocyclopropenyl cations, **2**.[21,22]



1a, R = H
b, R = CH_3

2

In this paper we present our data on the nuclear magnetic resonance spectroscopic observation of 2-cyclohexenyl (**3a**), 1-methyl-2-cyclohexenyl (**3b**), 1,5-dimethyl-2-cyclohexenyl (**3c**), 1,3-dimethyl-2-cyclohexenyl (**3d**), 1,3,5-trimethyl-2-cyclohexenyl (**3e**), 2-cyclo-

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(1) Part CXXVI: G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Amer. Chem. Soc.*, **94**, 1164 (1972).

(2) N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. T. Wisotsky, *ibid.*, **84**, 1498 (1962).

(3) N. C. Deno, H. F. Richey, N. Friedman, J. D. Hodge, J. J. House, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963).

(4) N. C. Deno and C. U. Pittman, Jr., *ibid.*, **86**, 1744, 1871 (1964).

(5) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, **87**, 2153 (1965).

(6) J. S. Sorensen, *ibid.*, **89**, 3782, 3794 (1967); **91**, 6397 (1969).

(7) The assumed observation of cyclohexenyl cation (G. A. Olah and W. S. Tolgyesi, *ibid.*, **83**, 5031 (1961)) must now be considered to be in error. See subsequent discussion.

(8) G. A. Olah and M. B. Comisarow, *ibid.*, **86**, 5682 (1964).

(9) N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 18.

(10) D. G. Farnum, A. Mostashari, and A. A. Hagedorn, *J. Org. Chem.*, **36**, 698 (1971).

(11) G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967).

(12) G. A. Olah, *Science*, **168**, 1297 (1970).

(13) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

(14) H. L. Goering and D. L. Towns, *J. Amer. Chem. Soc.*, **85**, 2295 (1963).

(15) M. Hanack and W. Keberle, *Chem. Ber.*, **96**, 2937 (1963).

(16) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

(17) M. Hanack and K. Riedlinger, *Chem. Ber.*, **100**, 2107 (1967).

(18) K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *J. Amer. Chem. Soc.*, **90**, 5338 (1968).

(19) E. L. Allred and C. R. Flynn, *ibid.*, **92**, 1064 (1970).

(20) Reference 12 and references quoted therein.

(21) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3224, 3245 (1961).

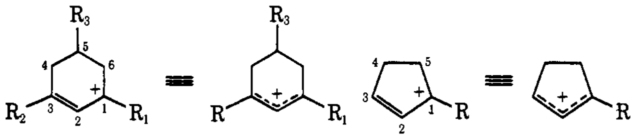
(22) S. Winstein, J. Sonnenberg, and L. de Vries, *ibid.*, **81**, 6523, 6524 (1959).

Table I. Pmr Parameters (δ) of Cycloalkenyl Cations at 60 MHz in FSO_3H-SbF_5-SO_2ClF at −70°

Cation	H_1,H_3	H_2	H_4,H_6	H_5	CH_3	$J_{2,3}$[a]	$J_{4,5}$
4a	11.26 (d)[b]	8.65 (t)	4.23 (s)[c]			4.2	
4b	10.60 (d)	8.36 (d)	4.05 (s)[c]		3.61 (s)	4.2	
3a	10.25 (d)	8.32 (t)	3.81 (t)	2.39 (p)		8.0	6.8
3b	9.73 (d)	8.18 (d)	3.60 (m)	2.42 (p)	3.36 (s)	8.0	6.4
3c	9.61 (d)	8.04 (d)	3.51 (m)	2.82 (m)	1.43 (d), 3.34 (s)	8.0	6.0
3d		8.04 (s)	3.60 (t)	2.60 (p)	3.14 (s)		6.0
3e		7.97 (s)	3.3–3.6 (m)	2.80 (m)	1.45 (d), 3.14 (s)		6.0

[a] In Hz. [b] d = doublet, t = triplet, s = singlet, p = pentuplet, m = multiplet. External TMS was used as reference. [c] Only the singlet was observed at all temperatures.

pentenyl (**4a**), and 1-methyl-2-cyclopentenyl (**4b**) cations



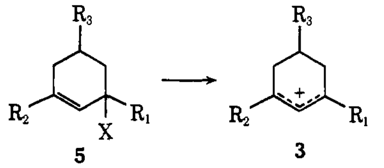
3

4a, R = H
b, R = CH_3

in fluorosulfuric acid–antimony pentafluoride-sulfuryl chloride fluoride or antimony pentafluoride-sulfuryl chloride fluoride solutions at low temperatures. The carbon-13 nmr data of both ions **3a** and **4a** have also been obtained.

Results and Discussion

A. Cyclohexenyl Cations. 2-Cyclohexenyl cation 3a has been generated from 2-cyclohexen-1-ol (**5**, X = OH), 3-chlorocyclohexene (**5**, C = Cl), and 3-bromocyclohexene (**5**, X = Br) in SbF_5SO_2, SbF_5-SO_2ClF,



5	**3**
a, $R_1 = R_2 = R_3 = H$; $X = OH$	a, $R_1 = R_2$; $R_3 = H$
b, $R_2 = CH_3$; $R_1 = R_3 = H$; $X = OH$	b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = CH_3$; $R_2 = R_3 = H$; $X = OH$	c, $R_1 = R_3 = CH_3$; $R_2 = H$
d, $R_2 = R_3 = CH_3$; $R_1 = H$; $X = OH$	d, $R_1 = R_2 = CH_3$; $R_3 = H$
e, $R_1 = R_2 = CH_3$; $R_3 = H$; $X = OH$	e, $R_1 = R_2 = R_3 = CH_3$
f, $R_1 = R_2 = R_3 = CH_3$; $X = OH$	

FSO_3H-SbF_5-SO_2, or FSO_3H-SbF_5-SO_2ClF solution at −78°. At −70°, solutions of the 2-cyclohexenyl cation in FSO_3H-SbF_5-SO_2ClF and in SbF_5-SO_2ClF give the spectrum shown in Figure 1 with proton absorptions at δ 2.39 (p, 2 H), 3.81 (t, 4 H), 8.32 (t, 1 H), and 10.25 (d, 2 H). Coupling constants are summarized in Table I. The assignments of the peaks are made by comparison with the pmr spectra of four other methyl-substituted cyclohexenyl cations, **3b**–**3e**.

2-Methyl-2-cyclohexenyl cation 3b was generated in the same acid media at −78° from 3-methyl-2-cyclohexen-1-ol (**5b**) and 1-methyl-2-cyclohexen-1-ol (**5c**). It shows the pmr absorptions at δ 2.42 (p, 2 H), 3.60 (br t, 4 H), 3.36 (s, 3 H), 8.18 (d, 1 H), and 9.73 (br d, 1 H).

1,5-Dimethyl-2-cyclohexenyl cation 3c was generated from 3,5-dimethyl-2-cyclohexen-1-ol (**5d**) in the same manner at −78°. It shows pmr absorptions at δ 1.43 (d, 3 H), 2.82 (br p, 1 H), 3.51 (m, 4 H), 3.34 (s, 3 H), 8.04 (d, 1 H), and 9.61 (br d of t, 1 H).

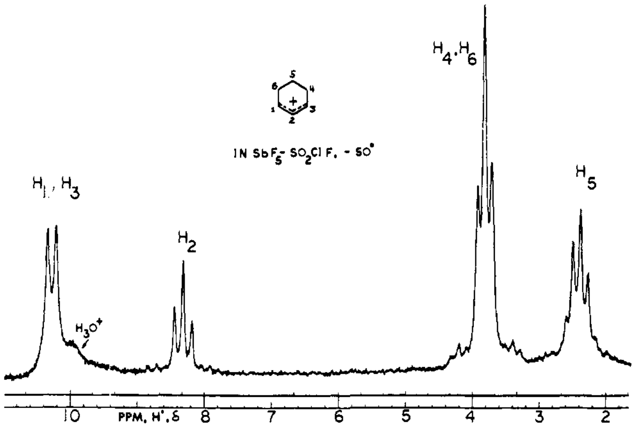


Figure 1.

1,3-Dimethyl-2-cyclohexenyl cation 3d was also generated in the same fashion from 1,3-dimethyl-2-cyclohexenen-1-ol (**5e**). It showed a pmr spectrum having absorptions at δ 2.60 (p, 2 H), 3.14 (s, 6 H), 3.60 (br t, 4 H), and 8.04 (s, 1 H).

1,3,5-Trimethyl-2-cyclohexenyl cation 3e was generated from 1,3,5-trimethyl-2-cyclohexen-1-ol (**5f**) in the same acid media at −78°, having pmr absorptions at δ 1.45 (d, 3 H), 2.80 (m, 1 H), 3.14 (s, 6 H), 3.3–3.6 (m, 4 H), and 7.97 (s, 1 H).

It can be clearly seen that when one or both terminal allylic protons are replaced by methyl groups, the central proton, which is a triplet in ion **3a**, is changed into a doublet and singlet in **3b** and **3c**, or **3d** and **3e**, respectively. All the cyclohexenyl cations (**3a**–**3e**) studied in superacid systems were found to be stable at temperatures below 0° despite the fact that many substituted cyclohexenyl cations were found to undergo ring contraction to form substituted cyclopentenyl cations in previously reported studies.[6,9,23] The formation of the cyclohexenyl cations from different precursors takes place directly and without rearrangement when the leaving group is directly attached to the carbon atom α to the double bond; thus the allylic system can be generated directly without intramolecular hydride shift. In contrast, when the leaving group is attached to the carbon atom at the homoallylic position, ring contraction or other rearrangement reactions take place, as discussed subsequently.

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(23) T. S. Soransen and K. Ranganazakulu, *ibid.*, **92**, 6534 (1970).

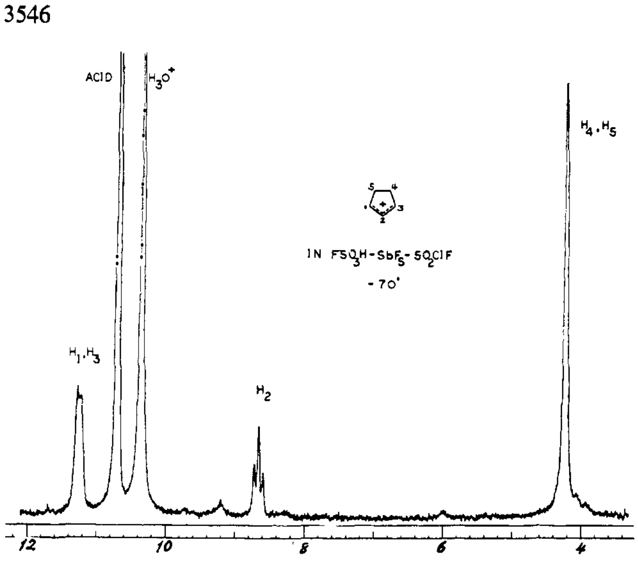
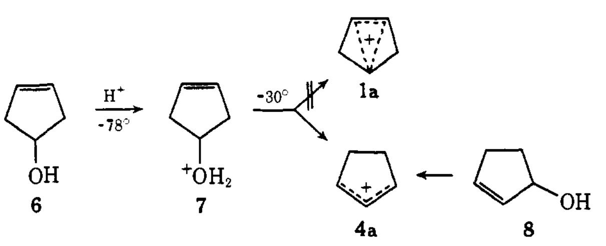
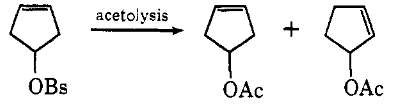


Figure 2.

B. Cyclopentenyl Cations. 2-Cyclopentenyl cation 4a has been generated from Δ^3-cyclopentenol (**6**)[24–26] and Δ^2-cyclopentenol (**8**)[27–29] in SbF_5-SO_2, SbF_5-SO_2ClF, $HF-SbF_5-SO_2ClF$, $FSO_3H-SbF_5-SO_2$ and $FSO_3H-SbF_5-SO_2ClF$ solutions at −78°. When **6** is dissolved in $FSO_3H-SbF_5-SO_2ClF$ or $HF-SbF_5-SO_2ClF$, at −78°, the protonated alcohol **13** is formed immediately. Preliminary studies of this system, in our laboratory, were carried out by Dr. J. Lukas.[30] When the solution is slowly heated to −30°, ion **4a** is completely formed. The pmr spectrum of ion **4a** (Figure 2) shows absorptions at δ 4.23 (s, 4 H), 8.65 (t, 1 H), and 11.26 (d, 2 H). Coupling constants are summarized in Table I. In SbF_5-SO_2ClF (or in SO_2) solution ion **4a** is formed from **6**, accompanied by a considerable amount of polymer. No pmr spectral characteristics corresponding to the bishomocyclopropenyl structure **1** are observed.

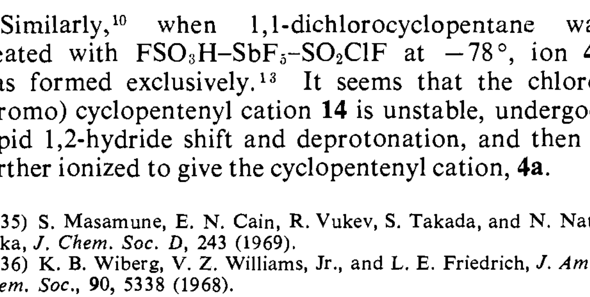


The anchimeric assistance to solvolysis by participation of double bonds in *anti*-7-norbornenyl,[31] 7-norbornadienyl,[32,33] and *endo*-bicyclo[3.2.1]oct-6-enyl-8[34] derivatives indicates that the developing positive charge in the transition state is effectively delocalized by the p orbitals of the double bonds. However, the presence of the double bond in the homoallylic position of the monocyclic compounds, such as 4-bromocyclopentene, does not accelerate the rate of solvolysis. On the contrary, a slight rate retardation was observed. In the case of simple monocyclic derivatives, the strain energy involved in reaching a suitable conformation in the transition state is greater than the stabilization afforded by orbital overlap. However, in the solvolytic reactions of 2-bicyclo[2.1.0]pentyl derivatives,[35] Δ^3-cyclopentenol was found as the only product indicating the potentially stable 3-cyclopentenyl cation in the course of reactions.[36] A similar observation was also made in the acetolysis of Δ^3-cyclopentenyl brosylate and *exo*-2,3-diazabicyclo[2.2.1]hept-2-en-5-yl derivatives.[37]



None of the discussed observations provides direct proof for the bishomocyclopropenyl cation **1a**. Indeed, the preferential formation of 3-cyclopentenyl products indicates the stability of the classical 3-cyclopentenyl cation or related structures of similar nature. Under stable ion conditions, when 3-cyclopenten-1-ol (**6**) was ionized at −78°, the allylic cyclopentenyl cation **4a** was immediately formed, indicating both the instability of the bishomocyclopropenyl cation **1** and the thermodynamical stability of ion **4a**. The 1,2-hydride shift is expected to be fast enough so that no differentiation of classical from nonclassical secondary ion **1a** is possible. Ion **4a** can also be formed, alternatively, from Δ^2-cyclopentenol (**8**) in SbF_5 in FSO_3H-SbF_5 diluted with SO_2ClF at −78°. No intermediate protonated alcohol is observed in the latter case.

The 2-cyclopentenyl cation **4a** was also obtained when 1,2-dihalocyclopentanes (**9**) (X = Cl or Br) were ionized in SbF_5-SO_2 (SO_2ClF) solution at −78°. The resulting solution showed the pmr spectrum of **4a**, identical with that obtained from previously discussed precursors, instead of the formation of acyclic halonium ions, **10**.[38] The mechanism involving the formation of **4a** from 1,2-dihalocyclopentanes can be depicted.



Similarly,[10] when 1,1-dichlorocyclopentane was treated with $FSO_3H-SbF_5-SO_2ClF$ at −78°, ion **4a** was formed exclusively.[13] It seems that the chloro-(bromo) cyclopentenyl cation **14** is unstable, undergoes rapid 1,2-hydride shift and deprotonation, and then is further ionized to give the cyclopentenyl cation, **4a**.

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(24) H. M. Hess and H. C. Brown, *J. Org. Chem.*, **32**, 4138 (1967); 34, 2206 (1969).

(25) G. A. Russell and A. Ito, *J. Amer. Chem. Soc.*, **85**, 2983 (1963).

(26) E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).

(27) K. Alder and F. H. Flock, *Chem. Ber.*, **89**, 1732 (1956).

(28) C. H. DePuy and H. L. Eilers, *J. Org. Chem.*, **24**, 1380 (1959).

(29) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3235 (1961).

(30) No promising results were obtained due to the solvent systems used.

(31) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955).

(32) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(33) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

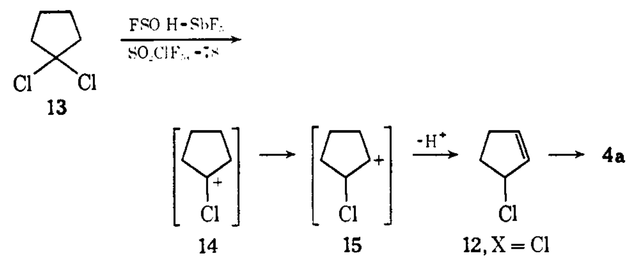
(34) H. A. Hess, Jr., *ibid.*, **93**, 1000 (1971).

(35) S. Masamune, E. N. Cain, R. Vukev, S. Takada, and N. Natatsuka, *J. Chem. Soc. D*, 243 (1969).

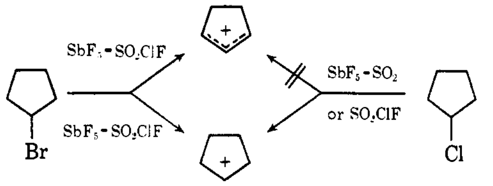
(36) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *J. Amer. Chem. Soc.*, **90**, 5338 (1968).

(37) E. L. Allred and C. R. Flyun, *ibid.*, **92**, 1064 (1970).

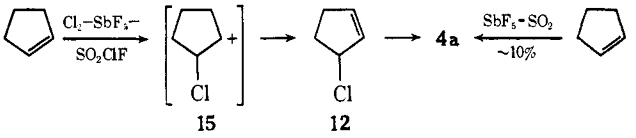
(38) S. Winstein and H. J. Lucas, *ibid.*, **61**, 1576, 2845 (1939).



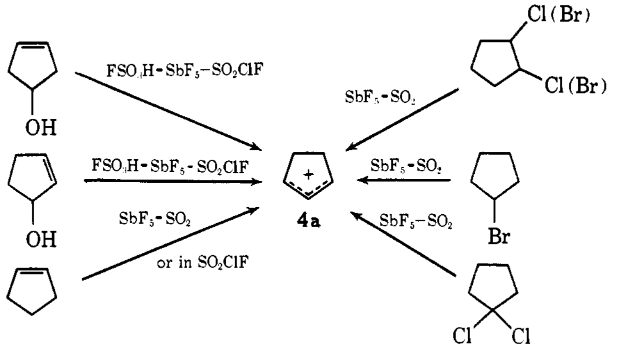
Furthermore, we found that even cyclopentyl bromide is ionized in SbF_5–SO_2 solution at −78° to give predominantly **4a** and a minor, yet unidentified species.[39] Cyclopentyl chloride in SbF_5–SO_2 (SO_2ClF) is known to give stable cyclopentyl cation.[40] Careful ionization of cyclopentyl chloride in the present study also showed that besides the cyclopentyl cation as the major product, a cycloalkenyl cation was also formed. It is believed to be the 1-chlorocyclopentenyl cation, since two highly deshielded absorptions were observed in the pmr spectrum. These two resonances were also observed when cyclopentyl bromide was treated with SbF_5–SO_2 at −78°. The structure of this ion is now under more detailed investigation. The cyclopentenyl cation **4a** was not found in the ionization of cyclopentyl chloride. The difference in the behavior between cyclopentyl chloride and bromide in superacid media is not yet fully understood.



As alkenes react with molecular chlorine to form the corresponding dichloroalkanes,[41] we found it possible to treat cyclopentene with SbF_5–Cl_2–SO_2ClF to give ion **4a** along with some polymers. The mechanism of this reaction may involve electrophilic chlorine attack on the double bond to give the chlorocyclopentyl cation which then deprotonates and further ionizes to give **4a**. We also examined the reaction of cyclopentene with SbF_5–SO_2 at low temperature. Polymeric products are mainly formed, but about 10% of cyclopentenyl cation **4a** is also present in the solution as evidenced by the characteristic pmr spectrum of **4a**. The mechanism for the formation of **4a** from cyclopentene in SbF_5–SO_2 can presently only be speculated upon. However, it may arise from the protolytic cleavage of the C–H bond by the small amount of protic superacid always present in SbF_5, or a radical ion process. Since SbF_5 is used in large excess, the formation of a donor–acceptor complex of cyclopentene with SbF_5 is likely. Either protolytic cleavage or hydride abstraction from this complex may lead to the formation of ion **4a**. The formation of cyclopentenyl cation **4a** from different precursors is summarized as shown in Scheme I.

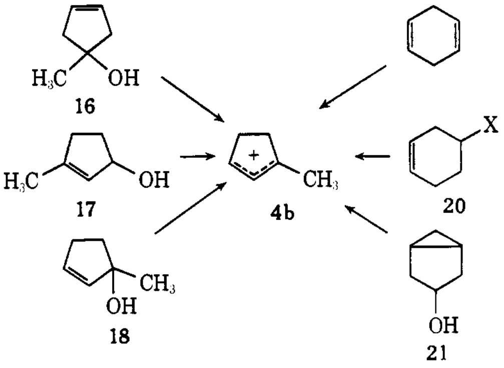


Scheme I



1-Methyl-2-cyclopentenyl cation 4b was generated from 1-methyl-3-cyclopenten-1-ol (**16**), 3-methyl-2-cyclopenten-1-ol (**17**), 1,4-cyclohexadiene, 1-methyl-2-cyclopenten-1-ol (**18**), 3-cyclohexen-1-ol (**20**) (X = OH), and *cis*-3-bicyclo[3.1.0]hexanol (**21**) in SbF_5–SO_2 (SO_2ClF) and FSO_3H–SbF_5–SO_2 (SO_2ClF) solutions at −78°, as described in the Experimental Section. The formation of ion **4b** from different precursors is summarized in Scheme II.

Scheme II



The pmr spectrum of ion **4b** shows proton absorptions at δ 3.61 (s, 3 H), 4.05 (br s, 4 H), 8.36 (d, 1 H), and 10.60 (d, 1 H). Protonation of 1,3-cyclohexadiene in FSO_3H–SbF_5–SO_2 (SO_2ClF) or in HF–SbF_5–SO_2 (SO_2ClF) was unsuccessful, as polymerization took place at all temperatures.

When 1-methyl-3-cyclopenten-1-ol (**16**) in SO_2ClF was slowly added to SbF_5–SO_2ClF at −78°, ion **4d** was formed, along with a small amount of polymer. Alcohol **16** could be protonated with partial ionization when it was carefully added to FSO_3H–SbF_5–SO_2ClF at −96°. Complete ionization of ion **4b** took place at −60°. No structural characteristics corresponding to **1b** are observed. Ion **4b** was further identified by the addition of the 3-methyl-2-cyclopenten-1-ol (**17**) and 1-methyl-2-cyclopenten-1-ol (**18**) to the same superacid solution at −78°, giving identical species and spectra.

The 7-methylnorbornenyl cation **19** was directly observed by Richey in 1966.[42] The presence of a methyl group at the C-7 position leads to little alteration in the chemical shifts of the other hydrogens in

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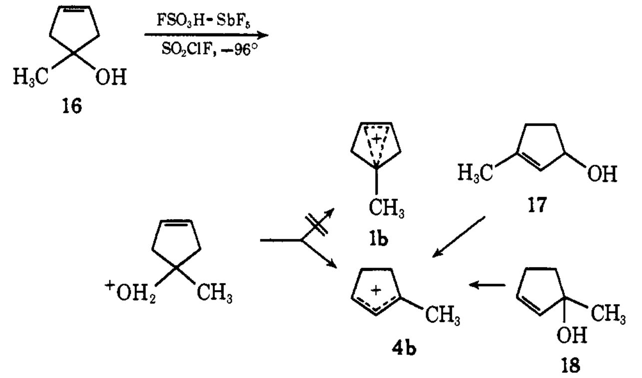
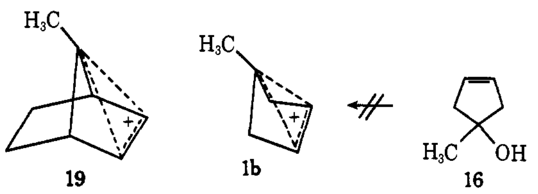
(39) Cyclopentyl bromide gives cyclopentyl cation when it is ionized in SbF_5–SO_2ClF at −78°; but in SbF_5–SO_2, it gives ion 4a. The effect of the solvent on ionization in this system is still not clear.

(40) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(41) For example, see M. L. Poutsma, *Science*, **157**, 997 (1967).

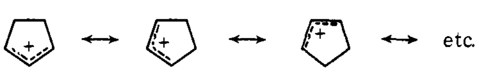
(42) H. R. Richey, Jr., and R. K. Lustgarten, *J. Amer. Chem. Soc.*, 88, 3136 (1966).



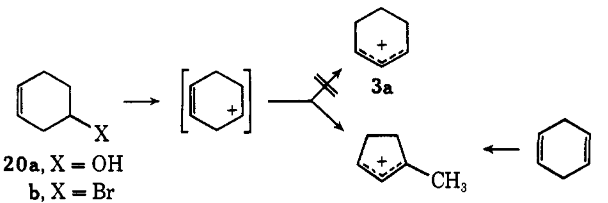


the ion. In the light of this observation, we hoped that a methyl-substituted bishomocyclopropenyl cation could be directly observed from methyl-substituted cyclopentenyl precursors. Thus, 1-methyl-3-cyclopenten-1-ol was synthesized and ionized in SbF_5-SO_2 (SO_2ClF) solution at −78°. The nmr spectra were too complicated to be interpreted. However, in FSO_3H-SbF_5-SO_2ClF (SO_2) solution, the alcohol was protonated at −78°, and its complete transformation into 1-methyl-2-cyclopentenyl cation took place at −60°. No evidence for either a classical or nonclassical tertiary structure was found. Clearly the initially formed *tert*-carbenium ion must undergo facile intramolecular hydride shift to give allylic ion **4b**.

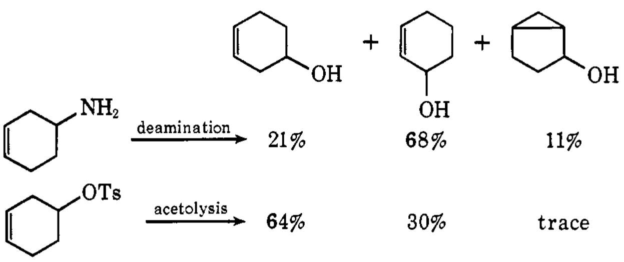
Interestingly, ion **4a** could also be obtained from cyclohex-3-en-1-ol (**20a**) in SbF_5-SO_2ClF at −78°. In FSO_3H-SbF_5-SO_2ClF or HF-SbF_5-SO_2ClF solution the latter alcohol was protonated and only partially ionized at −78°. Ion **4b** was found to be the only product when the temperature was raised to 0°. A degenerate system such as

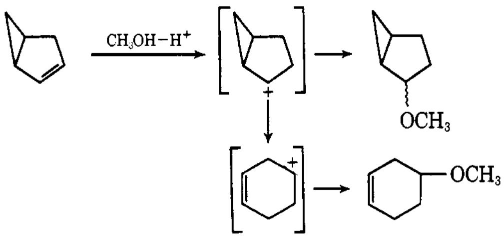


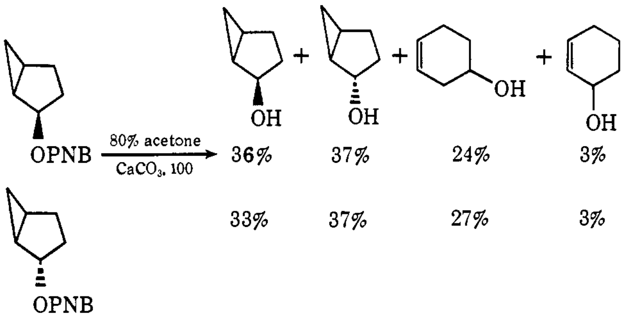
could be expected to occur at higher temperatures. However, this was not observed when the solution of **4a** was heated to 100° in a sealed nmr tube. Ion **4a** graduately decomposed at +110°, No 2-cyclohexenyl cation **3a** was formed in this case. Attempted ionization of both 4-bromo- and 4-chlorocyclohexenes (**20b** and **20c**) resulted in polymerization in superacid media. Protonation of 1,4-cyclohexadiene in FSO_3H-SbF_5-SO_2ClF solution resulted in the formation of ion **4b** with some concurrent polymerization.



Deno and Houser[43] first reported the rearrangement of cyclohexenyl to the corresponding cyclopentenyl cations. A number of such rearrangements were directly followed by continuous monitoring of the pmr spectra in the work of Deno and coworkers.[44] Deamination of 4-aminocyclohexene and acetolysis of 3-cyclohexenyl tosylate gave, in the work of Hanack, both allylic, homoallylic, and bicyclohexyl products.[45] Freeman and coworkers[16] reported the acid-catalyzed methanolysis of 2-bicyclo[3.1.0]hexene and found that 4-substituted cyclohexene was a major product. They suggested the mechanism and concluded that the 2-bicyclo[3.2.1]hexyl cation was more stable than the 3-bicyclo[3.1.0]hexyl cation.[46] Solvolysis of *endo*- and *exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates[47] gave the following product distribution. A common intermediate, independent of the geometric relationship of the leaving group and the cyclopropane ring, is believed to be involved in the solvolytic reactions. However, under solvolytic conditions, there is no methylcyclopentenyl product formed. Similar observations were also made by McDonald and his coworkers.[48,49] Allylic and homoallylic oxidation of cyclohexene by palladium salts was recently reported.[50]







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(43) N. C. Deno and J. J. Houser, *J. Amer. Chem. Soc.*, **86**, 1741 (1966).

(44) N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *ibid.*, **85**, 2995 (1963).

(45) M. Hanack and W. Keverle, *Chem. Ber.*, **96**, 2937 (1963).

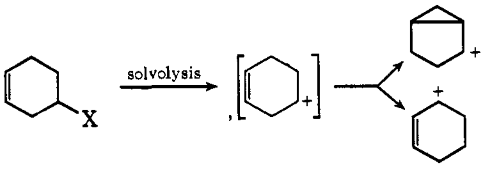
(46) F. A. Raymond, Ph.D. Thesis, University of Idaho, 1966; also, see R. R. Story and B. C. Clark, Jr., in "Carbonium Ions," Vol. 3, G. A. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, N. Y., in press.

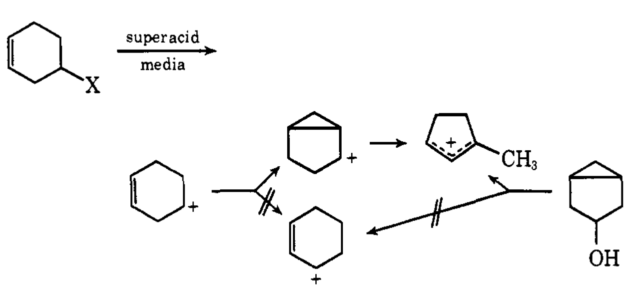
(47) E. C. Friedrich and M. A. Saleh, *Tetrahedron Lett.*, 1373 (1971).

(48) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).

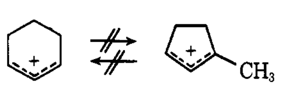
(49) R. N. McDonald and G. E. Davis, *Tetrahedron Lett.*, 1449 (1968).

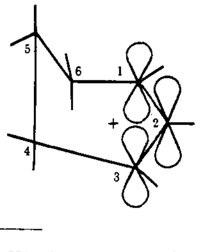
All the reported data indicate the tendency toward 1,2-hydride shift.[51] Nevertheless, under stable ion conditions, we did not find the similar hydride shift between 3-cyclohexenyl and 2-cyclohexenyl cations. For example, when 3-cyclohexen-1-ol was ionized in $FSO_3H-SbF_5-SO_2ClF$ at −78°, only 1-methyl-2-cyclopentenyl cation **4b** was found at all temperatures. The same ion could also be generated directly from 3-bicyclo[3.1.0]hexanol under the same ionizing condition. Thus, ring contraction of the cyclohexenyl cation to methylcyclopentenyl cation must take place prior to any intramolecular hydride shift; otherwise the allylic cyclohexenyl cation **3** would have been formed.

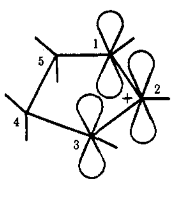




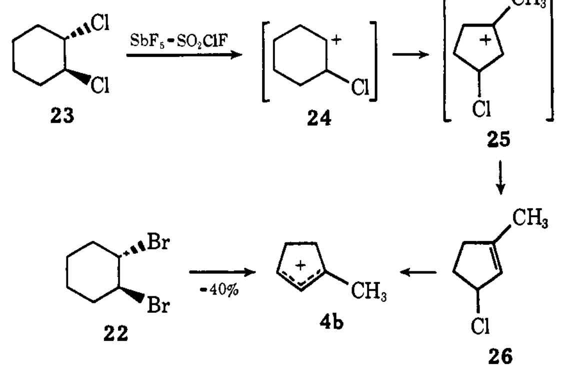
As was found, 2-cyclohexenyl cation could only be generated directly from 3-cyclohexenyl derivatives but not from 4-cyclohexenyl derivatives. The 2-cyclohexenyl cation was stable under the conditions studied and in no case was found to undergo ring contraction to give the methylcyclopentenyl cation. It was also found that both 1-methyl-, 1,3-dimethyl-, 1,5-dimethyl-, and 1,3,5-trimethyl-2-cyclohexenyl cations were stable in the same superacid solutions. Though many highly substituted cyclohexenyl cations were found to undergo ring contraction forming cyclopentenyl cations in mineral acid solutions, the 1,3-dimethylcyclohexenyl cation was found to be stable in 96% H_2SO_4.[52] Steric crowding factors might be least affecting the unsubstituted cyclohexenyl cation among all its homologs. Examining models shows that the cyclohexenyl cation could scatter all hydrogens present at C_4, C_5, and C_6 and retain relatively regular hybridized bond angles.[23,53]



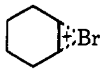




Ionization of 1,2-dihalocyclohexanes with SbF_5-SO_2 (SO_2ClF) solution also leads to ion **4b**. When *trans*-1,2-dichlorocyclohexane (**23**) was treated with SbF_5-SO_2ClF at −60°, the pmr spectrum showed the formation of 1-methyl-2-cyclopentenyl cation **4b** exclusively. No cyclohexenechloronium ion **27** was observed.[54] Ring construction of cyclohexyl cation to 1-methylcyclopentyl cation is well known.[55] Thus, the formation of **4b** from *trans*-1,2-dichlorocyclohexane can be rationized.



Ionization of **23** (X = Cl) should give 2-chlorocyclohexyl cation **24**. If a chlorine atom could stabilize the ion *via* halogen participation, then the cyclohexenechloronium ion **29** would be formed. Instead, it rearranges to a more stable *tert*-carbenium ion **25** which subsequently deprotonates to the chloroolefin **26** which upon further ionization can give the final stable 1-methylcyclopentenyl cation **4b**. In the case of *trans*-1,2-dibromocyclohexane, when treated with SbF_5-SO_2ClF solution, again 1-methyl-2-cyclopentenyl cation was obtained. A similar mechanism can be involved for both *trans*-1,2-dibromo- and 1,2-dichlorocyclohexanes. However, when *trans*-1,2-dibromocyclohexane was ionized in SbF_5-SO_2 solution at −40°, cation **4b** was formed (*ca.* 40%) along with other unidentified species. There are two singlet absorptions at δ 6.70 and 6.8 in the pmr spectrum. For such deshielded resonances, the methine protons in cyclic halonium ions **27** and **28** would seem possible. No attempt was made to assign the remainder of the rather complicated pmr spectrum. It is known that halonium ions are much more soluble in SO_2 than in SO_2ClF.[34] This may cause the different behavior in ionization of *trans*-1,2-dibromocyclohexane. A similar ion mixture was obtained when isomeric 1,4-dibromocyclohexanes were ionized in either SbF_5-SO_2 or $SbF_5-FSO_3H-SO_2$ solution at −60°, indicating that they both form similar ions. Furthermore, we found that cyclohexene also reacted with $Cl_2-SbF_5-SO_2ClF$ solution at −78° to



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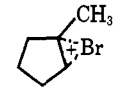

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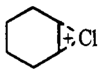

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(50) S. Wolfe and R. G. C. Campbell, *J. Amer. Chem. Soc.*, **93**, 1497 (1971).

(51) M. Hanack, *Suom. Kemistilehti*, **39**, 93 (1966).

(52) N. C. Deno and R. R. Lastomirsky, *J. Amer. Chem. Soc.*, **90**, 4089 (1968).

(53) T. S. Sorensen, *ibid.*, **91**, 6398 (1969). See also W. F. Sliwinski, Ph.D. Thesis, Princeton University, Princeton, N. J., 1971.

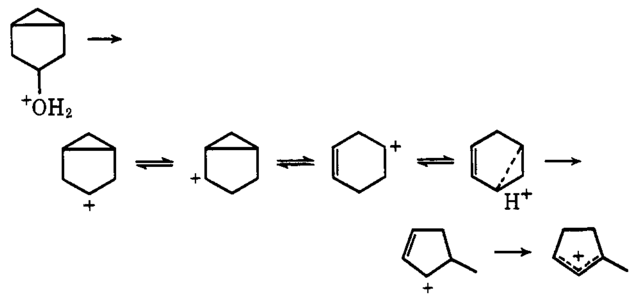
(54) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967).

(55) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *ibid.*, **89**, 2692 (1967).

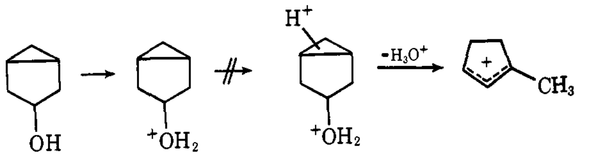
give cation **4b**. Obviously electrophilic chlorine would attack the double bond of cyclohexene to give 2-chlorocyclohexyl cation, which subsequently through the mechanism previously discussed would form cation **4b**.

In 1959, Winstein, Sonnenberg, and de Vries[22] reported the formation of the trishomocyclopropenyl cation **2** in the solvolysis of *cis*-3-bicyclo[3.1.0]hexyl systems. Ion **2** was depicted to be a symmetrical homolog of the cyclopropenyl cation. Rate acceleration, stereochemistry, special salt effect product analysis, and deuterium scrambling supported the trishomocyclopropenyl cation as the reaction intermediate in the solvolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate.[56,57] Contradictory data to the homoaromatic structure were, however, obtained in the deamination of both *cis*- and *trans*-3-bicyclo[3.1.0]hexylamines by Corey and Uda.[58,59] Similar indications against the nonclassical trishomocyclopenyl cation structure were given by Corey in the acetolysis of *cis*-diphenyl *p*-toluenesulfonate.[58] In addition to the solvolysis data, attempts to observe and determine the structure of the trishomocyclopropenyl cation were also made by several nmr studies.[16,60,61] Olah and Tolgyesi[7] reported the nmr spectrum of the fluoroborate salt obtained from 3-bromocyclohexene with silver hexafluoroantimonate or by the protonation of 1,4-cyclohexadiene by HF–SbF$_5$. This observation must now be considered to be that of rather poorly resolved (due to the solvent system used and side reactions) ion **4b** and not **2**. Sauers[62] and Broser[63] report on the nmr spectra of claimed derivatives of the trishomocyclopropenyl cation; their work must also be considered tentative.

Despite all of the chemical evidence either for or against the existence of the trishomocyclopropenyl cation, no verified report on the direct observation of the ion has been made. We therefore prepared *cis*-3-bicyclo[3.1.0]hexanol and attempted its ionization. When the alcohol was ionized in SbF$_5$–SO$_2$ (SO$_2$ClF) at −78°, no pmr spectrum corresponding to either a nonclassical or classical 3-bicyclo[3.1.0]hexyl cation was observed, but only polymeric materials were obtained. However, in FSO$_3$H–SbF$_5$–SO$_2$ClF (SO$_2$) a clear solution of the 3-methyl-2-cyclopentenyl cation **4b** was obtained. The same cation could also be directly generated from the corresponding 3-methyl- and 1-methyl-2-cyclopentenyl derivatives. Thus, the initially formed bicyclic cation must be so unstable that either hydride shift or ring contraction occurs immediately. Protonated 3-bicyclo[3.1.0]hexanol could be observed at low temperatures but it completely rearranges to 1-methyl-2-cyclopentenyl cation at −60°. Data can be rationalized according to the following mechanism.



The mechanism was further suggested by ionization of alcohol **21** in DF–SbF$_5$-SO$_2$ClF solution at −78°. The final rearranged allylic ion **4b** did not contain incorporated deuterium as indicated by the integration of the pmr spectrum of **4b**. Thus an alternate mechanism involving the protonation of the cyclopropyl ring followed by dehydration could be ruled out.



Even though a number of stable nonclassical carbocations have been directly observed under long-lived ion conditions,[11,12,46] our inability to observe either the bishomo- or trishomocyclopropenyl cations shows that both ions are unstable under conditions where other nonclassical ions were observed as stable entities. This is also reflected in the slower solvolytic rate of 3-cyclopentenyl derivatives (compared for simple norbornyl or cyclopropylcarbinyl systems) and the small cis/trans rate ratio of 3-bicyclo[3.1.0]hexyl derivatives.

Considerable information concerning the structure of cycloalkenyl cations has been obtained from nmr spectroscopic studies of the cations generated either in aqueous H$_2$SO$_4$[61] or in stronger acid systems.[11] In the substituted cyclopentenyl cations and cyclohexenyl cations, the central allylic proton has a chemical shift of generally δ 7–8. However, only few data concerning the terminal protons were available. Examination of pmr parameters of ions in Table I reveals several interesting features: (a) the terminal allylic protons in cyclopentenyl cations are much more deshielded than those in cyclohexenyl cations, (b) the coupling constants between the central and the terminal protons are smaller in cyclopentenyl cations than those in cyclohexenyl cations, and (c) the chemical shifts of the central and terminal protons are becoming less deshielded as the ring size and number of methyl substituents increase. Carbon-13 studies of both ions **3a** and **4a** show little or no evidence of C$_1$–C$_3$ interactions.[64] This kind of interaction was found important only in cyclobutenyl cations[11,65] (Table II). For the parent cyclopentenyl cation **4a**, the charge delocalization must be more substantial than that in the cyclohexenyl cation. Hoffmann and Olafson[66] suggested that delocalization could occur in cyclopentenyl cations by invoking both methylene groups in a hyperconjugative delocalization giving a cyclic 6π-electron system. The more deshielded nature of pmr chemical shift of the central allylic proton was also explained by ring current effect in the cation.[23]

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(56) S. Winstein, *Chem. Soc. Spec. Publ.*, No. 21, 5 (1967).

(57) S. Winstein, E. C. Fredrich, R. Baker, and Y-i Liu, *Tetrahedron*, 22, S221 (1966).

(58) E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, **85**, 1788 (1963).

(59) E. J. Corey and R. L. Dawson, *ibid.*, 85, 1782 (1963).

(60) P. M. Warder, Ph.D. Thesis, University of California, Los Angeles, 1970.

(61) N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 129 (1964).

(62) R. R. Sauers, *Tetrahedron Lett.*, 1015 (1962).

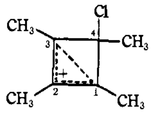
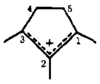
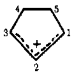
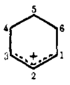
(63) W. Broser and D. Rahn, *Chem. Ber.*, 100, 3472 (1967).

(64) Carbon-13 nmr chemical shifts are obtained by the Fourier transformation method, using a Varian HA-100 nmr spectrometer at low temperatures.

(65) G. A. Olah, P. Clifford, R. Johanson, and Y. Halpern, *J. Amer. Chem. Soc.*, **93**, 4219 (1972).

(66) R. Hoffmann and R. A. Olafson, *J. Amer. Chem. Soc.*, **88**, 943 (1966).

Table II. Cmr Parameters (δ) of Cycloalkenyl Cations at 25.1 MHz in Superacid Solution at −70°

Cation	C_1,C_3	C_2	C_4,C_6	C_5
	-1.6^a	-16.9		
	-54.3^a	$+37.4$		
	-24.0^b	$+57.0$	$+145.0$	
	-41.0^b	$+48.0$	$+160.0$	$+180.5$

[a] Reference 65. [b] Reference 64; ^{13}C shifts are in parts per million from carbon disulfide.

Also, the smaller ring size of the cyclopentenyl cation brings the two terminal allylic carbon atoms closer together and causes the positive charge to disperse more onto the methylene carbons. This is reflected by the same deshielded nature of the methylene protons in cyclopentenyl cations. Another point is that the coupling constant between the central proton and the terminal allylic protons in cyclopentenyl cations is only about half of that in cyclohexenyl cations. This is in agreement with the well-known dependence of $J_{HC=CH}$ on ring size, observed in simple cycloolefins.[67]

Experimental Section

Nuclear Magnetic Resonance Spectra. A Varian Associates Model A56/60A nmr spectrometer equipped with variable-temperature probe was used for all spectra. External TMS (capillary tube) was used as reference.

Preparation of Ions. Solutions of the cations were prepared according to the previously reported procedure.[68] The superacid solutions were prepared by dissolving FSO_3H-SbF_5 (1:1, molar, 1.0 ml) or freshly distilled SbF_5 in SO_2ClF or SO_2 (1.0 ml) at Dry Ice–acetone temperature, to which was slowly added with vigorous stirring a solution of appropriate precursor (*ca.* 0.05 g) in SO_2ClF or SO_2 (0.5 ml) precooled at the same temperature. Ethanol–liquid nitrogen was used for the preparation of ions at −120°. The solution of the cation was then transferred into the nmr tube precooled at the same temperature for nmr spectra.

Materials. **Δ^3-Cyclopentenone** and **Δ^2-cyclopentenone** were prepared according to Brown's method,[24] having bp 32–33° (20 mm) and 50–53° (35 mm), respectively.

Δ^3-Cyclopentenol and **Δ^2-cyclopentenol** were prepared by LAH reduction of the corresponding ketones, having bp 67–68° (35 mm) and 66.5–68.5° (35 mm), respectively.

3-Methyl-2-cyclohexenol (5b) and **3,5-dimethyl-2-cyclohexenol (5d)** were prepared by LAH reduction of the corresponding ketones, 3-methyl-2-cyclohexenone and 3,5-dimethyl-2-cyclohexenone (Aldrich), respectively. Alcohols **5b** and **5d** have bp 72° (7.2 mm) and 68–69° (3.0 mm), respectively.

1,3-Dimethyl-2-cyclohexenol (5e) and **1,3,5-trimethyl-2-cyclohexenol (5f)** were prepared by methylmagnesium bromide addition to their corresponding ketones: 3-methyl-2-cyclohexen-1-one and 3,5-dimethyl-2-cyclohexen-1-one, respectively (Aldrich). **5e** and **5f** have bp 50–51° (2.5 mm) and mp 29–30°, respectively.

1-Methyl-3-cyclopenten-1-ol (16) and **1-methyl-2-cyclopenten-1-ol (18)** were prepared by Grignard addition of methylmagnesium bromide to Δ^3-cyclopentenone and Δ^2-cyclopentenone at 0°, respectively. **16** and **18** have bp 55–57° (25 mm) and 47–49° (15 mm), respectively.

***cis*-3-Bicyclo[3.1.0]hexanol (21)** was prepared according to Winstein's method.[21,22]

3-Methyl-2-cyclopentenol (17) was prepared by LAH reduction of the commercially available (Aldrich) 3-methyl-2-cyclopenten-1-one at room temperature, bp 73–75° (21 mm).

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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(68) G. A. Olah, D. H. O'Brien, and P. M. White, *ibid.*, **89**, 5694 1967).

Stable Carbocations. CXXX.[1] Carbon-13 Nuclear Magnetic Resonance Study of Halocarbenium Ions. Degree of Halogen "Back-Donation" and Relative Stability of Halocarbenium Ions

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received July 28, 1971*

Abstract: Carbon-13 nuclear magnetic resonance (cmr) studies of two series of halocarbenium ions, *i.e.*, dimethylhalocarbenium ions, $CH_3CX^+CH_3$ (**1-X**), and phenylmethylhalocarbenium ions, $C_6H_5CX^+CH_3$ (**2-X**), are reported. The degree of halogen "back-donation" is determined from the differences in cmr shifts ($\Delta\delta^{13}C$) between halocarbenium ions and their halo olefins ($RXC{=}CH_2$). The back-donation of fluorine is found to be greater than that of chlorine and bromine atoms. The relationship between relative stabilities of halocarbenium ions and their halogen back-donations (and also their sizes) is discussed.

Fluorine 2p–2p interaction (back-donation) has been well recognized both in organic[3] and inorganic systems.[4–6] The high electronegativity of fluorine results in the well-demonstrated inductive effect in organo-

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(1) Part CXXIX: G. A. Olah, K. Dunne, and D. P. Kelly, *J. Amer. Chem. Soc.*, in press.

(2) Research Associate, 1969–1971.

(3) W. A. Sheppard and C. M. Sharts in "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 18.

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