Table IV

% H_2SO_4	$-H_0$	ϵ_{obsd}[a]	ϵ_{calcd}[b]
15.1	0.67	79	75
30.2	1.73	89	90
40.4	2.44	94	101
50.2	3.40	115	117
55.2	3.94	127	128
60.4	4.51	146	141
65.2	5.10	167	162
67.3	5.40	186	177
70.4	5.86	221	210
72.6	6.18	245	241
74.1	6.40	279	270
75.3	6.60	294	297
78.5	7.11	367	373
80.0	7.34	424	410
81.7	7.61	446	450
84.7	8.08	535	510
88.2	8.65	567	554
89.7	8.90	577	566
94.5	9.75	585	588
98.6	10.5	595	595

[a] Zero-time extinction coefficient measured at 190 mμ. [b] Calculated from the equation log $[BH^+]/[B] = 0.62(-H_0 - 7.16)$ with $\epsilon_B = 65$, $\epsilon_{BH^+} = 598$, $g_B = -14.7$, $g_{BH^+} = 0$.[26]

7.25), and for *n*-propyl acetate the equation log $[BH^+]/[B] = 0.62 \cdot (-H_0 - 7.18)$. A typical set of experimental data for *n*-propyl acetate is given in Table IV. This was treated by a previously described[26] method to obtain the best fit of the experimental points to a calculated curve based on the equation log $[BH^+]/[B] = m(-H_0 - pK)$. The above method of obtaining *m* values was preferred over the more conventional logarithmic plots for two reasons. First, the log $[BH^+]/[B]$ *vs.* H_0 plots only utilize data obtained within a narrow range, usually 1.5–2.0 H_0 units either side of p*K*, whereas the previously described kinetic treatment using *m* involves data obtained over a much wider acidity range (15–98% sulfuric acid). Second, both the linearity and slopes of these log plots can be influenced by medium effects on the spectra of the base and conjugate acid forms. The present method reduces the seriousness of this possibility by correcting for medium effects. Unfortunately the rate of hydrolysis of isopropyl acetate is too high in acids above 90% to obtain reliable zero-time extinction coefficients. However, below this acidity, plots of log ε for isopropyl and *n*-propyl acetates against H_0 are strikingly similar, and it is reasonable to assume that the ionization behavior of isopropyl acetate closely resembles that of the *n*-propyl ester. Lane,[5] using a similar method, found the ionization behavior of ethyl acetate in sulfuric acid followed the equation log $[BH^+]/[B] = 0.65(-H_0 - 6.93)$. The close similarity of the indicator slopes and "p*K*" values for methyl, *n*-propyl, and ethyl acetates indicates that the protonation behavior of acetate esters is reasonably independent of structure. For the other acetates studied no reliable protonation data could be obtained either because of too rapid hydrolysis or because sulfonation interfered at the high acidities required to measure ϵ_{BH^+}. Therefore, in cases where no indicator slope could be measured, a value of $m = 0.62$ was assumed, and an approximate p*K* of −7.2 was used to correct for fraction protonated, where necessary.[21]

Acknowledgment. We are grateful to the National Research Council of Canada for continued financial support, and for the award of a studentship to R. A. M.

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(26) A. R. Katritzky, A. J. Waring, and K. Yates, *Tetrahedron*, **19**, 465 (1963).

Stable Carbonium Ions. XXXIV.[1]
The 1-Methylcyclopentyl Cation[2]

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received February 10, 1967*

Abstract: 1-Methyl-1-chlorocyclopentane, cyclopentylcarbinyl chloride, and cyclohexyl fluoride (chloride, bromide) in SbF_5–SO_2 solutions at −60° gave a stable solution of the 1-methylcyclopentyl cation. The same ion is also formed when 1-methylcyclopentanol or cyclohexanol were dissolved in FSO_3H–SbF_5 solutions. 1-Methylcyclopentene and cyclohexene are protonated in HF–SbF_5–SO_2 or FSO_3H–SbF_5–SO_2 solution to the 1-methylcyclopentyl cation, which is also formed by hydride abstraction from methylcyclopentane and cyclohexane in FSO_3H–SbF_5 solution. The structure of the 1-methylcyclopentyl cation was investigated based on its nmr spectrum.

The acid-catalyzed isomerization of methylcyclopentane and cyclohexane has long been recognized and studied and has provided much useful information concerning the carbonium ion chain mechanism for hydrocarbon isomerization.[4,5] In terms of product stability, cyclohexane is favored. The equilibrium mixture at 25° consists of 77% cyclohexane and 23% methylcyclopentane.[6] In terms of carbonium ion stability, however, the tertiary methylcyclopentyl cation I should be favored over the secondary cyclohexyl cation II. No good estimate is available concerning either the relative energy differences between these two

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(1) Part XXXIII: G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, in press.

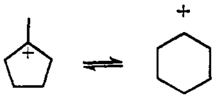
(2) For a preliminary report see G. A. Olah and M. W. Meyer in "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 645.

(3) (a) National Science Foundation Postdoctoral Research Investigator, 1966–1967. (b) National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

(4) C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, **66**, 1097 (1933).

(5) For reviews see (a) H. Pines and N. E. Hoffman, "Friedel-Crafts and Related Reactions," Vol. II, Part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 28; (b) F. E. Condon and P. H. Emmett, Ed., "Catalysis," Vol. VI, Reinhold Publishing Corp., New York, N. Y. 1958, Chapter 2.

(6) A. L. Glasebrook and W. G. Lovell, *J. Am. Chem. Soc.*, **61**, 1717 (1939), reported in accordance with ref 2 that the equilibrium mixture at 25° consists of 77% cyclohexane and 23% methylcyclopentane. D. P. Stevenson and J. H. Morgan, *ibid.*, **70**, 2773 (1948), found the equilibrium favors cyclohexane at lower temperatures, the amount of methylcyclopentane increasing with temperature.



I II

ions or the activation energy necessary for their interconversion.

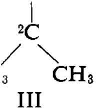
In the course of the investigation of stable carbonium ions in acidic solvent systems like SbF_5 or SbF_5–FSO_3H[7] we felt it of interest to attempt the observation of the carbonium ions formed from both 1-methylcyclopentyl and cyclohexyl precursors. We briefly reported on the observation of 1-methylcyclopentyl cation I in 1963,[2] but would like now to present in detail our observations relating to this ion.[8] As ion I was observed to be formed from a variety of precursors in strong acid media, its investigation also proved interesting with respect to applying a variety of methods in its generation.

Results and Discussion

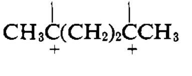
When 1-chloro-1-methylcyclopentane (**1**) was dissolved in SbF_5–SO_2 solution at −60° a stable solution of ion I was obtained. Ion I was also obtained from cyclopentanecarbinyl chloride (**2**) or cyclohexyl chloride (**3**) (or fluoride, bromide) in the same solvent at −60°. The primary cyclopentylcarbinyl cation and the secondary cyclohexyl cation thus rearrange with great ease even at −60° to the tertiary ion I which is the only ion observed by nmr spectroscopy.

Using FSO_3H–SbF_5 as the acid medium, 1-methylcyclopentanol-1 (**4**) and cyclohexanol (**5**) gave also exclusively ion I. 1-Methylcyclopentene-1 (**6**) and cyclohexene (**7**) were also protonated in HF–SbF_5–SO_2 or FSO_3H–SbF_5–SO_2 at −60° to give I. Furthermore, we observed that the extremely strong acid FSO_3H–SbF_5 is able to affect hydride ion abstraction from 1-methylcyclopentane (**8**) or cyclohexane (**9**) to form ion I.[9] Figure 1 summarized the different precursors and pathways leading to ion I.

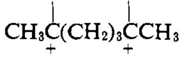
The pmr spectrum of the methylcyclopentyl cation I at −60° is shown in Figure 2. The substantially deshielded methyl (−3.98 ppm) and α-methylene (−4.20 ppm) protons adjacent to the positive charge are in the anticipated positions.[10] Particularly noteworthy is the long-range coupling (J_{H-H} = 4.0 cps) of the methylene and methyl hydrogens through the sp^2-hybridized center of ion I. Similar long-range coupling has been observed in simple alkylcarbonium ions. Thus



$$^{3}CH_2CH_3-\overset{+}{^{2}C}(^{1}CH_3)CH_3$$



$$CH_3\overset{+}{C}(CH_3)(CH_2)_2\overset{+}{C}(CH_3)CH_3$$



$$CH_3\overset{+}{C}(CH_3)(CH_2)_3\overset{+}{C}(CH_3)CH_3$$

III IV V

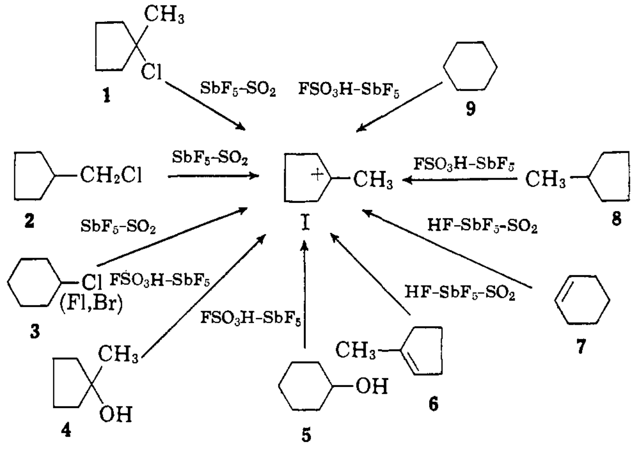


Figure 1.

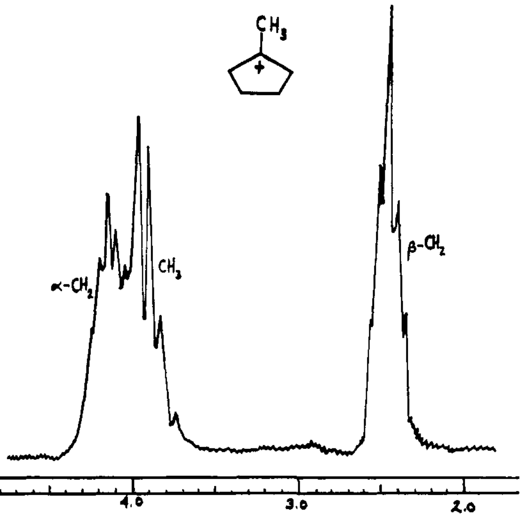


Figure 2.

in the dimethylethylcarbonium ion (*t*-amyl cation) (III), $J_{H_1-H_3}$ = 5.0 cps,[10] while for the dications IV and V, $J_{H_1-H_3}$ = 3.0 and 4.0 cps, respectively.[11] The β-methylene protons at −2.47 ppm show also the anticipated deshielding. Finally, quenching ion I in methanol at −70° gave a high yield (80%) of 1-methylcyclopentyl methyl ether[12] with smaller amounts of methylcyclopentene.

The fact that, starting from either 1-methylcyclopentyl or cyclohexyl precursors even at −60°, we were able to observe only the 1-methylcyclopentyl cation indicates that rearrangement of any initially formed cyclohexyl cation occurs too rapidly to be detected by nmr, at least under the experimental conditions used in the present work. Although the exact mechanistic details of this rearrangement are not yet known, we favor a mechanism not involving the intermediacy of a primary carbonium ion, which would represent a substantially high energy barrier. A rearrangement mechanism similar to the one proposed by Nenitzescu,[13] involving

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(7) See previous papers of this series.

(8) D. M. Brouwer and E. L. Mackor [*Proc. Chem. Soc.*, 147 (1964)] have also observed the methylcyclopentyl cation and claimed, based on line broadening, that above −20° the methyl group shifts along the ring. We cannot concur with this explanation and feel that line broadening was caused by other reasons.

(9) The application of FSO_3H–SbF_5 as a hydride-abstracting medium to generate carbonium ions from hydrocarbon is a general method: G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, **89**, 2227 (1967).

(10) In the dimethylethylcarbonium ion (*t*-amyl cation) observed in SbF_5–SO_2, the positions of the methyl and methylene groups adjacent to the positive charge are at 4.50 and 4.93 ppm: G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

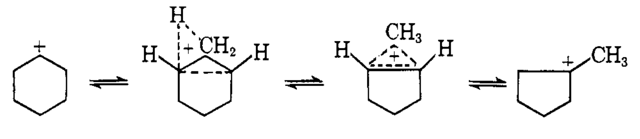
(11) J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *ibid.*, **89**, 156 (1967).

(12) G. A. Lutz, A. E. Bearse, J. F. Leonard, and F. P. Croxton, *ibid.*, **70**, 4139 (1948).

(13) C. D. Nenitzescu in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, Inc., New York, N. Y., in press.

Olah, et al. / 1-Methylcyclopentyl Cation

a protonated cyclopropane intermediate, merits consideration.



Experimental Section

All compounds with the exception of 1-chloromethylcyclopentane and 1-methylcyclopentyl methyl ether were commercially available. 1-Chloro-1-methylcyclopentane was prepared by the procedure of Merrwein and Mühlendyk.[14] 1-Methylcyclopentyl methyl ether was prepared according to the method of Lutz, *et al.*[12]

Nmr Spectra. The nmr spectra were obtained on a Varian Associates Model A56-60A spectrometer equipped with a variable-temperature probe. All spectra were run at −60°. The chemical shifts are recorded in parts per million relative to external TMS.

Preparation of Solutions of 1-Methylcyclopentyl Cation. a. **From Halides.** A saturated solution of antimony pentafluoride in sulfur dioxide was prepared (at −10°). Portions (2 ml) of this solution were cooled to −78°, causing some antimony pentafluoride to crystallize from solution. To this suspension was added with stirring approximately 0.2 g of the appropriate 1-methylcyclopentyl or cyclohexyl halide. Slight warming was required to complete the ionization, whereupon a homogeneous solution resulted with only slight traces of color. Ion concentrations were around 10%.

b. **From Alcohols.** The precursor alcohol (1-methyl-1-cyclopentanol or cyclohexanol) in SO_2 was cooled to −60° and added to a vigorously stirred 1:1 molar mixture of FSO_3H and SbF_5 at −60°. Generally an excess of SO_2 was used to prepare the solution which was then concentrated by pumping off SO_2 to give an approximately 8-10% concentration of the carbonium ion solution.

c. **From Cycloalkanes.** The cycloalkane (1-methylcyclopentane, cyclohexane) and a tenfold (weight) excess of acid (1:1 FSO_3-SbF_5) were vigorously stirred at room temperature until they formed a homogeneous colorless mixture.

d. **From Cycloalkenes (1-Methylcyclopentene and Cyclohexene).** A cold (−60°) solution of the cycloalkene in SO_2 was added slowly with stirring to a cold solution of HF-SbF_5 and FSO_3H-SbF_5 in SO_2. Excess SO_2 was pumped off in order to obtain a ~10% solution of the methylcyclopentyl cation.

Quenching the methylcyclopentyl cation in a suspension of methanol and potassium carbonate at −78° gave an 81% yield of 1-methylcyclopentene according to comparison with authentic samples.

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

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[14] H. Meerwein and M. Mühlendyk, *Ann.*, 405, 171 (1964).

Stable Carbonium Ions. XXXVIII.[1] Alkenyloxocarbonium Ions

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Received December 21, 1966

Abstract: An investigation of the alkenoyl fluoride–antimony pentafluoride complexes has been carried out. Acryloyl-, methacryloyl-, crotonoyl-, tigloyl-, β,β-dimethylacryloyl-, and cinnamoyl fluoride all form complexes with antimony pentafluoride, which based on infrared and nmr investigations are alkenyloxocarbonium ions.

No investigation of the complex formation of alkenoyl halides with Lewis acid halides has been reported in the literature. Deno, Pittman, and Wisotsky[3] investigated the behavior of crotonic, 2-methylcrotonic (tiglic), 3-methylcrotonic, and 2,4-hexadienoic (sorbic) acid in sulfuric acid and oleum. It was suggested, based on nmr studies, that an equilibrium exists between the oxocarbonium ions and protonated acids.

$$RCOOH_2^+ \rightleftharpoons RCO^+ + H_2O$$

In continuation of our previous work[4] on oxocarbonium ions it was of interest to attempt the preparation of alkenyloxocarbonium ion complexes ($RC^+{=}O$, R = unsaturated).

Results and Discussion

Stable alkenyloxocarbonium ion complexes were obtained by treating alkenoyl fluorides with antimony pentafluoride ("fluoride method" of oxocarbonium ion formation[4]).

$$RR'C{=}CR''COF + SbF_5 \rightleftharpoons RR'C{=}CR''C^+O\ SbF_6^-$$

The necessary alkenoyl fluorides were prepared from the corresponding acyl chlorides and anhydrous hydrogen fluoride except for acryloyl fluoride, methacryloyl fluoride, and crotonoyl fluoride, which were prepared from the corresponding acids and benzoyl fluoride. Yields were generally better than 90%. Table I summarizes the boiling points of the alkenoyl fluorides. Their purity, based on nmr and infrared spectra, was better than 98%.

The alkenoyloxocarbonium ion complexes were prepared by mixing cold 1,1,2-trifluorotrichloroethane (Freon 113) solutions of the corresponding alkenoyl fluorides with Freon 113 solutions of antimony pentafluoride. The complexes separate as liquids at room temperature except for the cinnamoyl complex which crystallizes (mp 75°). They are all brown in color except for the cinnamoyl complex which is bright red.

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[1] Part XXXVII: G. A. Olah, R. D. Chambers, and M. B. Comisarow, *J. Am. Chem. Soc.*, 89, 1268 (1967).

[2] National Science Foundation Predoctoral Research Investigator, 1965–1967.

[3] N. C. Deno, C. U. Pittman, Jr., and J. Wisotsky, *J. Am. Chem. Soc.*, 86, 4370 (1964).

[4] (a) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *ibid.*, 84, 2733 (1962); (b) G. A. Olah, *Rev. Chim., Acad. Rep. Populaire Roumaine*, 7, 1139 (1962); (c) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, 85, 1328 (1963); (d) G. A. Olah and M. B. Comisarow, *ibid.*, 88, 3313, 4442 (1966).