Preparation of the 4-Iodo-1,2,3,4-tetramethylcyclobutenyl Cation. Ultraviolet and Nuclear Magnetic Resonance Spectra of Cyclobutenyl Cations in Methylene Chloride, Sulfuric Acid, and Liquid Sulfur Dioxide[1]

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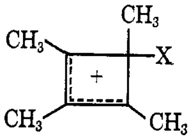
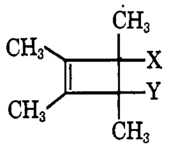
The 4-iodo-1,2,3,4-tetramethylcyclobutenyl cation (I, X = I) is formed when the corresponding diiodide (II, X = Y = I) is treated in methylene chloride solution with aluminum chloride, or in cold liquid sulfur dioxide with silver hexafluoroantimonate. The n.m.r. spectrum of this cation and the spectra of related cations of structure I were compared when the ions were prepared by the three following procedures: (1) the cyclobutenyl halide in methylene chloride was treated with aluminum chloride; (2) the cyclobutenyl halide was dissolved in concentrated sulfuric acid; and (3) the cyclobutenyl halide was treated with anhydrous silver hexafluoroantimonate in cold liquid sulfur dioxide. The ultraviolet spectra of cations I prepared by procedures 1 and 2 are compared.

Previously the cyclobutenyl cations (I), where X is CH_3, H, Cl, and Br, were synthesized by the reaction of the corresponding halides (II) in methylene chloride solution with aluminum chloride, and the proton n.m.r., ultraviolet, and infrared spectra of the ions prepared in this way were determined.[2] The n.m.r. spectra of two of the ions (in which X is CH_3 and Cl) were also determined in solutions in which the ions had been prepared in a different way, by reaction of the cyclobutenyl halide in sulfur dioxide with silver hexafluoroantimonate.



I



II

However, the spectroscopic properties of other carbonium ions,[3] particularly derivatives of the arylmethyl and tropylium ions, have usually been determined in sulfuric acid,[4] although recent studies have been carried out in a variety of other solvents, such as other acids,[4g,5] liquid hydrogen fluoride,[6] liquid sulfur dioxide,[7] antimony pentafluoride,[7c,d] and methylene chloride.[2b,4d,8] In correlating the data collected in the different solvent systems, it previously had been assumed that the effect of solvent changes could be neglected. An interpretation of differences between the ultraviolet and n.m.r. spectra of the cyclobutenyl cations and other allylic carbonium ions required this assumption, for while the cyclobutenyl cations were prepared mainly in methylene chloride from the cyclobutenyl halide and aluminum chloride,[2b] the other ions were prepared only from olefins and 96% sulfuric acid.[4i] In order to determine whether this difference was significant, the ultraviolet and n.m.r. spectra of some of the cyclobutenyl cations previously studied were redetermined in sulfuric acid and in sulfur dioxide.[9]

In addition, to complete the series of common halocyclobutenyl cations, the carbonium ion I, where X is iodine, was synthesized for the first time.

Results

For the present study, solutions of the cyclobutenyl cations were prepared by the following three procedures: (1) the cyclobutenyl halide in methylene chloride was treated with aluminum chloride; (2) the cyclobutenyl

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(1) Supported by grants from the Alfred P. Sloan Foundation and the National Science Foundation (NSF GP-748).

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(3) For reviews, see (a) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964); (b) G. A. Olah and M. W. Meyer, "Friedel-Crafts and Related Reactions," Vol. 1, G. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter VIII.

(4) (a) S. F. Mason, *Quart. Rev.* (London), **15**, 287 (1961); (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 226 ff, and references therein; (c) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); (d) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *ibid.*, **84**, 3349 (1962); (e) H. Hart, T. Sulzberg, and R. Rafos, *ibid.*, **85**, 1800 (1963), and references therein; (f) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952); (g) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959); (h) D. E. O'Reilly and H. P. Leftin, *J. Phys. Chem.*, **64**, 1555 (1960); *cf.* R. S. Berry, R. Dehl, and W. R. Waughan, *J. Chem. Phys.*, **34**, 1460 (1961); (i) N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2998 (1963), and preceding paper; (j) N. C. Deno and C. U. Pittman, Jr., *ibid.*, **86**, 1871 (1964).

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(7) (a) *Cf.* ref. 2a; (b) P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *J. Am. Chem. Soc.*, **85**, 3630 (1963); P. R. Story and M. Saunders, *ibid.*, **82**, 6199 (1960); (c) G. A. Olah, *ibid.*, **86**, 932 (1964); (d) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1390 (1964); (e) R. Dehl, W. R. Waughan, and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959); (f) G. A. Olah, *J. Am. Chem. Soc.*, **87**, 1103 (1965).

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

(9) Reported solvent effects on ultraviolet and n.m.r. spectra of carbonium ions include the following. (a) The ultraviolet spectrum of tropylium fluoborate in methylene chloride is similar to that of the ion in sulfuric acid, but the halides in the former solvent exhibit charge-transfer bands.[4d] (b) The ultraviolet spectra of triphenyl and tri-*p*-anisyl carbonium ions in a mixture of trifluoroacetic acid and its anhydride and in sulfuric acid are slightly different.[4g] (c) The n.m.r. spectra of triphenylmethylcarbonium ion in sulfur dioxide and in chlorosulfuric acid are moderately different, but those of phenyldimethyl, diphenylmethyl, and diphenyl carbonium ions in these solvents are similar.[5a,7c] (d) The n.m.r. spectra of the acetyl carbonium ion in fuming sulfuric acid and in antimony pentafluoride are the same.[10] (e) The n.m.r. spectra of some aliphatic carbonium ions in antimony pentafluoride and in sulfur dioxide are similar.[11] (f) The ultraviolet spectra of the conjugate acids of some organic bases,[12] but not others,[4b,13] shift slightly as the concentration of aqueous sulfuric acid is changed. (g) Moderately large solvent shifts have been observed in the n.m.r. spectra of some nonionic organic compounds, and even the relative shifts of two resonances of the same molecule have been observed to vary with solvent.[14]

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

(11) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

(12) (a) L. A. Flexer, L. P. Hammett, and A. Dingwell, *ibid.*, **57**, 2103 (1935); (b) J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).

(13) R. Stewart and T. Matthews, *Can. J. Chem.*, **38**, 602 (1960).

(14) N. Lumbroso and B. P. Dailey, *J. Phys. Chem.*, **67**, 2469 (1963).

halide was dissolved in concentrated sulfuric acid; and (3) the cyclobutenyl halide was treated with anhydrous silver hexafluoroantimonate in cold liquid sulfur dioxide. The spectra of the cations prepared in these ways are given in Tables I and II.

Table I

Ultraviolet Spectra of Cyclobutenyl Carbonium Ions

Starting halide (II)	λ_{max}, mμ (log ϵ_{max}) In CH_2Cl_2–$AlCl_3$	In 96% H_2SO_4
X = Y = Cl	253 (3.67)	246 (3.60)
X = CH_3, Y = Br (Cl)	245 (3.46)	242 (3.49)
X = H, Y = Cl	240 (3.48)	240 (3.40)

Table II

N.m.r. Spectra of Cyclobutenyl Carbonium Ions

Preparation	Chemical shifts	Relative intensities
II (X = Y = Cl) + $AgSbF_6$ in SO_2 (−60°)[a]	7.12, 7.60, 7.70	6:3:3
+ $AlCl_3$ in CH_2Cl_2[b]	7.09, 7.57, 7.72	6:3:3
+ H_2SO_4	7.48	
II (X = CH_3, Y = Br) + $AbSbF_6$ in SO_2 (−60°)	7.47, 7.68, 8.39	6:3:6
+ $AlCl_3$ in CH_2Cl_2[b]	7.36, 7.63, 8.40	6:3:6
+ H_2SO_4	7.50, 7.73, 8.46	6:3:6
II (X = H, Y = Cl) + $AlCl_3$ in CH_2Cl_2[b]	~5.5, 7.37, 7.63, 8.61	1:6:3:3
+ H_2SO_4	~5.6, 7.51, 7.73, 8.71	1:6:3:3
II (X = Y = I) + $AgSbF_6$ in SO_2 (−60°)	7.30, 7.59, 7.98	6:3:3
+ $AlCl_3$ in CH_2Cl_2 (−60°)	7.16, 7.40, 7.79	6:3:3

[a] Reference 2a. The peak positions given in the table are those reported plus 0.12, since in the present study the chemical shift of the tropylium hexafluoroantimonate used as the internal standard was found to be τ 0.67, not τ 0.55 as given by Mason.[4a] [b] Reference 2b.

The 1,2,3,4-tetramethyliodocyclobutenyl cation I (X = I), prepared by the reaction of the corresponding diiodide, II,[15] in methylene chloride with 1 mole of aluminum chloride at room temperature, exhibits an n.m.r. spectrum that consists of a single sharp line at τ 7.36. Cooling the solution broadens the line, and at −60° some resolution into separate components is observed. When this solution is quenched with tetra-*n*-butylammonium iodide, the starting diiodo compound II is recovered in 88% yield. If the reaction of the diiodide II in methylene chloride with aluminum chloride is conducted with 2 moles of the Lewis acid, the solution exhibits an n.m.r. spectrum that at 0° consists of a broad line at about τ 7.4, at +70° a sharp line at τ 7.37, and at −30 or −60° three lines, at τ 7.17, 7.42, and 7.81 of relative intensity 6.03:2.99:2.99.

If the solution is allowed to remain at room temperature for 1 day, the spectrum of the iodocyclobutenyl cation is replaced by the three-line spectrum characteristic of the 1,2,3,4-tetramethylchlorocyclobutenyl cation,[2] and a peak appears at τ 5.01, which might be due to the formation of CH_2ClI. The freshly prepared solutions of the iodocyclobutenyl cation in methylene chloride prepared from 1, 2, or 3 moles of aluminum chloride, whether at room temperature or at −65°, all exhibit similar infrared spectra, with intense absorption at 1460, 1430, 1370, 1178, and 1055 cm.^{-1}.[16] An attempt to determine the ultraviolet spectrum of the cation was frustrated by changes that occurred in the spectrum as it was repeatedly scanned.

If the diiodide II is treated at −70° in liquid sulfur dioxide solution with silver hexafluoroantimonate and filtered into an n.m.r. tube, which is then sealed, the spectrum at −62° exhibits three peaks, at τ 7.30, 7.59, and 7.98, approximately in the intensity ratio 2:1:1. However, other smaller peaks, attributed to impurities, mar the spectrum. After the sample is warmed to −10° the spectrum can still be observed, but warming to room temperature destroys the compound in solution, and recooling does not yield the characteristic three lines.

Discussion

The similarity of the three-line spectrum of the 4-iodo-1,2,3,4-tetramethylcyclobutenyl cation in methylene chloride at low temperatures with the spectra of the related chloro and bromo derivatives identifies the structure of the ion. The one-line spectrum observed in methylene chloride–aluminum chloride at high temperatures appears at a chemical shift which is the weighted average of the three lines observed in the cold, implying that the same material is present in solution, but that the iodine atom migrates around the ring rapidly with respect to n.m.r. frequencies, a hypothesis supported by the identity of the infrared spectra in the hot and cold samples. Failure to observe n.m.r. line fusion in the sulfur dioxide–silver hexafluoroantimonate preparation suggests that the migration does not occur intramolecularly, but more probably by equilibration of the cation I and iodide ion with II. When more aluminum chloride is employed in the experiment, the rate of this equilibration diminishes, and line fusion is observed only at higher temperatures.

From the data in Tables I and II, it can be seen that despite the difference in the solvents there is not great difference between the spectra. Since it is known that allylic carbonium ions are formed in concentrated sulfuric acid (from the measurement of freezing point depression constants[17]) and other ions in sulfur dioxide (from conductimetric and other measurements[18]),

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(15) (a) R. Riemenschneider and V. Becker, *Monatsh. Chem.*, **90**, 524 (1959); (b) R. Criegee, *Angew. Chem., Intern. Ed. Engl.*, **1**, 519 (1962).

(16) The other cyclobutenyl halides have similar spectra (*cf.* ref. 2b).

(17) N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 1499 (1962).

(18) N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963).

the implication of the similarities among the spectra of the cyclobutenyl cations in the three solvent systems is that aluminum chloride–methylene chloride also does more than form un-ionized complexes with the cyclobutenyl halides; it truly effects their ionization. The similarity of the spectra in the three solvents does not allow one to conclude the degree of ion pairing in methylene chloride[19] or in sulfur dioxide, for ionization and dissociation may not be easily distinguishable spectroscopically.[20] The observation is, however, useful to the study of the spectroscopic properties of carbonium ions since the manipulation is easier and the preparation is cleaner when the cations are made by procedure 1 than by either procedure 2 or 3.

Experimental Section

N.m.r. Spectra of Cyclobutenyl Cations in 96% Sulfuric Acid.—The cyclobutenyl halide and tetramethylammonium chloride, the internal standard, were dissolved in cold sulfuric acid by shaking the components vigorously in an n.m.r. tube. Spectra were determined on the Varian A-60 spectrometer and chemical shifts were assigned, assuming that the resonance of the tetramethylammonium ion appears at τ 6.90.[21] In sulfuric acid side reactions occur when $X = CH_3$ or H, and extraneous n.m.r. peaks are observed. The spectra were also determined in the absence of tetramethylammonium chloride.

N.m.r. Spectrum of Pentamethylcyclobutenyl Cation (I, $X = CH_3$) in Liquid Sulfur Dioxide.—A Pyrex tube divided by a sintered glass disk of medium porosity was attached on one side to an n.m.r. tube and on the other to a joint and was then connected to a vacuum manifold. To the open end of the tube there was added Celite to cover the disk and then anhydrous silver hexafluoroantimonate (344 mg, 0.92 mmole) and *ca.* 100 mg. of tropylium hexafluoroantimonate. The tube was evacuated on a high-vacuum manifold, and 102 mg. (0.34 mmole) of the pentamethylcyclobutenyl bromide (II, $X = CH_3$, $Y = Br$), *ca.* 1 ml. of liquid sulfur dioxide, and some tetramethylsilane (TMS) was distilled in. The tube was cooled (liquid N_2), evacuated (10^{-6} mm.), and sealed. The contents were shaken together for 5 min. while cooling in a bath at $-70°$ and then filtered at $-70°$ by inverting the tube. The n.m.r. tube was fused closed and separated from the remaining apparatus. The spectrum was determined on the Varian A-60 spectrometer while the sample was cooled to $-62°$. The chemical shifts of both the tropylium ion and the pentamethylcyclobutenyl cation were determined relative to the internal TMS with the aid of an audio side band oscillater. The tropylium cation resonance appeared at τ 0.67.

Preparation of 3,4-Diiodo-1,2,3,4-tetramethylcyclobutene.—In a 1-l. round-bottomed flask equipped with a stopcock on the bottom and fitted with a stirrer, reflux condenser, and flask for addition of solids, 3.55 g. (0.025 mole) of methyl iodide was added to 11.9 g. (0.490 mole) of Grignard magnesium in 500 ml. of dry ether. After 5 min. 119.0 g. (0.468 mole) of iodine was slowly added so that gentle reflux was maintained. After complete reaction, the colorless solution was rapidly stirred into 21.0 g. (0.117 mole) of 2,3-dichloro-1,2,3,4-tetramethylcyclobutene in 150 ml. of ether contained in a round-bottomed flask with reflux condenser. After stirring 15 min. the mixture was extracted twice with saturated brine containing some sodium thiosulfate (500 and 250 ml.), and the aqueous layers were extracted with 100 ml. of ether. The combined ether extract was dried over $MgSO_4$, filtered, and evaporated, leaving 36.0 g. (80%)[22] of 3,4-diiodo-1,2,3,4-tetramethylcyclobutene, m.p. 73–78°. Recrystallization from cold ($-15°$) acetone raised the melting point to 80–81.5° (lit.[15a] m.p. 80–82°): $\lambda_{max}^{CH_2Cl_2}$ 235 mμ (ϵ 14,700); $\lambda_{max}^{cyclohexane}$ 233 mμ (ϵ 15,400); n.m.r., two singlets at τ 7.66 and 8.42.

Preparation of the 4-Iodo-1,2,3,4-tetramethylcyclobutenyl Cation and Its Reaction with Iodide Ion.—To 0.370 g. (0.00275 mole) of anhydrous aluminum chloride at $-78°$, 1.0 g. (0.00275 mole) of 3,4-diiodo-1,2,3,4-tetramethylcyclobutene dissolved in 5 ml. of CH_2Cl_2 was rapidly added with stirring. The mixture was removed from the cooling bath until the reactants had dissolved, and it was then syringed into a stirred solution of 2.03 g. (0.0055 mole) of tetra-*n*-butylammonium iodide in 30 ml. of CH_2Cl_2 at $-78°$. After the sample had warmed to room temperature, the solvent was removed, leaving a brown oil. Solid impurities were removed by trituration with ether (30 ml.), filtration, and washed with two more 30-ml. portions of ether. Evaporation of the ether left 0.885 g. (88%) of 3,4-diiodo-1,2,3,4-tetramethylcyclobutene, m.p. 75–80°, which after recrystallization from acetone had a melting point and mixture melting point with an authentic sample of 80–81.5°. The n.m.r. and infrared spectra of the material were identical with those of the authentic sample.

Spectra of the 4-Iodo-1,2,3,4-tetramethylcyclobutenyl Cation in Methylene Chloride. A. N.m.r.—The n.m.r. samples were prepared at $-78°$ using 5 mmoles of the diiodide in 0.3 ml. of CH_2Cl_2 and varying amounts of $AlCl_3$ in the way described previously. The n.m.r. spectra were determined at 60 Mc. using the Varian A-60 instrument and the methylene chloride solvent was used as the internal standard.

B. Infrared.—Methylene chloride solutions containing about 8% of the diiodide were treated with $AlCl_3$ as in A above, and spectra were determined in Irtran cells using a Perkin-Elmer 421 spectrometer.

N.m.r. Spectrum of the 4-Iodo-1,2,3,4-tetramethylcyclobutenyl Cation (I, X = I) in Liquid Sulfur Dioxide.—The technique was identical with that used above for I ($X = CH_3$) except that TMS was absent and 1.024 g. (2.7 mmoles) of silver hexafluoroantimonate and 362 mg. (1.0 mmole) of II ($X = Y = I$) were used. The spectrum was the same at -60 and 10°. It consisted of the three main lines and some small extraneous ones. On warming to 10° the sample decomposed; the lines broadened, decreased in intensity, and disappeared, and they did not reappear when the sample was cooled to $-60°$.

Ultraviolet Spectra of the Cyclobutenyl Cation in 96% Sulfuric Acid.—The cyclobutenyl halides were dissolved in cold concentrated H_2SO_4, and the spectra were determined in 0.1-mm. quartz cells using the Cary Model 14 spectrometer.

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[19] See ref. 4d and K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Am. Chem. Soc.*, **84**, 120 (1962).

[20] Reference 18, pp. 90–93.

[21] N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963); D. G. Farnum, M. A. T. Heybey, and B. Webster, *ibid.*, **86**, 673 (1964).

[22] This is a much higher yield than was obtained using sodium iodide in acetone.[15a] Another preparation was recently reported: R. Criegee, H. Kristinsson, D. Seebach, and F. Zanker, *Chem. Ber.*, **98**, 2331 (1965).