Cyclopropenyl Cation. Synthesis and Characterization[1a,2]

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Abstract: Three salts of cyclopropenyl cation (I) have been prepared from 3-chlorocyclopropene. The nmr spectrum of the cation is consistent with expectations, and the infrared spectrum has only four bands which have been assigned to the four allowed modes for a molecule with D_{3h} symmetry. The pK_{R^+} of I was determined to be -7.4 ± 0.1 by an nmr method. Comparison with an estimated pK_{R^+} for allyl cation shows that I is 18 kcal/mole more stabilized. This compares well with a gas-phase value of 17–18 kcal/mole determined from appearance potentials.

Salts of the cyclopropenyl cation (I) are of interest since I is the simplest possible aromatic system, with two delocalized π electrons. The first derivative of this system, triphenylcyclopropenyl cation (II), was prepared[3] in 1957. Since that time, diphenyl,[4] substituted triaryl,[5] alkyl,[6] and halo[5b,7] derivatives of I have been described.

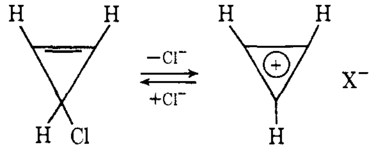
Their properties, in particular their high thermodynamic stabilities in equilibria with the corresponding alcohols, confirm the aromatic character of the cyclopropenyl cation system. Furthermore, by extrapolation many of the properties of the parent cation I could be deduced. Thus, for instance, an extrapolation[6a] of the pK_{R^+}'s of tripropyl- and dipropylcyclopropenyl cation suggested a pK_{R^+} of -6.3 for cation I. However, direct measurements on the parent cation were obviously of greater interest and reliability.

As we reported in a preliminary communication,[8] it is possible to prepare crystalline salts of I from 3-chlorocyclopropene.[2] At the same time, Farnum reported[9] the observation of cation I in solution, obtained by another approach. In this paper, we detail our studies on the salts of I prepared by our[8] procedure.

Results and Discussion

Simple mixing of 3-chlorocyclopropene with antimony pentachloride, aluminum trichloride, or silver fluoroborate as described in the Experimental Section led to the salts of cyclopropenyl cation Ia, Ib, and Ic. Phosphorus pentachloride was too weak a Lewis acid to produce the cation under these conditions. The hexachloroantimonate (Ia) was produced in quantitative yield and analytical purity as a clean white solid, stable for several days at room temperature and indefinitely at $-20°$. The tetrachloroaluminate (Ib) was also isolated as a white solid, but the tetrafluoroborate (Ic) was handled only in solution.

The spectroscopic data (*vide infra*) overwhelmingly confirm the structure assignments. Extra chemical evidence was obtained by quenching Ia with chloride ion to regenerate 3-chlorocyclopropene. The resulting 3-chlorocyclopropene was identified by nmr spectroscopy and by conversion to adducts with tetracyclone (**XIX** and **XX** of ref 2) in 47% over-all yield, indicating 72% efficiency of reconversion to 3-chlorocyclopropene.



Ia, $X = SbCl_6$
b, $X = AlCl_4$
c, $X = BF_4$

Similarly, Ia abstracted chloride from chlorotriphenylmethane to afford a 94% yield of 3-chlorocyclopropene, and a residue with λ_{max} at 403 and 432 nm characteristic of trityl cation.

Spectra. The nmr spectrum of I in nitromethane, acetonitrile, or sulfur dioxide showed a sharp singlet in the region of δ 11.1–11.2. This position is as expected from what is known of other cyclopropenyl cations; we have discussed the contributing effects elsewhere.[6a] The ^{13}C satellites are also singlets with half-width less than 0.5 Hz, and $J_{^{13}C-H}$ is 265 ± 1 Hz.

Although this very large coupling constant may reflect factors[10] in addition to the amount of s character in the carbon hybrid orbital of the C–H bond, by the standard relationship[11] between $J_{^{13}C-H}$ and s character this corresponds to 53% s in the carbon orbital. Olah has shown[12] that the positive charge *per se* does not affect the relation; ^{13}C–H coupling constants for unstrained sp^2 hybridized carbonium ions are similar to the ^{13}C–H coupling constants of ordinary olefins. If the C–H bond does use an approximately sp hybrid orbital, as our coupling constant suggests, the bonding in I can be described quite simply. Each carbon uses an sp orbital to hydrogen, two sp^3 orbitals in the plane for the bent single bonds, and a p orbital for the π system (Figure 1).

The fact that the ^{13}C satellites are sharp singlets indicates a very small (≤ 0.25 Hz) H–H coupling constant. This small ring effect, leading to small vicinal coupling

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[1] (a) Support of this work by the National Institutes of Health and intellectual and experimental contributions by Mr. Gordon Ryan are gratefully acknowledged. (b) NIH Predoctoral Fellow, 1966–1969.

[2] *Cf.* R. Breslow, G. Ryan, and J. T. Groves, *J. Am. Chem. Soc.*, **92**, 988 (1970).

[3] R. Breslow, *ibid.*, **79**, 5318 (1957).

[4] (a) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961); (b) D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

[5] (a) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961); (b) R. West, *Accounts Chem. Res.*, in press.

[6] (a) R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962); (b) *cf.* G. L. Closs, "Advances in Alicyclic Chemistry," Vol. I, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N. Y., 1966, p 102 *ff*, for a review.

[7] S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964).

[8] R. Breslow, J. T. Groves, and G. Ryan, *ibid.*, **89**, 5048 (1967).

[9] G. Farnum, G. Mehta, and R. S. Silberman, *ibid.*, **89**, 5049 (1967).

[10] (a) G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **86**, 3574 (1964); (b) D. Grant and W. Litchman, *ibid.*, **87**, 3994 (1965); (c) K. B. Wiberg, *Tetrahedron*, **21**, 2749 (1965).

[11] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

[12] G. A. Olah and M. B. Comisaro, *J. Am. Chem. Soc.*, **88**, 1818 (1966).

Table I. Infrared Spectra (cm^{-1})

Principal component	$C_3H_3^+$	$C_3D_3^+$	$C_3Cl_3^+$	$C_3Br_3^+$	D_{3h}	D_{6h}	C_6H_6	C_6D_6
C–X stretch	3105	2327	735	575	E′	E_{1u}	3099	2293
C–C stretch	1276	1239	1312	1276	E′	E_{1u}	1485	1333
C–X in-plane bending	908	665	(200)		E′	E_{1u}	1037	813
C–X out-of-plane bending	736	542			A_2''	A_{2u}	671	503

constants, has been noted previously.[13] The $^{13}C–C–H$ coupling constant of 50 Hz is similar to the value, 50.8 Hz, for the ethynyl proton in propyne.[14]

The infrared spectrum of Ia shows only four bands at 3105, 1276, 908, and 736 cm^{-1} due to the cation, and one at 340 cm^{-1} for the anion. The same four bands were found in Ib and in solution spectra in which the Nujol region is clear. Exactly four infrared bands are expected for a species with D_{3h} symmetry, three E′ modes and one A_2'' mode.[15] Although coupling is strong, and none of these bands corresponds to a single vibration of only part of the molecule, one of the E′ bands involves mainly a C–H stretch, another mainly a C–C stretch, and a third mainly a C–H inplane bending. The A_2'' mode involves C–H out-of-plane bending. Accordingly, the assignments were made as in Table I.

The assignments were tested by the synthesis of Ia-d_3 which had infrared bands at 2327, 1239, 665, and 542 cm^{-1} (and 340 cm^{-1}). If the original bands had in fact corresponded to pure C–H or C–C vibrations, and our assignments were correct, a reduced mass calculation predicts that the bands of Ia-d_3 would come at 2280, 1276, 667, and 542 cm^{-1}. The actual values indicate appreciable mixing of C–H and C–C vibrations, at least in the two highest energy bands.

The infrared spectra of I and I-d_3 indicate a symmetrical, delocalized structure for the cation. They correlate well with the assignments by West[16] for the spectra of trichloro- and tribromocyclopropenyl cations to infrared modes of the D_{3h} group. These are also listed in Table I. In addition, since the D_{3h} point group is contained in the D_{6h} group, corresponding bands are expected in benzene and benzene-d_6. The gas-phase spectra of benzene and benzene-d_6 have four intense bands which correspond well in position and deuterium isotope effect to those in I and I-d_3. These are also included in Table I.

Stability. The thermodynamic quantity of greatest interest for a carbonium ion is its pK_{R^+}, the negative logarithm of the hydrogen ion activity required to establish a 1:1 equilibrium in water between the carbonium ion and the derived alcohol. This quantity, by

$$R^+ \underset{H_2O}{\overset{K}{\rightleftarrows}} ROH + H^+$$

$$pK_{R^+} = -\log K$$

referring the carbonium ion to its derived alcohol, corrects in large measure for miscellaneous strain factors which contribute to the over-all free energy of formation of the carbonium ion. However, the correction is by no means perfect, as we have discussed[6] elsewhere.

The pK_{R^+} for most carbonium ions has been determined by the use of electronic spectra, but I and alkylcyclopropenyl cations generally have uv transitions below 200 nm,[6] as expected from both naive and sophisticiated molecular orbital calculations. For the alkylcyclopropenyl cations, we and others[6] have used potentiometric titration to determine pK_{R^+}, but since for I the expected value is far below zero, this is not feasible here. Accordingly, we were forced to devise a technique using nmr spectroscopy.

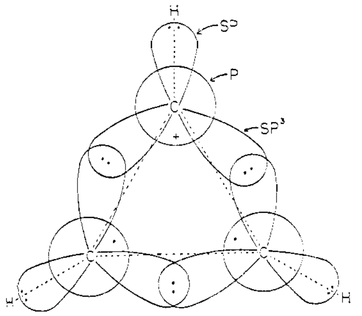
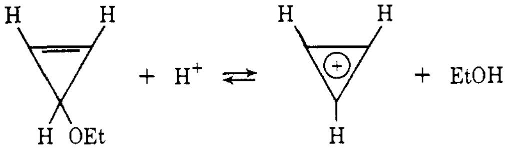


Figure 1. A hybridization scheme for cyclopropenyl cation which is consistent with the $^{13}C–H$ coupling constant.

When chlorocyclopropene is dissolved in ethanol it is converted to the ethyl ether, but in the presence of acid this compound has not the AB_2 ring pattern for such a structure, but instead a singlet at δ 6.58. The ether equilibrates rapidly with its congruent isomers, probably *via* the cation I. With very strong acid the solution has the singlet at δ 11.08 of cation I, as the equilibrium is displaced to the right. With intermediate acid strengths a singlet is still seen, but at intermediate chemical shifts. The nmr signal involves an averaging of the set of congruent isomers of ethoxycyclopropene with each other and also with the cation. A signal at δ 8.85, halfway between δ 6.6 and δ 11.1, should correspond to a 1:1 mixture of ether and carbonium ion if the internal standard correctly mirrors nmr medium effects. The data are presented in Table II and plotted in Figure 2.



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The medium is of course not the standard one for pK_{R^+} determinations, so it was calibrated with two carbonium ions of known pK_{R^+} using the usual uv

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(13) (a) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963); (b) O. L. Chapman, *ibid.*, **85**, 1014 (1963); (c) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2017 (1963).

(14) G. J. Karabatsos *J. Phys. Chem.*, **65**, 1657 (1961).

(15) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, New York, N. Y., 1956, pp 91 ff, 363 ff.

(16) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2478 (1966).

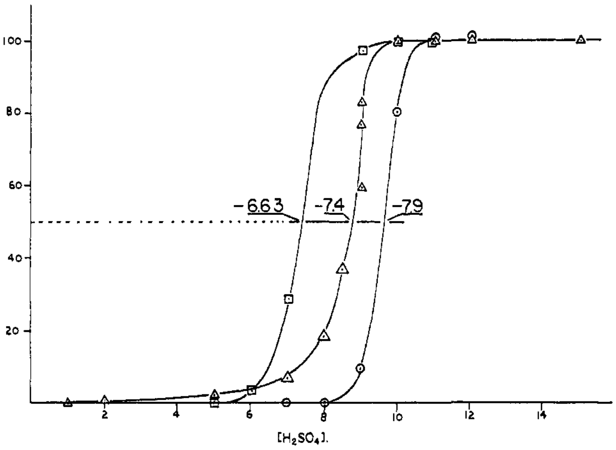

Figure 2. Titration curves for cyclopropenyl, triphenylmethyl, and *p*-methoxybenzhydryl cations: ⊡, $(C_6H_5)_3C^+$; ⊙, $H_3COC_6H_4C^+HC_6H_5$; △, *c* – $C_3H_3^+$.

technique.[17] These are also included in Figure 2. Since we have so far been unable to isolate and handle 3-ethoxycyclopropene, it was formed *in situ*, as described, from 3-chlorocyclopropene. Accordingly, the medium contains HCl, and this was also added in the calibrating experiments. It is apparent from Figure 2 that all three titrations curves are reasonably parallel in this system. Interpolation between the two known pK_{R^+}'s indicates –7.4 ± 0.1 for the pK_{R^+} of I. The error relates to the precision of measurement, and the actual uncertainty limits are somewhat wider.

Table II. Nmr Shifts of 3-Chlorocyclopropene in 95% Ethanol as a Function of Sulfuric Acid Concentration

$[H_2SO_4]$, *M*	δ_{obsd}	% C^+
17.0	11.1	100
12.0	11.08	100
11.0	11.08	100
10.0	11.1	100
9.0	10.3	82.7
9.0	10.04	76.9
9.0	9.26	59.6
8.5	8.32	39.5
8.0	7.40	18.2
8.0	7.0	9.3
7.0	7.0	9.3
7.0	6.9	7.1
5.0	6.68	2.2
2.0	6.60	0.05
1.0	6.58	0.0

This value of the pK_{R^+} is somewhat lower than the –6.3 extrapolated[6] from tripropylcyclopropenyl cation (pK_{R^+} = +7.2) and dipropylcyclopropenyl cation (pK_{R^+} = +2.7). Apparently these alkyl stabilizing effects are not quite additive, and the third propyl substituent is proportionally less stabilizing than the first two. It is also interesting that Wiberg[18] had reported hydride abstraction from cyclopropene by triphenylmethyl cation, although our p*K*'s and direct comparisons show that simple hydride transfer to produce I is contrathermodynamic. In his experiment the cyclopropene was converted to polymeric material. It may be that hydride transfer, with a somewhat better acceptor, could still prove a convenient synthesis of I from cyclopropene; the present synthesis of I is satisfactory, but tedious.

We have already discussed[6] in detail the factors, including aromaticity, which contribute to such a pK_{R^+}. It is interesting, however, to compare it with the estimated pK_{R^+} for allyl cation, the open-chain analog of I. Deno[17] has determined a pK_{R^+} of –19 for benzyl cation, and solvolysis data[19] in which allyl cation forms ten or so times more slowly than benzyl cation suggests a pK_{R^+} for allyl cation of approximately –20. Thus allyl cation is about 13 p*K* units less stable than cyclopropenyl cation, corresponding to a $\Delta\Delta F°$ of 18 kcal/mole. This number reflects only part of the extra stabilization of I by aromatic resonance, since it has been diminished by strain-energy differences between the two.

A related comparison can be performed with gas-phase data. Wiberg and Lossing[20] have reported appearance potentials of *m*/*e* 39 from cyclopropene, and of *m*/*e* 41 from propylene. Although they handled the

$$\text{cyclopropene} + e \longrightarrow C_3H_3^+ + H\cdot + 2e \qquad 11.15\ \text{V}$$
$$\text{propylene} + e \longrightarrow C_3H_5^+ + H\cdot + 2e \qquad 11.95\ \text{V}$$

data somewhat differently, a direct substraction of these two expressions produces a form in which the appearance potential data reflect the same energy difference as did the pK_{R^+} comparison, with the usual assumption that appearance potentials are thermodynamic.

$$\text{cyclopropene} + C_3H_5^+ \rightleftharpoons C_3H_3^+ + \text{propylene}\ \Delta F° = -0.80\ \text{eV}$$

Professor Lossing has also kindly determined appearance potentials of the same ions from 3-chlorocyclopropene and allyl chloride. The difference, 0.84

$$\text{3-chlorocyclopropene} + e \longrightarrow C_3H_3^+ + Cl\cdot + 2e \qquad 10.20\ \text{V}$$
$$\text{allyl chloride} + e \longrightarrow C_3H_5^+ + Cl\cdot + 2e \qquad 11.04\ \text{V}$$

V, is similar to that for the hydrocarbons above. Since 0.84 eV is 19.3 kcal/mole, these gas-phase data also correspond well with the 18 kcal/mole difference in solution p*K*'s. All confirm the extra stabilization in cyclopropenyl cation, and the close correspondence between solution and gas-phase energy differences indicates that solvation energies of the two ions must be quite similar.

Experimental Section

Cyclopropenyl Hexachloroantimonate (Ia). Antimony pentachloride (0.32 g, 1.069 mmoles) was dissolved in 10 ml of dry methylene chloride. The mixture was flushed with argon and cooled to –77° in a Dry Ice–acetone bath. 3-Chlorocyclopropene (0.073 g, 0.098 mmole), prepared and purified as described in the accompanying paper, was dissolved in 0.5 ml of methylene chloride and added to the above solution dropwise with thorough mixing. A fine white precipitate separated immediately. The mixture was centrifuged in a jacketed tube packed with Dry Ice, and the pale yellow supernatant liquid carefully withdrawn and discarded. The centrifugate was repeatedly washed with methylene chloride, the last traces of solvent being removed with a stream of argon followed by vacuum drying at 0°. Cyclopropenyl hexachloroantimonate thus prepared was a fine white powder, stable for extended periods

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[17] (a) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); (b) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); (c) N. C. Deno, H. Berkheimer, W. Evans, and H. Peterson, *ibid.*, **81**, 2344 (1959); (d) N. C. Deno, P. T. Groves, J. J. Jaruzelski, and Myron N. Lugasch, *ibid.*, **82**, 4719 (1960).

[18] K. B. Wiberg, Abstracts, 131st National Meeting of the American Chemical Society, Miami Beach, Fla., April 7-12, 1957, p 39-O.

[19] R. E. Robertson and J. M. W. Scott, *J. Chem. Soc.*, 1596 (1961).

[20] K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 3980 (1962).

at room temperature under vacuum or argon but extremely sensitive to atmospheric moisture (0.366 g, 100%). The material was best stored in a sealed tube at −20°: nmr (CH_3NO_2)δ 11.20 (s) relative to CH_3NO_2, 4.33, $J_{^{13}C-H} = 265 \pm 1$ Hz, $J_{^{13}C-C-H} = 50$ Hz, $J_{H-H} \leq 0.25$ Hz; ir (Nujol mull) 3105, 1276, 908, 738, and 340 cm^{-1}. An analytical sample of Ia was prepared by precipitation in a manner identical with that described above. The precipitate was filtered on a fine fritted glass funnel and washed with dry methylene chloride at room temperature in a drybox. The sample was sealed in a glass tube and stored at −20°.

Anal. Calcd for $C_3H_3SbCl_6$: C, 9.66; H, 0.812. Found: C, 9.46; H, 0.897.

Cyclopropenyl Hexachloroantimonate-d_3. Cyclopropenyl hexachloroantimonate-d_3 was prepared from 3-chlorocyclopropene-d_3 and isolated in a manner identical in every respect with that used to prepare Ia: ir (Nujol mull), 2327, 1239, 665, 542, and 336 cm^{-1}.

Cyclopropenyl Tetrachloroaluminate (Ib). A 30-mg sample of 3-chlorocyclopropene was added to 0.2 cc of dry nitromethane saturated with aluminum trichloride at −50° under an argon atmosphere to afford a pale amber solution. The resulting mixture was diluted with 5 cc of methylene chloride to yield a fine white precipitate which was isolated by centrifugation in a manner similar to that used to isolate Ia: ir (Nujol mull) 3080, 1275, 915, and 742 cm^{-1}; nmr (CH_3NO_2) δ 11.20 (s).

Cyclopropenyl Tetrafluoroborate (Ic). Dry silver fluoroborate (0.805 g, 0.413 mmole) was dissolved in 0.5 cc of dry acetonitrile or SO_2 and the resulting solution was cooled to −50°. Upon the addition of 3-chlorocyclopropene (0.04 g, 0.413 mmole), silver chloride precipitated leaving a yellow supernatant solution. The nmr spectrum of this solution showed a strong sharp singlet at δ 11.04 indicative of I and a slightly broadened band of variable intensity at δ 9.2–9.4 which was attributed to unidentified decomposition products. All attempts to isolate solid Ic from this solution failed and this procedure was not further investigated.

Reaction of Ia with Tetraethylammonium Chloride. A sample of Ia (0.336 g, 0.980 mmole) was placed in a 25-cc round-bottomed flask at −77° under argon. Tetraethylammonium chloride (0.1823 g, 1.1 mmoles) was dissolved in 2 cc of nitromethane and added to the flask containing the cyclopropenyl hexachloroantimonate with stirring. The mixture was allowed to warm slowly to 0° as all volatile material was vacuum distilled into a trap cooled to −77°. The distillate was a clear liquid with the strong distinctive odor of 3-chlorocyclopropene. The nmr spectrum of this solution showed a strong slightly broadened singlet at δ 6.6, identical with the nmr spectrum of a nitromethane solution of authentic 3-chlorocyclopropene. The entire distillate was diluted with 2 cc of carbon tetrachloride and tetraphenylcyclopentadienone (0.377 g, 0.98 mmole) was added to the mixture with stirring. After 2 hr at room temperature, the solvent was removed under a vacuum and the residue was dissolved in chloroform-*d*. The nmr spectrum of the resulting solution showed, besides aryl hydrogen, absorbances indicative of a 1:1 mixture of the previously described[2] adducts XIX and XX: δ 3.35 (t, $J = 1.5$); 2.67 (d, $J = 1.5$ Hz); 3.0 (t, $J = 1.5$ Hz); 2.54 (d, $J = 1.5$ Hz). The ratio of aryl hydrogen (δ 6.8–7.5) to cyclopropyl hydrogen (δ 2.5–3.5) was found to be 43:3 (20:3, theoretical) indicating a 47% yield of the two 1:1 adducts XIX and XX, or a 72% quench of Ia. After removal of the chloroform-*d* under vacuum and trituration of the residue with ether, the white solid residue had an ir spectrum identical with that of authentic XX.

Reaction of Ia with Triphenylmethyl Chloride. Triphenylmethyl chloride (200 mg, 0.718 mmole) in 4 cc of nitromethane was added to a sample of Ia (0.0861, 0.23 mmole) in a 25-cc round-bottomed flask at −77°. A brilliant yellow developed immediately. The reaction mixture was allowed to warm to 0° while 2 cc of volatile material was vacuum distilled into a trap maintained at −77°. To the distillate was added tetraphenylcyclopentadienone (0.275 g, 0.718 mmole) and 2 cc of carbon tetrachloride. The resulting mixture was allowed to stand at room temperature for 2 hr. After removal of the solvent under vacuum, the entire reaction product was dissolved in chloroform-*d*. The nmr spectrum of the resulting solution showed a complex aryl absorption (δ 6.8–7.5) and cyclopropyl hydrogens of XIX and XX (δ 2.5–3.5) in a ratio of 283:16.8, indicating a yield of adducts of 61% based on Ia, or a quenching yield of 94%.

Cyclopropenyl Cation pK_{R^+} Determination. A titration curve was obtained by plotting the nmr absorbance chemical shift of acidic ethanol solutions of 3-chlorocyclopropene against the molarity of sulfuric acid in the same solution. A typical point was obtained as follows. Sulfuric acid (96.9%) was weighed into a 10-cc volumetric flask which was then made up to the mark with 95% ethanol. The acidic ethanol solution (0.2 cc) was placed in an nmr tube, flushed with argon, and cooled to −77°. 3-Chlorocyclopropene (10–15 mg) was added to the nmr tube with a fine capillary pipet and mixed thoroughly to give a homogeneous solution. With solutions of high acid concentration, it was necessary to allow the solution to warm to 0° to facilitate mixing. The resulting solution was allowed to warm to 40° in the nmr probe and the nmr spectrum was determined as quickly as possible. Absorbance positions were recorded relative to the methyl absorption of the ethanol, the highest field absorbance of the triplet taken to be δ 1.10. There appeared to be negligible solvent shifts of this resonance over the range of acidities, although a second triplet near δ 1 appeared at high acid concentrations. The above nmr titration curve was calibrated by titrating triphenylcarbinol (p$K_{R^+} = -6.63$) and *p*-methoxybenzhydrol (p$K_{R^+} = -7.9$) spectrophotometrically in a medium identical with that used above according to the method of Deno.[17] A typical point was obtained as follows. Sulfuric acid (96.9%) was weighed into a 10-cc volumetric flask and 1.0 cc of 2.75×10^{-4} *M* triphenylcarbinol in 95% ethanol stock solution was added and mixed with cooling at −20°. A 4-cc sample of 2.85 *M* hydrochloric acid in 95% ethanol was added and the flask was made up to the mark with more ethanol. The OD of the solution at 431 nm was determined as quickly as possible to avoid excessive loss of hydrogen chloride.

The pK_{R^+} of cyclopropenyl cation was determined by linear extrapolation from the half-ionization points of the calibration curves (Figure 2) to give a value of -7.4 ± 0.1.