

The Behavior of Chloroalkenes in Sulfur Trioxide-Sulfuric Acid and in Fluorosulfonic Acid

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Allyl cations in which the terminal carbons of the allyl system are completely substituted by methyl or chloro groups are stable in sulfur trioxide-sulfuric acid and in fluorosulfonic acid. Chloroalkenes which can directly ionize to such ions do so. Less substituted chloroalkenes generally produce carboxylic acid derivatives, in one case with a 1,2-chloro shift.

The literature contains a number of examples of the solvolysis of CCl_3 to COOH and CCl_2 to CO . These reactions generally take place in strong acid systems such as sulfuric acid or sulfur trioxide-sulfuric acid. In the past, the products have been isolated by addition of the reaction mixtures to water so that the actual species present in the strongly acidic reaction mixtures were not known. A representative collection of these systems have now been examined by proton magnetic resonance (pmr) spectroscopy.

The results were largely forecast by the following considerations. Electron impact studies of the reaction



have been used to estimate the stabilizing effect of R on the methyl cation.^{1,2} Relative to zero for R equal H, Cl and CH_3 stabilized RCH_2^+ to the extent of 32 and 36 kcal mole⁻¹. It is apparent that Cl has about the same effect as CH_3 when directly attached to the carbonium center.³

In simple allyl cations, the terminal carbons of the allyl system must be completely alkylated to achieve stability in oleum.⁴ This fact combined with the comparable stabilizing effect of Cl and CH_3 led to the expectation that to produce a stable chloro-substituted allyl cation, all four terminal positions must be substituted by chloro or alkyl groups. The results were in accord with this expectation, and stable allyl cations were observed only where loss of OH^- or Cl^- led to such a tetrasubstituted allyl cation. In less substituted cases, carboxylic acid derivatives were the ultimate product.

Chloro Allyl Cations.—Cations I-III (Chart I) were formed in over 95% yield in fluorosulfonic acid at -50° . Cation III was also stable in 34% oleum at 25° . The structures of the ions and their precursors are shown below. The numbers indicate the pmr band positions in parts per million (δ) downfield from tetramethylsilane using tetramethylammonium chloride (3.10 ppm) as an internal standard.

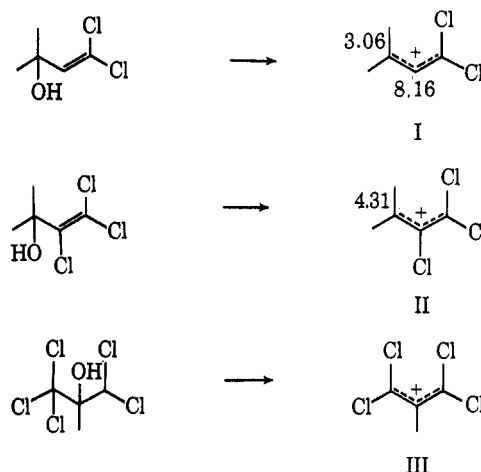
(1) Ph.D. Thesis of R. H. Martin, directed by F. W. Lampe and R. W. Taft, Jr., The Pennsylvania State University, 1965.

(2) R. W. Taft, Jr., R. H. Martin, and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 2490 (1965).

(3) This conclusion is in moderate accord with the results of solvolysis studies. The relative rates for $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, $\text{C}_6\text{H}_5\text{CHCl}_2$, and $\text{C}_6\text{H}_5\text{CCl}_3$ were 0.10:1:1:50 [J. Hine and D. E. Lee, *ibid.*, **73**, 22 (1951)]. The rates were measured in 50% aqueous acetone at 30° . The relative rates for $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, $\text{C}_6\text{H}_5\text{CHCl}_2$, and $\text{C}_6\text{H}_5\text{CCl}_3$ were 0.076:1:573 (A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 44). The first two rates were measured in ethanol and the last in 90% aqueous acetone, all at 25° and all referred to the rate for $(\text{CH}_3)_3\text{CCl}$. The chloro substituent increases the rate by factors of 10 and 50, whereas the factors for methyl are 13 and 573.

(4) N. 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).

CHART I



The 6:1 ratio of the band areas in the spectrum of I along with the band positions constituted the proof of structure. The band positions are quite similar to those of other allyl cations.⁵ There were no extraneous bands other than the broad band centering around -13 due to the strongly acidic hydrogens of the solvent.

The single band of II at 4.31 was somewhat more downfield than usual for allyl cations. The precursor, 2-methyl-3,4,4-trichloro-3-buten-2-ol, was recovered in 60% yield by adding the fluorosulfonic acid solution of II to ice and water and extracting with carbon tetrachloride. This recovery along with the pmr spectrum of II served as strong evidence for the assigned structure. The identity and purity of the recovered precursor was demonstrated by the pmr spectrum.

The single band of III at 2.05 is typical of a methyl group on C-2 of a cyclopentenyl cation.⁵ The structural assignment was further assured by a recovery experiment. Drowning of III in water would be expected to produce 2,3,3-trichloroisobutyric acid and this acid was isolated in 65% yield by adding a 34% oleum solution of III to ice and water.

Cations I-III are not the only chloro carbonium ions that have been directly observed. The pentachlorocyclopentadienyl cation,⁶ the trichlorocyclopropenyl cation,⁷ the α,α -dichlorobenzyl cation,⁸ and the penta-

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

(6) H. P. Fritz and L. Schafer, *J. Organometal. Chem.* (Amsterdam), **1**, 318 (1964).

(7) R. West, A. Sado, and S. W. Tobey, *J. Am. Chem. Soc.*, **88**, 2488 (1966).

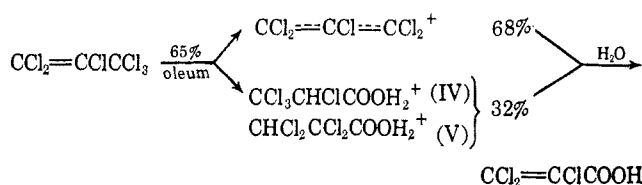
(8) R. J. Gillespie and E. A. Robinson, *ibid.*, **86**, 5676 (1964); N. Deno, N. Friedman, and J. Mockus, *ibid.*, **86**, 5676 (1964); E. A. Robinson and J. A. Ciruna, *ibid.*, **86**, 5677 (1964).

chloroallyl cation (discussed in the next section) have been reported.

Behavior of Hexachloropropene.—At the outset, it was expected that this olefin would ionize a Cl^- to directly produce the pentachloroallyl cation. This cation has been formed from hexachloropropene and aluminum chloride,^{9,10} antimony trichloride,¹⁰ and gallium trichloride.¹⁰ Furthermore, not only is the comparable 2,4-dimethylpentenyl cation completely stable in oleum,⁴ but the pentachloroallyl cation is structurally prevented from undergoing the usual destruction reaction which is alkylation of the equilibrating diene.⁵

The actual results were more complex than anticipated. Addition of hexachloropropene to 65% oleum produced two sharp pmr bands, one at 4.40 ppm and the other at 4.70 ppm. At the time of the first pmr measurement (2 min), the areas of the two bands were equal. With time, the 4.40 band increased at the expense of the 4.70 band so that the ratio is 75:25 after 1 hr and 78:22 after 2 days. The sum of the areas remained constant. It is attractive to assign these bands to the two isomeric protonated tetrachloropropionic acids (IV and V) since the band positions are comparable with those of the model species, $\text{ClCH}_2\text{COOH}_2^+$ (4.67)⁵ and CH_2Cl_2 (5.30), and drowning of the oleum solution in ice-water produced trichloroacrylic acid in 97% yield *via* loss of HCl.

However, there are two facts that show that IV and V are not the only species present. The solution exhibits a λ_{max} at 420 $\text{m}\mu$ with an extinction coefficient, based on added hexachloropropene, of 1.03×10^4 . This can in no way be attributed to IV or V or any of their derivatives. Secondly, the sum of the pmr band areas was equivalent to 0.32 mole of hydrogen atoms/mole of hexachloropropene added.¹¹ Thus 68% of the added hexachloropropene is in a form that does not contain an added H^+ . It can hardly be hexachloropropene, which would be insoluble.¹² Two candidates are protonated trichloroacrylic acid and pentachloroallyl cation, but only the latter could account for the absorption spectra. It is provisionally concluded that 68% of the hexachloropropene is converted to the pentachloroallyl cation and that this ion has λ_{max} at 420 $\text{m}\mu$ with an extinction coefficient of 1.58×10^4 . This ion is not in equilibrium with IV and V since IV and V change their ratios without changing their total amount. The reactions are summarized in the following sequence.



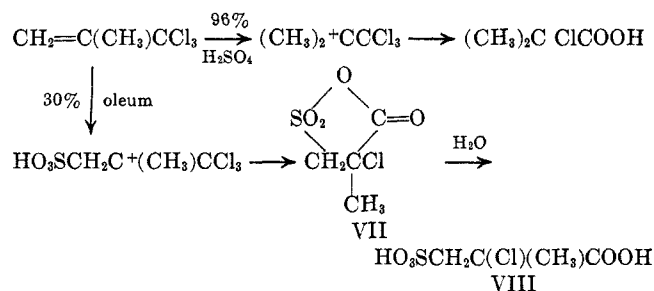
Hexachloropropene slowly reacts with 20% oleum to produce pmr bands at 4.40 and 4.70 and similar re-

sults are obtained with fluorosulfonic acid. The quantitative aspects of those systems were not investigated.

Behavior of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CX}_3$.—It has already been discovered that addition of 1,1,1-trichloro-2-methyl-2-propanol (chloreton) to 94% sulfuric acid produces 2-chloroisobutyric acid.¹³ This result has been confirmed. Addition of chloreton or its dehydration product (3,3,3-trichloro-2-methylpropene) to 96% sulfuric acid gave a single band at 1.88 ppm¹⁴ which is identical with that given by 2-chloroisobutyric acid. This reaction would appear to be a case of an internal 1,2-chlorine shift in a carbonium ion.

The products in 20–34% oleum are quite different. Either chloreton or its dehydration product produce a product with pmr bands at 2.10, 4.31, and 4.36 in the ratio 3:1:1. This spectrum is stable for days. Drowning of the solution in ice and water forms a water-soluble product with bands at 1.86 and 3.80 in the ratio 3:2. None of these spectra correspond to that of α -methylacrylic acid or its protonated or acyl cation form.¹⁵

A plausible interpretation is that in oleum, the products arose by sulfonation of VI whereas in 96% sulfuric acid they arose by protonation of VI. In either case a 1,2-chloro shift follows. Structure VII would



account for the pmr spectrum in oleum and structure VIII would account for the spectrum in water.

Support for the above interpretation arises from the behavior of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CBr}_3$ in 20–34% oleum. Although the product is different as shown by direct comparison of the pmr spectra, the pmr spectrum is very similar consisting of bands at 2.22, 4.37, and 4.33 in the ratios 3:1:1. It is attractive to assign this spectrum to the bromo analog of VII.

Although chloreton and brometone showed similar behavior in 20–34% oleum, their behavior in 96% sulfuric acid was strikingly different. The conversion of chloreton to 2-chloroisobutyric acid was discussed above. Addition of $(\text{CH}_3)_2\text{C}(\text{OH})\text{CBr}_3$, brometone, to 96% sulfuric acid produced protonated acetone as recognized by its single pmr band which varies from 2.94 in 96% H_2SO_4 to 3.04 in 20% oleum. However, its formation required perhaps 10 min for completion during which time gas (presumably CO) evolution occurred and a band at 2.12 (shown to be that of protonated 2-hydroxyisobutyric acid by direct compari-

(13) D. G. Kundiger, E. A. Ikenberry, E. B. W. Ovist, J. G. Patterson, and C. R. Dick, *J. Am. Chem. Soc.*, **78**, 6099 (1956); **82**, 2953 (1960).

(14) The position of this band is somewhat sensitive to acid concentration so that comparison to establish identity must be made in a single solution.

(15) α -Methylacrylic acid in CCl_4 exhibits pmr bands for the methyl group and the two vinyl hydrogens at 1.95, 5.65, and 6.26. The corresponding values for the protonated acid in 96% H_2SO_4 are 2.02, 6.30, and 6.59, and for the acyl cation (RCO^+) in 65% oleum, they are 2.50, 7.91, and 8.10. The band areas are in the ratios 3:1:1 in all three cases as required by the structure.

(9) S. Heilbronner, private communication.

(10) R. West and P. T. Kwitowski, *J. Am. Chem. Soc.*, **88**, 5280 (1966).

(11) Tetramethylammonium chloride was used to standardize areas.

(12) Hexachlorobutadiene and perchloropropene are insoluble. This demonstrates that the internal pressure of 65% oleum is large enough to prevent solubility of C_6 species [cf. N. Deno and H. E. Berkheimer, *J. Chem. Eng. Data*, **5**, 1 (1960)].

son) disappeared. The acetone does not arise by fragmentation of the initial alcohol to acetone plus bromoform because the 6.85 band of the latter was not present. Instead the acetone arises *via* 2-hydroxyisobutyric acid which undergoes a conventional Koch decarbonylation *via* the acyl cation.

1,1,1-Trifluoro-2-methyl-2-propanol gave a single pmr band at 1.53 ppm when dissolved in 96% sulfuric acid. The spectrum was stable for days and is presumably either the starting alcohol or its protonated form. In 34% oleum, a number of bands appeared which were not further examined.

Experimental Section

Pmr Spectra.—All spectra were measured on a 60-Mc instrument. The solvent was carbon tetrachloride unless otherwise specified. Band positions are expressed in δ , the chemical shift, in parts per million downfield from tetramethylsilane.

Preparation of Cation Precursors.—All such compounds were previously known and were either purchased or prepared by published directions. A brief outline of the method of preparation is given along with the literature reference and the pmr spectrum. The latter have not heretofore been reported.

4,4-Dichloro-2-methyl-3-buten-2-ol was prepared by acetylation of 1,1-dichloroethylene followed by treatment of the 4,4-dichloro-3-buten-2-one with CH_3MgBr .¹⁶

2-Methyl-3,4,4-trichloro-3-buten-2-ol was prepared from methyl trichloroacrylate and CH_3MgBr .¹⁷ The pmr spectrum exhibited bands at 1.62 and 2.90 in the required 6:1 ratio.

2-Methylpentachloro-2-propanol was prepared by chlorination of chloretone (2-methyl-1,1,1-trichloro-2-propanol) using sulfuric oxychloride in carbon tetrachloride with periodic addition of dibenzoyl peroxide at the reflux temperature.¹³ A 16% yield was obtained. No yield was reported in the original reference.

Chloretone is commercially available. The pmr spectrum consists of bands at 1.63 and 2.66 in the ratio 6:1. The dehydration product, 2-methyl-3,3,3-trichloropropene, was prepared as described.¹⁸

The bromo analog, 2-methyl-1,1,1-tribromo-2-propanol, has been prepared by the base-catalyzed condensation of acetone and bromoform.¹⁹ No yields or details of preparation were given although the compound was satisfactorily characterized by analyses. The melting point was given as 167–176°. We have prepared material of mp 163–165° using a procedure identical with that recommended for making chloretone²⁰ with the exception that bromoform was used in place of chloroform. As noted by Aldrich,¹⁹ the product is difficult to separate from unreacted bromoform and our yield of pure product was only 4%

after the purification by steam distillation and recrystallizations. The product of mp 163–165° does appear to be very pure as evidenced by a single band at 1.70 in the pmr spectrum and the melting point should now be regarded as 165° rather than the 167–176° reported earlier.

The fluoro analog, 2-methyl-1,1,1-trifluoro-2-propanol, was prepared from ethyl trifluoroacetate and CH_3MgBr as reported.²¹ The pmr spectrum consisted of bands at 1.38 and 3.23 in the required ratio of 6:1.

Recovery Experiments.—A solution of the 2-methyltetrachloroallyl cation (III) in oleum was added to ice. The mixture was extracted with ether and the ether solution extracted with 5% aqueous sodium hydroxide. The aqueous extract was acidified with hydrochloric acid and ether extracted, and the ether extract was dried with sodium sulfate. Distillation of this solution gave a 65% yield (based on the original 2-methyl-1,1,3,3-tetrachloro-2-propanol), bp 70–80° (14 mm), of 2,3,3-trichloroisobutyric acid. The identification was based on agreement with the reported boiling point²² and the pmr spectrum which showed single bands at 1.98, 6.23, and 11.38 in the ratio 3:1:1 due to the CH_3 , CHCl_2 , and COOH groups, respectively. The compound was reported to melt at 50°, but we were unable to crystallize our sample despite no indication of impurities in the pmr spectrum.

Addition of hexachloropropene to 65% oleum to produce a 10% solution and addition of this solution to ice gave a white precipitate of trichloroacrylic acid in 97% yield. The acid was identified by its melting point of 73–74° (lit.²³ mp 75°), a single pmr band at -12 , neutral equivalent of 179 (calcd 176), and the infrared spectrum, which consisted of a broad band at 2.9–3.3 μ (OH) and narrow bands at 5.85 (C=O), 6.50 (C=C), and 8.3 μ .

Several authors have reported the formation of trichloroacrylic acid by various sulfuric acid or nitric acid treatments of hexachloropropene.²⁴ The method described above seems preferable to the older ones, particularly in view of explosion hazards introduced by the heating involved in the older methods.²⁵

Registry No.—Sulfuric acid, 7664-93-9; fluorosulfonic acid, 7789-21-1; sulfur trioxide, 7446-11-9; 2,3,3-trichloroisobutyric acid, 10027-62-0; trichloroacrylic acid, 2257-35-4.

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(16) I. Heilbron, E. R. H. Jones, and M. Julia, *J. Chem. Soc.*, 1430 (1949).

(17) H. L. Schlichting and E. D. Weil, Belgium Patent 622,421; *Chem. Abstr.*, **59**, 11255 (1962).

(18) D. G. Kundiger, H. Pledger, and L. E. Ott, *J. Am. Chem. Soc.*, **77**, 6659 (1955).

(19) T. B. Aldrich, *ibid.*, **33**, 387 (1911).

(20) C. H. Weizman, E. Bergmann, and M. Sulzbacher, *ibid.*, **70**, 1189 (1948); R. Lombard and R. Boesch, *Bull. Soc. Chim. France*, 733 (1953).

(21) A. L. Henne, J. W. Shepard, and E. J. Young, *J. Am. Chem. Soc.*, **72**, 3577 (1950); A. L. Henne, T. Alderson, and M. S. Newman, *ibid.*, **67**, 918 (1945).

(22) J. Gottlieb, *J. Prakt. Chem.*, [2] **12**, 1 (1875).

(23) T. V. Zincke and A. Rohde, *Ann.*, **299**, 380 (1898).

(24) F. K. Beilstein, "Handerbuch der Organischen Chemie," Vol. II, Suppl 3, 1961, p 1247.

(25) F. Bergmann and L. Haskelberg, *J. Am. Chem. Soc.*, **63**, 1438 (1941).