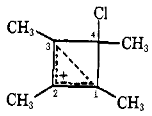
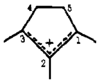
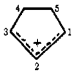
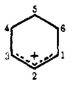
**Table II.** Cmr Parameters ($\delta$) of Cycloalkenyl Cations at 25.1 MHz in Superacid Solution at −70°

| 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 $SbF_3$ 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.** **$\Delta^3$-Cyclopentenone** and **$\Delta^2$-cyclopentenone** were prepared according to Brown's method,[24] having bp 32–33° (20 mm) and 50–53° (35 mm), respectively.

**$\Delta^3$-Cyclopentenol** and **$\Delta^2$-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 $\Delta^3$-cyclopentenone and $\Delta^2$-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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(67) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 2017 (1963).

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

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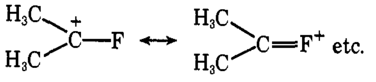
(1) Part CXXIX: G. A. Olah, K. Dunne, and D. P. Kelly, *J. Amer. Chem. Soc.*, in press.

(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.

(4) H. S. Gutowsky and D. W. McCall, *J. Phys. Chem.*, **57**, 481 (1953).

fluorine compounds.[7] On the other hand, when the nonbonded electron pairs of fluorine are capable of interacting with an empty orbital of the bonding atom, both inductive and resonance (back-donation) effects are playing an important part. The simplest example studied is the dimethylfluorocarbenium ion, $CH_3CFCH_3^+$ (**1**-F), the proton and fluorine-19 nmr spectra of which have been reported in our previous work.[8] The extensive deshielding of the fluorine resonance shift ($\phi$ −181.9) clearly indicates that 2p–2p interaction indeed plays an important role in the structure of the ion.



Our interest in the study of carbon-13 nmr parameters of halocarbenium ions was directed to an attempt to answer the following questions: (i) what is the degree of back-donation of other halogens compared to that of fluorine; (ii) is there a correlation of cmr shifts of halocarbenium ions and electronegativities of halogens; and (iii) what is the relationship between halocarbenium ion stability and halogen back-donation?

## Results and Discussion

We have undertaken a study of the cmr shifts by the indor method[9] of the two known series of halocarbenium ions, dimethylhalocarbenium ions, $CH_3CX^+CH_3$ (**1**-X), and phenylmethylhalocarbenium ions, $C_6H_5CX^+CH_3$ (**2**X, where X = F, Cl, and Br). All these halocarbenium ions (**1**-X and **2**-X) are known and can be prepared from their corresponding dihalides by ionizing with $SbF_5$-$SO_2$ at −78°. The results of carbon-13 nmr studies of halocarbenium ions (**1**-X and **2**-X) are summarized in Table I. For comparison with

$$\begin{array}{lcl} CH_3CX_2CH_3 & \xrightarrow{SbF_5\text{-}SO_2,\ -78^\circ} & CH_3\overset{+}{C}XCH_3 + SbF_5X^- \\ X = F, Cl, Br & & \quad \mathbf{1\text{-}X} \end{array}$$

$$\begin{array}{lcl} C_6H_5CX_2CH_3 & \xrightarrow{SbF_5\text{-}SO_2,\ -78^\circ} & C_6H_5\overset{+}{C}XCH_3 + SbF_5X^- \\ X = F, Cl, Br & & \quad \mathbf{2\text{-}X} \end{array}$$

the cmr parameters of these ions, the $^{11}B$ and $^{31}P$ shifts of boron trihalides[5] and phosphorous trihalides[4] are also shown.

In the boron and phosphorus trihalides, the magnitude of the $^{11}B$ and $^{31}P$ chemical shift differences between the fluorides and chlorides is large and has been considered by Onak[5] and Gutowsky,[4] respectively, in terms of fluorine back-donation of the type

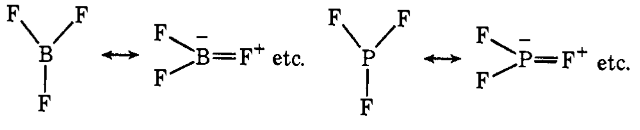


Table I. Comparison of Nmr ($^{13}C$, $^{11}B$, and $^{31}P$) Parameters of Halocarbenium Ions, Boron Trihalides, and Phosphorus Trihalides

| | F | Cl | Br | I |
|---|---|---|---|---|
| $CH_3CXCH_3^{+\,a}$ | −142.7 | −120.0 | −126.0 | |
| $C_6H_5CXCH_3^+$ | −39.5 | −42.4 | −46.3 | |
| $BX_3$ [b] | 66.0 | −29.2 | −22.7 | −23.3 |
| $PX_3$ [c] | 97 | −210 | −227 | −178 |

[a] The carbon shifts are those of carbenium carbon atoms and are referred to $CS_2$ in ppm. [b] Chemical shifts measured in ppm from boron trifluoride etherate external reference.[5] [c] Chemical shifts measured in ppm from 85% $H_3PO_4$ aqueous solution external reference.[4]

Table II. Comparison of Carbon-13 Chemical Shifts of Halocarbenium Ions with Those of Haloalkanes and Haloalkenes, and Their Differences ($\Delta\delta^{13}C$) in ppm[a]

| Model compd | $\delta^{13}C$ | Carbenium ions | $\delta^{13}C$ | $\Delta\delta^{13}C$ |
|---|---|---|---|---|
| $FH\overset{*}{C}{=}CH_2$ | 33.0 | $(CH_3)_2{}^+\overset{*}{C}F$ | −142.7 | 175.7 |
| $Cl\overset{*}{C}H{=}CH_2$ | 68.2[c] | $(CH_3)_2{}^+\overset{*}{C}Cl$ | −120.0 | 188.2 |
| $Br\overset{*}{C}H{=}CH_2$ | 78.7[c] | $(CH_3)_2{}^+\overset{*}{C}Br$ | −126.0 | 204.7 |
| $H\overset{*}{C}H{=}CH_2$ | 69.9 | $(CH_3)_2{}^+\overset{*}{C}H$ | −125.0[g] | 194.2 |
| $CH_3\overset{*}{C}H{=}CH_2$ | 55.4 | $(CH_3)_2{}^+\overset{*}{C}CH_3$ | −135.4[g] | 190.8 |
| $CH_3F\overset{*}{C}{=}CH_2$ | 32.6 | $(CH_3)_2{}^+\overset{*}{C}F$ | −142.7 | 175.3 |
| $CH_3Cl\overset{*}{C}{=}CH_2$ | 55.9 | $(CH_3)_2{}^+\overset{*}{C}Cl$ | −120.0 | 175.9 |
| $CH_3Br\overset{*}{C}{=}CH_2$ | 62.3 | $(CH_3)_2{}^+\overset{*}{C}Br$ | −126.0 | 188.3 |
| $CH_3H\overset{*}{C}{=}CH_2$ | 55.4 | $(CH_3)_2{}^+\overset{*}{C}H$ | −125.0[g] | 180.4 |
| $(CH_3)_2\overset{*}{C}{=}CH_2$ | 49.1 | $(CH_3)_2{}^+\overset{*}{C}CH_3$ | −135.4[g] | 184.5 |
| $F\overset{*}{C}H(CH_3)_2$ | 105.5 | $(CH_3)_2{}^+\overset{*}{C}F$ | −142.7 | 248.2 |
| $Cl\overset{*}{C}H(CH_3)_2$ | 138.9[d] | $(CH_3)_2{}^+\overset{*}{C}Cl$ | −120.0 | 258.9 |
| $Br\overset{*}{C}H(CH_3)_2$ | 148.6[d] | $(CH_3)_2{}^+\overset{*}{C}Br$ | −126.0 | 274.6 |
| $H\overset{*}{C}H(CH_3)_2$ | 178.2 | $(CH_3)_2{}^+\overset{*}{C}H$ | −125.0[g] | 303.2 |
| $CH_3\overset{*}{C}H(CH_3)_2$ | 169.1 | $(CH_3)_2{}^+\overset{*}{C}CH_3$ | −135.4[g] | 304.5 |
| $F\overset{*}{C}(CH_3)_3$ | 101.2 | $(CH_3)_2{}^+\overset{*}{C}F$ | −142.7 | 243.9 |
| $Cl\overset{*}{C}(CH_3)_3$ | 126.1[b,d] | $(CH_3)_2{}^+\overset{*}{C}F$ | −120.0 | 246.1 |
| $Br\overset{*}{C}(CH_3)_3$ | 132.1[d] | $(CH_3)_2{}^+\overset{*}{C}Br$ | −126.0 | 258.1 |
| $H\overset{*}{C}(CH_3)_3$ | 169.1[e] | $(CH_3)_2{}^+\overset{*}{C}H$ | −125.0[g] | 294.1 |
| $CH_3\overset{*}{C}(CH_3)_3$ | 165.9[f] | $(CH_3)_2{}^+\overset{*}{C}CH_3$ | −135.4[g] | 301.3 |

[a] Carbon shifts refer to $CS_2$. [b] This work, +125.0. [c] G. E. Maciel, *J. Phys. Chem.*, **69**, 1947 (1965). [d] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon, London, 1968, p 995. [e] D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964). [f] R. A. Friedel and H. L. Retcofsky, *ibid.*, **85**, 1300 (1963). [g] Reference 9.

The small differences in cmr shifts of dimethylhalocarbenium and phenylmethylhalocarbenium ions compared to the related boron and phosphorus trihalides are due to the fact that only a single halogen atom is involved here in such an interaction. For increased in-

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(5) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, paper presented to the Division of Inorganic Chemistry, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959.

(6) F. A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry," Interscience, London, 1966, p 256.

(7) (a) A. L. Henne and C. J. Fox, *J. Amer. Chem. Soc.*, **76**, 479 (1954); (b) J. M. Birchall and R. N. Haszeldine, *J. Chem. Soc.*, 3653 (1969).

(8) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **91**, 2955 (1969).

(9) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

sight into the question of halogen back-donation of halocarbenium ions, these data are not sufficiently informative, they are all very similar. Furthermore, even in the $BX_3$ and $PX_3$ series, back-donations of halogens other than fluorine were not taken into account in the evaluation of the nmr parameters.

A better approach to the problem is to compare the cmr shifts of halocarbenium ions, $CH_3CX^+CH_3$, to those of the corresponding halo olefins and haloalkanes. The results are summarized in Table II. The purpose of comparing cmr shift differences, $\Delta\delta^{13}C$, instead of cmr shifts is to eliminate the influence of the inductive effect of halogen atoms. Thus, only resonance effects are taken into account. The cmr shift differences, $\Delta\delta^{13}C$, increase with the decrease of the electronegativities of halogen, indicating back-donation is greater in fluorine than in chlorine and bromine atoms.

In addition, $\Delta\delta^{13}C$ between alkylcarbenium ions, such as *tert*-butyl and isopropyl cations, and their corresponding alkenes and alkanes are also taken into consideration. In comparison with haloalkenes and haloalkanes, these cmr shift differences, $\Delta\delta^{13}C$, are always greater than those with fluoro- and chlorocarbenium ions. On the other hand, the cmr shift differences, $\Delta\delta^{13}C$, with dimethylbromocarbenium ion, $CH_3CBrCH_3^+$, are greater than those with alkylcarbenium ions when comparison is made only to $sp^2$ hybridization in haloalkenes and smaller when comparison is made to $sp^2$–$sp^3$ hybridizations in haloalkanes. We prefer the former comparison since the carbon hybridization remains unchanged. Thus, back-donation of bromine in halocarbenium ions can be neglected.

A linear correlation of carbon-13 shift with electronegativities of some haloorganic compounds has been observed.[10] With the data available in the literature and those obtained in the present work, we are also able to correlate cmr shifts of halo olefins of the type $RXC{=}CH_2$ (lines A-1 and A-2 in Figure 1) and haloalkanes of the type $(CH_3)_2CRX$ (lines B-1 and B-2 in Figure 1) against electronegativity of the halogens. In all cases, a linear correlation is obtained. It is interesting to note that the cmr shift differences, $\Delta\delta^{13}C$, between homologous halo olefins and haloalkanes are about 70 ppm. Such a difference arises from a change in hybridization of the related carbon atoms. The good correlation between cmr shifts and electronegativities indicates that the deshielding of the carbon atom is mostly effected inductively. It is, however, due to the back-donation of halogen atoms that halocarbenium ions do not hold such relationships with electronegativity of the halogens (Figure 1, dotted lines).

The slopes of the plots of the cmr shifts against halogen electronegativities in haloalkanes and halo olefins are equal. Another straight line passing through the point of the dimethylbromocarbenium ion (**1-Br**) with identical slope can be obtained for halocarbenium ions by assuming the absence of halogen back-donation (see solid lines C-1 and C-2 in Figure 1). This is because as we have already demonstrated back-donation of bromine in **1**-Br is almost insignificant. Thus, the deviations between the assumed values in the absence of back-donation (solid lines C-1 and C-2) and the experimentally observed slope (dotted lines) are due to the differences in cmr shifts arising from back-donation of fluorine and chlorine atoms in the corresponding halocarbenium ions. Consequently, the back-donation of halogens in halocarbenium ions is in the order of F > Cl ≫ Br. Back-donation decreases as the atomic sizes of halogen increases. Obviously, such p–p interaction is more feasible in the case of fluorine because of the similar size of the charged carbon (empty p orbital) and fluorine atoms. As the size of halogen is increased, such interaction between the empty 2p orbital and halogen lone pair becomes unlikely, as observed in the case of $CH_3CBr^+CH_3$.

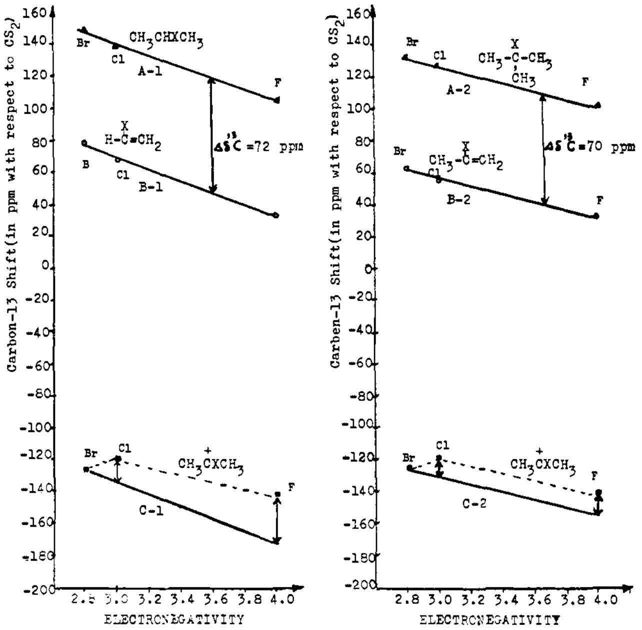
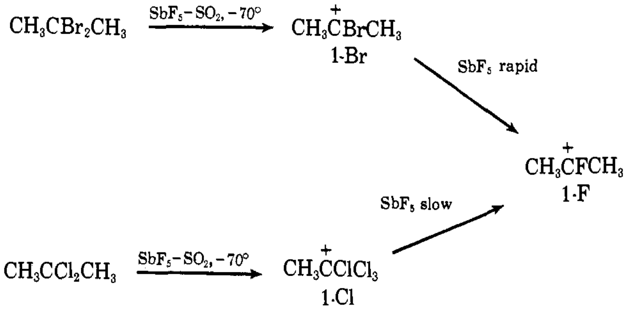


Figure 1. Relationship of carbon-13 nmr shifts to halogen electronegativities.

Back-donation of halogens is also related to the stability of halocarbenium ions. Olah and Comisarow[8] found that dimethylbromocarbenium ion, $CH_3CBr^+CH_3$, is converted to dimethylfluorocarbenium ion, $CH_3CF^+CH_3$, above −70°. The conversion of $CH_3CCl^+CH_3$ to $CH_3CF^+CH_3$ under similar conditions is much slower.

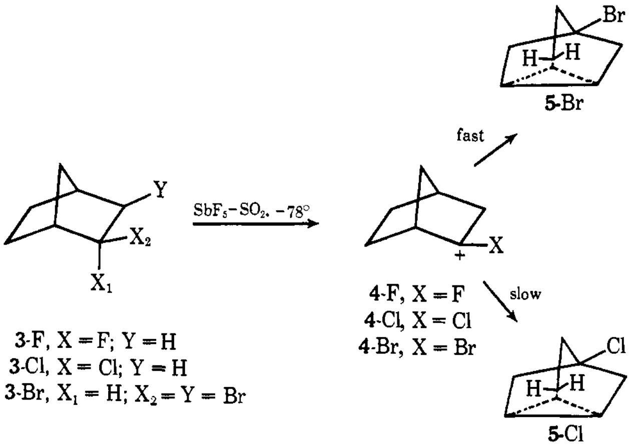


Attempted preparation of dimethyliodocarbenium ion, $CH_3CI^+CH_3$, from ionization of 2,2-diiodopropane in $SbF_5$–$SO_2$ solution was not successful. The pmr spectrum of this solution has a singlet at δ 3.1 which is almost identical with the precursor, $CH_3CI_2CH_3$ (δ 3.0), in $SO_2$. Furthermore, we also found that even isopropyl iodide was not ionized to isopropyl cation under similar conditions. Only the diisopropyliodonium ion, $[(CH_3)_2CH]_2I^+$, was obtained even when a large excess of $SbF_5$–$SO_2$ was used. The failure to prepare iso-

(10) See Table II, footnote *d*.

propyl cation from isopropyl iodide in $SbF_5$–$SO_2$ solution indicates to us that the preparation of dimethyliodocarbenium ion, $CH_3CICH_3^+$, may face the same fate. Consequently, comparison of rate in iodine–fluorine exchange reaction of dimethyliodocarbenium ion is not possible.

In addition to the halogen–fluorine exchange reactions, similar results were also obtained when 2,2-dihalonorbornanes (**3-X**) were ionized in $SbF_5$–$SO_2$ solution.[11] Indeed, 2-bromonorbornyl cation **4-Br** was never directly observed as it immediately rearranged to the 4-bromonorbornonium ion **5-Br** while the corresponding 2-chloronorbornyl cation **4-Cl** was found in a mixture with the 4-chloronorbornonium ion **5-Cl**. Ion **4-F** was found stable and did not rearrange to the 4-fluoronorbornonium ion under similar conditions. In comparison, we have also studied the ionization of 1,1-dihaloethanes in $SbF_5$–$SO_2ClF$ solution at −78°. The results show that the rate of halogen–fluorine exchange is faster in the case of 1,1-dibromoethane than in 1,1-dichloroethane.



## Experimental Section

**Materials.** 2,2-Difluoropropane was prepared according to the literature[12] or from methylacetylene saturated with hydrogen fluoride. 2,2-Dichloro- and 2,2-dibromopropanes were obtained from J. T. Baker and K and K Laboratories, respectively. 2,2-Diiodopropane was prepared according to Pross and Sternhell's method.[13] The preparation of $\alpha,\alpha$-dihaloethylbenzenes has been reported in our early work.[8] Isopropyl and *tert*-butyl fluorides were prepared from the reactions of silver fluoride with their corresponding alkyl bromides. 2-Fluoropropene was obtained from Peninsular Chemresearch Inc. 2-Chloro- and 2-bromopropenes were obtained from Columbia Organic Chemical Co.

**Nmr Spectra.** Proton and fluorine nmr spectra were obtained on a Varian Model A56/60A nmr spectrometer equipped with a variable-temperature probe. External TMS and $CFCl_3$ were used as references for $^1H$ and $^{19}F$ spectra, respectively. Carbon-13 nmr spectra were obtained on a Varian Model HA100 nmr spectrometer by irradiation of the 100-MHz proton spectrum with a swept 25.1-MHz frequency source (indor method). The detailed techniques employed have been described previously.[9] Modified instrumentation using a Monsanto 3300A digital frequency synthesizer as the 25.1-MHz frequency source was employed for all the measurements. $^{13}C$ shifts were computed with respect to TMS as a reference and converted to the carbon disulfide standard by adding 194.6 ppm.

**Preparation of the Ions.** Solutions of ions in antimony pentafluoride–sulfur dioxide solutions were prepared as described previously.[8]

**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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[11] G. A. Olah, P. R. Clifford, and C. L. Jeuell, *J. Amer. Chem. Soc.*, **92**, 5531 (1970).

[12] W. K. Hasek, W. C. Smith, and V. A. Englehardt, *ibid.*, **82**, 543 (1960).

[13] A. Pross and S. Sternhell, *Aust. J. Chem.*, **23**, 989 (1970).

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# Stable Carbocations. CXXXII.[1] Protonated Unsaturated Aldehydes and Ketones

**George A. Olah,* Yuval Halpern, Y. K. Mo, and Gao Liang**

*Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.* *Received August 30, 1971*

**Abstract:** Protonated $\alpha,\beta$-unsaturated aldehydes and ketones were studied in $HSO_3F$–$SbF_5$ (1:1, mol/mol)–$SO_2ClF$ solution. Proton and carbon-13 nmr studies indicate that the site of protonation is the carbonyl oxygen atom and the ions are of hydroxyallyl cation nature. The positive charge is shown to be distributed between the carbonyl oxygen atom and the carbon skeleton. Carbon-13 nmr measurements indicate that the charge density at C-3 is greater than at C-1 and that there is practically no positive charge at C-2. $\beta,\gamma$-Unsaturated ketones were found to isomerize to $\alpha,\beta$-unsaturated ketones in superacid. In the case of $\gamma,\delta$-unsaturated ketones, only the five-membered ring oxonium ions were observed.

Saturated carbonyl compounds[2] and $\alpha,\beta$-unsaturated carboxylic acids[3] were found to be protonated on oxygen by superacids. Cyclohexadienones were found to be oxygen protonated by concentrated sulfuric acid.[4] It is thus of interest to study the behavior of $\alpha,\beta$-unsaturated carbonyl compounds in superacid media. Olefins are known to protonate in superacids forming

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[1] Part CXXXI: G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Org. Chem.*, 37, 1169 (1972).

[2] For a review, see G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, 70, 561 (1970).

[3] G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 405 (1968), and references given therein.

[4] E. C. Friedrich, *J. Org. Chem.*, **33**, 413 (1968).