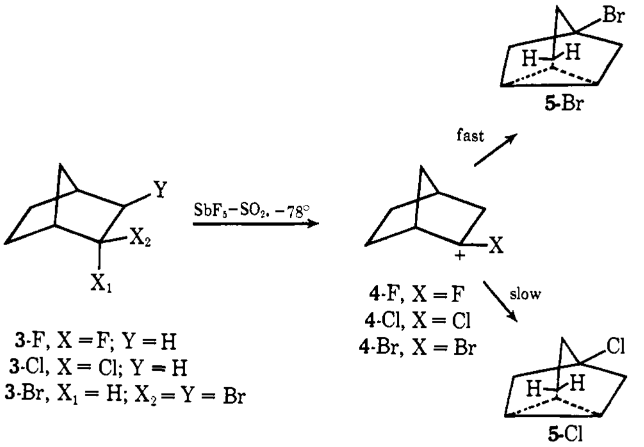
propyl cation from isopropyl iodide in SbF_5–SO_2 solution indicates to us that the preparation of dimethyliodocarbenium ion, $CH_3CICH_3^+$, may face the same fate. Consequently, comparison of rate in iodine–fluorine exchange reaction of dimethyliodocarbenium ion is not possible.

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.



3-F, X = F; Y = H
3-Cl, X = Cl; Y = H
3-Br, X_1 = H; X_2 = Y = Br

4-F, X = F
4-Cl, X = Cl
4-Br, X = Br

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 α,α-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).

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

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Abstract: Protonated α,β-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. β,γ-Unsaturated ketones were found to isomerize to α,β-unsaturated ketones in superacid. In the case of γ,δ-unsaturated ketones, only the five-membered ring oxonium ions were observed.

Saturated carbonyl compounds[2] and α,β-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 α,β-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.

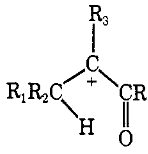
[4] E. C. Friedrich, *J. Org. Chem.*, **33**, 413 (1968).

Table I. Pmr (60 MHz) Parameters for Protonated α,β-Unsaturated Aldehydes and Ketones[a,b]

		R₁		R₂		R₃			
Ion	CH_3	H	CH_3	H	CH_3	H	CH_3	H′	H″
4a		7.60, d of t, $J = 9, 17$ (−1.20)		8.30, d, $J = 9$ (−1.90)		8.50, d, $J = 17$ (−2.10)		9.70, t, $J = 9$ (−0.20)	13.65, d, $J = 9$
4b			2.48 s (−0.68)	8.00, s (−1.90)		8.12, s (−1.77)		9.60, d, $J = 8$ (−0.10)	13.55, d, $J = 8$
4c		7.80, d of d, $J = 8, 14$ (−1.60)			3.00, d, $J = 7.5$ (−0.90)	9.30, d of q, $J = 7.5, 14$ (−2.30)		9.50, t, $J = 8$ (0.00)	12.50, d, $J = 8$
4d			2.40 s (−0.70)	8.90, q, $J = 7$ (−1.22)			2.88, d, $J = 7$ (−0.90)	9.35, d, $J = 8$ (+0.15)	12.55, d, $J = 8$
syn-**6a**	3.40 s (−1.17)	7.40, d of d, $J = 10, 16$ (−1.52)		7.74, d, $J = 10$ (−1.54)		8.11, d, $J = 16$ (−1.87)			13.63, s
anti-**6a**	3.40 s (−1.17)	7.44, d of d, $J = 10, 16$ (−1.56)		7.83, d, $J = 10$ (−1.63)		8.11, d, $J = 16$ (−1.87)			13.33, s
6b	3.40 s (−1.07)		2.50 s (−0.59)	8.56, s (−2.52)		8.87, s (−2.76)			13.40, s
6c	3.24 s (−1.10)	7.24, d, $J = 16$ (−1.24)			2.80, d, $J = 8$ (−0.90)	7.98, d of q, $J = 8, 16$ (−1.20)			12.93 (syn) 12.63 (anti)
6d	3.14 s (−1.13)	7.20 s (−1.20)			2.84, s (−1.08)		3.00, s (−0.99)		12.09, s
6e	3.28 s (−1.10)		2.38 s (−0.58)	8.91, q, $J = 7$ (−2.11)			2.73, d, $J = 7$ (−0.82)		12.76, s

[a] Chemical shifts in ppm (δ) from external TMS and coupling constants in Hz; s = singlet, d = doublet, t = triplet, and q = quartet.
[b] The differences in proton shifts between protonated and unprotonated α,β-unsaturated carbonyl compounds are shown in parentheses.

stable carbocation.[5] If α,β-unsaturated aldehydes and ketones were protonated on the double bond, the cation which would form would have the structure of **1** or **2**,



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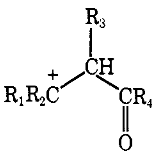

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depending on substituents. Our previous attempts to prepare these types of cations by treating α- or β-halo ketones or aldehydes with SbF_5–SO_2ClF were unsuccessful.

On the other hand, if protonation occurs on the carbonyl oxygen atom and the charge is delocalized over the carbon skeleton, the cations formed will have the structure of hydroxyallyl cations **4** and **6**. While the charge distribution in some allyl cations has been reported,[6] it was of interest to study hydroxyallyl systems. We have therefore undertaken, using both proton nmr (pmr) and carbon-13 nmr (cmr) techniques, a study of protonated α,β-unsaturated aldehydes and ketones.

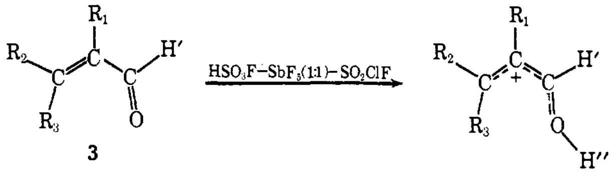
In addition, protonation of β,γ- and γ,δ-unsaturated ketones was also of interest and we also studied the interconversion of β,γ- and of γ,δ-unsaturated ketones to α,β-unsaturated ketones in superacids.

Results

A. Pmr Studies. Protonation of α,β-unsaturated aldehydes and ketones was investigated in HSO_3F–$SO_2ClF(SO_2)$ solution at −80°. Protonated species are generally characterized by deshielded proton shifts in the pmr spectra. The protons on oxygen are rapidly exchanging with the acidic solvent systems and therefore are not observed. Only in the case of protonated tiglaldehyde (**4d**) could the proton on oxygen be ob-

Scheme I

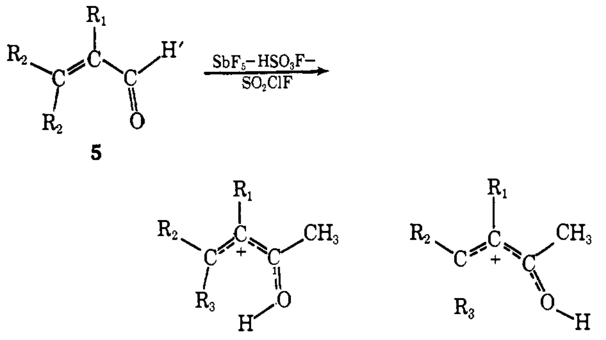
α,β-Unsaturated aliphatic aldehydes



3 **4**

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = R_3 = H$; $R_2 = CH_3$
d, $R_1 = R_3 = CH_3$; $R_2 = H$

α,β-Unsaturated aliphatic ketones



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syn-**6** *anti*-**6**

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_2 = CH_3$; $R_1 = R_3 = H$
d, $R_1 = R_3 = CH_3$; $R_2 = H$
e, $R_2 = R_3 = CH_3$; $R_1 = H$

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(5) G. A. Olah and Y. Halpern, *J. Org. Chem.*, **36**, 2354 (1971).
(6) G. A. Olah, P. R. Clifford, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 4219 (1972).

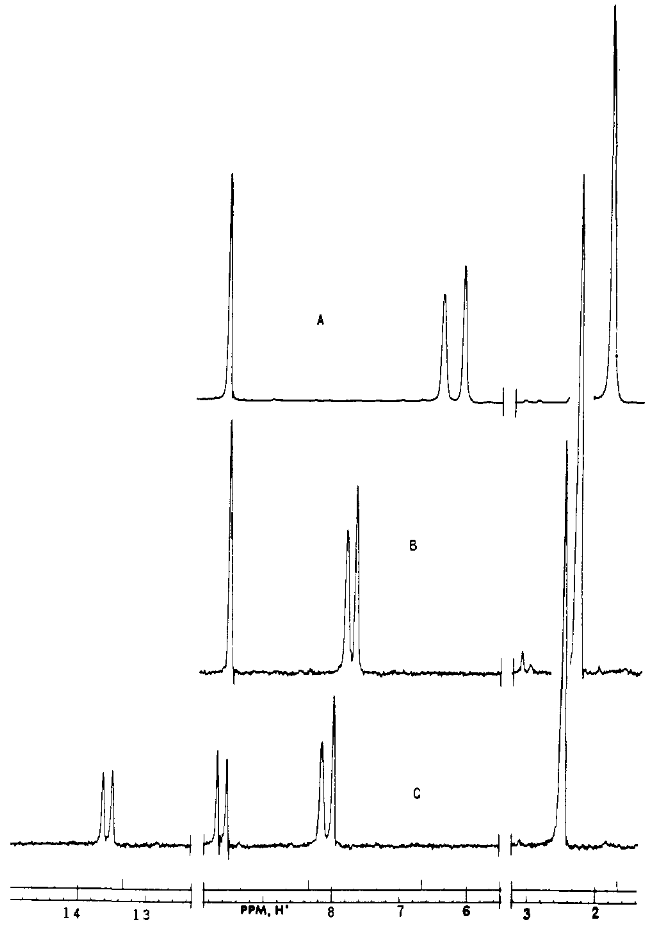


Figure 1. Pmr spectra of: A, 2-methylpropanal (**3b**), in SO_2ClF; B, protonated **3b** in HSO_3F-SO_3ClF; C, protonated **3b** in HSO_3F-SbF_5-SO_2ClF at −60°.

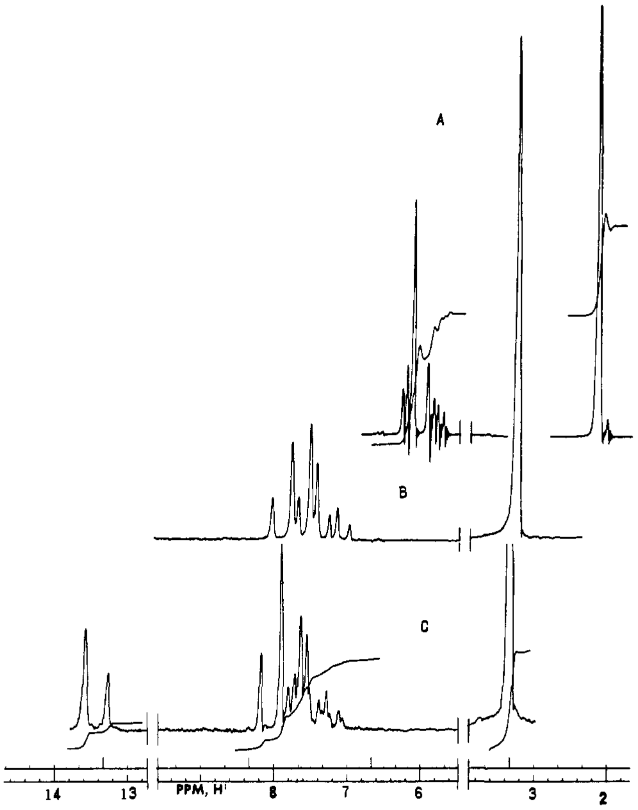


Figure 2. Pmr spectra of: A, methyl vinyl ketone (**5a**) in SO_2ClF; B, protonated methyl vinyl ketone in HSO_3F-SO_2ClF; C, protonated methyl vinyl ketone in HSO_3F-SbF_5-SO_2ClF (**6a**, syn and anti) at −60°.

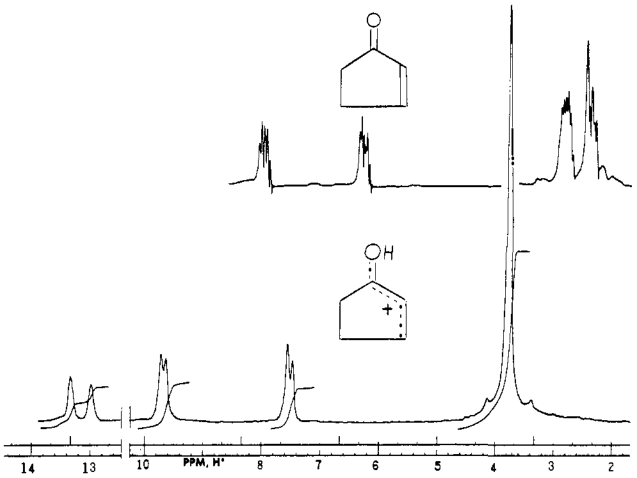


Figure 3. Pmr spectra of: A, 2-cyclopenten-1-one (**7a**) in SO_2ClF; B, protonated 2-cyclopenten-1-one in HSO_3F-SbF_5-SO_2ClF (syn and anti) at −60°.

served by cooling the solution to −110°. Addition of SbF_5-SO_2ClF to the HSO_3F-SO_2ClF solutions caused further deshielding of the proton absorptions and slowed the rate of the exchange process so that the proton on oxygen could be observed. The same results were obtained by treating α,β-unsaturated aldehydes and ketones directly with HSO_3F-SbF_5-SO_2ClF solution.

The protonated α,β-unsaturated aliphatic aldehydes and ketones studied are shown in Scheme I. The pmr data are summarized in Table I. Representative spectra are shown in Figures 1–3.

When R_2 and R_3 are both either hydrogen atoms or methyl groups (Scheme I), their assignment is made on the assumption that the cis group (R_3) is more deshielded than the trans group (R_2) due to proximity to the carbonyl group.[7] When $R_1 = R_2 = R_3 = H$ (**3a**, **4a**, **5a**, and **6a**) the assignment of R_2 and R_3 is based on the general experience that $J_{\mathrm{HH\ trans}}$ (J_{R_1,R_3}) is larger than $J_{\mathrm{HH\ cis}}$ (J_{R_1,R_2}).[8] In protonated acrolein (**4a**) the doublet at δ 8.50 has a coupling constant J_{R_1,R_3} = 17 Hz and the coupling constant for the higher field doublet at δ 8.30 is J_{R_1,R_2} = 9 Hz. From decoupling experiments in the case of **4a** it was found that the multiplet at δ 7.60 is in fact a doublet of triplets with $J_{\mathrm{H'R_1}} = J_{R_1,R_2}$ = 9 Hz and J_{R_1,R_3} = 17 Hz.

For protonated methyl vinyl ketone (**6a**) it was found that J_{R_1,R_3} = 16 Hz and J_{R_1,R_2} = 10 Hz. Decoupling experiments in the case of protonated crotonaldehyde (**4c**) showed that the multiplet at δ 7.80 is composed of two doublets with $J_{\mathrm{H'R_1}}$ = 8 Hz and J_{R_1,R_3} = 14 Hz; the multiplet at δ 9.30 is a doublet of quartets with J_{R_2,R_3} = 7.5 Hz and J_{R_1,R_3} = 14 Hz. In the protonated α,β-unsaturated ketone **6c**, J_{R_1,R_3} = 16 Hz and J_{R_2,R_3} = 8 Hz.

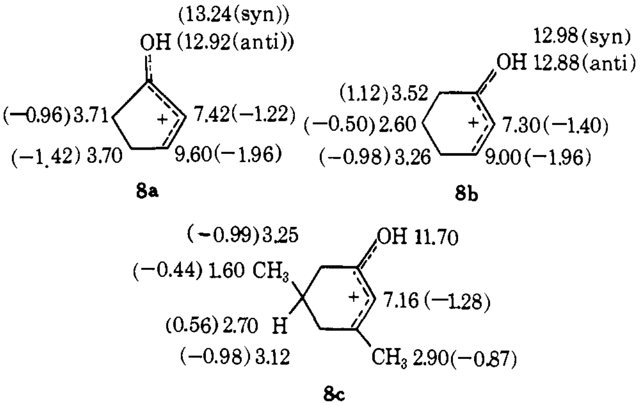
In addition, α,β-unsaturated alicyclic ketones were protonated in SbF_5-HSO_3F(1:1, mol/mol)-SO_2ClF.

[7] F. A. Bovey in "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 72–76.

[8] L. M. Jackman and S. Sternhell in "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, p 301.

2-Cyclopenten-1-one, 2-cyclohexen-1-one, and 3,5-dimethyl-2-cyclohexen-1-one (**7a**, **7b**, and **7c**, respectively) formed the corresponding protonated α,β-unsaturated alicyclic ketones **8** (Chart I).

Chart I[a]

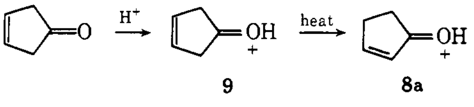


[a] The proton chemical shifts are shown in ppm from external TMS. In parentheses are shown the differences ($\Delta\delta$) in proton chemical shifts of protonated and parent compounds.

In all the protonated α,β-unsaturated aldehydes in HSO_3F–SbF_5–SO_2ClF, the protons on oxygen appear as a sharp doublet with the coupling constant J_{HH} = 8–9 Hz indicating that only the anti isomer is formed (Scheme I).[9] The doublets start to broaden without a change in the coupling constant only at temperatures above +30°, indicating that a rapid exchange process between the proton on oxygen and the acid occurs at these temperatures. α,β-Unsaturated ketones **5a**, **5c**, **7a**, and **7b** form, upon protonation, both the syn and anti isomers, each of which shows a deshielded pmr singlet for the proton on oxygen. On warming to −10°, the two singlets merge, indicating that rotation about the carbon–oxygen bond occurs.

When α,β-unsaturated aldehydes and ketones were treated with deuterated superacid, SbF_5–DSO_3F(1:4)–SO_2ClF, the pmr spectra indicated that deuteration on oxygen occurred but that no proton–deuterium exchange took place in the temperature range of −80 to −20°. In the cases of both **8b** and **8c**, no ring contraction to the protonated methylcyclopentenone derivatives was observed in the temperature range of −80 to −20°. Hogeveen[10] reported ring contraction occurs in some protonated cyclohexenones at higher temperatures.

Reflecting the greater stability of conjugated protonated α,β-unsaturated ketones, protonated Δ^3-cyclopentenone (**9**) undergoes thermal transformation to



the more stable protonated 2-cyclopenten-1-one (**8a**) in FSO_3H–SbF_5–SO_2ClF as well as in HF–SbF_5–SO_2ClF solutions. The protonated Δ^3-cyclopentenone was immediately formed when Δ^3-cyclopentenone was slowly added to FSO_3H–SbF_5–SO_2ClF at −96°. The same was also obtained when the ketone was protonated in HF–SbF_5–SO_2ClF at −85°. The pmr spectrum of **9** shows proton absorptions at δ 4.32 (s, 4 H), 6.55 (s, 2 H), and 15.08 (s, 1 H). Furthermore, when the solution of **9** in FSO_3H–SbF_5–SO_2ClF was warmed to −70°, isomerization started to take place slowly. Complete transformation to protonated 2-cyclopenten-1-one (**8a**) is observed when the temperature is raised to 20°. Figure 4 shows time and temperature change as protonated Δ^3-cyclopentenone is interconverted to protonated Δ^2-cyclopentenone.

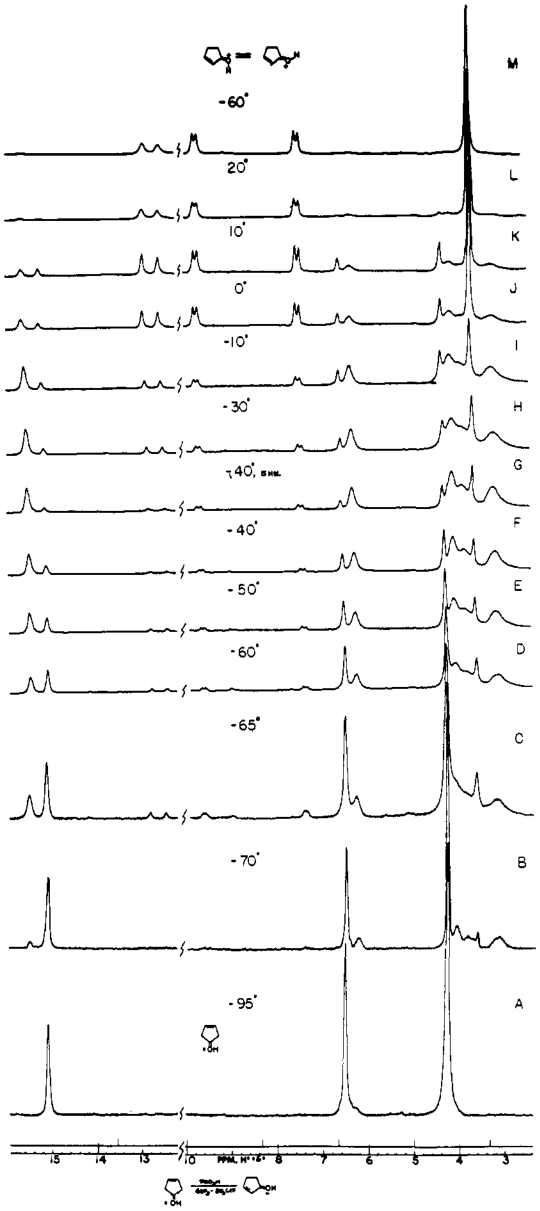
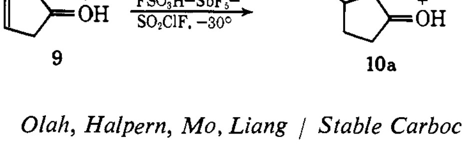


Figure 4. Pmr spectra of interconversion of Δ^3-cyclopentenone to Δ^2-cyclopentenone in SbF_5–HSO_3F–SO_2ClF.

Concerning the isomerization of protonated Δ^3-cyclopentenone (**9**) to protonated Δ^2-cyclopentenone (**8a**), an intermediate protonated ketone was observed as revealed in Figure 4. When a solution of **9** (in FSO_3H–SbF_5–SO_2ClF) was heated at −30° for 15 min, the intermediate was completely formed, with structure **10a** identified by its proton and fluorine spectra.



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(9) G. A. Olah, D. H. O'Brien, and M. Calin, *J. Amer. Chem. Soc.*, **89**, 3582 (1967).

(10) H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **87**, 1295 (1968).

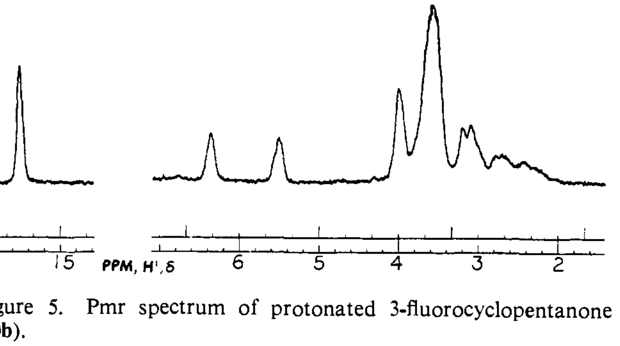
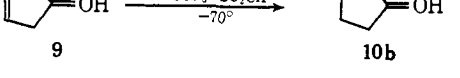


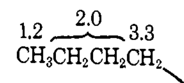
Figure 5. Pmr spectrum of protonated 3-fluorocyclopentanone (**10b**).

10a has a fluorine shift at ϕ 42.0. Similar reaction is also found in HF-SbF$_5$–SO$_2$ClF solution. When Δ^3-cyclopentenone was carefully protonated at −90°, the protonated Δ^3-cyclopentenone was immediately formed. However, it was not as stable as in FSO$_3$H–SbF$_5$–SO$_2$-ClF and was converted completely to the protonated 3-fluorocyclopentanone (**10b**) when the solution was allowed to warm to −70°. The isomerization temperature of **9** to **8a** in HF–SbF$_5$–SO$_2$ClF solution was also much lower than in FSO$_3$H–SbF$_5$–SO$_2$ClF. When the solution of **10b** was warmed to −60°, protonated 2-cyclopentenone was completely formed within 5 min. The structure of **10b** was also confirmed by its proton nmr spectrum (Figure 5) and its fluorine nmr spectrum shows the fluorine resonance at ϕ 135.0 (br d, J_{HF} = 52.0 Hz).

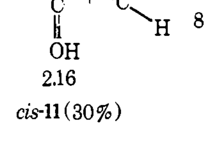


9 **10b**

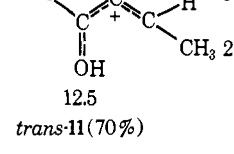
Similarly, 1-octen-4-one was found to be isomerized to both protonated cis (30%) and trans (70%) α,β-unsaturated ketones **11** in SbF$_5$–HSO$_3$F–SO$_2$ClF solution at −78°. The structures of ions **11** were confirmed by their pmr spectra. In addition, isomerization of alicyclic β,γ- and γ,δ-unsaturated ketones to the corresponding α,β-unsaturated ketones was found. When (2-cyclopenten-1-yl)acetone and (1-cyclopenten-1-yl)-acetone were dissolved in SbF$_5$–HSO$_3$F–SO$_2$ClF solution at −78°, parent protonated unsaturated ketones were formed immediately, yet both were unstable and rapidly transformed into their conjugated ketones, protonated cyclopentylideneacetone, **12**. The pmr spectra of both solutions were identical and consistent with the formation of a hydroxyallyl cation.



$$\mathrm{CH_3CH_2CH_2CH_2\underset{\underset{\displaystyle O}{\|}}{C}CH_2CH{=}CH_2} \xrightarrow[\mathrm{SO_2ClF}]{\mathrm{SbF_5-HSO_3F-}}$$



cis-**11** (30%)



trans-**11** (70%)

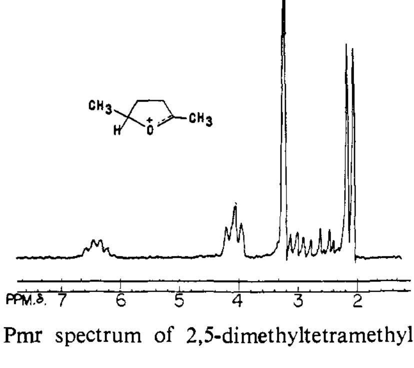


Figure 6. Pmr spectrum of 2,5-dimethyltetramethyleneoxonium ion **13**.

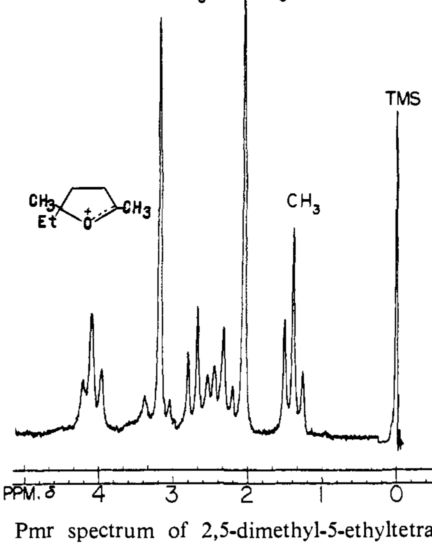
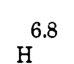
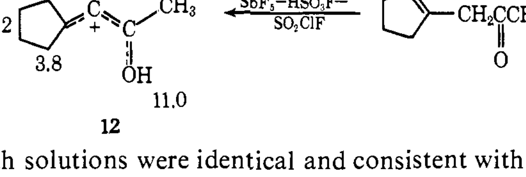


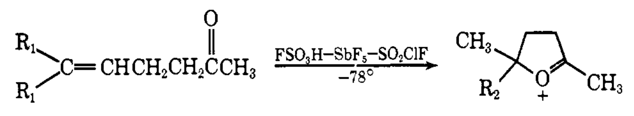
Figure 7. Pmr spectrum of 2,5-dimethyl-5-ethyltetramethyleneoxonium ion **14**.





12

On the other hand, aliphatic γ,δ-unsaturated ketones, such as 5-hexen-2-one and 6-methyl-5-hepten-2-one, reacted with SbF$_5$–HSO$_3$F–SO$_2$ClF solution at −78° to form cyclic oxonium ions **13** and **14**, respectively. Isomerization to α,β-unsaturated ketones was not found under these experimental conditions. The pmr spectra of ions **13** and **14** are shown in Figures 6 and 7, respectively.



$R_1 = H$ or CH_3

13, $R_2 = H$
14, $R_2 = CH_3CH_2$

B. Cmr Studies. The cmr spectra of protonated α,β-unsaturated aldehydes and ketones as well as their precursors were obtained in SO_2ClF solution at low temperature using the indor method.[11] The cmr parameters are summarized in Table II. Cmr data of some parent α,β-unsaturated aldehydes and ketones obtained at room temperature were previously reported by Stothers.[12,13] In these cases, our cmr data showed good agreement with the reported shifts. Cmr results for the protonated α,β-unsaturated aldehydes and ketones show both C_3 and C_1 are deshielded as compared with the parent compounds, while the chemical shifts of C_2 remain about the same. In all cases, the deshielding ($\Delta\delta^{13}C$)[14] caused by protonation is larger for C_3 than for C_1.

Table II. Cmr Data for Protonated α,β-Unsaturated Aldehydes and Ketones[a]

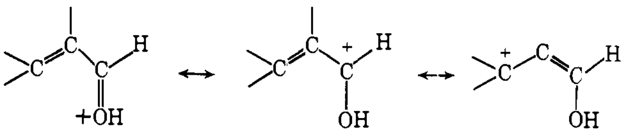
Ion	δC_1	δC_2	δC_3	$\Delta\delta C_1$	$\Delta\delta C_2$	$\Delta\delta C_3$	Charge density[b] at C_3
4a	−19.0	59.4	16.0	−19.4	+3.0	−40.8	0.22
4b	−19.1	47.3	18.5	−17.0	+0.6	−38.9	0.21
4c	−13.4	61.9	−8.6	−14.8	+1.9	−49.3	0.27
4d	−12.7	51.5	−5.6	−9.9	−1.1	−47.9	0.26
6a	−33.0	59.3	34.9	−28.6	+3.1	−30.2	0.17
6b	−31.7	51.3	33.7	−26.5	−3.0	−21.1	0.12
6c	−27.0	63.2	11.8	−23.3	+2.9	−38.2	0.21
6d	−29.0	56.2	7.1	−23.8	+1.9	−47.7	0.26
6e	−23.0	70.0	10.7	−19.6	+0.2	−29.3	0.16
8a	−38.3	59.6	10.3	−23.0	−0.3	−38.9	0.21
8b	−31.5	65.0	1.2	−27.2	+0.6	−41.8	0.23
8c	−19.1	70.1	14.9	−14.7	+2.3	−57.7	0.32

[a] Chemical shifts in ppm from CS_2. [b] Estimated charge density is based on a $\Delta(\delta^{13}C^+ - \delta^{13}C)$ of 180 ppm per unit charge at the carbon atom (see text).

Discussion

The highly deshielded proton absorption due to the proton on oxygen and the deshielding of the vinyl protons and those of the C_1 and C_3 carbons show that protonation of α,β-unsaturated aldehydes and ketones takes place on the carbonyl oxygen rather than at the double bond. The positive charge is distributed between the oxygen and the carbon skeleton of the protonated α,β-unsaturated aldehydes and ketones. Qualitatively, this charge distribution is indicated by the fact that the proton on oxygen does not appear in the pmr spectra at as low field as in protonated aliphatic aldehydes or ketones.[9,15] Rather the signal appears at a higher field, similar to the chemical shifts of the proton on oxygen in protonated α,β-unsaturated carboxylic acids.[3] From cmr data, particularly the deshielding values ($\Delta\delta^{13}C$) obtained by comparison of the protonated species with the parent compounds, a somewhat more quantitative conclusion can be obtained. In protonated α,β-unsaturated aldehydes and ketones where there is little or no charge in the carbon sp^2 hybridization (as shown by the constancy of the vinylic J_{HH} coupling constants before and after protonation), deshieldings in the cmr spectra can be related to positive charge density on carbon.[16] Since positive charge on an sp^2-hybridized carbenium atom generally causes a cmr deshielding of about 180 ppm[17] compared with the uncharged precursor having the same substituted groups, it is possible to calculate the positive charge densities on C_2 and C_3. $\Delta\delta^{13}C$ for C_2 in all the cases is no more than ±3 ppm and hence it bears little, if any, positive charge. On the other hand, C_3 exhibits significant deshielding upon protonation and, according to the relationship between $\Delta\delta^{13}C$ and charge density, there is, in all the protonated α,β-unsaturated aldehydes and ketones, a significant amount of positive charge on this carbon. The highest amount is in the case of **8c** and the lowest in **6b** (~0.3 and 0.1 unit of positive charge, respectively). The amounts of positive charge on C_3 depend on the substituents on the carbon skeleton. Even though there is no change in its hybridization, there is no direct correlation between $\Delta\delta^{13}C$ of C_1 and its charge density due to the fact that there is a change in the nature of substituents by the protonation process (from carbonylic oxygen to at least partial hydroxylic nature). Nevertheless, even the relative small deshielding of C_1 indicates that there is partial positive charge on this carbon. This positive charge can result either inductively from the protonated carbonylic oxygen atom **15** or from the hydroxylic resonance form **16**.

In α,β-unsaturated aldehydes, the aldehydic methine proton is strongly deshielded due to the anisotropy of the carbonyl group[7] and appears at low field (≈ δ 9.5) in the pmr spectrum. In the protonated forms, charge delocalization occurs through the resonance forms **16** and **17** in which there is no longer a carbonyl group. In a species such as **15** the methine proton would be highly deshielded (about δ 12–13 analogous to the shift of δ 13 for the methine proton in the isopropyl cation[19]) while in **17** it should appear much more shielded (approximately δ 6, compared with a vinylic proton). The observed chemical shift (δ 9.5) is the result of contribution



15 **16** **17**

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(11) A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).

(12) J. B. Stothers and L. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964).

(13) D. H. Marr and J. B. Stothers, *ibid.*, **43**, 596 (1965).

(14) $\Delta\delta^{13}C$ is the difference (in ppm) between the ^{13}C chemical shift of a carbon in the parent α,β-unsaturated aldehydes or ketones and the chemical shift of the same carbon in the protonated form.

(15) (a) G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 938 (1968); (b) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

(16) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *ibid.*, **91**, 1057 (1969), and references therein.

(17) The relationship between charge density and carbon shift of sp^2-hybridized carbon was evaluated to be 160 ppm/electron.[16,18a] Experimental results obtained in our laboratory show this value to be approximately 180 ppm/electron.[18b]

(18) (a) P. C. Lauterbur, *Tetrahedron Lett.*, 274 (1961); H. Spiesecke and W. G. Schneider, *ibid.*, 468 (1961); (b) G. A. Olah, Y. Halpern, and Y. K. Mo, unpublished results.

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

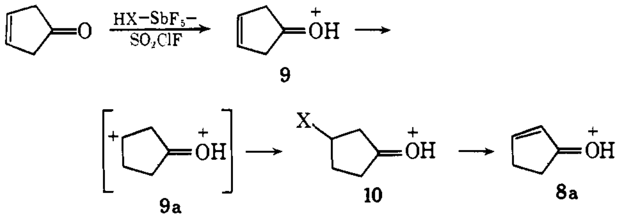
of the above resonance forms. These forms also explain the lack of positive charge on C_2.

Among protonated aldehydes previously investigated,[4] only acetaldehyde showed two observable stereoisomers (syn and anti) which differ in the position of the proton on oxygen relative to the methyl group. The higher homologs showed only the anti isomer. This observation was explained by the assumption that in these cases, the syn isomer is sterically unfavorable. Present results for protonated α,β-unsaturated aldehydes where only the anti isomer is observed are in good agreement with the above observations. The results are somewhat different for protonated α,β-unsaturated ketones. While in some cases both the syn and anti isomers are observed, in others only one isomer is detectable. Long-lived carbocations, observed in superacid media, generally are the thermodynamically most stable isomeric species. If the stability difference between the two isomers (due, for example, to steric effects caused by substituents on the carbon skeleton) is minor, both isomers are found. On the other hand, if there is a substantial energy difference between the isomers, only the most stable one is observed. The major factor which is responsible for the steric hindrance in protonated α,β-unsaturated ketones and aldehydes is the relative size of the substituents on the carbonyl carbon. In the case of α,β-unsaturated aldehydes, when one of the substituents is an aldehydic proton, one alkyl group on C_2 is sufficient to hinder the formation of the syn isomer. On the other hand, in the case of α,β-unsaturated aliphatic ketones, when one of the substituents on the carbonyl carbon is a methyl group it is necessary to have no hydrogen at all either on C_2 (**6d**) or C_3 (**6e**) in order to hinder the formation of the syn isomer. This is also in good agreement with the results obtained for both protonated α,β-unsaturated alicyclic ketones (**8**) and protonated saturated ketones.[15b]

The isomerization of the protonated 3-cyclopentenone to the protonated 2-cyclopentenone is an example of the interconversion between α,β- and β,γ-unsaturated ketones. Even though the isomerization between the α,β- and β,δ-unsaturated ketones has been known for a long time, no report has been made for such reactions in the presence of strong ionizing solvents, such as HF and FSO_3H.

The mechanism of the isomerization of the protonated Δ^3-cyclopentone (**9**) to the protonated Δ^2-cyclopentenone can be rationalized as shown in Scheme II.

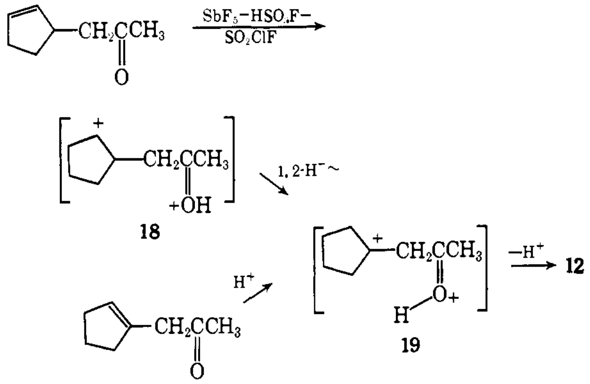
Scheme II



The initially formed protonated Δ^3-cyclopentenone must be further protonated to give the unstable transient dication **9a**, which was quickly trapped by either fluorosulfonate anion or fluoride ion before 1,2-hydride shift took place to form **10**. **10** could then eliminate HX (X = FSO_3 or F) to form **8a**. Attempts to isolate either **10a** or **10b** were unsuccessful. Under each experimental condition (a base such as pyridine was used), both **10a** and **10b** give off HX quickly and only Δ^2-cyclopentenone is isolated.

The facile transformation of the 3-cyclopentenone to 2-cyclopentenone under strong acid conditions might be controlled either by the strong affinity of the acid, addition to the double bond of the former ketone (β,γ-unsaturated ketone), or the suitable planar geometry in the latter required for the conjugation. The observation of the unstable intermediates **10a** and **10b** shows that the protic solvent does play an important role in the isomerization between unconjugated and conjugated cycloalkenones.

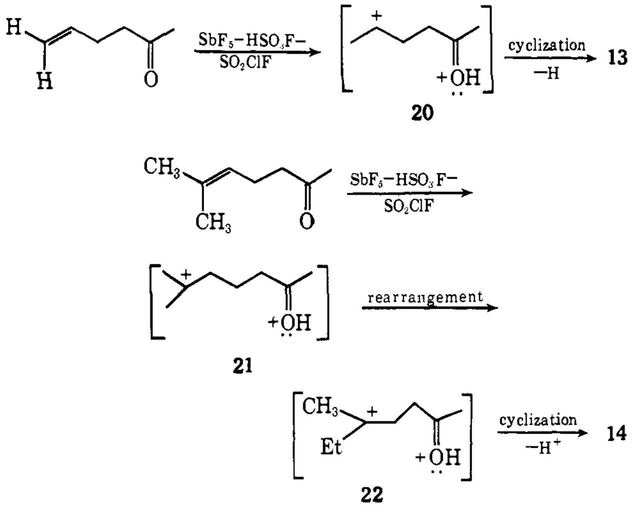
On the other hand, protonation of acyclic 1-octen-4-one in superacid showed no observable intermediate such as $C_4H_9CO^+HCH_2CH(SO_3F)CH_3$. Isomerization of 1-octen-4-one to ions **11** may or may not involve such an intermediate. However, it seems likely that protonation took place at the oxygen atom before the π bond. The second protonation step is suggested to involve a relatively unstable dication, quite similar to **9a**. It subsequently would deprotonate to form the thermodynamically more stable ions **11**. Alternatively, it could react with OSO_2F^- from the medium to form $C_4H_9CO^+HCH_2CH(SO_3F)CH_3^+$, which immediately eliminates HSO_3F to form ions **11**. Similarly, isomerization of (1-cyclopenten-1-yl)acetone to the protonated α,β-unsaturated ketone **12** may also involve the same mechanism. But the isomerization of (2-cyclopenten-1-yl)acetone to ion **12** in superacid could involve direct diprotonation to form ion **18**. Simple 1,2-hydride shift will give the more stable tertiary ion **19**.



Deprotonation of ion **19** would give the observed ion **12**. (2-Cyclopenten-1-yl)acetone is the only γ,δ-unsaturated ketone found to isomerize to the more stable α,β-unsaturated ketone. In the case of acyclic γ,δ-unsaturated ketones, only the cyclic five-membered oxonium ions **13** and **14** were formed. The different behavior between cyclic and related acyclic γ,δ-unsaturated ketones in superacid media is most likely caused by steric factors and also the relative stability of the intermediate dications (**18**, **20**–**22**). The mechanism for the formation of cyclic five-membered onium ions **13** and **14** can be rationalized as shown in Scheme III.

5-Hexen-2-one is presumed to be diprotonated in superacid to ion **20**. However, it underwent neither deprotonation nor 1,2-hydride shift to form the conjugated ketone. Indeed, its empty p orbital interacts with the unshared electron pair of oxygen to form a σ bond, followed by deprotonation to give ion **13**. In the case of 6-methyl-5-hepten-2-one, diprotonation is

Scheme III



expected to give ion **21**. Dications are generally stable when two or more methylene carbons separate the charged carbons.[20] Dication **21** did not cyclize to form the cyclic six-membered oxonium ion, but rearranged to dication **22**. Ion **22** is considerably more stable than ion **21** and cyclized to form the five-membered ring oxonium ion **14**. Similar behaviors are found in the preparation of cyclic halonium ions.[21] To our knowledge, no six-membered ring halonium ions have been observed.

Experimental Section

Materials. All unsaturated aldehydes and ketones used were commercially available except for Δ^3-cyclopentenone, which was prepared according to Hess and Brown.[22]

Nmr Spectra. A Varian Model A56/60A nmr spectrometer was used to obtain pmr and fmr spectra. A Varian Model HA-100 nmr spectrometer was used to obtain the indor carbon-13 nmr spectra[23] and for the proton–proton decoupling experiments. Both instruments were equipped with variable-temperature probes.

Protonation of α,β-Unsaturated Aldehydes and Ketones. Samples were prepared by dissolving ~1.5 ml of 1:1 (mol/mol) FSO$_3$H–SbF$_5$ in an equal volume of SO$_2$ClF at −80°. The α,β-unsaturated aldehyde or ketone (approximately 0.3 ml) was dissolved in about 1 ml of SO$_2$ClF at −80° and slowly added to the acid solution with vigorous stirring.

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[20] J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

[21] G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. Brinich, *ibid.*, **94**, 1164 (1972).

[22] H. M. Hess and J. C. Brown, *J. Org. Chem.*, **32**, 4138 (1967).

[23] For details, see G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

Hydroboration. XXXI. The Cyclic Hydroboration of Dienes with Borane in Tetrahydrofuran in the Molar Ratio of 1:1

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Abstract: Glpc conditions for determining the exact quantities of *B*-methoxyboracyclanes are established. The hydroboration of a representative series of dienes with borane in the molar ratio of 1:1 with the diene-to-borane mode of addition is examined by (1) active hydride analyses, (2) ir, (3) glpc analyses of the methanolysis products, and (4) glpc analyses of the oxidation products. The total amount and product distribution of monomeric cyclic boranes formed under the ordinary hydroboration conditions are determined. The methoxy derivatives of the monomeric cyclic boranes are isolated and identified whenever possible. A tentative generalization which would permit one to understand and predict the course of hydroboration of acyclic dienes is made.

In spite of the fact that a number of publications dealing with the hydroboration of dienes and polyenes have appeared, little effort had been made until recently to control the hydroboration of dienes with borane in the molar ratio of 1:1 in order to produce the corresponding boracyclanes.[2,3] In our recent study[4] we described a simple diagnostic test for the formation of cyclic organoboranes *via* intramolecular cyclic hydroboration. Unfortunately, the test does not appear valid when borane itself (or diborane) is used.

In our earlier study[5] on the hydroboration of monoolefins with excess borane, the hydride-containing species formed were first converted to the corresponding *B*-methoxyboranes by methanolysis, and the *B*-methoxyboranes were distilled for quantitative determination. Although the method appeared reliable, the distillation step was quite tedious.

We have recently demonstrated the feasibility of a much more convenient glpc analysis of *B*-dimethoxy-

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[1] (a) Postdoctoral Research Associate on a research grant, DA 31-134 ARO(D) 453, supported by the U. S. Army Research Office (Durham). (b) Graduate Assistant on a research grant, GM 10937, supported by the National Institutes of Health.

[2] R. Köster, *Angew. Chem.*, **72**, 626 (1960).

[3] (a) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280 (1968); (b) H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **26**, C67 (1971); (c) *ibid.*, **28**, C1 (1971).

[4] H. C. Brown and C. D. Pfaffenberger, *J. Amer. Chem. Soc.*, **89**, 5475 (1967); for experimental detail, see C. D. Pfaffenberger, Ph.D. Thesis, Purdue University, 1967.

[5] H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Amer. Chem. Soc.*, **82**, 4703 (1960).