Methyl and ethyl diacetoacetate were prepared by acetylation of the corresponding acetoacetates.[22]

All other starting materials were commercially available.

Spectra. Infrared spectra were obtained on a Beckman IR 10 spectrophotometer, using IRTRAN or AgCl plates.

Proton NMR spectra were obtained on a Varian Associates Model A56/60A equipped with variable temperature probes. External Me_4Si (capillary) was used as reference.

Carbon-13 NMR spectra were obtained on Varian Associates Model HA-100 and XL-100 spectrometers both equipped with a broad-band decoupler, Fourier transform accessory, and a variable temperature probe. External ^{13}C-enriched Me_4Si (capillary) was used as reference.

Preparation of Ions. Acetoacetylium Ion. (a) A cold solution of acetoacetyl fluoride (2 mmol) in 1 ml of liquid SO_2 was added, with vigorous stirring, to a solution of SbF_5 (6 mmol) in 1 ml of SO_2 at −78°. For NMR studies, an aliquot of the about 10% solution was used after transfer to an NMR tube. For ir studies, the solvent was removed under vacuum to give a somewhat viscous semicrystalline product.

(b) Acetoacetic esters were added to a 1:1 *M* HSO_3F–SbF_5 mixture at −20°, using the general reaction conditions described previously.[9]

Diacetoacetylium Ion. Crystalline diacetoacetylium tetrachloroaluminate was prepared as described.[2]

Diacetoacetic anhydride–$3BF_3$ was prepared according to Meerwein.[16]

Diacetoacetylium hexafluoroantimonate was prepared by adding the anhydride–$3BF_3$ adduct (2 mmol) in SO_2 (2 ml) to a solution of 1:1 *M* HF–SbF_5 (6 mmol) in SO_2 (2 ml) at −78°. The reaction was carried out in a sealed reaction tube fitted with a pressure screw cap. After 5 hr at room temperature, the sealed tube was cooled and opened and the solvent removed under vacuum.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

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Stable Carbocations. CLXXXIII.[1a] Haloacetylium Ions

George A. Olah,* Alain Germain,[1b] and Henry C. Lin[1b]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received September 21, 1974*

Abstract: Haloacetylium ions were prepared using methods previously developed for obtaining acylium fluoroantimonate salts. The monochloro-, monobromo-, and monoiodoacetylium ions were obtained as stable species and studied by NMR spectroscopy in SO_2, while the monofluoroacetylium ion was found to be in equilibrium with its oxygen and fluorine coordinated donor–acceptor complexes. Dichloro- and difluoroacetylium and, in contrast to previous reports, also the trifluoroacetylium ion could not be obtained as stable species due to their rapid decarbonylation. The ^1H, ^{19}F, and ^{13}C NMR spectra of prepared haloacetylium ions are discussed in relation to structural aspects and the stability of the halogen substituted acetylium ions.

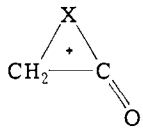
Acylium ions constitute by now a well-characterized class of stable carbocations.[2] However, no study of halogenated aliphatic acylium ions, except the work of Lindner and Kranz concerning the trifluoroacetylium ion,[3] has previously been reported. These ions are of interest as intermediates in haloacylation reactions and also of theoretical interest concerning the effect of introduction of halogen atoms on the stability of acylium ions and the possibility of halogen participation.

In carbenium ions, halogen substitution of the carbenium center affects stabilization by electronic "back-donation",[4] i.e., by conjugation of the nonbonded halogen electron pairs into the vacant p orbital. Halogen substitution at adjacent or further removed carbons on the other hand causes destabilization due to the inductive electronic effect of the electronegative halogen atoms. This is clearly the case for fluorine but, with chlorine, bromine, and iodine, halogen participation involving halonium ion type mesomeric forms can also be expected.[5a,b]

In the case of acylium ions, three mesomeric forms (**1**, **2**, and **3**) are involved in providing stabilization of the ions. All

$$\underset{\mathbf{1}}{R{-}C{\equiv}O^{+}} \longleftrightarrow \underset{\mathbf{2}}{R{-}\overset{+}{C}{=}O} \longleftrightarrow \underset{\mathbf{3}}{\overset{+}{R}{=}C{=}O}$$

these mesomeric forms will be destabilized by the inductive effect of halogen substitution. While possible chlorine, bromine, or iodine neighboring group participation could lead to the stabilizing halonium ion form **4**, such an effect is un-



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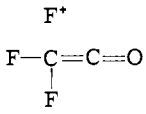
likely in fluoro-substituted compounds, due to the high electronegativity of fluorine. Fluorine substitution thus is unlikely to be stabilizing, particularly in the case of perfluoroacylium ions, where the "ketene like" form **3** would signify a cationic fluorine hyperconjugative effect **5**. Despite



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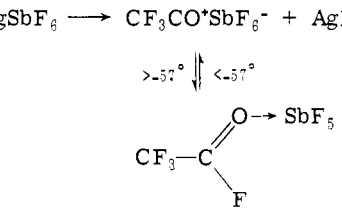
these considerations, Lindner and Kranz reported the preparation of trifluoroacetylium hexafluoroantimonate, using the silver salt method.[3] From infrared spectroscopic and conductivity data, they concluded that a temperature dependent equilibrium exists between the acetylium ion and the oxygen coordinated donor-acceptor complex:



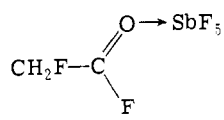
These studies seemingly contradict our expectations regarding the stability of fluoro-substituted carbocations and indicated the need for further study.

We report now our investigations of the preparation and NMR spectroscopic study of halogen substituted acetylium ions.

Results

Fluoroacetylium Ion. (a) The Fluoroacetyl Fluoride–Antimony Pentafluoride System. NMR study of SO_2 solution of fluoroacetyl fluoride with excess of SbF_5 shows a temperature dependent equilibrium between three species, **6, 7,** and **8**. (The ratio of **6:7:8** is 20:50:30 at −70° and 27:38:35 at −30°.) Figure 1 shows the proton and fluorine-19 NMR spectra. Proton, fluorine-19, and carbon-13 NMR data are summarized in Tables I and II.

Oxygen Coordinated Donor–Acceptor Complex 6. The presence of hydrogen–fluorine coupling clearly shows that, in **6**, the carbonyl–fluorine bond is not broken. Although



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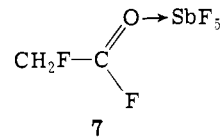
somewhat deshielded, all chemical shifts and coupling constants are close to those of the precursor. The proton deshielding effect (0.34 ppm) together with the maintained coupling (J_{HF}) indicates the carbonyl oxygen coordinated donor–acceptor complex. The observation of a broadened absorption for the -COF fluorine, instead of the expected two triplets (J_{HF} = 4.7 Hz) can be explained by a long range coupling with SbF_5.

Fluorine Coordinated Donor–Acceptor Complex 7. ^1H and ^{19}F NMR shifts for **7** are intermediate between those



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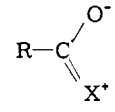
expected for ions **6** and **8**. No proton fluorine coupling is observable, although the fluorine–fluorine and the carbon–fluorine couplings are still observed. The COF fluorine signal is drastically changed. Its deshielding of 23.9 ppm from the precursor and the quintet nature of the absorption suggests, as the only reasonable structure, a donor–acceptor complex with fluorine to antimony pentafluoride coordination.

The significant deshielding of the carbonyl carbon (+20.6 ppm) agrees with this structure. Indeed, it is generally accepted[6a] that the more shielded carbonyl shifts of acid halides, compared with those of ketones, are due to the contribution of the mesomeric form **9**, resulting in a higher



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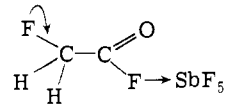
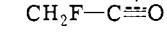
electron density at the carbonyl carbon. The interaction of a Lewis acid with an acyl halide, decreasing the contribution of form **9**, explains the observed deshielding effect.

The changes of the carbon–fluorine coupling constants are more difficult to analyze. The larger one bond coupling constant (J_{CF}) of the CH_2F group (+13 Hz) is consistent with the enhanced π character of this bond[6b] because of increased electron withdrawal.



But, on the other hand, smaller one- and two-bond coupling constants of the -COF fluorine ate with the α and β carbons ($J_{CO\text{-}F}$ and $J_{C\text{-}CO\text{-}F}$) would be expected according to the decreasing π character of the CO–F bond. Instead, however, the two-bond coupling constant $J_{C\text{-}CO\text{-}F}$ decreases (−39 Hz), while the one-bond constant $J_{CO\text{-}F}$ increases (+33 Hz). This is in contrast with the usual trend of the change in the magnitude of the corresponding two coupling constants (one-bond $J_{C\text{-}F}$ and two-bond $J_{C\text{-}C\text{-}F}$), in the same direction,[6b] and at this time, cannot be satisfactorily explained based on our present understanding of carbon–fluorine coupling constants.

Fluoroacetylium Ion 8. The absence of a fluorine absorption and fluorine coupling for a COF bond and also the much deshielded proton resonance (1.84 ppm from the precursor) in the third species **8** are only consistent with the formation of the fluoroacetylium ion.



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The shielding of the carbonyl carbon-13 resonance (−14.6 ppm from the precursor) is also consistent with the increased triple bond character of the carbonyl bond.[6] The larger one- and two-bond carbon–fluorine coupling constants (48 and 9 Hz, respectively) also agree with the increase of the π character of the C–F bond.

For the fluoroacetyl species (**6, 7,** and **8**), the variation of the fluorine chemical shift of the CH_2F group is unexpected. Indeed, while the proton NMR absorption shifts to lower field from complex **6** to complex **7** and ion **8**, a reverse

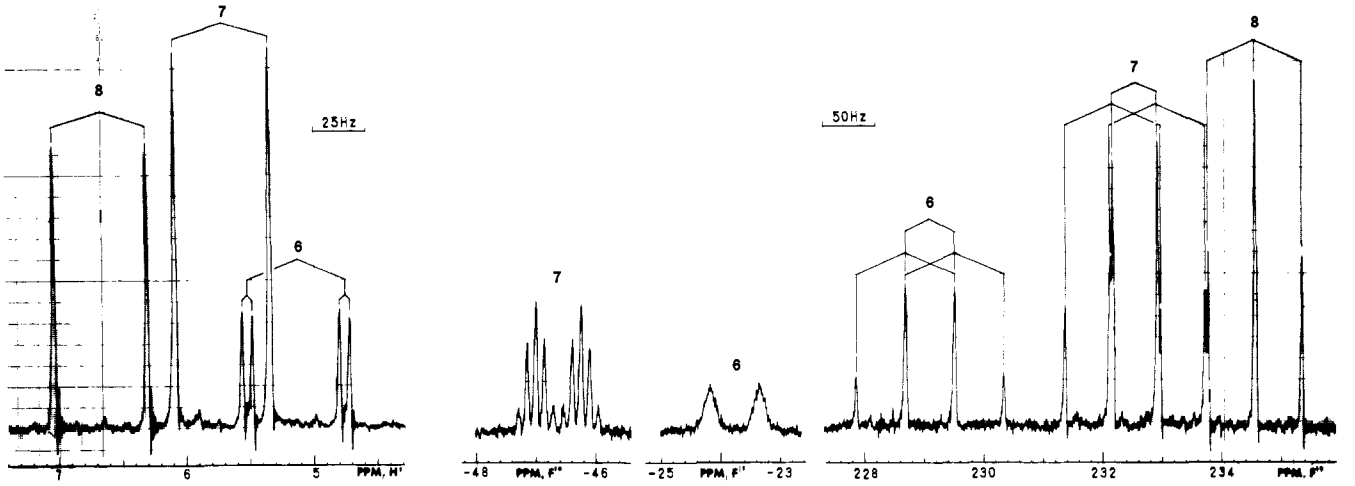
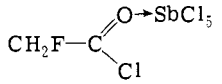


Figure 1. Proton and fluorine-19 NMR spectrum of CH_2FCOF–SbF_5 in SO_2 at −60°

effect is observed for the fluorine absorption. Generally, the development of a positive charge in the α position to a fluorine atom results in a deshielding of the fluorine shift.[7] However, the observed shift differences of species **6, 7,** and **8** are small and not significant in comparison with the large fluorine absorption range. Further it should be noted that many other factors besides charge distribution can contribute to the fluorine chemical shifts.[8] Thus no simple explanation for the shielding differences can be offered.

Treating fluoroacetyl chloride with an excess of SbF_5 in SO_2 leads to the same proton and fluorine NMR spectra as discussed for the fluoroacetyl fluoride system indicating chlorine-fluorine exchange. On the other hand, only the oxygen donor-acceptor complex **10** is obtained when treating fluoroacetyl chloride with $SbCl_5$, while the reaction of fluoroacetyl fluoride with $SbCl_5$ leads to an equilibrium between the two donor-acceptor complexes **10** and **11.**



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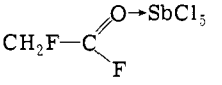

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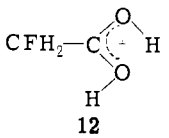
The proton deshielding observed in $SbCl_5$ complexes is smaller than that observed for the SbF_5 donor-acceptor complexes, in agreement with the weaker Lewis acidity of $SbCl_5$.

(b) Fluoroacetic Acid in HSO_3F–SbF_5 ("Magic Acid") Solution. Protonated fluoroacetic acid is obtained by dissolving sodium fluoroacetate in HSO_3F–SbF_5–SO_2 solution at −70°. Proton and fluorine NMR data are given in Table III. As is generally observed for protonated carboxylic acids,[9-11] the two OH protons are nonequivalent at low temperature. In this case, they are also differently coupled with the α-fluorine atom. Only one isomer is observed, and the nonequivalence of the OH protons is interpreted by the structure **12.**



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12 does not dehydrate, even in neat HSO_3F–SbF_5 at room temperature, to the fluoroacetylium ion **8.**

Difluoroacetylium Ion. (a) Difluoroacetyl Fluoride–Antimony Pentafluoride System. When difluoroacetyl fluoride was treated with SbF_5 in SO_2 at −78°, the proton and fluorine NMR spectra show the formation of the oxygen coordinated donor-acceptor complex **13** (see Tables IV and V). This assignment is based on the deshielded proton absorption (+0.85 ppm) and the maintaining of coupling between

Table I. Proton and Fluorine NMR Data of Fluoroacetyl Fluoride and Chloride and Their Complexes with Antimony Pentafluoride and −chloride[a]

Compd		Chemical shift, ppm[b] δ_{CH_2F}	Φ_{CH_2F}	Φ_{COF}
CH_2FCOF		4.99 (dd = 46.6; 5.1)	229.4 (dt[c] = 46.6; 46.8)	−22.7 (dt = 46.8; 5.1)
CH_2FCOF–SbF_5	(6)	5.33 (dd = 46.0; 4.7)	229.0 (dt[c] = 46.0; 46.5)	−23.8 (bd = 46.5)
	(7)	5.89 (d = 44.6)	232.4 (dt = 44.6; 43.2)	−46.6 (dq = 43.2; 8.1)
	(8)	6.83 (d = 43.8)	234.6 (t = 43.8)	
CH_2FCOCl		4.89 (d = 46.5)	208.8 (t = 46.5)	
CH_2FCOCl–$SbCl_5$	(10)	4.97 (d = 46.5)	208.9 (t = 46.5)	
CH_2FCOCl–SbF_5	(10)	5.03 (d = 46.5)	209.2 (t = 46.5)	
	(11)	4.99 (dd = 45.5; 5.0)	229.1 (dt[c] = 45.5; 46.7)	−23.9 (dt = 46.7; 5.0)

[a] In SO_2 at −70°. [b] Proton chemical shifts (δ) are referred to external Me_4Si. Fluorine chemical shifts (Φ) are referred to external CCl_3F. Multiplicity and coupling constants (in hertz) are given in parentheses. d = doublet; t = triplet; dd = doublet of doublet; dt = doublet of triplet; dq = doublet of quintet; bd = broad doublet. [c] Because the two coupling constant are very similar, the signal looks like a quartet.

Table II. Carbon-13 NMR Data of Fluoroacetyl Fluoride and Its Complexes with Antimony Pentafluoride[a]

Compd	Chemical shift, ppm[b] CH_2F	CO
CH_2FCOF	75.4 (dd = 180; 84)	159.7 (dd = 358; 25)
6	75.9 (dd = 174; 82)	162.1 (dd = 360; 25)
7	77.1 (dd = 193; 45)	180.3 (dd = 391; 23)
8	75.4 (d = 228)	145.1 (d = 34)

[a] In SO_2 at −60°. [b] Chemical shifts are referred to external Me_4Si. Multiplicity and carbon–fluorine coupling constants (in hertz are given in parentheses. d = doublet; dd = doublet of doublet.

Table III. Proton and Fluorine NMR Data of Protonated Fluorinated Acetic Acids

Acid	Solvent[a] (temp, °C)	Chemical shift, ppm[b] OH	H	F
CH_2FCO_2H	A	*c*		
	B (−70)	13.25 (d = 3.5) 13.95 (d = 4.5)	5.95 (d = 45)	231.5 (tt = 45; 4[e])
	C (RT)	*d*	6.20 (d = 45)	232.1 (t = 45)
CHF_2CO_2H	A (−70)	9.82	6.00 (t = 53.5)	129.1 (d = 53.5)
	B (−90)	14.28 (b) 14.75 (b)	6.98 (t = 51.5)	130.2 (d = 51.5)
	C (RT)	*d*	7.08 (t = 51.5)	129.2 (d = 51.5)
CF_3CO_2H	A (−50)	10.2		76.7
	B (−90)	15.33 (b)		73.5
	C (RT)	*d*		73.6

[a] A = SO_2; B = HSO_3F–SbF_5 (1:1)–SO_2; C = HSO_3F–SbF_5 (1:1). [b] Proton chemical shift (δ) are referred to external Me_4Si. Fluorine chemical shift (Φ) are calculated from external CCl_3F. Multiplicity and coupling constants (in hertz) are given in parentheses. d = doublet; t = triplet; tt = triplet of triplet; b = broad. [c] The monofluoroacetic acid was used like its sodium salt. [d] Fast exchange with solvent. [e] Because the two β-hydrogen–fluorine coupling constants are too close, the fluorine spectrum shows a seeming triplet of triplets.

Table IV. Proton and Fluorine NMR Data of Difluoroacetyl Fluoride and Its Antimony Pentafluoride Complex[a]

	Temp, °C	Chemical shift, ppm[b] δCHF_2	ϕCHF_2	ϕCOF
CHF_2COF	−70	5.14 (dt = 52.0; 2.5)	130.4 (dd = 52.0; 8.7)	−21.3 (dt = 8.7; 2.3)
CHF_2COF–SbF_5 (13)	−80	5.99 (dt = 52.0; 2.5)	129.7 (dd = 52.0; 8.7)	−22.1 (dt = 8.7; 2.3)
(14)	−30	6.43 (q = 80.3)	78.4 (d = 80.3)	
CF_3H	RT	6.25[c] (q = 79.7)	78.6[c] (d = 79.7)	

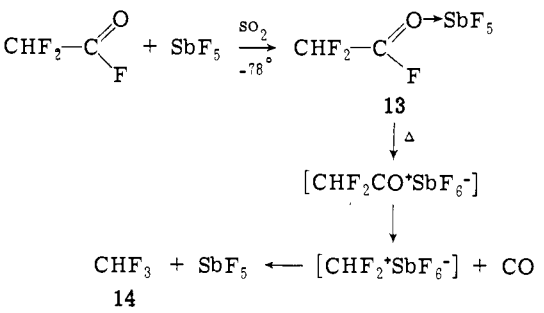
[a] In SO_2. [b] Proton chemical shifts (δ) are referred to external Me_4Si. Fluorine chemical shifts (Φ) are referred to external CCl_3F. Multiplicity and coupling constants (in hertz) are given in parentheses. d = doublet; q = quarter; dd = doublet of doublet; dt = doublet of triplet. [c] In cyclohexane, ref 12.

Table V. Fluorine NMR Data of Trifluoroacetyl Fluoride and Its Antimony Pentafluoride Complex[a]

Compd	Temp, °C	Chemical shifts, ppm[b] CF_3	COF
CF_3COF	−70	76.7 (d = 6.2)	−13.7 (q = 6.2)
CF_3COF–SbF_5	−78	75.4 (d = 6.2)	−15.6 (q = 6.2)
CF_3COF–SbF_5	−30	74.2 and 73.4	

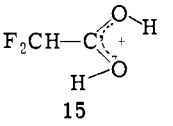
[a] In SO_2. [b] Fluorine chemical shifts (Φ) are referred to external CCl_3F. Multiplicity and coupling constants (in hertz) are given in parentheses. d = doublet; q = quartet.

the COF fluorine and the proton and fluorine atoms of the CHF_2 group. Like the fluoroacetyl fluoride–SbF_5 oxygen coordinated donor–acceptor complex **6**, the fluorine chemical shifts do not change significantly upon warming the solution. Cleavage, however, occurs with simultaneous CO evolution, giving fluoroform **14** (characterized by its proton



and fluorine NMR spectra[12,13]). Figure 2 shows the fluorine and proton NMR spectra obtained during the reaction. No difluoroacylium ion was observed. The formation of fluoroform is explained by the decarbonylation of the unstable, difluoroacetylium ion intermediate.

(b) Difluoroacetic Acid in HSO_3F–SbF_5 ("Magic Acid") Solution. In HSO_3F–SbF_5–SO_2 solution, difluoroacetic acid is protonated. The proton and fluorine NMR data are given in Table III. At −90°, the two hydroxyl protons are nonequivalent, but no coupling with fluorine can be observed because of fast exchange with the solvent. As in the case of protonated fluoroacetic acid, the observation of two different hydroxyl signals suggests the structure **15.**



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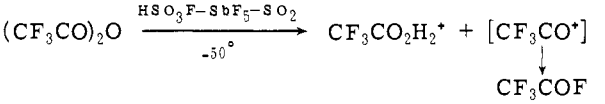
No dehydration occurs even in neat HSO_3F–SbF_5 at room temperature to the difluoroacetylium ion.

Trifluoroacetylium Ion. We have previously reported the protolytic cleavage of trifluoroacetic anhydride.[14] While the cleavage of carboxylic anhydrides generally gives the corresponding acylium ions and protonated acids, no trifluoroacetylium ion was obtained, but only trifluoroacetyl fluoride was observed besides protonated trifluoroacetic acid.



This behavior is in accord with the previously discussed instability of the difluoroacetylium ion. The observed instability of the intermediately formed trifluoroacetylium ion, even in the low nucleophilicity HSO_3F–SbF_5–SO_2 system, contrasts with the reported isolation of trifluoroacetylium hexafluoroantimonate by Lindner and Kranz.[3] We have consequently attempted to prepare the trifluoroacetylium ion, in order to be able to characterize it by NMR spectroscopy, with the silver salt method used by Lindner and Kranz and the protolytic cleavage of trifluoroacetic acid and esters.

(a) Trifluoroacetyl Halide–Antimony Pentafluoride Systems. When treated with excess of SbF_5 in SO_2 at −78°, trifluoroacetyl fluoride maintains fluorine–fluorine coupling in the ^{19}F NMR spectrum. As in the case of the other fluorinated acetyl fluorides, the fluorine chemical shifts do not change significantly. In analogy with the previously discussed systems, formation of the carbonyl oxygen coordinated donor–acceptor complex is indicated. Warming the solution to around −50° produces CO evolution, and two very low intensity fluorine NMR absorptions are observed at φ 74.2 and 73.4, respectively, while the COF signal disappears. The same spectrum is obtained by introducing trifluoroacetyl fluoride into SbF_5–SO_2 at −30°. The SO_2 so-

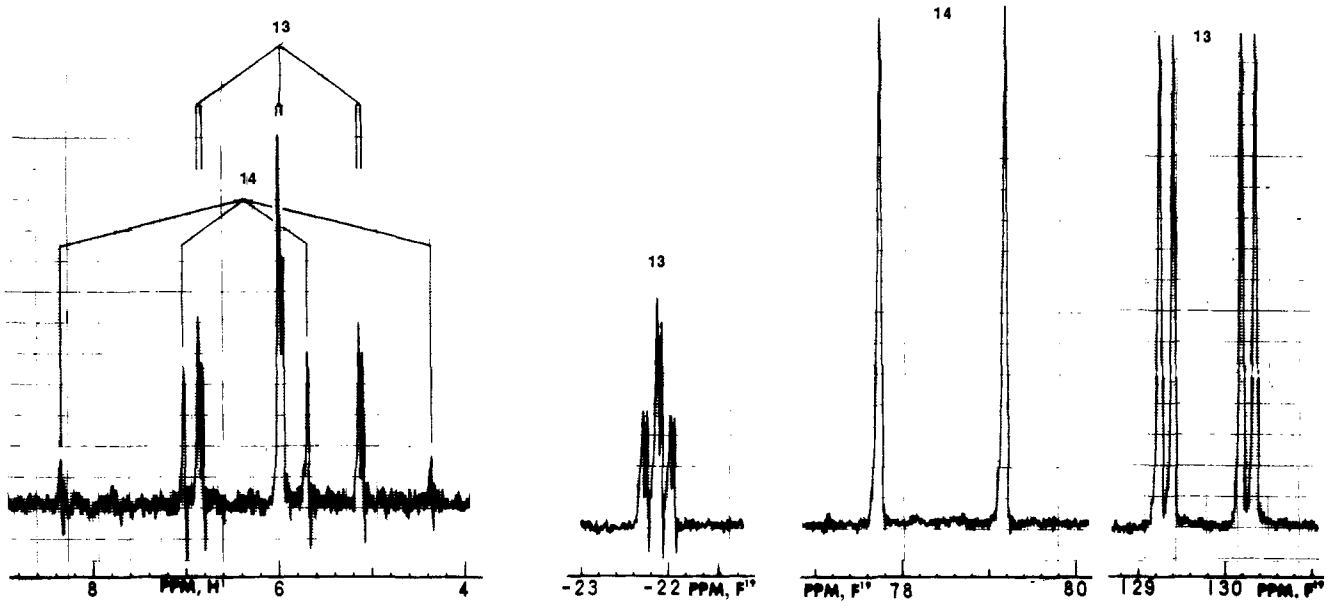


Figure 2. Proton and fluorine-19 NMR spectrum of CHF_2COF–SbF_5 in SO_2 at −50°, showing the formation of CHF_3.

lution does not react with benzene to give α,α,α-trifluoroacetophenone, and none of the NMR absorptions is attributable to the trifluoroacetylium ion but only to carbon tetrafluoride and its weak SbF_5 complex (ϕ_{CF_4} 63.4 in cyclohexane and ϕ_{69} neat).[12,13] Decarbonylation of the unstable intermediate trifluoroacetylium ion, similarly to that of the difluoroacetylium ion, is thus indicated.

$$CF_3COF + SbF_5 \xrightarrow[-78°]{SO_2} CF_3-C(=O\rightarrow SbF_5)F \xrightarrow{\Delta} [CF_3CO^+SbF_6^-] \longrightarrow CF_4 + SbF_5 \longleftarrow [CF_3^+SbF_6^-] + CO$$

The same behavior is observed with trifluoroacetyl chloride and bromide.

(b) Silver Salt Method. Trifluoroacetyl chloride reacts slowly at −30° in SO_2 with silver hexafluoroantimonate. The SO_2 solution, separated from the silver chloride, shows a small fluorine NMR signal at ϕ 75.9 that is attributed to uncomplexed carbon tetrafluoride.

Contrary to the results of Lindner and Kranz,[3] in our hands trifluoroacetyl bromide did not react with anhydrous silver hexafluoroantimonate in SO_2 solution at low temperature and gave only CF_4 at higher temperatures.

(c) Protolytic Cleavage of Trifluoroacetic Acid and Its Esters. Only protonated trifluoroacetic acid is obtained by treating trifluoroacetic acid with HSO_3F–SbF_5. Even at 60° in neat "Magic Acid", no cleavage occurs. In SO_2 solution, the two hydroxyl protons have only one ^1H NMR absorption even at −90° (see proton and fluorine NMR data in Table III), indicating rapid exchange with the acid-solvent system. The very low nucleophilicity of trifluoroacetate explains this behavior. The more deshielded OH proton resonance, compared with those of protonated acetic acid (δ_{OH} = 12.33 and 13.03 ppm),[9] fluoroacetic and difluoroacetic acid, can be attributed to the higher electronegativity of the $-CF_3$ group.

All of the studied alkyl trifluoroacetates undergo alkyl-oxygen cleavage in neat HSO_3F–SbF_5 solution, including methyl and ethyl trifluoroacetate (see Table VI). Boron tris(trifluoroacetate), on the other hand, cannot undergo boron-oxygen cleavage but gives carbon tetrafluoride (ϕ 74.6), indicating the intermediacy of the unstable trifluoroacetylium ion, which then immediately decarbonylates. In HSO_3F–SbF_5–SO_2 at low temperature, NMR spectra of

$$(CF_3CO_2)_3B \xrightarrow{3H^+} [(CF_3CO_2H)_3B]^{3+} \xrightarrow{3H^+} [B(OH_2)_3]^{3+} + [3CF_3CO^+] \xrightarrow{SbF_6^-} CF_4 + SbF_5$$

the protonated trifluoroacetate esters were obtained, but in no case was fluorine-proton coupling observed. With FSO_3H in SO_2, chemical shifts intermediate between those of the precursors and the protonated esters are observed. These are not considered to be average chemical shifts, due to a fast equilibrium between protonated and parent unprotonated esters, but to be due to the formation of hydrogen bonded interaction between the carbonyl oxygen atom and fluorosulfuric acid. Indeed, the observation of two isomers in the case of the isopropyl ester eliminates the possibility of a fast proton exchange. The bulkiness of HSO_3F and the isopropyl group explains the existence of two conformers.

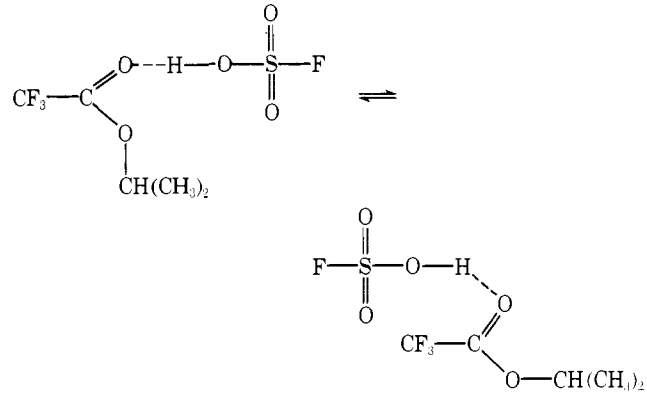


Table VI. Proton and Fluorine NMR Data of Protonated Trifluoroacetic Acid Esters and Their Cleavage in HSO_3F-SbF_5 Solutions

			Chemical shift, ppm[b]				
	Solvent[a]	Temp, °C	CF_3	OH	H_1	H_2	Products of cleavage
$CF_3CO_2CH_3$	A	−70	76.1		3.87		
1	B	−70	75.7	*c*	4.20		
	C	−70	72.7	16.03 (b)	5.23		
	D	60	73.6	*c*	5.03		$CF_3CO_2H_2^+ + CH_3OSO_2F$
$CF_3CO_2CH_2CH_3$	A	−70	75.8		4.28 (q = 7.3)	1.18 (t = 7.3)	
1 2	B	−70	75.6	*c*	4.47 (q = 7.3)	1.25 (t = 7.3)	
	C	−70	72.6	15.55 (b)	5.67 (q = 7.3)	1.90 (t = 7.3)	
	D	20	73.5	*c*	Fast polymerization		$CF_3CO_2H_2^+ + [CH_3CH_2^+]$ polymer
$CF_3CO_2CH_2CH_2CH_2CH_3$	A	−70	75.8		4.24 (q = 6.2)	0.57 to 1.72 (m)	
	B	−70	75.5	*c*	4.45 (t = 6.2)	0.63 to 1.90 (m)	
1 2	C	−70	72.6	15.50 (b)	5.51 (q = 6.2)	0.82 to 2.45 (m)	
	D	30	73.5	*c*		4.45	$CF_3CO_2H_2^+ + (CH_3)_3C^+$
$CF_3CO_2CH(CH_3)_2$	A	−70	75.8		5.05 (s = 6.4)	1.17 (d = 6.4)	
1 2	B	−70	*d* 75.7		5.50 (s = 6.5)	1.42 (d = 6.5)	
			76.2		5.42 (s = 6.5)	1.52 (d = 6.5)	
	C	−70	73.0	15.07 (b)	6.57 (s = 6.2)	1.93 (d = 6.2)	
	D	30	73.4		4.50 (m)	3.27 (d = 4.2)	$CF_3CO_2H_2^+ + (CH_3)_2CH\text{-}C^+(CH_3)_2$
$CF_3CO_2CH{=}CH_2$	A	−70	75.9		7.17 (dd = 6.2 and 13.8)	4.86 (dd = 6.2 and 2.7); 5.11 (dd = 13.8 and 2.7)	
1 2							
	B	−70	76.0		7.04 (q = 5.5)[e]	1.82 (d = 5.5)[e]	
	C		Decomposes				
$(CF_3CO_2)_3B$	A	−70	78.1				
	C	−90	73.4	15.33 (b)			
	D	20[f]	74.6 (small)				CF_4

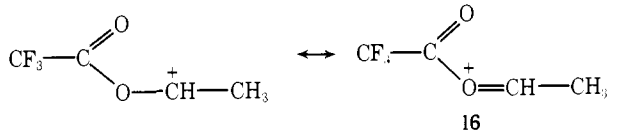
[a] A = SO_2; B = HSO_3F-SO_2; C = HSO_3F-SbF_5(1:1)−SO_2; D = HSO_3F-SbF_5 (1:1). [b] Proton chemical shifts (δ) are referred to external Me_4Si. Fluorine chemical shifts (Φ) are referred to external CCl_3F. Multiplicity and coupling constants (in hertz) are given in parentheses. d = doublet; t = triplet; q = quartet; s = septet; dd = doublet of doublet; m = multipler; b = broad. [c] Fast exchange with solvent. [d] Equilibrium between two species. [e] Protonation on the vinyl group. [f] After 15 hr at +70°.

Table VII. Proton and Carbon-13 NMR Data of Halogenated Acetylium Ions and Their Precursor[a]

	Chemical shift, ppm[b]			
	Proton	$^{13}C_\alpha$	^{13}CO	$^{13}CF_3$
CH_3COF	2.07 (d = 8.0)	18.1 (d = 56)	162.7 (d = 356)	
CH_3CO^+	4.27	6.8	152.0	
ICH_2COCl[c]	4.26	7.2	169.0	
ICH_2CO^+	5.40	−38.7	150.6	
$BrCH_2COF$	4.15 (d = 5 ≅ 0)	23.9 (d = 74.5)	158.9 (d = 355)	
$BrCH_2CO^+$	5.47	4.2	147.1	
$ClCH_2COF$	4.23 (d = 3.8)	38.7 (d = 80)	159.8 (d = 355)	
$ClCH_2CO^+$	5.94	30.0	146.4	
FCH_2COF[d]	4.99 (dd = 5.1; 46.6)	75.4 (dd = 84; 180)	159.7 (dd = 358; 25)	
FCH_2CO^+[d]	6.82 (d = 43.8)	75.5 (d = 229)	145.3 (d = 34)	
CF_3CH_2COF[e]	3.47 (dq = 4.09; 9.6)	36.8 (dq = 64; 32)	155.7 (d = 358)	122.1 (q = 276)
$CF_3CH_2CO^+$[f]	5.79 (q = 6.7)	30.5 (q = 40)	145.8	118.1 (q = 251)

[a] In SO_2 at −60°. [b] Protonated and carbon chemical shift are referred to external Me_4Si. Multiplicity and coupling constant (in hertz) are given in parentheses (d = doublet; q = quartet; dd = doublet of doublet; dq = doublet of quartet). [c] The fluoride has not been obtained. [d] For fluorine data see Table I. [e] Fluorine-19 data (in parts per million from external CCl_3F), ϕ = 61.9 (dt = 12.6,9.6). [f] Fluorine-19 data (in parts per million from external CCl_3F), ϕ = 53.7 (t = 6.7).

Vinyl trifluoroacetate treated with HSO_3F–SbF_5 decomposes, even in SO_2 solution at −70°, into yet undetermined products but, with HSO_3F in SO_2, protonation occurs at the vinyl group to give ion **16.**



16

Thus in our hands, the trifluoroacetylium ion was never observed as a long-lived species.

Chloro-, Bromo-, Iodo-, and Trifluoromethylacetylium Ions. Monohalogenated acetylium ions, as well the trifluoromethyl substituted pseudo-halide derivative, were obtained by treating the corresponding acyl fluorides (the chloride in the case of the iodo derivative) with SbF_5 in SO_2 solution. All are stable at low temperatures, and the chloro- and bromoacetylium ions even could be isolated[15] as stable fluoroantimonate salts. Proton and carbon NMR data, including those of the precedingly discussed fluoroacetylium ion (and for comparison also of the parent, unsubstituted acetylium ion), are summarized in Table VII. The deshieldings of the proton absorptions (between 2.27 and 1.14 ppm), compared with the shift of the precursors, as well as those of the carbonyl carbon-13 shifts (between 152.0 and 145.1 ppm) are in good agreement with the formation of the acylium ions.

Dichloroacetylium Ion. Attempts to obtain the dichloroacetylium ion were unsuccessful. Dichloroacetyl fluoride (δ 6.68 in SO_2) when treated with SbF_5 in SO_2 at −30° gives a proton NMR signal at δ 6.35 that broadens at −70°. This signal can be attributed to the dichlorofluoromethane–SbF_5 complex **17,** undergoing fluorine exchange, similarly to the fluoromethane–SbF_5 complex.[16] Because of the fast fluorine exchange with SbF_5, no fluorine NMR signal can be observed. In SO_2ClF solution, where SbF_5 is not complexed as strongly with the solvent,[17] complete halogen exchange occurs at −30°, leading to fluoroform (as previously characterized). Thus, like the difluoro- and trifluoroacetylium ions, the dichloroacetylium ion is also unstable and undergoes decarbonylation.

$$CHCl_2COF + SbF_5 \xrightarrow[-30°]{SO_2} [CHCl_2CO^+SbF_6^-] \longrightarrow CHCl_2F{\rightarrow}SbF_5 + CO$$

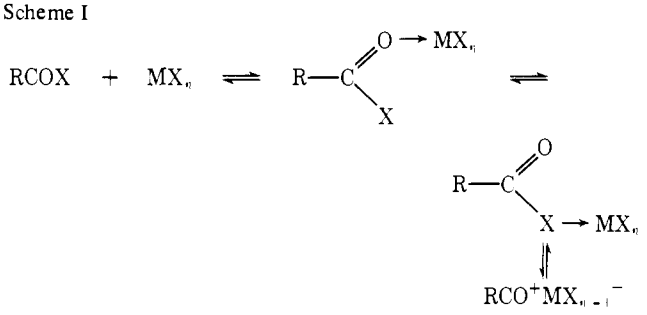
17

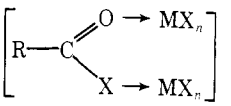
$$CHCl_2COF + SbF_5\ (\text{excess}) \xrightarrow[-30°]{SO_2ClF} CHF_3 + CO$$

Discussion and Conclusions

Monohalogenated acetylium ions are stable in SO_2 at low temperature. It must be noted, however, that the fluoroacetylium ion is in equilibrium with its two donor-acceptor complexes. It is the first time that a halogen coordinated donor-acceptor complex formed between an acyl halide and a Lewis acid halide was observed. This result is particularly interesting, because such a complex can be considered the direct precursor for the formation of the acylium ion, according to Scheme I. It can be speculated, that the mechanism leading to the formation of the halogen coordinated donor-acceptor complex could involve a second Lewis acid molecule through an intermediate 1:2 complex like **18.**

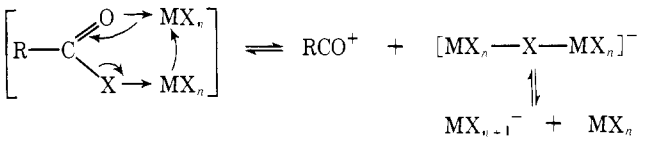
Scheme I





18

18 could also give directly, the acylium ion:



The observation of ionic complexes with dimeric counterions, such as $ArCO^+$, $Ti_2Cl_9^-$,[18] would be consistent with this possibility.

The fluoroacetylium ion, although less stable than the other monohalogenated acetylium ions, was observed. The difluoro- and trifluoroacetylium ion, however, like the dichloroacetylium ion, could not be obtained as stable species, as all undergo rapid decarbonylation. These results are in contrast to the reported preparation of the trifluoroacetylium hexafluoroantimonate by Lindner and Kranz. However, Professor Lindner communicated to us since that he too observed that, even at −40°, the trifluoroacetylium salt is not stable and that traces of proton acid can catalyze the rapid CO elimination.[19] This is in accord with our findings on the lack of stability of the ion in acid solution. Indeed, in the presence of SbF_5 or other acid catalysts, the decomposition of $-CF_2COF$ groups is an efficient way to introduce the $-CF_3$ group via decarbonylation of the intermediate $-CF_2CO^+$ ion[20] and subsequent fluoride abstraction from SbF_6^-.

The carbonyl carbon-13 chemical shifts of monohalogenated acetylium cations (XCH_2CO^+) showed the following order of deshielding:

$$CH_3CO^+ > ICH_2CO^+ > BrCH_2CO^+ > ClCH_2CO^+ > CF_3CH_2CO^+ > FCH_2CO^+$$

This order is the reverse of the Pauling electronegativities of the halogens, the position of the CF_3- group being intermediate between Cl and F.[21] This order can be interpreted as caused by the diminution of the participation of the "ketene-like" mesomeric form **3** and the augmentation of the oxonium-like mesomeric form **1,** when the electronegativity of the halogen substituents increases. Indeed, the shielding effect on the carbonyl carbons of acylium ions agrees with the effect expected by comparison with the carbonyl carbon shift of ketene (δ_{13C} 194.7),[22] and an increase of the triple bond character of the C–O bond.[6]

Concerning possible halogen participation in haloacetylium ions, i.e., formation of bridged halonium ions **4,** the data do not permit a definitive conclusion. An equilibrium between open haloacetylium ions and assymetrically bridged halonium ions **19** could be envisaged and could explain partially (in addition to the diminution of the electronegativity effect) the deshielding effect on the carbonyl carbon-13 chemical shifts of the chloro-, bromo-, and iodoa-

cetylium ions, compared with the fluoro- and trifluoromethylacetylium ions.

19

The α-carbon chemical shifts are difficult to interpret since they are also directly affected by the halogen substituents and the α-halogen substituent effects are not yet completely understood.[6c] The α-carbon shift of the fluoroacetylium ion is unchanged from that of the precursor, in agreement with the absence of delocalization of positive charge to the α carbon. The very shielded absorption of the iodoacetylium ion (from the unsubstituted, parent acetylium ion) is, however, surprising. It is shielded by 45.5 ppm, while the shielding of iodomethane (−20.5 ppm) compared with methane (−2.1 ppm) is only of 18.4 ppm.[6c] Either one must envisage a more important "ketene-like" form participation for the iodo derivative, than for the parent ion, $I^+CH_2{=}C{=}O$, or assume participation by an asymmetric bridged halonium **19** (the three-membered ring interaction causing a shielding effect, as is the case in the shielding of cyclopropane[6d]). Delocalization of part of the positive charge onto the halogen atom, however, should cause a reverse effect, as well as the diminution of the triple bond character of the C–O bond. Thus an equilibrium between the open-chain haloacetylium ion and bridged halonium ion **19** does not in itself explain the observed α-carbon chemical shifts.

Experimental Section

Materials. Except for trifluoroacetyl fluoride (Peninsular Chemresearch, Inc.), all acyl fluorides were prepared from the corresponding carboxylic acids or their sodium salts and benzoyl fluoride using the procedure previously described.[23] Fluoroacetyl chloride was prepared in a similar manner from the sodium salt with benzoyl chloride.

All the other starting materials were commercially available.

Preparation of Haloacylium Ions or Donor–Acceptor Complexes. (a) **Superacid Systems.** Antimony pentafluoride (6 mmol) or 1:1 *M* FSO_3H–SbF_5 (3 g) was diluted with 1 ml of liquid SO_2 at −78°. To the resulting solution was added with vigorous stirring a solution of the acid halide and corresponding carboxylic acid or ester (2 mmol) in liquid SO_2 (1 ml). An aliquot of the solution was then transferred to a precooled NMR tube for spectral studies.

(b) **Silver Salt Method.** A solution of the haloacyl halide (6 mmol) in SO_2 (2 ml) was added slowly, with vigorous stirring, to a solution of $AgSbF_6$ (8 mmol) in SO_2 (5 ml). The resulting solution was warmed up to −30° for 30 min. After removing AgCl by filtration, an aliquot of the clear solution was transferred to an NMR tube for spectral studies.

NMR Spectroscopy. Proton and fluorine NMR spectra were obtained on a Varian Associates Model A-5052 spectrometer equipped with variable temperature probe. External Me_4Si and $CFCl_3$ (capillary) were used as reference.

Carbon-13 NMR spectra were obtained on Varian Associates Model HA-100 and XL-100 spectrometers both equipped with a broad-band decoupler, Fourier transform accessory, and variable temperature probe. External ^{13}C-enriched Me_4Si (capillary) was used as reference.

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References and Notes

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