Stable Carbonium Ions. XXVII.[1a] Cyclo- and Polycycloalkyloxocarbonium Ions

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Abstract: Complex formation of mono-, di-, and polycycloalkylcarbonyl fluorides (chlorides) with antimony pentafluoride (chloride) was investigated. Stable cycloalkyloxocarbonium hexahaloantimonate complexes were obtained from the following carbonyl halide precursors: cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cycloundecyl, 2-*exo*-norbornyl, and 1-adamantyl. The structure of the oxocarbonium (acylium) ions was proved by infrared and nmr studies. The tertiary 1-adamantyloxocarbonium ion readily decarbonylates in solution to yield the 1-adamantyl cation. All the isolated cycloalkyloxocarbonium ion complexes are effective acylating agents in C, O, N, and S acylations.

In previous investigations relating to acyl cations,[2-4] it was shown that when acyl fluorides were allowed to react with SbF_5 in an inert solvent stable crystalline oxocarbonium (acylium) salts could be obtained. These salts have strong infrared absorption bands at approximately 2250 cm^{-1} which were assigned to the oxocarbonium ions (acyl cations: $R-C^+O$). The proton magnetic resonance spectra (in SO_2 solution) show the proton(s) α relative to the carbonyl group at approximately -4.0 ppm (from external tetramethylsilane as reference). This resonance is deshielded approximately 2 ppm from the resonance of the α proton in the acyl fluoride (-2.2 ppm for acetyl fluoride). It was similarly shown that the protons β to the -COF group are deshielded approximately 1 ppm on formation of the oxocarbonium ion.

The oxocarbonium complexes could be formed with a variety of Lewis acids (BF_3, PF_5, AsF_5), but it was found that the complexes tended to be more stable both as isolated solids and in solution, when formed from an acyl fluoride and antimony pentafluoride.

Recently, Deno, Pittman, and Wisotsky[5] have shown that stable acylium ions are also formed by dissolving carboxylic acids in H_2SO_4 which contain 0–30% SO_3.

$$RCOOH \xrightleftharpoons{H_2SO_4} RCOOH_2HSO_4^- \xrightleftharpoons{0\text{–}30\%\ SO_3\text{–}H_2SO_4} RCO^+HSO_4^-$$

Besides aliphatic fatty acids, the method was also applied to cyclopropane, cyclobutane, and cyclohexanecarboxylic acids.

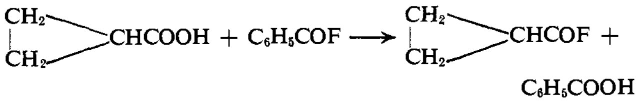
In this paper we report an extension of our previous work to the antimony pentafluoride complexes of cyclic and polycyclic carbonyl fluorides (and in certain cases, of the corresponding acyl chlorides with antimony pentachloride).

Results and Discussion

The preparation of the cycloalkylcarbonyl fluoride–antimony pentafluoride complexes was carried out according to the "fluoride method" described in previous work[2,4] in cold 1,1,2-trifluorotrichloroethane solution.

$$\widehat{(CH_2)_n CH}COF + SbF_5 \rightleftharpoons \widehat{(CH_2)_n CH}CO^+SbF_6^-$$

The needed cycloalkylcarbonyl fluorides, not previously reported in the literature, with the exception of cyclopropylcarbonyl fluoride[6a] and cyclohexylcarbonyl fluoride,[6b] were prepared from the corresponding acyl chlorides with anhydrous hydrogen fluoride. Cyclopropylcarbonyl fluoride was obtained more conveniently by the metathetic reaction of cyclopropanecarboxylic acid with benzoyl fluoride. The isolated complexes were found by analytical data to be 1 : 1 acyl fluoride–antimony pentafluoride complexes. Their analytical data and melting points (in sealed capillary tubes) are listed in the Experimental Section.



$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>CHCOOH + C_6H_5COF \longrightarrow \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>CHCOF + C_6H_5COOH$$

We also investigated the complex formation of cycloalkylcarbonyl chlorides with antimony pentachloride. From 1,1,2-trifluorotrichloroethane solution 1:1 complexes could be isolated with the exception of the cyclopentyl, cycloundecyl, and adamantyl systems. The stability of the chloride complexes is generally less than that of the fluoride complexes and they decompose more readily on standing.

Spectroscopic Investigations. A. Infrared Spectra. The spectra were obtained as neat films (of the low-melting complexes) or as mulls (of the higher melting crystalline complexes) in a fluorinated hydrocarbon (Fluorolube).

The main characteristic absorption data are summarized in Tables I and II.

All the complexes are ionic oxocarbonium ions as evidenced by the strong absorption frequencies around 2200–2250 cm^{-1} and the absence of carbonyl absorption (1600 to 1550 cm^{-1}) assignable to the donor–acceptor complexes. Figure 1 shows the spectrum of the cyclopropyloxocarbonium ion as a characteristic example of all the spectra. It was observed that the absence of carbonyl absorption was dependent on the complete

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[1] (a) Part XXVI: G. A. Olah, C. U. Pittman, Jr., and T. S. Sorensen, *J. Am. Chem. Soc.*, **88**, 2331 (1966); (b) National Science Foundation Predoctoral Research Fellow.

[2] G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Am. Chem. Soc.*, **84**, 2733 (1962).

[3] G. A. Olah, *Rev. Chim.*, **7**, 1139 (1962).

[4] G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, **85**, 1328 (1963).

[5] N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *ibid.*, **86**, 4370 (1964).

[6] (a) M. Hanack and H. Eggensperger, *Ber.*, **96**, 1341 (1963); (b) Y. Yamase, *Bull. Chem. Soc. Japan*, **34**, 480 (1961).

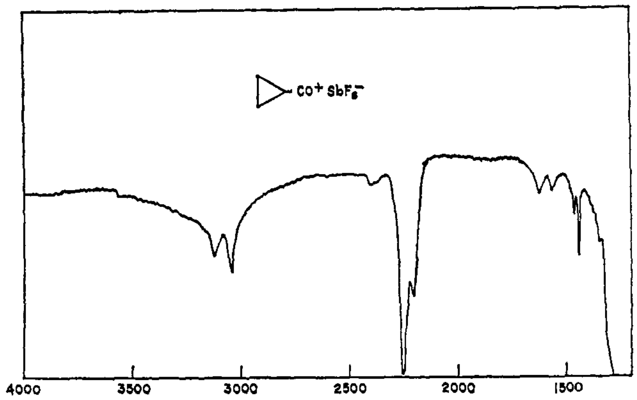


Figure 1.

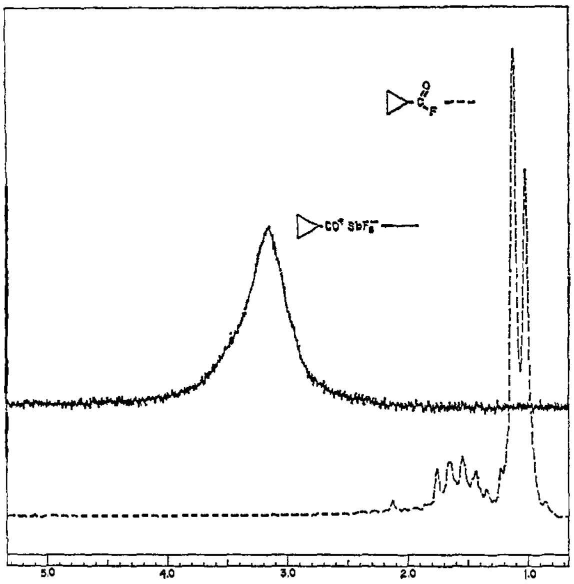


Figure 2.

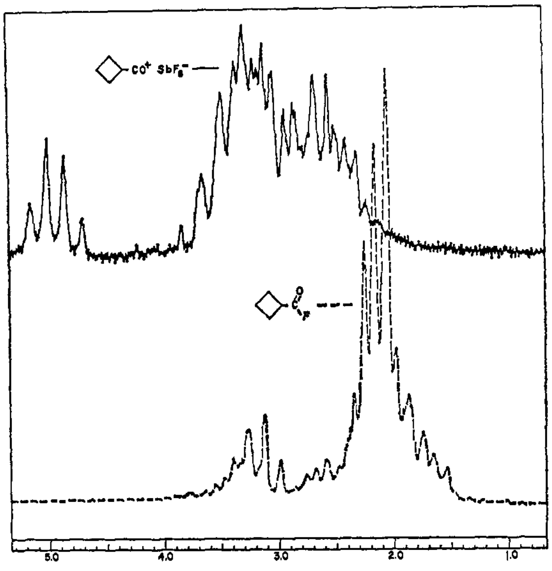


Figure 3.

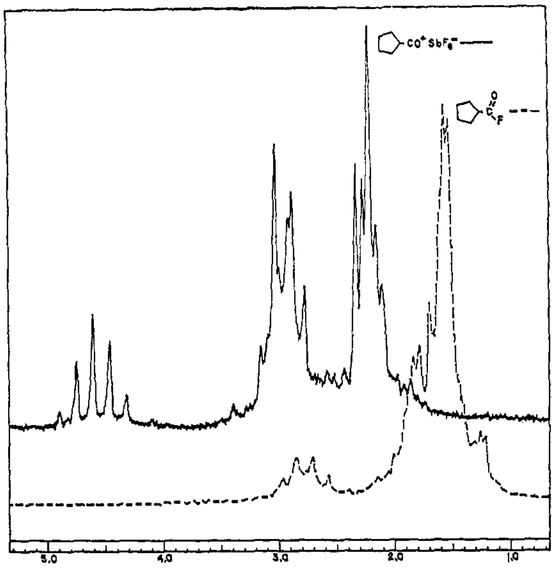


Figure 4.

absence of moisture from the systems. Water hydrolyzes antimony pentafluoride to hydroxyantimony fluorides, which are weaker Lewis acids, and therefore, instead of ionizing the C–F bonds of acyl fluorides, complex the carbonyl oxygen atom. This was evidenced by studying several spectra of a given complex after addition of known amounts of water to the system. As a broad absorption band at 3500–3000 cm^{-1} (OH stretching frequency) appeared, the 2250-cm^{-1} oxocarbonium ion absorption decreased in intensity and new donor–acceptor absorption bands (1550 and 1600 cm^{-1}) appeared.

Table I. Infrared Stretching Frequencies of Cycloalkylcarbonyl Fluorides and Their Antimony Pentafluoride Complexes

R	Acyl fluoride ν_{CO}, cm^{-1}	Complex ν_{CO^+}, cm^{-1}
Cyclopropyl	1815	2225
Cyclobutyl	1825	2205
Cyclopentyl	1830	2260
Cyclohexyl	1835	2255
Cycloheptyl	1825	2210
Cycloundecyl	1840	2260
2-*exo*-Norbornyl	1840	2250
1-Adamantyl	1835	2255

B. Nuclear Magnetic Resonance Spectra. All of the cycloalkylcarbonyl fluoride–antimony pentafluoride complexes are ionic oxocarbonium ions in sulfur dioxide

Table II. Infrared Stretching Frequencies of Cycloalkylcarbonyl Chlorides and Their Antimony Pentachloride Complexes

R	Acyl chloride ν_{CO}, cm^{-1}	Complex ν_{CO^+}, cm^{-1}
Cyclopropyl	1780	2245
Cyclobutyl	1800	2239
Cyclopentyl	1790	2240
Cyclohexyl	1800	2240
Cycloheptyl	1790	. . .[a]
Cycloundecyl	1795	. . .[a]
2-*exo*-Norbornyl	1800	2240
1-Adamantyl	1740	. . .[a]

[a] Too unstable to permit observation.

Table III. Proton Magnetic Resonance Shifts[a] of Cycloalkylcarbonyl Fluorides and the Derived Cycloalkyloxocarbonium Ions in Sulfur Dioxide Solution at −60°

	Acyl fluoride				Oxocarbonium complex			
	H_α	H_β	H_γ	H_δ	H_α	H_β	H_γ	H_δ
Cyclopropyl	1.55 (M)[a]	1.1 (D)			3.1 (B)	3.1 (B)		
Cyclobutyl	3.18 (M)	2.20 (M)	1.98 (M)		4.95 (Q)	3.30 (M)	2.6 (M)	
Cyclopentyl	2.85 (M)	1.76 (M)	1.58 (M)		4.55 (U)	3.00 (M)	2.25 (M)	
Cyclohexyl	2.40 (B)	1.60 (B)	1.35 (B)	1.17 (B)	4.50 (M)	2.60 (B)	2.10 (B)	1.80 (B)
Cycloheptyl	2.55 (B)	1.8 (S)			4.50 (B)	2.60 (B)		
Cycloundecyl	2.60 (B)	1.65 (S)	1.53	1.37	4.35 (B)	2.65 (B)	2.05 (B)	1.60 (B)

[a] In ppm from external TMS. M = multiplet; D = doublet (spacing 6 cps); B = broad peak, poorly resolved fine structure; Q = quartet; U = quintet, J_{H-H} = 7 cps; S = shoulder.

solution as shown by the 2-ppm deshielding of the protons α and the 1-ppm deshielding of the protons β to the carbonyl group. The nmr data are summarized in Table III. The spectra are shown in Figures 2–7.

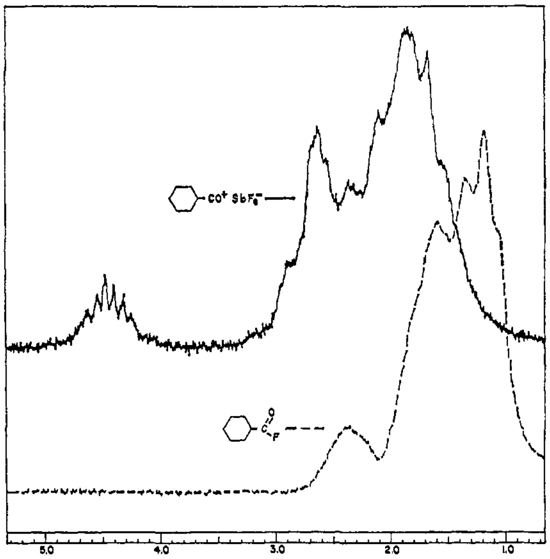


Figure 5.

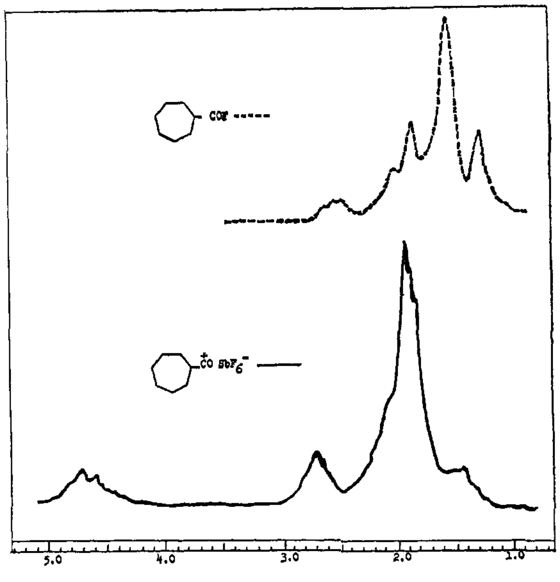


Figure 6.

In no case was any donor–acceptor complex observable. However, if water was added to the solution of the complexes, the nmr spectra showed chemical shifts upfield from those of the acylium ions, but deshielded from those of the starting fluorides, which can be assigned to the donor–acceptor complexes. The cycloalkylcarbonyl chloride–antimony pentachloride complexes decompose in sulfur dioxide solutions and no meaningful nmr data could be therefore obtained.

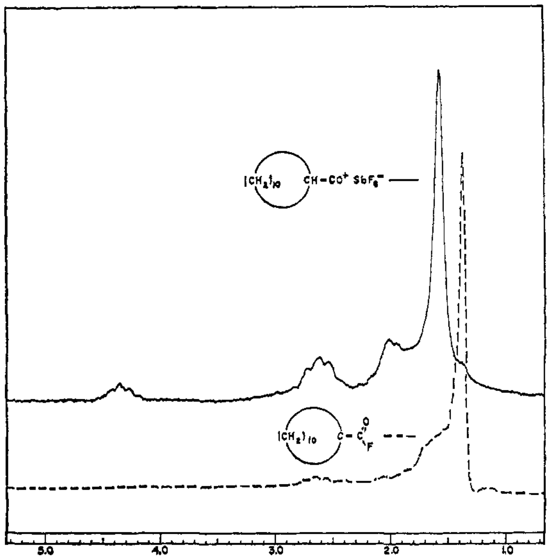
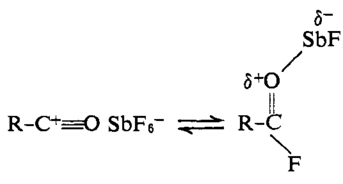


Figure 7.

In previous nmr work on oxocarbonium ions,[2–4] the presence of both donor–acceptor complexes and oxocarbonium ions was observed. These data were interpreted to indicate that in solution an equilibrium is established between the oxocarbonium ion and the donor–acceptor complex.



$$R\text{-}C^+\!\equiv\!O\ SbF_6^- \rightleftharpoons R\text{-}C(\!=\!\overset{\delta+}{O}\!-\!\overset{\delta-}{SbF_5})F$$

We now wish to report our observation that the presence of donor–acceptor complexes in previous work was due in all probability to impurity moisture present in the samples. Preparation of the oxocarbonium ion complexes and their solutions using highly purified reagents and extreme precautions to exclude moisture (see Experimental Section) resulted in obtaining solutions of the complexes the spectra of which showed chemical shifts corresponding to only the

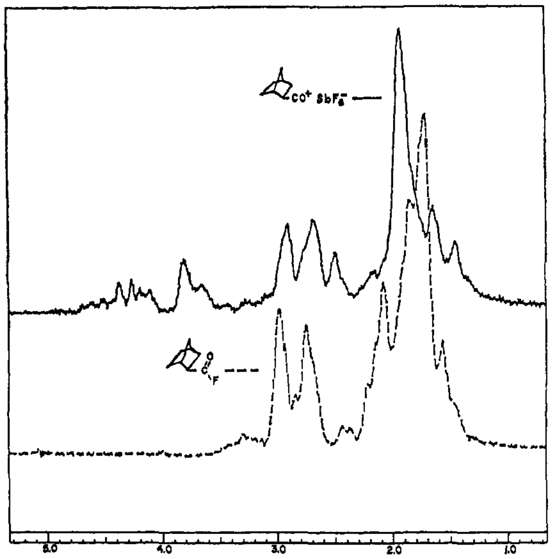


Figure 8.

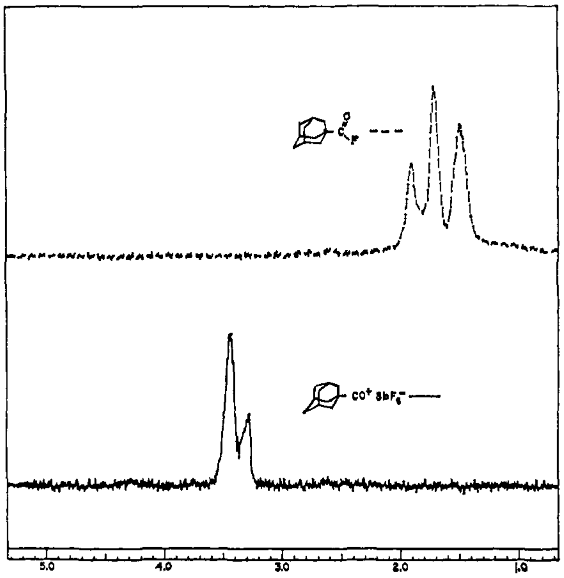
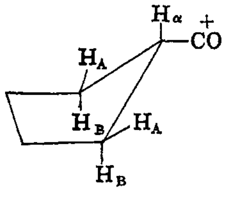


Figure 9.

oxocarbonium ions. If donor–acceptor complexes were present at all, their concentration in equilibrium must be below the limit of spectroscopic observations (2–3%).

As pointed out previously,[24] acyl fluoride–antimony pentafluoride complexes form oxocarbonium ions, the charge being substantially localized on the carbonyl carbon atom. Proof of this suggestion was obtained from H^1 and C^{13} nmr data. Present data further substantiate this suggestion. The large deshielding effects observed on the α-hydrogen atoms and substantial deshielding on the β (and γ) hydrogens cannot be explained with charge localization primarily on the carbonyl oxygen atom. Boer[7] recently convincingly demonstrated this conception through the X-ray structure of the methyloxocarbonium ion ($CH_3CO^+SbF_6^-$).

The nmr spectrum of the cyclopentyloxocarbonium ion is particularly interesting (Figure 4). The α proton appears as a 1:4:6:4:1 quintet ($J_{H-H} = 7$ cps) indicating equal coupling to four other protons. This can be accounted for by the following model.

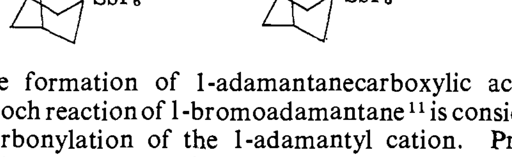


The energy of monosubstituted cyclopentanes is minimized in the "envelope" conformation.[8a] Fieser–Dreiding models predict dihedral angles between H_α and H_A of about 25° and between H_β and H_B of about 150°. From the dependence of coupling constants on dihedral angles[8b] coupling constants of about 7.5 cps are predicted for both $J_{H\alpha-H\beta}$ and $J_{H\alpha-H\beta}$, in good agreement with the above model. This does not imply that the above conformation of the cyclopentyloxocarbonium ion is the only conformation present but rather that it is the predominant one. The nmr shifts of the α proton in other oxocarbonium ions are not resolved well enough to permit a similar simple analysis of the coupling constants.

Decarbonylation and Chemical Reactivity. Tertiary (and to a much lesser degree secondary) alkyloxocarbonium ions were shown to decarbonylate in solution of the corresponding carbonium ions.[4] It was shown that the *t*-butyloxocarbonium (pivalylium) ion loses CO readily[4] to form the stable *t*-butyl carbonium ion. In view of the known high stability of the norbornyl[9] and adamantyl[10] cations it was felt of interest to examine the decarbonylation of the corresponding oxocarbonium ion complexes.

The 2-*exo*-norbornyloxocarbonium ion (in the form of the SbF_6^- complex in SO_2 in a sealed nmr tube) was allowed to stand at room temperature for 1 week while its nmr spectrum was periodically monitored (Figure 8). Although the sample decomposed after a week as evidenced by the loss of an nmr signal and precipitation of a tarry substance, at no time did peaks corresponding to the norbonyl cation[8a] appear.

When the 1-adamantyloxocarbonium ion (Figure 9) was similarly treated, the spectrum of the adamantyl cation[9] appeared, and the oxocarbonium ion spectrum completely disappeared after 1 day.



The formation of 1-adamantanecarboxylic acid in the Koch reaction of 1-bromoadamantane[11] is considered as carbonylation of the 1-adamantyl cation. Present experimental observation of the decarbonylation of the 1-adamantyloxocarbonium ion proves the reversibility of the process.

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(7) F. P. Boer, *J. Am. Chem. Soc.*, **88**, 1572 (1966).

(8) (a) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1961; (b) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(9) P. von R. Schlayer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964).

(10) P von. R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 4195 (1964).

The cycloalkyloxocarbonium complexes are highly effective acylating agents in C, O, N, and S acylations of a variety of organic compounds. These modified Friedel–Crafts type reactions will be reported in detail separately elsewhere. At the present time we would like to observe only qualitatively on their behavior.

Aromatic hydrocarbons like benzene, when allowed to react with cycloalkyloxocarbonium hexafluoroantimonates, preferably in nitromethane solution, give the corresponding aryl cycloalkyl ketones

$$ArH + RCO^+SbF_6^- \longrightarrow ArCOR + HF + SbF_5$$

Reaction of 1-adamantyloxocarbonium hexafluoroantimonate with benzene yields predominantly 1-phenyladamantane. Cycloalkylations are believed to take place through primary decarbonylation of the adamantyloxocarbonium ion. This is in accordance with previous observations on the Friedel–Crafts reaction of adamantanylcarbonyl chloride with benzene[11] giving only 1-phenyladamantane.

It is interesting to observe the reaction of 2-*exo*-norbornyloxocarbonium hexafluoroantimonate with benzene. Acylation exclusive of concurrent alkylation is observed. This is in accordance with the $AlCl_3$-catalyzed reaction of 2-*exo*-norbornyl chloride with benzene giving exclusively phenyl 2-*exo*-norbornyl ketone.[12]

Cycloalkyloxocarbonium salts are also highly effective acylating agents for O-acylation of alcohols giving esters

$$ROH + R'CO^+SbF_6^- \longrightarrow ROOCR' + HF + SbF_5$$

for S-acylation of mercaptans giving thiol esters

$$RSH + R'CO^+SbF_6^- \longrightarrow RSOCR' + HF + SbF_5$$

and for N-acylation of primary and secondary amines yielding amides

$$2RHN_2 + R'CO^+SbF_6^- \longrightarrow RNHOCR' + RNH_2\cdot HSbF_6$$

Experimental Section

Antimony pentafluoride was obtained from the Ozark Mahoning Corp., Tulsa, Okla. The commercial material was twice distilled in all-glass standard type apparatus (Kel-F grease was used to grease the joints), and the middle 60% fraction from the second distillation was used. The purified SbF_5 was stored in Teflon bottles and kept in a dessicator.

The necessary acyl chlorides if not commercially available were prepared from the corresponding acids with $SOCl_2$. All of the used cycloalkanecarboxylic acids and some of the acyl chlorides are commercially available (Aldrich, Eastman).

Preparation of Acyl Fluorides. Cyclopropylcarbonyl Fluoride. Cyclopropanecarboxylic acid (42 g, 0.5 mole), benzoyl fluoride (70 g, 0.56 mole), and NaF (3 g), were mixed together, and the mixture was slowly distilled from a standard glass distillation apparatus over a period of 3 hr. The distillation was stopped when the distillate temperature reached 100°. The product was then distilled twice from a few grams of NaF, bp 82°.

Cyclobutylcarbonyl Fluoride. Cyclobutylcarbonyl chloride (100 g, 0.85 mole), was cooled to 0° in a 1-qt polyethylene bottle equipped with a gas inlet and drying tube. The cyclobutylcarbonyl chloride was magnetically stirred while 20 g (1.0 mole) of anhydrous HF was introduced over a period of 1 hr. The reaction mixture was then allowed to warm to room temperature, while dry N_2 was bubbled through to remove excess HF. The cyclobutylcarbonyl fluoride was then twice distilled from a few grams of NaF, bp 95–96°.

Cyclopentylcarbonyl fluoride (bp 58–60° (80 mm)), cyclohexylcarbonyl fluoride (bp 80–81° (80 mm)), cycloheptylcarbonyl fluoride (bp 90–92° (50 mm)), cycloundecylcarbonyl fluoride (bp 89° (1 mm)), and 2-*exo*-norbornylcarbonyl fluoride (bp 53° (10 mm)) were prepared (and purified) using the same method.

In general for acyl fluorides boiling above 100° (1 atm) it is more convenient to remove excess HF by bubbling dry N_2 through the reaction mixture than by using dry NaF, as used previously.

1-Adamantylcarbonyl Fluoride. Adamantylcarbonyl chloride, 50 g (0.23 mole), was added to 100 g (10 moles) of cold (−20°) anhydrous liquid HF in a 1-qt, wide-mouth plastic bottle equipped with an inlet tube and drying tube. The reaction mixture was allowed to warm to room temperature and then dry N_2 was blown through the bottle to remove excess HF. The product was then twice distilled from dry NaF, bp 98° (8 mm).

All the acid fluorides were stored in polyethylene bottles kept refrigerated.

Preparation of Diacyl Fluoride–Antimony Pentafluoride Complexes. All operations with the complexes should be done in a drybox as the complexes are very sensitive to moisture.

The following procedure was used to prepare all of the complexes. The acyl fluoride (0.05 mole) was dissolved in 100 ml of cold (0°) Freon 113 and slowly added to a cold solution of 12 g (0.06 mole) of SbF_5 in 200 ml of 1,1,2-trifluorotrichloroethane (Freon 113). The complexes separated from the solution. After standing for 0.5 hr to complete precipitation, the mother liquid was decanted, and the complexes were washed twice with Freon 113 and pumped dry. Most of the complexes are liquids at room temperature and their melting point was determined as given below. (The acyl chloride–antimony pentachloride complexes were prepared using an analogous procedure.)

The melting points of the crystalline complexes were determined in sealed capillaries on a Gallenkamp melting point apparatus. The melting points of low-melting complexes were determined in the following way. A solution of 0.01 mole of acyl fluoride in 100 ml of cold (−50°) dichlorofluoromethane (Freon 12) was added slowly to a solution of 3 g of SbF_5 in 200 ml of cold (−50°) Freon 12. The complexes immediately precipitate as a solid. The solutions were then magnetically stirred and allowed to slowly warm up while the temperature of the solution was monitored with a low-temperature thermometer. If a complex melted higher than the boiling point of Freon 12 (−29°), 100 ml of cold (−30°) Freon 113 was added and the warming continued, while the Freon 12 was allowed to distill off.

Table IV. Cycloalkylcarbonyl Halide–Antimony Pentahalide Complexes

R	Fluoride complex, mp, °C	Chloride complex, mp, °C
Cyclopropyl	−35 to −30	79–80
Cyclobutyl	−10 to −5	65–67
Cyclopentyl	20–25[a]	69–75[b]
Cyclohexyl	35–40[a]	53–54[b]
Cycloheptyl	25–30[a]	*c*
Cycloundecyl	25–30[a]	*c*
2-*exo*-Norbornyl	58–65	80–81[b]
1-Adamantyl	*d*	*c*

[a] Slowly melts at room temperature. [b] Decomposes overnight at room temperature. [c] Decomposes on formation. [d] Not determined, liquid at room temperature.

All the complexes were analyzed for antimony and fluoride (chloride) in the manner described previously.[2,4] Owing to the somewhat lower stability of the complexes the accuracy of the analyses was less accurate, but all complexes clearly showed the diacyl halide-2 antimony pentahalide stoichiometry.

Infrared Investigations. The spectra were obtained on Perkin-Elmer, Model 337, and Beckman, Model IR-10, grating spectrometers. The spectra of the liquid complexes were scanned as neat liquids between two Irtran plates. The solid complexes were examined as mulls (Fluorolube). The spectrum of the cyclopropyloxocarbonium complex is shown in Figure 1 as a representative

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[11] H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, 92, 1628 (1959).

[12] J. Sauer, H. Wiest, and A. Mielert, *ibid.*, 97, 3183 (1964).

example of the infrared spectra. The infrared data are summarized in Tables II and III.

A study of the effect of added water on the infrared spectra was carried out in the case of the cyclopentyl and cyclobutyl complexes. Smears of the neat complexes were prepared between two Irtran plates in a drybox. The smears were then taken out of the drybox and the two Irtran plates separated. The films were exposed to air for periods of 30 sec, 1 min, 3 min, and 5 min, then the plates were pressed together and the spectra obtained.

Nmr Investigations. The spectra were obtained on Varian Associates Model A60, A56-60, and HA60 spectrometers in sulfur dioxide solution at −20 to −70°. The spectra were found temperature independent. The spectra are shown in Figures 2 to 8 and the data are summarized in Table III. The chloride complexes decompose when dissolved in SO_2 and no meaningful spectra could be obtained.

Reaction of Oxocarbonium Salts with Aromatic Compounds. **(A) Without Solvent.** The cycloalkyloxocarbonium salt (0.2 mole) was added to 0.5 mole of well-stirred aromatic hydrocarbon (benzene, toluene). The complex salts are generally not soluble in the aromatics. In most cases gentle heating was necessary to start the reaction. The formed ketones give complexes with the by-product Lewis acids and separate from the excess aromatic as a separate lower layer. After washing the reaction mixtures with water, they were dried over Na_2SO_4 and the products isolated in the usual manner.

(B) In Solution. In these experiments, the reaction was carried out in nitromethane solutions in which the aromatics and the oxocarbonium salts are both soluble. The reactions are much slower in solvent, and owing to the partial decomposition of the oxocarbonium salts in nitromethane the yields are lower.

Reaction of Oxocarbonium Salts with Alcohols. Oxocarbonium salt (0.1 mole) was added as nitromethane solution or in small portions as a solid into excess of the appropriate stirred and cooled alcohol. A fast reaction takes place. The resulting mixture was washed with water, dried over Na_2SO_4, and fractionated.

Reaction of Oxocarbonium Salts with Mercaptans. The oxocarbonium salt (0.1 mole) was added in nitromethane solution or in small fractions as a solid to an excess of well-stirred and cooled mercaptan. The reaction is very fast. After completion of the reaction, the mixture was washed with water, dried over Na_2SO_4, and fractionated.

Reaction of Oxocarbonium Salts with Amines. The solution of 0.1 mole of oxocarbonium salt in nitromethane solution was added to excess of the sitrred and cooled primary or secondary amine. The products, after water washings, were isolated.

Acknowledgment. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society.

Carbenoid Intermediates from Polyhalomethanes and Chromium(II). The Homogeneous Reduction of Geminal Halides by Chromous Sulfate

C. E. Castro and W. C. Kray, Jr.

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Abstract: The rapid homogeneous reduction of a wide array of geminal halides and polyhalomethanes by chromous sulfate in aqueous dimethylformamide has been examined at room temperature. The products, reactivities, and kinetics suggest a mechanism involving metal ion complexes of α-halomethyl radicals and carbenes. A dimethylmethyl fragment could be transferred to olefins to result in *gem*-dimethylcyclopropanes.

Earlier studies[1] of the homogeneous oxidation of chromous sulfate by alkyl halides have pointed up the unusual rapidity of the reaction of methylene bromide with this salt in aqueous dimethylformamide. The present work portrays the general scope and mechanism of the interaction of geminal halides and polyhalomethanes with this reagent.

Based upon ion exchange and elemental analysis of the resulting solution, a red ion noted to result from the addition of chloroform[2] to aqueous chromous perchlorate was assigned the formula $(CrCHCl_2)^{2+}$. Warming the solution of the ion resulted in the production of a green solution of Cr(III) that contained

$$HCCl_3 + Cr^{2+} \longrightarrow CrCl^{2+} + (CrCHCl_2)^{2+} \longrightarrow Cr(III) + Cl^- \quad (1)$$

chloride ion (eq 1). No organic products were detected. The existence of such an ion was in keeping with reports of the production of benzylchromium,[3] $(PhCH_2Cr)^{2+}$, by a process similar to eq 1. Subsequently, the rates of production of a series of substituted benzylchromium ions[4a] and their decomposition[4b] to bibenzyl and toluene have been examined. Quite recently solutions of air-stable ions derived from haloethyl- and halomethylpyridinium salts and Cr(II) have been observed.[5]

Several isolated cases of the oxidation of transition metal species by polyhalomethanes have been reported. Thus, carbon tetrachloride has been noted to oxidize cobaltocene,[6] bis(ethylbenzene)chromium,[7] and chromous chloride.[2,8a,b] Benzal chloride has been converted to a mixture of stilbenes and ethers, and diphenyldichloromethane to *sym*-tetraphenylethylene,

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