

# Stable Carbonium Ions. XXV.<sup>1a</sup> Alkylene- (Arylene-) dioxodicarbonium Ions (Acyl Dications)

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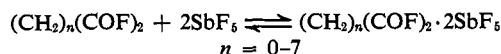
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**Abstract:** Complex formation of dicarboxylic acid fluorides with antimony pentafluoride was investigated. Succinyl fluoride forms a 1:2 complex which based on infrared and nmr studies is a monooxocarboxonium ion, mono-donor-acceptor complex ( $\text{SbF}_6 \cdot \text{FOC}(\text{CH}_2)_2\text{CO}^+\text{SbF}_6^-$ ). Glutaryl, adipyl, pimelyl, suberyl, and azelayl fluoride, as well as terephthaloyl fluoride, all form 1:2 complexes with antimony pentafluoride, which according to infrared and nmr studies are acyl dication complexes ( $\text{SbF}_6^- + \text{OC}(\text{CH}_2)_2\text{CO}^+\text{SbF}_6^-$ ). The acyl dication complexes could be isolated as crystalline, well-defined salts. They are effective diacylating agents in C-, O-, N-, and S-acylation reactions.

No investigation of the complex formation of dicarboxylic acid halides with Lewis acid halides was reported so far in the literature. In continuation of previous work relating to stable oxocarboxonium ions (acyl cations)<sup>1-4</sup> we considered it of interest to extend our investigation to the complexes of dicarboxylic acid fluorides with antimony pentafluoride.

## Results and Discussion

Preparation of the dicarboxylic acid fluoride-antimony pentafluoride complexes was carried out according to the previously reported "fluoride method" using excess antimony pentafluoride.<sup>2,3</sup>



Dicarboxylic acid fluorides needed for these investigations were prepared from the corresponding acyl chlorides with anhydrous hydrogen fluoride.<sup>5</sup>

Of the dicarboxylic acid fluorides, oxalyl,<sup>6</sup> malonyl,<sup>7</sup> succinyl,<sup>8</sup> adipyl,<sup>8</sup> and terephthaloyl<sup>7</sup> fluoride were reported in the literature; the others were newly prepared compounds.

The complex formation of acyl fluorides with antimony pentafluoride was generally carried out in 1,1,2-trifluoroethane (Freon 113) solution at  $-5$  to  $0^\circ$ . The azelayl complex was preferentially prepared in difluorodichloromethane (Freon 12) solution at lower temperature ( $-30^\circ$ ). Terephthaloyl fluoride is practically insoluble in fluorinated alkanes. Its complex formation therefore was carried out in sulfur dioxide-SbF<sub>5</sub> solution.

The crystalline complexes obtained were found by analytical data to be 1:2 acyl fluoride-antimony pentafluoride complexes of high purity. Their analytical data and melting points (in sealed capillary tubes) are listed in the Experimental Section.

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## Spectroscopic Investigations

**A. Infrared Spectra.** A Perkin-Elmer Model 337 grating spectrometer was used to record the spectra. Emulsions of the solid, isolated complexes in a fluorinated hydrocarbon (Fluorolube S30, Hooker Chemical Co.) were pressed between Irtran-2 plates, all operations being carried out in a drybox, as the complexes are sensitive to moisture.

The main characteristic data obtained are summarized in Table I. As an illustrative example the spectrum of  $\text{SbF}_6^- + \text{CO}(\text{CH}_2)_3\text{CO}^+\text{SbF}_6^-$  is shown in Figure 1.

Table I. Infrared Stretching Frequencies ( $\text{cm}^{-1}$ ) of Diacyl Fluoride-Antimony Pentafluoride Complexes

	Acyl fluoride		Complex		
	$\nu_{\text{CO}}$	$\nu_{\text{CF}}$	$\nu_{\text{CO}^+}$	$\nu_{\text{CO} \rightarrow \text{SbF}_6^-}$	$\nu_{\text{SbF}_6^-}$
Succinyl	1845, 1792	1085	2300	1550, 1630	663
Glutaryl	1842	1080	2290		664
Adipyl	1840	1075	2290		662
Pimelyl	1836	1082	2286		665
Suberyl	1836	1070	2285		665
Azelayl	1837	1073	2282		665
Terephthaloyl	1812	1040	2262		660

With the exception of the succinyl fluoride complex all the other investigated complexes show *no* carbonyl absorption, only the presence of an intense band around  $2300 \text{ cm}^{-1}$  indicating dioxodicarbonium ions without donor-acceptor complex character. The lower CO stretching frequency in the terephthaloyl complex compared with the alkylendioxodicarbonium complexes can be attributed to the conjugation of the CO groups with the ring. The spectrum of the succinyl fluoride-antimony pentafluoride complex (Figure 2) shows both the  $2300 \text{ cm}^{-1}$  band indicative of the oxocarboxonium ion nature and shifted carbonyl stretching frequency bands at 1550 and  $1630 \text{ cm}^{-1}$  indicative of donor-acceptor complex nature.<sup>2</sup> Thus the succinyl fluoride complex in the solid state is a mixed oxocarboxonium ion donor-acceptor complex. There is present also a band



at  $1810 \text{ cm}^{-1}$ . The presence of bands at 2300, 1810, 1600, and 1550 seems to be general for C<sub>4</sub> diacyl fluoride-antimony pentafluoride complexes.<sup>9</sup> The  $1800\text{-cm}^{-1}$

(9) G. A. Olah and M. B. Comisarow, *ibid.*, in press.

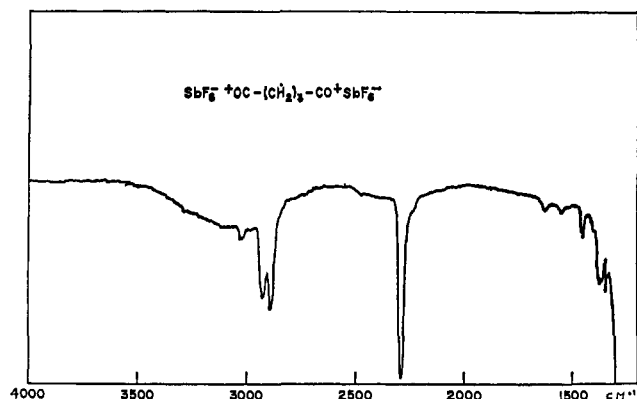


Figure 1.

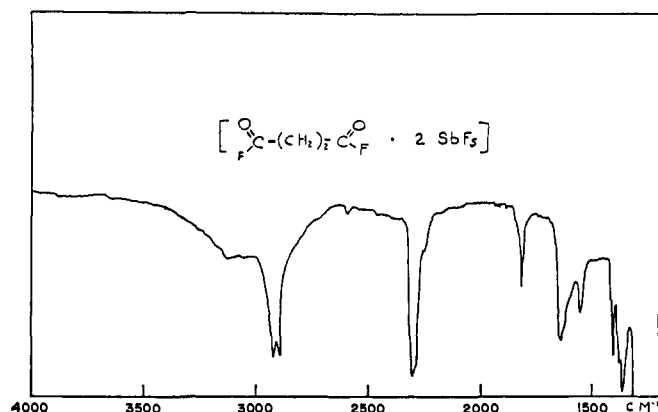
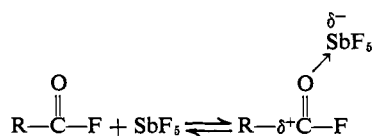


Figure 2.

band characteristic of the acyl fluoride CO stretching frequency could be due to an equilibrium between uncomplexed and complexed acyl fluoride. The in-



stability of the oxalyl and malonyl fluoride-antimony pentafluoride systems has not allowed their investigation.

**B. Nuclear Magnetic Resonance Spectra.** To obtain information on the structure of the diacyl fluoride-antimony pentafluoride (1:2) complexes in solution (as contrasted with infrared investigation of the solid complexes) nuclear magnetic resonance investigations were carried out. Sulfur dioxide solutions of the complexes were used at temperatures ranging from  $-30$  to  $60^\circ$ . Both  $\text{H}^1$  and  $\text{F}^{19}$  spectra were investigated

The proton spectra of the complexes was investigated on the Varian Model A-60 spectrometer equipped with a variable-temperature probe. Characteristic spectra are displayed in Figures 3-8. The data are summarized in Table II. All spectra are given in

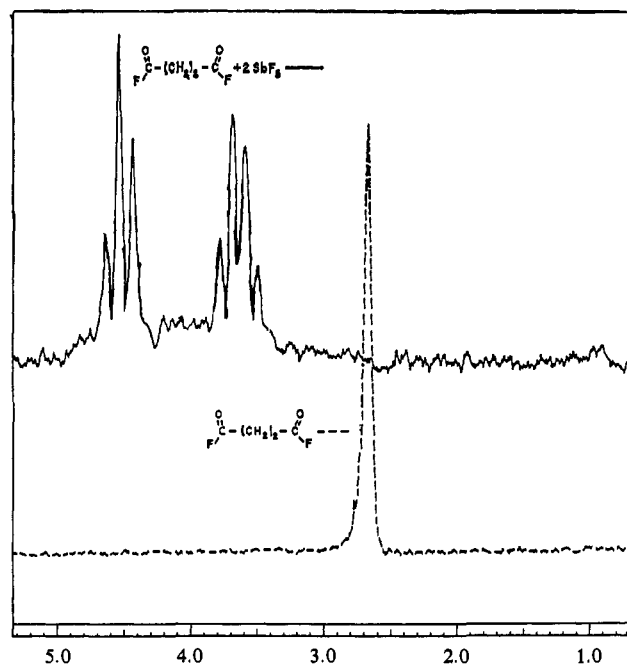


Figure 3.

**Table II.**  $\text{H}^1$  Nuclear Magnetic Proton Resonance Shifts of Diacyl Fluoride-Antimony Pentafluoride Complexes in  $\text{SO}_2$  Solution (ppm from TMS)

Compound	Temp, $^\circ\text{C}$	-Diacyl fluoride-2SbF <sub>5</sub> Complex-		
		Diacyl fluoride	$\text{SbF}_6^- \cdots \text{OC}(\text{CH}_2)_n \cdots \text{CO}^+ \text{SbF}_6^-$	$\text{SbF}_6^- \cdots \text{OC}(\text{CH}_2)_n \cdots \text{COF} \cdot \text{SbF}_6^-$
Succinyl	-17	-2.79	-4.60	-3.73
Glutaryl	-25	-2.63 $\alpha$	-4.58 $\alpha$	
		-1.83 $\beta$	-3.34 $\beta$	
Adipyl	-26	-2.42 $\alpha$	-4.20 $\alpha$	
		-1.53 $\beta$	-2.52 $\beta$	
Pimelyl	-32	-2.37 $\alpha$	-4.13 $\alpha$	
		-1.32 $\beta$	-2.24 $\beta$	
		-1.10 $\gamma$	-1.78 $\gamma$	
Suberyl	-32	-2.23 $\alpha$	-4.02 $\alpha$	
		-1.40 $\beta$	-2.20 $\beta$	
Azelayl	-25	-1.17 $\gamma$	-1.60 $\gamma$	
		-2.62 $\alpha$	-4.00 $\alpha$	
		-1.70 $\beta$	-2.10 $\beta$	
Terephthaloyl		-1.15 $\gamma$	-1.40 $\gamma$	
		-1.29 $\delta$	-1.29 $\delta$	
		-7.59 (main peak)	-8.07 (main peak)	

ppm from external tetramethylsilane (in a sealed capillary tube centered in the middle of the nmr tubes).

The acyl fluorides investigated exhibit  $\text{H}^1\text{-F}^{19}$  coupling of varying magnitude (generally  $^3J_{\text{H-F}} = 7$  cps). None of the glutaryl fluoride to azelayl fluoride complexes investigated exhibit any H-F coupling. No coupling would, of course, be expected in the oxocarboxonium ion forms. Fast exchange in a highly polarized donor-acceptor complex, however, could equally well result in the absence of observable H-F coupling<sup>2,4</sup> and therefore absence of H-F coupling cannot be used as conclusive evidence of ionic dissociation.

The nmr spectrum of the succinyl fluoride-antimony pentafluoride complex is shown in Figure 3. This spectrum can be accounted for by the monooxocarboxonium ion monodonor-acceptor structure already suggested from the infrared investigations. The low-field peak (at  $-4.6$  ppm) is assigned to the methylene group adjacent to the charged oxocarboxonium carbon atom and is split into a triplet ( $^3J_{\text{HH}} = 6$  cps) by the adjacent  $\text{CH}_2$  group. The high-field peak ( $-3.73$  ppm) can be assigned to the  $\text{CH}_2$  group adjacent to the

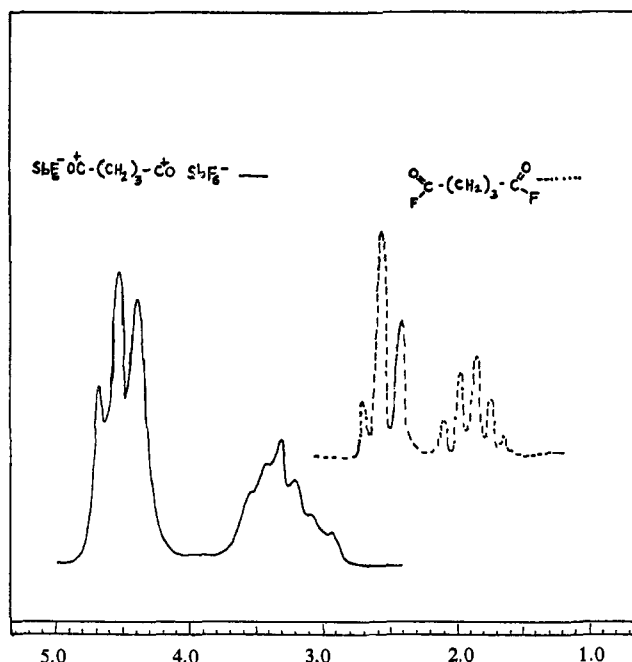


Figure 4.

donor-acceptor complex and arises as a quartet as follows. The low-field methylene group gives rise to a triplet which is further split by the fluorine of the acyl fluoride. If  $J_{H-F} = J_{H-H}$  a 1:3:3:1 quartet will result. The splitting by the fluorine of the acyl fluoride in the donor-acceptor complex was not observed previously in the case of acetyl fluoride and propionyl fluoride donor-acceptor complexes.<sup>2</sup> Thus the above assignment implies that fluorine is exchanging very slowly or not at all in the succinyl fluoride donor-acceptor complex. This seems to indicate that both ends of the molecule are solvated by a single solvation shell which prevents fluorine exchange. That the  $C_4$  skeletal integrity was maintained in complex formation was shown by the reaction of the complex with methanol to form dimethyl succinate and with benzene to form 1,4-diphenylbutane-1,4-dione.

The nmr spectrum of the glutaryl fluoride-antimony pentafluoride complex is shown in Figure 4. The low-field triplet ( $^3J_{H-H} = 7$  cps) at  $-4.5$  ppm is assigned to the two methylene groups adjacent to the acylium ion and the peak at  $-3.3$  ppm to the center methylene group. This peak is deshielded 1.4 ppm which is more than the normal 1-ppm deshielding the  $\beta$  protons undergo on formation of an acylium ion, because the center methylene protons are  $\beta$  to both positively charged ends of the molecule.

The adipyl, pimelyl, suberyl, and azelayl fluoride-antimony pentafluoride 1:2 complexes (Figure 5, 6, 7, and 8) all show nmr spectra in accordance with dioxodicarbonium structure (Table III). Terephthaloyl fluoride also forms a dioxodicarbonium ion, indicated by the substantial deshielding of the main proton peak (as compared with the deshielding effect noted in the phenyloxocarbonium ion<sup>2</sup>), but the ring protons are not well resolved.

Oxalyl and malonyl fluoride do not form sufficiently stable complexes with antimony pentafluoride that spectra could be obtained prior to partial decomposition. The same was the case with carbonyl fluoride.

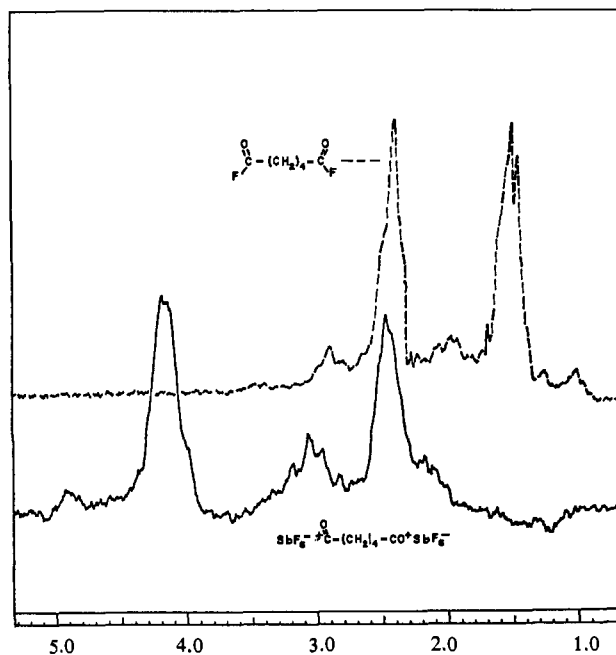


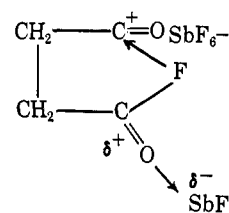
Figure 5.

Table III. Diacyl Fluoride-Antimony Pentafluoride Complexes

Diacyl fluoride · 2SbF <sub>6</sub>	Mp, °C <sup>a</sup>	—Calcd, %—		—Found, %—	
		F	Sb	F	Sb
Succinyl	66–69	41.7	43.5	42.1	43.2
Glutaryl	68–70	40.7	42.5	41.0	42.1
Adipyl	80–83	39.8	41.5	40.4	41.0
Pimelyl	68–70	38.8	40.5	39.0	40.3
Suberyl	68–71	37.9	39.5	38.3	39.4
Azelayl	40–44	37.1	38.6	37.0	38.1
Terephthaloyl	93–95	38.5	40.1	38.1	39.6

<sup>a</sup> With heating rate of 3°/min.

The fact that dioxodicarbonium (diacylium) ions are found only starting with glutaryl fluoride indicates the effect of charge-charge repulsion in the case of the lower members of the homologous series (FOC-(CH<sub>2</sub>)<sub>n</sub>COF,  $n < 2$ ). The monoacylium ion mono-donor-acceptor complex in the case of succinyl fluoride is further stabilized by cyclic interaction. When  $n \geq 4$ , cyclic interaction would be decreased by the steric in-



stability of larger rings. Spectroscopic data support this reasoning. So does the fact that the corresponding dicarboxylic acids preferentially form monomeric anhydrides.

The F<sup>19</sup> resonance spectra, obtained on Varian A-56-60 and HA-60 spectrometers equipped with a variable-temperature probe, showed good agreement with the proton resonance spectra. The glutaryl, adipyl, pimelyl, suberyl, azelayl, and terephthaloyl complexes all displayed only the SbF<sub>6</sub><sup>-</sup> fluorine atoms around +100

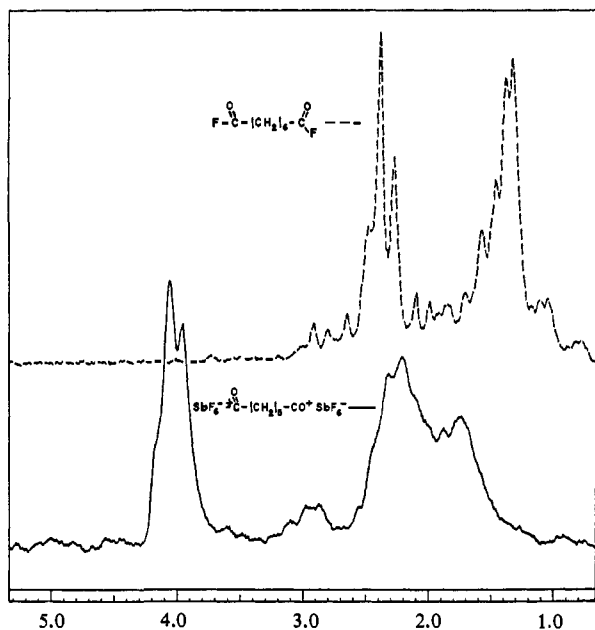


Figure 6.

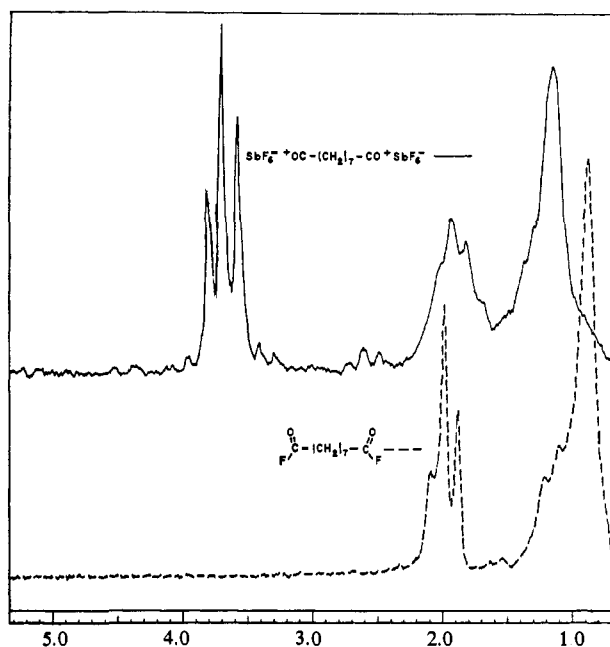


Figure 8.

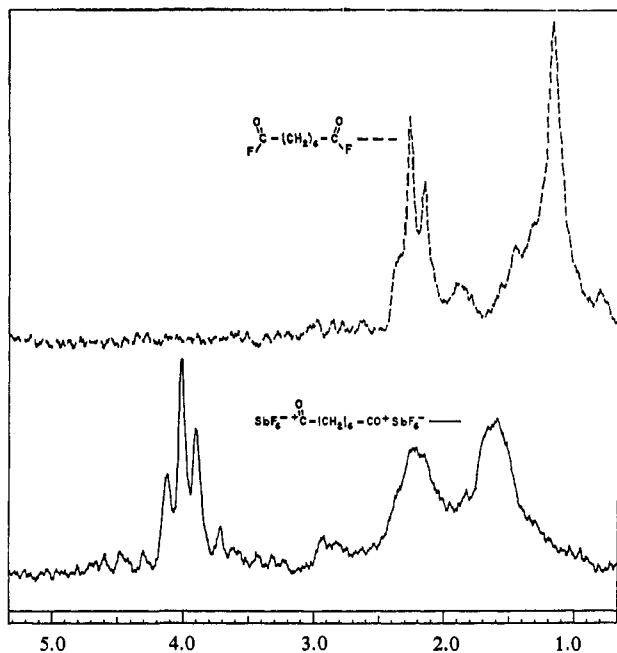


Figure 7.

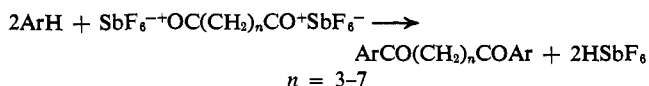
ppm (from external  $\text{CCl}_3\text{F}$ ) with no indication of aliphatic acyl fluoride atoms present. The succinyl fluoride-antimony pentafluoride complex (1:2) at  $-60^\circ$  in  $\text{SO}_2$  solution shows a 1:2:1 triplet ( $J_{\text{H-F}} = 5$  cps) at  $-35.5$  ppm (external  $\text{CCl}_3\text{F}$ ) and the antimony-fluorine peaks around  $+100$  ppm. Thus the nature of the monocation monodonor-acceptor complex suggested, based on the proton resonance data, is fully substantiated by the fluorine resonance investigations.

#### Chemical Reactivity

The isolated alkylenedioxodicarbonium ion complexes were found effective acylating agents in C, O, N, and S acylations of a variety of organic compounds. The scope of these reactions was not yet fully evaluated

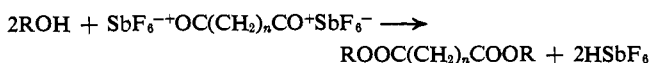
but the following examples are felt to sufficiently demonstrate some of the most important reaction types.

Aromatic hydrocarbons when treated with alkylenedioxodicarbonium ions in nitromethane solution (but also under heterogeneous reaction conditions) give the expected diketones

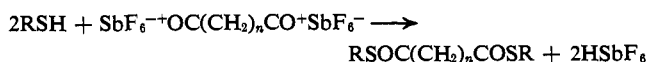


Yields with benzene and toluene, based on product diketone isolated, generally varied between 72 and 89%. No attempt was made to optimize reaction conditions.

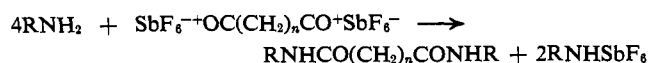
Alkylenedioxodicarbonium hexafluorantimonates are also highly effective acylating agents for O acylation of alcohols giving diesters



for acylation of mercaptans giving dithioesters



and for acylation of primary and secondary yielding diamides



These reactions proceed practically quantitatively.

#### Experimental Section

All of the starting acids and some of the acid chlorides are commercially available (Aldrich, Eastman Kodak). When the necessary acid chlorides were not available, they were prepared from the acids and  $\text{SOCl}_2$ .

Antimony pentafluoride was obtained from the Ozark-Mahoning Corp., Tulsa, Okla., and was purified as described previously.<sup>2</sup>

Succinyl fluoride (bp  $154-156^\circ$ ), glutaryl fluoride (bp  $98-100^\circ$  (59 mm)), adipyl fluoride (bp  $82^\circ$  (12 mm)), pimelyl fluoride (bp  $96-95^\circ$  (12 mm)), suberyl fluoride (bp  $104-107^\circ$  (12 mm)), and azelanyl fluoride (bp  $118-119^\circ$  (12 mm)) were prepared from the corresponding acid chlorides and anhydrous hydrogen fluoride in analogy with

the procedure for the preparation of 1-cyclobutanecarbonyl fluoride.<sup>9</sup> Terephthaloyl fluoride was similarly prepared and purified by sublimation at 4 mm. All acyl fluorides showed strong carbonyl (around 1825  $\text{cm}^{-1}$ ) and carbon-fluorine (around 1070  $\text{cm}^{-1}$ ) stretching frequencies.

**Preparation of Diacyl Fluoride-Antimony Pentafluoride Complexes.** In order to exclude moisture all preparations were carried out in efficient drybox (Keewaunee). Diacyl fluoride (0.05 mole) was dissolved in 100 ml of cold ( $0^\circ$ ) 1,1,2-trifluoroethane (Freon 113) and slowly added to a well-stirred (Teflon-covered magnetic stirrer) solution of 25 g (0.12 mole) of  $\text{SbF}_5$  in 200 ml of cold ( $0^\circ$ ) Freon 113. The complexes crystallize on formation, with the exception of the azeloyl complex which separates as a liquid. The complexes were then twice washed with 100-ml portions of Freon 113 and dried under vacuum. If needed, they were recrystallized from sulfur dioxide. The azeloyl complex could be prepared as a crystalline solid (mp  $40\text{--}44^\circ$ ) by using the above procedures but with dichlorodifluoromethane (Freon 12) as solvent and at a lower temperature ( $-30^\circ$ ).

As terephthaloyl fluoride is insoluble in chlorofluoroalkanes the following method was used for preparation of its antimony pentafluoride complex. Terephthaloyl fluoride (1.5 g) was added to a  $-10^\circ$  solution of 5 g of antimony pentafluoride in 500 ml of sulfur dioxide. The reaction mixture was stirred for 1 hr. The solution (containing the dissolved complex) was filtered from insoluble material. Sulfur dioxide was distilled off. The remaining solid complex was washed with Freon 113 to remove excess antimony pentafluoride. The crystalline white complex was then dried under vacuum. The analytical data and melting points of the isolated complexes are listed in Table III.

The nmr spectra of the complexes and the parent fluorides were taken at  $-30$  to  $-60^\circ$  in  $\text{SO}_2$  solvent on a Varian Model A-60 spectrometer equipped with a variable-temperature probe. The spectrum of terephthaloyl fluoride was taken at room temperature (sealed tube) because of the low solubility of the fluoride in  $\text{SO}_2$  at lower temperature.

Infrared spectra were taken on a Perkin-Elmer Model 337 Infrared spectrometer. The acyl fluorides were examined as neat liquids between KBr plates. The complexes were examined as fluorolube mulls. All operations with acyl fluorides or their com-

plexes were carried out in a drybox. The infrared data are summarized in Table I.

**Reaction of Alkylenedioxycarbonium Dihexafluoroantimonates with Aromatic Compounds.** The following procedure is for the reaction of the succinyl complex with benzene, but similar procedures were used for the other complexes with aromatics like benzene, toluene, and fluorobenzene.

The succinyl complex (10 g) was added slowly to 100 ml of benzene and the stirred mixture was heated gently ( $30\text{--}40^\circ$ ) to start the reaction. After being stirred for 30 min, the reaction was poured onto ice and the product was extracted with ether. After washings with water, the ethereal layer was dried ( $\text{MgSO}_4$ ), and 1,4-diphenylbutanedione was isolated after evaporation of the ether in yield of 56%.

**Reaction of Alkylenedioxycarbonium Salts with Alcohols.** The following procedure is for the succinyl complex but similar procedures were used for the other complexes. The succinyl complex (2 g) was dissolved in 100 ml of cold ( $-75^\circ$ )  $\text{SO}_2$  and added to a cold ( $-75^\circ$ ) stirred solution of 30 ml of methanol in 100 ml of  $\text{SO}_2$ . After being stirred for 1 hr at  $-70^\circ$ , the reaction mixture was poured onto a cold ( $-20^\circ$ ) ether-ice mixture. Sulfur dioxide was distilled off. The ethereal solution was washed with water and neutralized with  $\text{NaHCO}_3$ . Ether was distilled off and dimethyl succinate was isolated in yield of 74%.

**Reaction of Alkylenedioxycarbonium Dioxoantimonates with Mercaptans and Amines.** The reaction between dioxycarbonium ions and amines and mercaptans was carried out using conditions described previously for monooxycarbonium complexes.<sup>4</sup>

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