<u>3-(4-Chloro-3-pivaloylamino-2,6-dimethoxyphenyl)-5-phenyl-2-isoxazoline (XII)</u> was obtained analogously to (XI).

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ELECTROPHILIC ISOMERIZATION OF FLUOROALIPHATIC

OXYGEN-CONTAINING COMPOUNDS

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An unusual electrophilic cyclization of fluorine-containing carbonyl compounds and  $\alpha$ -oxides was discovered. Upon the action of SbF<sub>5</sub>, perfluorinated ketones, diketones, and  $\alpha$ -oxides isomerize to oxolanes. This reaction proceeds with the obligatory participation of the terminal CF<sub>3</sub> group.

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In previous work [1], we have shown that heating 2,3-bis(fluorosulfato)perfluoro-(2-methylpentane) (I) in the presence of  $SbF_5$  gives 2-fluorosulfatoperfluoro-(2-methyl-3pentanone) (II) as well as an unusual cyclization product, namely, perfluoro-2,2- dimethoxy-3-oxolanone (III), which is formally the cyclocondensation product of (II).\*



An analogy for this reaction is found in the isomerization of perfluoro(2-methyl-2-pentene) oxide (IV) upon its heating with a mixture of perfluorotoluene and  $SbF_5$ , leading to perfluoro(2,2-dimethyloxolane) (V) [2].<sup>†</sup>



Such reactions accompanied by the cleavage of a C-F bond in an unactivated  $CF_3$  group far removed from any functional group, double bond, or aromatic system, do not find analogy in the chemistry of organofluorine compounds.

<sup>\*</sup>In the present work, we found that heating (I) in the presence of  $SbF_5$  in an autoclave at 150°C for 12 h leads to the formation of (III) in 87% yield. <sup>†</sup>Oxide (IV) does not react with  $SbF_5$  in the absence of perfluorotoluene upon heating to 300°C [3].

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TABLE 1. Isomerization of	fι	(I),	(IV),	(VI),	(VIII),	and	(XI)
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Starting compound g (mole)	SbF <sub>5</sub> , g (mole)	<b>T</b> , °C	Time, h	Product	Yield,	Bp, ℃	Method of identification
(I), 22(0,05)	21 (0,09)	150	12	(111)	87	44-46	<sup>19</sup> F NMR, mass spectrometry (cf. [1])
(1V), 3(0,0075)	3(0,014) SbF <sub>5</sub> + 2,5 (0,01)	100	16	(V)	83	51-52	Cf. [2]
(VI), 1,2(0,003)	C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub> 2,4(0,01)	100	7	(VII)	84	50-52	<sup>19</sup> F NMR, mass spectrometry (cf. [4])
(VIII), 0,5 (0,002)	3(0,014) SbF <sub>5</sub> + 1,5(0,007)	100	13	(IX)	76	28	<sup>19</sup> F NMR, mass spectrometry (cf. [5])
(X),	$C_6F_5CF_3$ 3(0,014)	150	20	Starting	-	49-50	
2 (0,0052) (XI), 17 (0,054)	4,5 (0,02)	200	10	ketone (VII)+(X) (1:1)	90% mix-	49	<sup>19</sup> F NMR, GLC
					ture		

TABLE 2. Isomerization of (XII), (XIV), (XVI), (XVIII), (XXI), and Indices of Products Obtained

Starting		(e)		ч	÷	%	0		Found, % Calculated		Chemical
compour g (molo	e)	SbF <sub>5</sub> g (mo]	т, "С	Time,	Produc	Yield,	Bp, °(	vC=0, <b>C⊞−1</b>	с	F	formula
(XII);	7,0 (0,03)	12,0 (0,06)	150	8	(XIII)	83	29-32	1831	_	-	
(XIV);	15,0 (0,05)	21,0 (0,1)	100	6	(XV)	81	50-51	1824	$\tfrac{24,28}{24,49}$	$\tfrac{64,88}{64,63}$	$C_{6}F_{10}O_{2}$
(XVI);	<b>3,0</b> (0,01)	3,7 (0,02)	100	9	(XVII)	80	72-74	<b>182</b> 3	$\tfrac{\underline{24,08}}{\underline{24,42}}$	$\tfrac{65,84}{66,27}$	$C_7F_{12}O_2$
(XVIII);	34,0 (0,12)	50,0 (0,2)	150	8	(XIX)	65	57-58	1801	$\frac{23.91}{24,49}$	$\tfrac{64,60}{64,63}$	$C_6F_{10}O_2$
<b>(X</b> XI);	11,8 (0,04)	16,0 (0,07)	100	20	(XIX)	96	57-58	1801			

In the present work, we studied the behavior of a number of fluorine-containing carbonyl compounds and  $\alpha$ -oxides upon the action of SbF<sub>5</sub>.

Perfluoro(4-methyl-2-pentanone) (VI) readily cyclizes upon heating with  $SbF_5$  at 100°C for 7 h to give perfluoro(2,4-dimethyloxolane) (VII).



The cyclization of linear perfluoro-2-pentanone (VIII) is accomplished with considerably greater difficulty. Upon heating at 100°C for 13 h in the presence of  $SbF_5$ , the conversion of (VIII) does not exceed 2-3% but the use of the  $C_6F_5CF_3/SbF_5$  system gives the conversion of (VIII) to perfluoro(2-methyloxolane) (IX) under the same conditions.



Attempts to carry out this reaction for perfluoro(2-methyl-3-pentanone) (X), perfluoro(2,6,6-trimethyl-3-heptanone), and perfluoro-2-octanone were unsuccessful. Under comparable conditions featuring heating at 150-170°C for 20-30 h, the starting compounds were recovered unchanged.

Thus, these results permit us to determine the limiting conditions for this reaction. The electrophilic cyclization of oxo- and epoxyperfluoroalkanes is accomplished with the obligatory participation of the terminal  $CF_3$  group only in cases leading to the formation of a five-membered ring.

The exclusive formation of oxolanes is especially clearly seen in the behavior of perfluoro(4-methyl-2-pentene) oxide (XI). According to Zapevalov et al. [3], (XI) isomerizes upon heating to 200°C in the presence of  $SbF_5$  to give a 1:1 mixture of (VI) and (X). According to our data, a 1:1 mixture of (VII) and (X) is formed quantitatively upon the action of freshly distilled  $SbF_5$  on (XI) under the same conditions.<sup>\*</sup>



Independently of the question whether (VI) and (X) are formed initially or the isomerization of (XI) to (VII) occurs directly without intermediate formation of a ketone, the cyclization proceeds only when the formation of a five-membered ring is possible.

Perfluoro( $\alpha$ -diketones),  $R_{F}C(0)C(0)CF_{3}$  ( $R_{F} = C_{2}F_{5}$ ,  $n-C_{3}F_{7}$ ,  $i-C_{3}F_{7}$ ,  $C(CF_{3})_{3}$ ) cyclize in the presence of SbF<sub>5</sub> at 100-150°C to give substituted perfluoro-3-oxolanones or 2-trifluoroacetylperfluorooxolane (for  $R_{F} = n-C_{3}F_{7}$ ).



\*A mixture of (VI) and (X) is indeed formed upon the action of undistilled  $SbF_5$  on (XI) in accord with the data of Zapevalov [3].

## TABLE 3. Mass Spectra of Starting (XIV) and (XVI) and Products (XIII), (XIX), (XV), (XVII), (VII), and (IX)

Compound	m/z (I, %)
(IX)	$[M^+] 294 (1,5); [C_4F_7O]^+, 197 (25,7); [C_3F_7]^+, 169 (13,1); [C_3F_5]^+, 131 (3,8); [C_2F_3O]^+, 97, (24,6); [CF_3]^+, 69 (100)$
(XVI)	$ [M-CCCF_3]^+, 247 (24,5); [C_4F_7]^+, 181 (4,8); [C_4F_5O]^+, 159 (12,2); \\ [C_2F_3O]^+ 97 (24,3); [CF_3]^+, 69 (100) $
(XIII)	$\begin{array}{llllllllllllllllllllllllllllllllllll$
(XIX)	$\begin{array}{llllllllllllllllllllllllllllllllllll$
(XV)	[M-COF], 247 (2,1); $[C_3F_6]^+$ , 150 (100); $[C_3F_5]^+$ , 131 (26,5); $[C_3F_3O_2]^+$ , 125 (7,5); $[C_2F_4]^+$ , 100 (57,1); $[CF_3CO]^+$ , 97 (13,1); $[C_2FO_2]$ , 75 (1,9); $[CF_3]^+$ , 69 (36,1)
(XVII)	$      \begin{bmatrix} M^+ ], \ 344 \ (1,5); \ [M-F]^+, \ 325 \ (1,7); \ [C_4F_8]^+, \ 200 \ (100); \ [C_4F_7]^+, \ 181 \ (87,3); \\ [C_8F_5O]^+, \ 159 \ (10,5); \ [C_8F_6^+], \ 150 \ (9,8); \ [C_8F_8]^+, \ 131 \ (32,7); \ [C_3F_3O_2]^+, \\ 125 \ (10,0); \ [C_2F_3O]^+, \ 97 \ (16,5); \ [C_2F_4]^+, \ 100 \ (6,2); \ [C_2FO_2]^+, \ 75 \ (8,6); \\ [CF_3]^+, \ 69 \ (96,7)                                    $
(VII)	$ \begin{bmatrix} M-F \end{bmatrix}^+, 297 (15,4); \ [M-CF_3]^+, 247 (5,0); \ [C_4F_9]^+, 219 (16,7); \ [C_4F_6]^+, 200 (15,2); \ [C_4F_7]^+, 181 (42,19); \ [C_8F_6]^+, 150 (14,0); \ [C_3F_5], 131 (60,6); \ [C_2F_4]^+, 100 (12,3); \ [CF_3]^+, 69 (100) $
(IX)	$ \begin{array}{l} [MF]^+, \ 247\ (2,2); \ [MCF_3]^+, \ 197\ (4,6); \ [C_3F_7]^+, \ 169\ (23,7); \ [C_3F_6]^+, \\ 150\ (12,4); \ [C_3F_5]^+, \ 131\ (15,3); \ [C_2F_4]^+, \ 100\ (25,5); \ [C_2F_3O]^+ 97\ (29,2); \\ [CF_3]^+, \ 69\ (100) \end{array} $

Clearcut behavior is found in the cyclization of  $\alpha$ -diketones as in the case of monocarbonyl compounds. Ring formation requires the presence of a CF<sub>3</sub> group on one end of a chain consisting of five atoms and a carbonyl oxygen atom on the other. Independently of the structure of perfluoroalkyl substituent, the carbonyl group not participating in the cyclization must be either in the ring or outside the ring in a trifluoroacetyl fragment. If this rule is violated, the cyclization does not proceed at all as seen in the case of perfluoro-2,3-octadione (XX), which does not cyclize under comparable conditions and undergoes considerable decomposition under more vigorous conditions.

 $CF_{3} - C - C_{5}F_{11} \xrightarrow{SbF_{5}}_{150^{\circ}, 16 \text{ h}} \cdot$ 

The first reaction step in the cyclization of perfluorinated ketones or  $\alpha$ -diketones is apparently the electrophilic attack of SbF<sub>5</sub> on the carbonyl group oxygen atom, leading to a carbenium site. The next step features isomerization of the secondary carbocation into a primary carbocation with subsequent intramolecular alkylation at the oxygen atom (scheme 1).

The driving force for the isomerization is the generation of a cation stabilized by the interaction of the vacant orbital of the carbon atom with the p-electrons of the two geminal fluorine atoms.



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TABLE 4. <sup>19</sup>F NMR Spectral Parameters for Compounds Obtained\*



\*The spectra are highly coupled multispin systems. These spectra were not calculated. The table gives the differences of the corresponding frequencies. \*\*The assignment of the signals for the cis and trans isomers

for (XV) was carried out using the constants for through space coupling  $\rm J_{b-c}$  = 9.5 Hz (cis) and <1 Hz (trans).

The isomerization of the secondary carbenium ion to a primary carbenium ion is most likely accomplished by the direct attack of the cationic site on a fluorine atom of the trifluoromethyl group and not by the consecutive migration of a fluorine atom along the chain. At least the formation of oxolanone (XVII) from diketone (XVI) unequivocally indicates the actual migration of a fluorine atom through space since the presence of a quaternary carbon atom excludes migration along the carbon chain. This hypothesis is also supported by the facility of the cyclization of the ketones and  $\alpha$ -diketones with a branched chain in comparison with linear analogs.

The isomerization of oxiranes to oxolanes described above apparently proceeds through an analogous mechanism except that the initially formed secondary carbocation is generated by means of electrophilic attack of  $SbF_5$  onto the oxygen of the  $\alpha$ -oxide (scheme 2).



The tendency to five-membered ring formation is clearly seen also in the recyclization of perfluoro(2-methyl-3-oxolanone) (XXI),\* which undergoes ring contraction upon the action of  $SbF_5$  and isomerizes to give perfluoro(2-acetyloxolane) (XIX).



In conclusion, we should note the promoting role of perfluorotoluene in these reactions. When the  $C_6F_5CF_3/SbF_5$  system is used as the isomerization catalyst, the initial step is apparently attack of the perfluorobenzyl cation on the oxygen atom of the carbonyl group or oxirane ring. The greater facility of formation of oxonium or carbonium ions upon the attack of a positively charged species in comparison with the neutral  $SbF_5$  molecule as well as the approximation in energy of the vacant 2p orbital of this cation and the occupied 2p orbital of the oxygen atom are possible factors facilitating the interaction of the perfluorobenzyl cation with the oxygen atom in these compounds.

## EXPERIMENTAL

The <sup>19</sup>F NMR spectra were taken on a Bruker WP-200 SY spectrometer using  $CF_3CO_2H$  as the external standard. The chemical shifts are given in ppm, while the coupling constants are given in Hz. The Raman spectra were obtained on a Ramanor spectrometer with excitation by an argon laser at 514.5 nm. The mass spectra were obtained on a GV7070E mass spectrometer. The energy of the ionizing radiation was 70 eV.

Isomerization of Perfluoroketones, Perfluorodiketones, and Substituted Perfluorooxiranes by the Action of  $SbF_5$  (typical procedure). A mixture of the starting compound and  $SbF_5$  was heated in a sealed glass ampul. The ampul was then cooled to -196°C and opened. The reaction mixture was poured into concentrated sulfuric acid and distilled over concentrated sulfuric acid. The isomerization conditions and indices of the compounds obtained are given in Tables 1 and 2. Reaction products (III), (VII), (IX), and (V) were identified by <sup>19</sup>F NMR and Raman spectroscopy and mass spectrometry. The reactions of (I) and (XI) were carried out in an autoclave.

The mass spectra of the compounds obtained as well as several starting reagents (for comparison of the decomposition) are given in Tables 3 and 4. The mass spectra of the perfluorooxalanones differ markedly from the spectra of the corresponding starting  $\alpha$ -diketones. The decomposition of the cyclic molecular ion, in general, proceeds along two pathways:

<sup>\*</sup>A sample of (XXI) was kindly supplied by Chemical Sciences Candidate V. G. Poludnenko.



The first fragment and product of its subsequent decomposition  $[FC(0)-C=0]^-$  (m/z 75) are the same for all three compounds, while the second fragment is specific. The corresponding ions in all cases have 100% intensity. The smaller fluorocarbon fragments may be seen as products of subsequent decomposition of  $[CF_2=CXY]^+$  ions.

The mass spectra of the other compounds are much more similar to the spectra of the starting isomers. Ring opening and subsequent fragmentation similar to the fragmentation of the ketones apparently occurs to a great extent upon electron impact. Nevertheless, the enhanced content of olefinic fragments ( $C_4F_8$ ,  $C_3F_6$ , and  $C_2F_4$  in the case of (VII),  $C_3F_6$  and  $C_2F_4$  in the case of (IX), and  $C_2F_4$  in the case of (XIX)) is in accord with the general rules for ring decomposition [6] and supports the proposed structures.

The <sup>19</sup>F NMR spectra are given in Table 4.

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