

# Reaction of Polyfluoro-3-chloro(bromo)-1-butenes with Sodium Hypohalites and Properties of Epoxides Derived Therefrom

A. Ya. Zapevalov, T. I. Filyakova, M. I. Kodess, and V. I. Saloutin

*Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences,  
ul. S. Kovalevskoi 20, Yekaterinburg, 620219 Russia  
e-mail: saloutin@ios.uran.ru*

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**Abstract**—Epoxidation of 3-chloro(bromo)heptafluoro-1-butenes and 3,4-dichlorohexafluoro-1-butene with aqueous solutions of sodium hypohalites is accompanied by cleavage of the carbon skeleton at the double bond and formation of polyfluorocarboxylic acid sodium salts as by-products. 3-Chloro(bromo)-1,2-epoxyheptafluoro- and 3,4-dichloro-1,2-epoxyhexafluorobutanes were synthesized and subjected to isomerization into carbonyl compounds by the action of cesium fluoride or antimony pentafluoride.

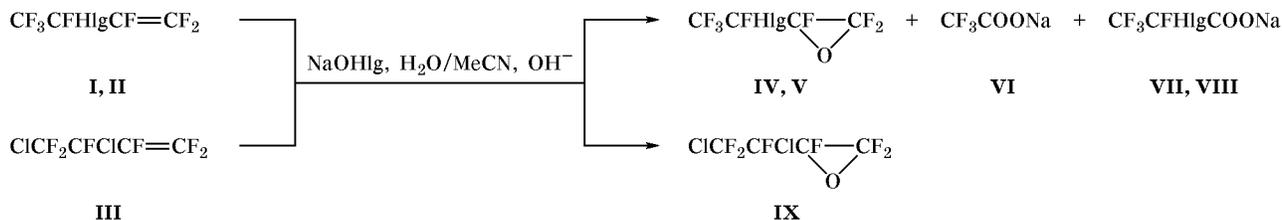
We previously demonstrated a wide synthetic potential of the hypohalite procedure for epoxidation of polyfluoroalkenes, which makes it possible to obtain various polyfluorinated epoxy derivatives [1–5]. We found that the structure of the initial alkene largely determines the mechanism of its reaction with hypohalite ions. In the epoxidation of internal and cyclic perfluoroalkenes, the yields of the corresponding epoxy derivatives were nearly quantitative [1–4], whereas in the reactions with terminal perfluoroalkenes the yields were somewhat lower because of side processes [1, 2, 5]. The selectivity of epoxidation is also reduced when the substrate contains chlorine or bromine atoms in the  $\alpha$ - or  $\beta$ -position with respect to the double bond [6, 7].

The goal of the present study was to get a deeper insight into the mechanism of hypohalite oxidation of fluoroalkenes, prepare the corresponding epoxides, and determine their structure and properties. For this

purpose, we examined reactions of sodium hypohalites with polyfluoro-1-butenes having a chlorine or bromine atom in position 3: 3-chloroheptafluoro-1-butene (**I**), 3-bromoheptafluoro-1-butene (**II**), and 3,4-dichlorohexafluoro-1-butene (**III**).

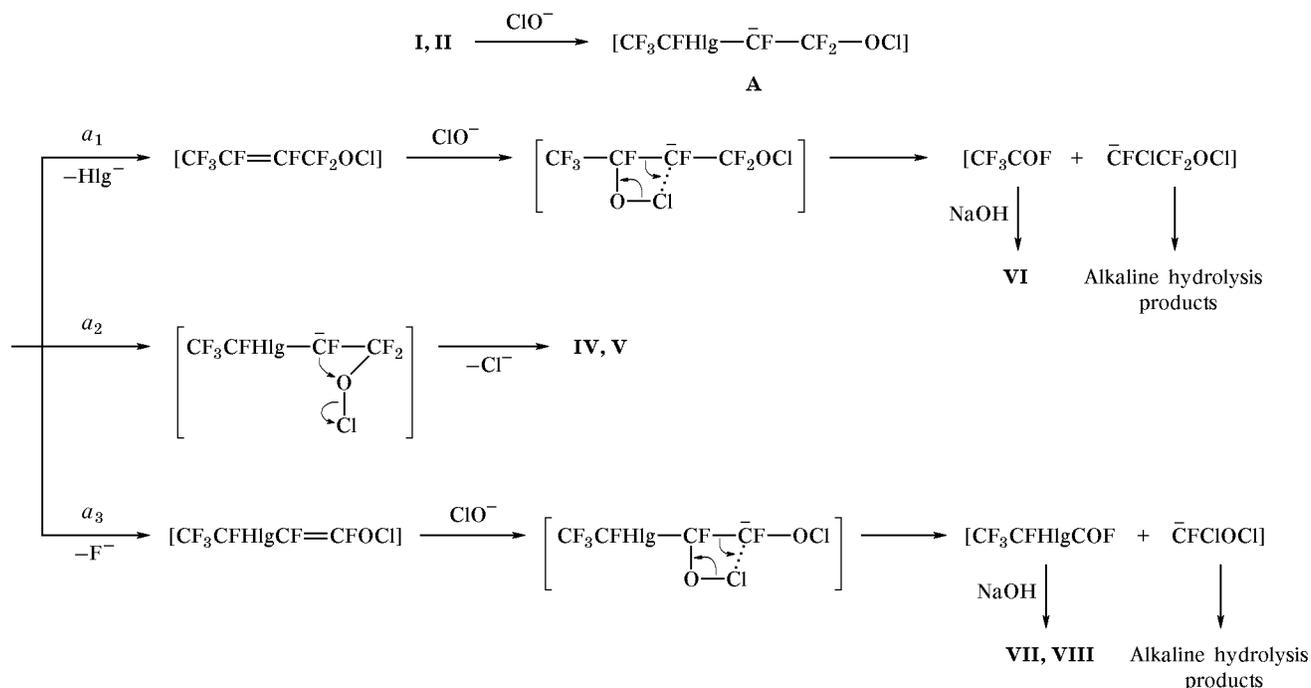
The synthesis and some properties of alkenes **I** and **II** were described by us previously [8]. Compound **III** was synthesized by pyrolysis of sodium 4,5-dichloropentanoate. Alkenes **I–III** readily react with sodium hypohalites in a mixture of water with an aprotic solvent; however, the presence of chlorine or bromine atom gives rise to alternative paths for stabilization of intermediate carbanions. Despite the reactions were not strictly selective, we succeeded in isolating epoxy derivatives of all the above alkenes (Scheme 1). The by-products were mainly sodium salts of polyfluorocarboxylic acids, which are soluble in water (polyfluorinated peroxides are insoluble in water).

Scheme 1.



**I, IV, VII, Hlg = Cl; II, V, VIII, Hlg = Br.**

Scheme 2.



The reaction is likely to follow Scheme 2. Carbanionic intermediate **A** can be stabilized according to pathways  $a_1$  and  $a_2$  with equal probabilities. The yields of epoxy derivatives **IV** and **V** are 52 and 40%, respectively; sodium trifluoroacetate is the major component of the salt products. However, the formation of a small amount of compounds **VII** and **VIII** (7–9% of the overall amount of the salt products) indicates that stabilization pathway  $a_3$  also exists.

The product composition and the yield of epoxy derivatives **IV**, **V**, and **IX** depend on the initial alkene structure, reaction temperature, and the way of mixing of the reactants. The maximal yields of 1,2-epoxybutanes **IV** and **IX** were obtained when an aqueous solution of sodium hypochlorite was added at 5 to 10°C to a solution of polyfluoroalkene **I** or **III** in acetonitrile. The yield decreases on raising the temperature, while the fraction of alkaline hydrolysis products increases. No by-products were isolated in

the reaction with dichloroalkene **III**. Presumably, oxygen-containing anions undergo further transformation, as follows from evolution of a small amount of CO and CO<sub>2</sub>. This is consistent with the results obtained in the epoxidation of 1,4-dichlorohexafluoro-2-butene [6], where we failed to detect by-products as well. However, following the above procedure, from alkene **II** we obtained 1-bromoheptafluoro-2-butene (**X**) as the major product (Scheme 3). We previously reported [8] that alkene **II** extremely readily undergoes isomerization into compound **X** by the action of both nucleophilic and electrophilic reagents [8]. Addition of a few drops of a solution of NaOCl to a solution of polyfluorobutene **II** in acetonitrile (i.e., the reaction occurs in fact in aprotic medium) leads to elimination of bromide ion (pathway  $a_1$  in Scheme 2) which promotes isomerization of **II** into **X**. The latter process is accompanied by elimination of the allylic bromine atom, giving rise to a specific “chain” reaction (Scheme 3).

Scheme 3.

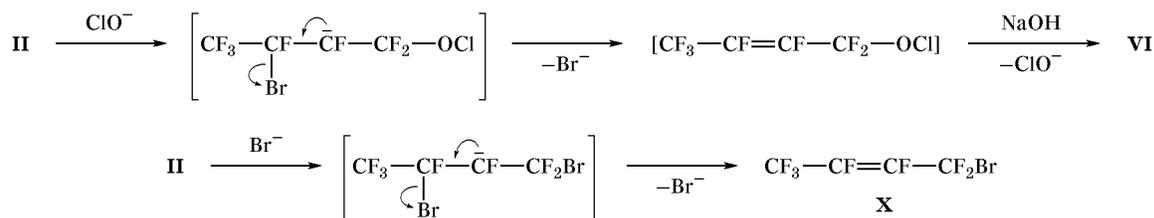
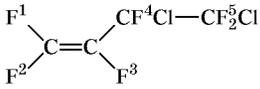
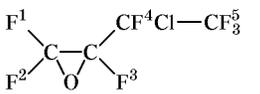
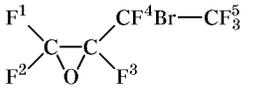


Table 1.  $^{19}\text{F}$  NMR spectra of compounds **III**–**V**, **VII**–**IX**, **XIII**, and **XVI**<sup>a</sup>

| Comp. no.                | Formula  | Chemical shifts, $\delta_{\text{F}}$ , ppm   | Coupling constants $J_{\text{F,F}}$ , Hz  |
|--------------------------|--|--|---|
| <b>III</b>               |                       | 108.24 d.d.d.d (1-F);<br>89.64 d.d.d.m (2-F);<br>166.94 d.d.d.d (3-F);<br>128.34 d.d.d.d (4-F);<br>66.32 d.d.d (5-F <sub>A</sub> );<br>65.23 d.d.d (5-F <sub>B</sub> )   | $J_{1,2} = 58.2$ , $J_{1,3} = 126.3$ ,<br>$J_{1,4} = 48.8$ , $J_{1,5A} = -J_{1,5B} = 4.0$ ,<br>$J_{2,3} = 42.8$ , $J_{2,4} = 2.8$ , $J_{3,4} = 22.8$ ,<br>$J_{3,5A} = 9.0$ , $J_{3,5B} = 8.2$ ,<br>$J_{4,5A} = 12.1$ , $J_{4,5B} = 13.0$ ,<br>$J_{5A,5B} = 177.1$   |
| <b>IV</b>                |                       | Isomer <b>1</b> (60%):<br>107.86 d.d.m (1-F);<br>107.26 d.d (2-F); 143.27 m (3-F);<br>133.87 m (4-F); 79.11 d.d (5-F)<br>Isomer <b>2</b> (40%):<br>108.57 d.d.m (1-F);<br>110.60 d.d (2-F); 147.68 m (3-F);<br>135.15 m (4-F); 77.90 d.d (5-F)   | $J_{1,2} = 41.0$ , $J_{1,3} = J_{2,3} = 17.0$ ,<br>$J_{1,4} = 24.5$ , $J_{3,5} = J_{4,5} = 8.3$<br>$J_{1,2} = 42.0$ , $J_{1,3} = 18.0$ ,<br>$J_{1,4} = 20.5$ , $J_{2,3} = 18.0$ ,<br>$J_{2,4} = 2.0$ , $J_{3,5} = 7.3$ , $J_{4,5} = 9.8$  |
| <b>V</b>                 |                       | Isomer <b>1</b> (70%):<br>107.86 d.d (1-F); 106.67 d.d (2-F);<br>140.68 m (3-F);<br>137.61 m (4-F); 77.82 d.d (5-F)<br>Isomer <b>2</b> (30%):<br>109.04 d.d.m (1-F);<br>111.49 d.d (2-F); 147.54 m (3-F);<br>138.51 m (4-F); 76.34 d.d (5)   | $J_{1,2} = 39.0$ , $J_{1,3} = 17.1$ ,<br>$J_{1,4} = 25.6$ , $J_{2,3} = 17.1$ ;<br>$J_{2,4} = 3.7$ ; $J_{3,5} = J_{4,5} = 9.8$<br>$J_{1,2} = 42.7$ , $J_{1,3} = 18.3$ ,<br>$J_{1,4} = 20.8$ , $J_{2,3} = 18.3$ ,<br>$J_{2,4} = 2.4$ , $J_{3,5} = J_{4,5} = 9.8$  |
| <b>VII</b>               | $\overset{1}{\text{CF}}_3-\overset{2}{\text{CFCl}}-\text{COONa}$                                       | 78.54 d (1-F); 123.95 q (2-F)  | $J_{1,2} = 6.1$   |
| <b>VIII</b>              | $\overset{1}{\text{CF}}_3-\overset{2}{\text{CFCl}}-\text{COONa}$                                       | 76.83 d (1-F); 124.54 q (2-F)  | $J_{1,2} = 8.5$   |
| <b>IX</b>                | $\overset{1}{\text{CF}}_3-\overset{2}{\text{CFBr}}-\text{COONa}$                                       | Isomer <b>1</b> (75%):<br>107.88 d.d.d.m (1-F);<br>108.70 d.d.m (2-F); 143.56 m (3-F);<br>127.30 m (4-F); 61.81 d.d (5-F <sub>A</sub> );<br>66.04 d.m (5-F <sub>B</sub> )<br>Isomer <b>2</b> (25%):<br>109.64 d.d.d.m (1-F);<br>112.69 d.d.d.m (2-F); 148.90 m (3-F);<br>127.92 m (4-F);<br>63.67 d.d.m (5-F, AB center) | $J_{1,2} = 40.0$ , $J_{1,3} = 17.0$ ,<br>$J_{1,4} = 26.0$ , $J_{1,5A} = 2.0$ ,<br>$J_{1,5B} = 1.0$ , $J_{2,3} = 16.0$ ,<br>$J_{3,4} = 18.0$ , $J_{3,5A} = 15.0$ ,<br>$J_{3,5B} = 13.0$ , $J_{4,5A} = 8.5$ ,<br>$J_{4,5B} = 11.0$ , $J_{5A,5B} = 176.0$<br>$J_{1,2} = 43.0$ , $J_{1,3} = 18.0$ ,<br>$J_{1,4} = 21.0$ , $J_{2,3} = 19.0$ ,<br>$J_{2,4} = 2.0$ , $J_{3,4} = 6.5$ ,<br>$J_{3,5} = 14.5$ , $J_{4,5} = 9.5$ |
| <b>XIII</b> <sup>b</sup> | $\overset{1}{\text{ClCF}}_2-\overset{2}{\text{CFCl}}-\overset{3}{\text{CF}}_2-\overset{4}{\text{COF}}$ | -13.6 m (1-F, AB center);<br>57.3 m (2-F); 33.43 m (3-F <sub>A</sub> );<br>34.67 m (3-F <sub>B</sub> );<br>-97.3 m (4-F)   | $J_{3A,3B} = 175$   |
| <b>XVI</b>               | $\overset{1}{\text{CF}}_3-\text{CO}-\overset{2}{\text{CFCl}}-\overset{3}{\text{CF}}_2\text{Cl}$        | 73.04 d.t (1-F); 134.34 m (2-F);<br>63.84 d.d.q (3-F <sub>A</sub> );<br>65.34 d.d.q (3-F <sub>B</sub> )  | $J_{1,2} = 5.8$ , $J_{2,3A} = 8.6$ ,<br>$J_{2,3B} = 10.0$ , $J_{1,3A} = J_{1,3B} = 1.9$ ,<br>$J_{3A,3B} = 176.9$  |

<sup>a</sup> The  $^{19}\text{F}$  NMR spectra of compounds **XIV** and **XV** coincided with those reported in [6].<sup>b</sup> Relative to  $\text{CF}_3\text{COOH}$  (external reference).

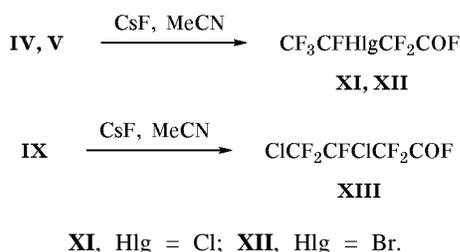
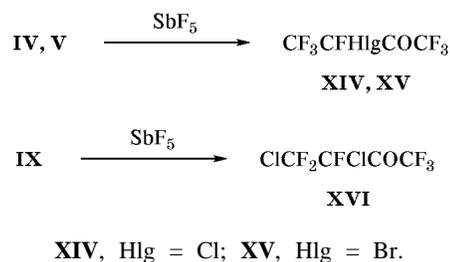
**Table 2.** Yields, boiling points, and IR spectra of compounds **III–V**, **IX**, and **XI–XVI**

| Compound no. | Yield, % | bp, °C | IR spectrum, $\nu$ , $\text{cm}^{-1}$ |
|--------------|----------|--------|---------------------------------------|
| <b>III</b>   | 73       | 66–67  | 1770 (C=C)                            |
| <b>IV</b>    | 52       | 30–31  | 1540 (oxirane)                        |
| <b>V</b>     | 44       | 46–47  | 1535 (oxirane)                        |
| <b>IX</b>    | 57       | 65–66  | 1540 (oxirane)                        |
| <b>XI</b>    | 88       | 36–37  | 1880 (COF)                            |
| <b>XII</b>   | 90       | 57–58  | 1880 (COF)                            |
| <b>XIII</b>  | 92       | 70–71  | 1865 (COF)                            |
| <b>XIV</b>   | 86       | 31–32  | 1785 (C=O)                            |
| <b>XV</b>    | 75       | 45–46  | 1775 (C=O)                            |
| <b>XVI</b>   | 84       | 64–65  | 1780 (C=O)                            |

No isomerization products were obtained from alkenes **I** and **III** under analogous conditions. The observed difference in the behaviors of bromine-containing polyfluorobutene (**II**) and alkenes **I** and **III** may be explained by more facile elimination of bromine as bromide ion and higher nucleophilicity of bromide ion as compared to chloride ion [9].

3-Bromo-1,2-epoxyheptafluorobutane (**V**) was obtained in 41% yield by addition of alkene **II** in a dropwise fashion to a solution of NaOCl containing acetonitrile at 0 to 10°C. According to the  $^{19}\text{F}$  NMR data, compounds **IV**, **V**, and **IX** are formed as mixtures of two diastereoisomers due to the presence in their molecules of two chiral centers (Table 1).

Epoxy polyfluoroalkanes **IV**, **V**, and **IX**, as well as their perfluorinated analogs, are capable of undergoing rearrangement into carbonyl compounds by the action of Lewis acids and bases. In the presence of fluoride ion, these compounds give rise to acyl fluorides **XI–XIII** (Scheme 4). The rearrangement was performed in acetonitrile under reflux to avoid formation of oligomeric products. Compounds **IV**, **V**, and **IX** readily react with  $\text{SbF}_5$  at room temperature to afford  $\alpha$ -chloro(bromo)polyfluoroketones **XIV–XVI** (Scheme 5).

**Scheme 4.****Scheme 5.**

## EXPERIMENTAL

The  $^{19}\text{F}$  NMR spectra were recorded on Tesla BS-567A (94.1 MHz) and Tesla BS-587A spectrometers (75.3 MHz) using acetone- $d_6$  and methanol- $d_4$  as solvents and  $\text{C}_6\text{F}_6$  as internal reference; also, a Perkin-Elmer R-32 instrument (84.6 MHz) was used with  $\text{CF}_3\text{CO}_2\text{H}$  as external reference. The chemical shifts are given in ppm relative to  $\text{CFCl}_3$  (positive values correspond to increasing field strength). The  $^{19}\text{F}$  NMR data are collected in Table 1. The IR spectra were measured on a Specord 75IR spectrometer from samples prepared as thin films or solutions in  $\text{CCl}_4$ . GLC analysis was performed on an LKhM-72 chromatograph equipped with a thermal conductivity detector and steel columns (6500  $\times$  4 mm) packed with 15% of SKTFT-100 or FS-1265 on Chromosorb W; carrier gas helium.

4,5-Dichloroheptafluoropentanoic acid was synthesized by the procedure described in [10], and alkene **III** was prepared by pyrolytic decarboxylation of sodium 4,5-dichloroheptafluoropentanoate at 250–280°C. The yields, boiling points, and some IR bands of the compounds prepared are given in Table 2.

Solutions of sodium hypochlorite [1] and sodium hypobromite [11] were prepared by known methods.

**Reaction of alkene I with NaOCl.** An aqueous solution of NaOCl, 50 ml, was added at 5 to 10°C under vigorous stirring to a solution of 4.8 g (22.17 mmol) of alkene **I** in 6 ml of acetonitrile. The mixture was stirred for 1 h, and the organic layer was separated, washed with water, dried over  $\text{MgSO}_4$ , and distilled. Yield of epoxy derivative **IV** 2.7 g. Found, %: C 20.34; Cl 15.12; F 56.90.  $\text{C}_4\text{ClF}_7\text{O}$ . Calculated, %: C 20.65; Cl 15.27; F 57.20. The aqueous phase was evaporated, and the salt residue was dried and dissolved in  $\text{CD}_3\text{OD}$ . According to the  $^{19}\text{F}$  NMR data, it was a 61:39 mixture of salts **VI** and **VII**.

**Reaction of alkene II with NaOCl.** *a.* The reaction was carried out in a similar way. From 10 g (38.31 mmol) of alkene **II**, 8 ml of acetonitrile, and 50 ml of a solution of NaOCl we obtained 8.4 g of

alkene **X** containing a small amount (~5%, according to GLC and  $^{19}\text{F}$  NMR) of compound **V**.

*b.* Alkene **II**, 6.0 g (23 mmol), was added dropwise at 0 to 10°C under vigorous stirring to 50 ml of an aqueous solution of NaOCl and 6 ml of acetonitrile. The mixture was stirred for 1 h, and the bottom layer was separated, washed with water, dried over  $\text{MgSO}_4$ , and distilled. Yield of compound **V** 2.8 g. Found, %: C 17.25; Br 29.30; F 41.07.  $\text{C}_4\text{BrF}_7\text{O}$ . Calculated, %: C 17.45; Br 29.09; F 41.45. According to the  $^{19}\text{F}$  NMR data, the aqueous phase contained salts **VI** and **VIII** at a ratio of 91:9.

**Reaction of alkene II with NaOBr.** Alkene **II**, 4.0 g (15.33 mmol), was added dropwise at ~5°C under vigorous stirring to a mixture of 20 ml of an aqueous solution of NaOBr and 2 ml of acetonitrile. The mixture was stirred for 1 h. The organic phase was separated, washed with water, dried over  $\text{MgSO}_4$ , and distilled. We isolated 2.8 g of a mixture of compounds **V** and **X** at a ratio of 70:30 (GLC,  $^{19}\text{F}$  NMR). From the aqueous phase, a mixture of salts **VI** and **VIII** (93:7;  $^{19}\text{F}$  NMR) was isolated.

**Reaction of alkene III with NaOCl.** An aqueous solution of NaOCl, 100 ml, was added dropwise at 0 to 10°C under vigorous stirring to a solution of 20.0 g (85.8 mmol) of alkene **III** in 10 ml of acetonitrile. The mixture was stirred for 1 h and was subjected to appropriate treatment to isolate 12.2 g of compound **IX**. Found, %: C 19.56; Cl 28.05; F 45.33.  $\text{C}_4\text{Cl}_2\text{F}_6\text{O}$ . Calculated, %: C 19.28; Cl 28.51; F 45.78. No organofluorine compounds were detected in the aqueous phase by  $^{19}\text{F}$  NMR spectroscopy.

**Reaction of 3-chloro-1,2-epoxyheptafluorobutane (IV) with CsF.** Compound **IV**, 1.25 g (5.38 mmol), was added dropwise with stirring to a mixture of 0.3 g (1.96 mmol) of freshly calcined CsF and 3 ml of freshly distilled (over  $\text{P}_2\text{O}_5$ ) acetonitrile, heated to the boiling point. The mixture was stirred for 0.5 h, filtered, and distilled. We isolated 1.1 g of 3-chlorohexafluorobutanoyl fluoride (**XI**).

**Reaction of 3-bromo-1,2-epoxyheptafluorobutane (V) and 3,4-dichloro-1,2-epoxyhexafluorobutane (IX) with cesium fluoride.** Following the above procedure, from 1.6 g (5.8 mmol) of compound **V** or 2.5 g (10.0 mmol) of compound **IX** and 0.5 g (3.27 mmol) of CsF in 4 ml of acetonitrile we obtained 1.4 g of fluoride **XII** or 2.3 g of fluoride **XIII**.

**Reaction of compound IV with  $\text{SbF}_5$ .** Antimony pentafluoride, 0.1 ml, was added dropwise to 1.0 g (4.3 mmol) of compound **IV**. The mixture was kept for 0.5 h and was then distilled over concentrated sulfuric acid to isolate 0.86 g of ketone **XIV**.

**Reaction of compounds V and IX with  $\text{SbF}_5$ .** Following the above procedure, from 1.2 g (4.3 mmol) of compound **V** or 1.8 g (7.23 mmol) of **IX** and 0.1 ml of  $\text{SbF}_5$  we obtained, respectively, 0.9 g of ketone **XV** or 1.5 g of ketone **XVI**.

## REFERENCES

1. Filyakova, T.I., Zapevalov, A.Ya., and Kolenko, I.P., USSR Inventor's Certificate no. 666176; *Byull. Izobret.*, 1979, no. 21.
2. Zapevalov, A.Ya., Filyakova, T.I., Peschanskii, N.V., Kodess, M.I., and Kolenko, I.P., *Zh. Org. Khim.*, 1988, vol. 24, p. 371.
3. Sokolov, L.F., Valov, P.I., and Sokolov, S.V., *Usp. Khim.*, 1984, vol. 53, p. 1229.
4. Zapevalov, A.Ya., Filyakova, T.I., Peschanskii, N.V., Kodess, M.I., and Kolenko, I.P., *Zh. Org. Khim.*, 1985, vol. 21, p. 2113.
5. Filyakova, T.I., Peschanskii, N.V., Kodess, M.I., and Kolenko, I.P., *Zh. Org. Khim.*, 1990, vol. 26, p. 256.
6. Filyakova, T.I., Matochkina, E.G., Peschanskii, N.V., Kodess, M.I., and Zapevalov, A.Ya., *Zh. Org. Khim.*, 1992, vol. 28, p. 25.
7. Filyakova, T.I., Kodess, M.I., and Zapevalov, A.Ya., *Russ. J. Org. Chem.*, 1998, vol. 34, p. 1256.
8. Filyakova, T.I. and Zapevalov, A.Ya., *Zh. Org. Khim.*, 1991, vol. 27, p. 1824.
9. Mathieu, J. and Panico, R., *Mecanismes reactionnels en chimie organique*, Paris: Hermann, 1972. Translated under the title *Kurs teoreticheskikh osnov organicheskoi khimii*, Moscow: Mir, 1975, pp. 152, 156.
10. Plashkin, V.S., Zapevalova, T.B., Zapevalov, A.Ya., and Selishchev, B.N., *Zh. Org. Khim.*, 1980, vol. 16, p. 540.
11. Bräuer, G., *Handbuch der Präparativen anorganischen Chemie*, Stuttgart: Enke, 1981. Translated under the title *Rukovodstvo po preparativnoi neorganicheskoi khimii*, Moscow: Inostrannaya Literatura, 1956, p. 165.