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CATALYSIS

Catalytic Synthesis of Certain Perfluorinated Ketones and Study of Their Structure by ^{19}F NMR Spectroscopy

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Abstract—An efficient catalyst of a perfluorinated ketone synthesis of a high selectivity in the absence of solvent was proposed. Products of reaction of perfluorinated fluorides of various structures with tetrafluoroethylene and hexafluoropropylene in the presence of efficient catalysts without solvent were examined. The structure of the resulting products and their isomeric composition were identified by ^{19}F NMR spectrscopy.

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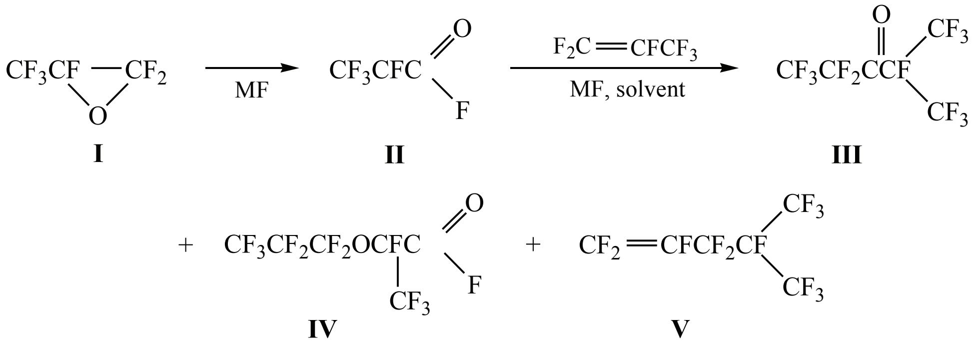
Synthesis of perfluoroethylisopropyl ketone (**III**) (perfluoro-2-methylpentan-3-one) by interaction of perfluoropropionic acid fluoride (**II**) or hexafluoropropylene epoxide (HFPE) (**I**) with hexafluoropropylene (HFP) in the presence of cesium or potassium fluoride in a polar aprotic solvents was described in [1–8]:



Reproduction of these studies showed that the yield of ketone **III** ranges from 20 to 63.5% depending on the conditions of synthesis and the moisture content in the solvent. Along with the formation of ketone solvation of fluoride anion by aprotic solvent leads to condensation of metal perfluoropropanoate with **I** resulting in a perfluoro-2-methyl-3-oxahexanoyl fluoride (**IV**) (HFPO dimer), and also to dimerization of hexafluoropropene with formation of perfluoro-4-methylpentene-1 (**V**) (HFP dimer) with the participation of the derived perfluoroisopropyl carbanion. The rates of formation of the ketone **III** and dimers **IV**, **V** under these conditions were comparable.

In the synthesis of perfluorinated ketones using less reactive perfluorinated fluorides the formation of the dimers **IV**, **V** may become the main reaction [9, 10].

This fact as well as the difficulties associated with deep dehydration and regeneration of solvents led to the search for a catalyst for deriving different perfluorinated ketones of high selectivity in the absence of solvent.

Table 1. Content of the synthesis products in the mixture depending on the catalyst type and the process temperature (according to GLC data)

Catalyst	T, °C	Composition, wt %				Yield of ketone **III**, mol %
		II	**IV**	**V**	**III**	
–	150	<0.1%	–	–	–	0
Cr/Mg (GIPKh-55)	130–200	–	–	–	–	4
CsF	130	14.8	0.19	0.05	85	12.4
	180	30.29	0.21	0.1	69.4	13.8
CaF_2 + NaF + KF	130	20.8	0.64	0.06	78.5	21.6
CaF_2 + NaF + CsF	130	10.3	0.6	0.1	89	77.6
BAU	130	5.6	15.8	5.1	73.5	64
BAU-A-2	160	19.0	16.5	5.9	58.6	52
KF on BAU-A-2	130	16.5	1.2	0.2	82	62
	160	23.6	1.2	0.2	75	58
CsF on BAU-A-2	130	5.85	0.1	0.05	94	92.4
	160	13.84	0.1	0.06	86	85

Table 2. Structures of the produced compounds according to ^{19}F NMR data

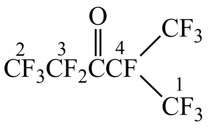
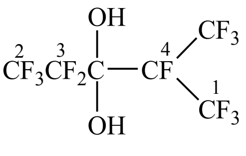
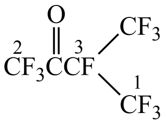
Structure of compound	Atom no.	$-\delta_{CCl_3F}$, ppm	Number of fluorine nuclei	NMR signal	$J_{F^*-F^{**}}$, Hz
Perfluoroethylisopropyl ketone (**III**)					
	1	72.5	6	d.t	$F^1–F^4$ 6.8; $F^1–F^3$ 2.9
	2	80.8	3	d	$F^2–F^4$ 6.4
	3	119.1	1	d.qn	$F^3–F^4$ 28.7; $F^3–F^1$ 2.8
	4	189.2	1	t.sx	$F^4–F^3$ 28.8; $F^4–F^1$ 6.8
Perfluoro-2-methylpentane-3-diol [hydrate (**III**)]					
	1	69.2	6	t.t	$F^1–F^4$ 10.1; $F^1–F^4$ 5.0
	2	77.4	3	t	$F^2–F^4$ 6.5
	3	121.3	2	d.qn	$F^3–F^4$ 17.4; $F^3–F^1$ 10.0
	4	180.3	1	t.m	$F^4–F^3$ 17.2; $F^4–F^2$ 6.1; $F^4–F^1$ 4.7
Perfluoromethylisopropyl ketone (**VII**)					
	*1*	72.7	6	d	$F^1–F^3$ 7.2
	2	74.3	3	d	$F^2–F^3$ 19.2
	3	190.3	1	q.m	$F^3–F^2$ 19.3; $F^3–F^1$ 6.9

Table 2. (Contd.)

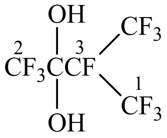
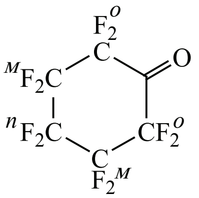
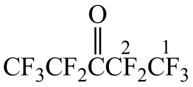
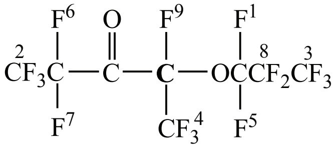
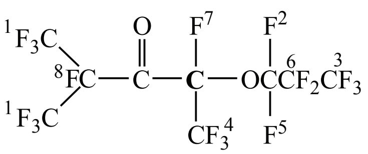
Structure of compound	Atom no.	$-\delta_{CCl_3F}$, ppm	Number of fluorine nuclei	NMR signal	$J_{F^*–F^{**}}$, Hz
Perfluoro-2-methylbutan-3-diol [hydrate (**VII**)]					
	*1*	69.9	6	d	F^1–F^3 7.2
	2	79.6	3	d	F^2–F^3 6.3
	3	181.7	1	m	F^3–F^1 6.8; F^3–F^2 5.8
Perfluorocyclohexanone (**IX**)					
	*o*	117.2	2	m	F^M–F^n 7.7
	m	132.1	2	br.s	
	p	149.9	1	t.t	F^n–F^M 7.7; F^n–F^o 6.9
Perfluoroethyl ketone (**X**)					
	*1*	82.6	3	t	F^1–F^2 1.5
	2	121.3	2	q	
Perfluoroethyl-1-methyl-2-oxapentyl ketone (**XI**)					
	*1*	75.8	0.3	d.d.q	F^1–F^5 150.5; F^1–F^9 17.6; F^1–F^3 7.0
	1′	77.0	1		
	2	77.9	0.3	s	
	2′	79.8	3		
	3	81.59	0.3	t	F^3–$F^{1;5}$ 7.3
	3′	81.62	3		
	4	81.20	0.3	s	
	4′	80.25	3		
	5	81.8	1.0	q	F^5–F^1 150.4
	6	118.46	1.0	d.d.sp	F^6–F^7 320; F^6–F^9 24.0; F^7–F^9 21.8; $F^{7;6}$–F^2 5.0
	7	118.56	1.0	d.d.m	
	8′	128.5	2	s	
	8	128.6	0.3		
	9	135.7	1.0	q	F^9–$F^{1;6;7}$ 21.8

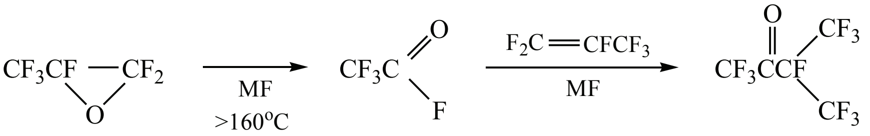
Table 2. (Contd.)

Structure of compound	Atom no.	$-\delta_{CCl_3F}$, ppm	Number of fluorine nuclei	NMR signal	$J_{F^*-F^{**}}$, Hz
Perfluoroisopropyl-1-methyl-2-oxapentyh ketone (**XII**)					
	*1*	72.4	6	m	F^1–F^8 6.0
	1′	72.7	6	sp	$F^{1'}$–$F^{8'}$ 6.9
	2	77.1	2	d.d	F^2–F^6 150.1; F^2–F^6 12
	3	78.96	3	s	
	3′	79.0	3	s	
	4	80.64	3	d	F^4–F^7 7.6
	4′	80.66	3	d	F^4–F^7 7.6
	5	82.1	2	d	F^5–F^2 150.1
	6	128.41	2	s	
	6′	128.43	2	s	
	7	134.36	1	s	
	7′	134.48	1	s	
	8	187.18	1	t.sp	F^8–F^7 13; F^8–F^1 6.5
	8′	187.30	1	t.sp	$F^{8'}$–$F^{7'}$ 12.5; $F^{8'}$–$F^{1'}$ 6.5

RESULTS AND DISCUSSIONS

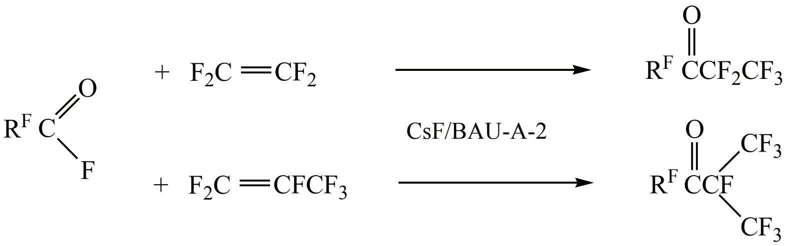
For investigating the catalytic activity of catalysts the reaction of HFPO with HFP in the absence of solvent was chosen as a model in the temperature range 130–180°C. The catalysts used anhydrous potassium and cesium fluorides both individually and in mixtures with sodium and calcium fluoride or applied to a surface of active carbon BAU [11–13].

Table 1 shows the results of a study of the products derived from the reaction of HFPO with HFP and yields of the ketone **III** identified by ^{19}F NMR spectrum (Table 2). Among byproducts were also detected pentafluoropropionyl fluoride (**II**), HFPO dimer **IV** and HFP dimer **V**. With increasing the synthesis temperature to 160°C trifluoroacetyl fluoride (**VI**) is formed due to thermal decomposition of HFPO [14]. Interaction of **VI** with HFP results in the formation of perfluoro(methyl isopropyl) ketone (**VII**) according to ^{19}F NMR spectrum (Table 2):



I **VI** **VII**

Table 1 shows that the maximum yield of the ketone **III** was achieved at a temperature of 95–130°C using cesium fluoride as a catalyst in an amount of 20 wt% deposited on the activated carbon BAU-A-2. There with yields of dimer **IV**, **V** does not exceed 0.1%. This catalyst was used for synthesis of a number of perfluorinated ketones by interaction of perfluoroolefins with perfluoroacyl fluorides of different structures (Table 3):

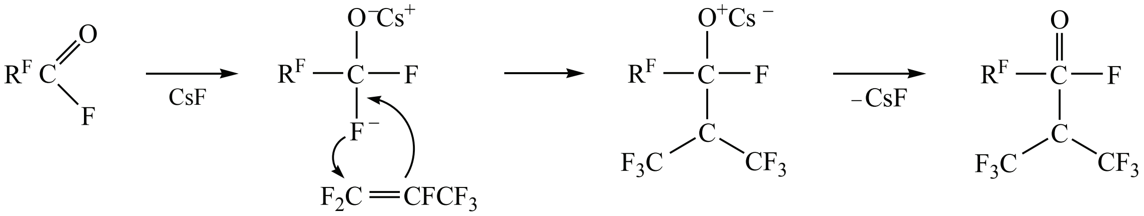


The resulting perfluorodialkyl ketones were identified according to ^{19}F NMR spectra (Table 2).

Table 3 shows that the interaction of HFP with different perfluoroacyl fluorides leads to formation of the corresponding perfluoroisopropylalkyl ketones with sufficiently high yields.

Unlike HFP in interaction of perfluoroacyl fluorides with tetrafluoroethylene the yields of corresponding ketones are significantly reduced, while in reaction with perfluorocyclohexylcarbonyl fluoride (**VIII**) identification of an expected perfluoroethylcyclohexyl ketone failed. This is probably due to the asymmetry of the HFP structure and, as a consequence, to the distribution of charges in its structure, which facilitates the opening of the double bond at the nucleophilic fluorine atom at difluoromethylene group of cesium perfluoropropionate acetate formed in the first stage of HFPO interaction with cesium fluoride. In the case of symmetrical tetrafluoroethylene an attaching requires its polarization that is difficult in the absence of solvent.

HFP bond conjugation is accompanied by a transfer of fluoride anion with the formation of an isopropyl group followed by decomposition of secondary cesium alkoxide, unstable at high temperatures, with the formation of corresponding perfluoroisopropyl ketone:



In tougher conditions in the products of interaction of **VIII** with tetrafluoroethylene perfluorocyclohexanone (**IX**) was identified, the spectrum of which is also shown in Table 2. Its formation is probably the result of pyrolysis of perfluoroacyl fluoride (**VIII**) and oxidation of the intermediate fromed perfluorocyclohexene.

In the reaction of perfluoroolefins with perfluoroacyl fluoride (**IV**) in the structure of formed perfluorodialkyl ketones an asymmetric carbon atom appears and stereoisomerism of the products occurs, which leads to a doubling signals of ^{19}F NMR spectra shown in Table 2. A ratio of intensities of these signals also shows the differences in the interaction of HFP and TFE with acyl fluorides. If ketones derived by reaction of acyl fluoride with HFP, form a mixture of stereoisomers with a ratio of 1 : 1, the ratio of stereoisomers for tetrafluoroethylene is 9 : 1.

The product of the reaction of **VIII** with HFP, extracted in rectification, contained 98 wt % of pefluoroisopropylcyclohexyl ketone (**XIII**) according to GLC on a standard phase. However, in the course of GLC analysis with perfluorinated stationary phase there were two non-separated peaks with heights ratio of 2 : 3 in the chromatogram at 90°C. ^{19}F NMR spectra of these products (Table 4), apparently, also suggest conformational

Table 3. Structure and yields of perfluoroketones obtained by reaction of a number of perfluoroacyl fluorides of various structure in the absence of solvent on the catalyst CsF/BAU-A-2

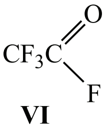
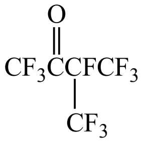
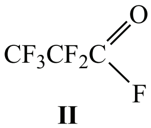
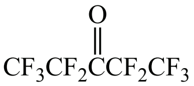
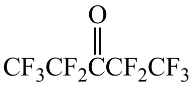
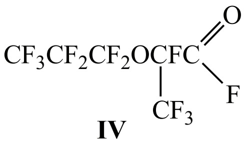
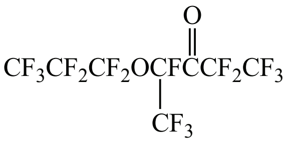
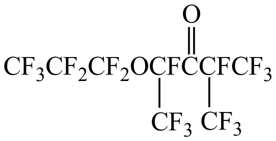
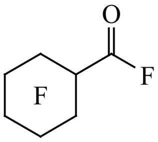
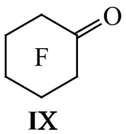
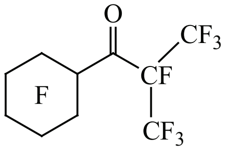
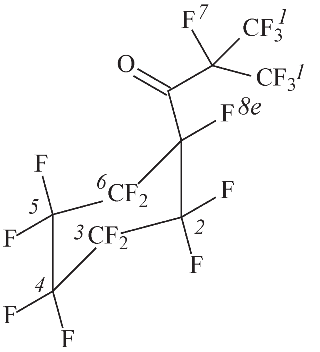
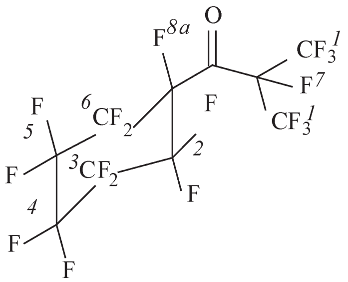
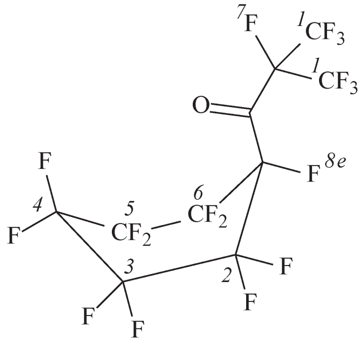
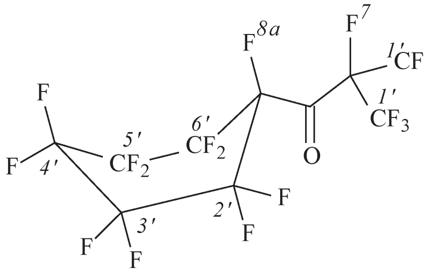
Perfluoroacyl fluoride	Perfluoroolefin	Parameters		Perfluoroketone (bp, °C)	Yield, mol%
		T, °C	*P*, MPa		
 **VI**	$CF_3CF=CF_2$	65–130	0.25	 $CF_3\overset{\overset{O}{\|}}{C}\underset{\underset{CF_3}{\|}}{C}FCF_3$ **VII** (24–25)	92
 **II**	$CF_2=CF_2$	110 170	1.4 2.1	 $CF_3CF_2\overset{\overset{O}{\|}}{C}CF_2CF_3$ **(X)** (25–28)	25 50
	$CF_3CF=CF_2$	65 95 130	0.25	 $CF_3CF_2\overset{\overset{O}{\|}}{C}CF_2CF_3$ **(X)** (25–28)	91.5 95 95
 **IV**	$CF_2=CF_2$	65 140	1.3 2.1	 $CF_3CF_2CF_2O\underset{\underset{CF_3}{\|}}{C}F\overset{\overset{O}{\|}}{C}CF_2CF_3$ **XI** (98–102)	11 21
	$CF_3CF=CF_2$	65–140	0.38–0.75	 $CF_3CF_2CF_2O\underset{\underset{CF_3}{\|}}{C}F\overset{\overset{O}{\|}}{C}\underset{\underset{CF_3}{\|}}{C}FCF_3$ **XII** (119–122)	42–64
 **VIII**	$CF_2=CF_2$	65–75 120–130	1.5 2.1	 **IX** _ (54–55)	– 17
	$CF_3CF=CF_2$	110 140	0.82 1.75	 **XIII** (142–145)	72.3 80.5

Table 4. Conformational isomerism of perfluoroisopropyl cyclohexyl ketone **XIII**

Structure of compound	Atom no.	$-\delta_{CCl_3F}$, ppm	Number of fluorine nuclei	NMR signal	J_{F*-F**}, Hz
Conformation chair					
	1	71.9	6	s	
	2a, 6a	116.9	2	d.d	F^2–F^5 298; F^2–F^4 12
	3a, 5a	121.1	2	d	F^3–F^6 286
	4a	122.0	1	d.m	F^4–F^7 290; F^4–$F^{2;6}$ 12
	2e, 6e	127.7	2	d	F^2–F^5 298
	3e, 5e	137.3	2	d	F^6–F^3 286
	4e	140.0	1	d	F^7–F^4 286
	7	185.7	1	s	
	8e	185.8	0.3	s	
	8a	185.9	0.7	s	
Conformation bath					
	1'	71.5	3	t.s	F^1–F^x 6.9
	1	71.7	6	sx	$F^{1'}$–F^x 6.9
	2'a, 6'a	113.7	1	d	$F^{2'}$–$F^{5'}$ 274
	2a, 6a	115.5	2	d	F^2–F^5 280
	3'a, 5'a	115.6	1	d	$F^{3'}$–$F^{6'}$ 275; $F^{3'}$–F^x 17
	3a, 5a	119.6	2	d	F^3–F^6 268
	4'a	119.9	0.5	d	F^4–F^7 269
	4a	120.0	1	d.t	$F^{4'}$–$F^{7'}$ 267; $F^{4'}$–$F^{2'6'}$ 15
	2'e, 6'e	120.3	1	d.t	$F^{5'}$–$F^{3'}$ 267; $F^{5'}$–$F^{2'7'}$ 15
	2e, 6e	122.8	2	d	F^5–$F^{2'}$ 266; F^5–F^7 19
	3e, 5e	123.3	2	d.d	F^6–F^3 278; F^6–F^7 14
	3'e, 5'e	129.6	1	d	$F^{6'}$–$F^{3'}$ 275
	4e	128.2	1	d	F^7–F^4 269
	4'e	129.7	0.5	d	F^7–F^4 269
	7	186.0	1.5	s	
	8e	186.5	1	s	
	8a	186.9	0.5	s	

isomerism associated with an axial or equatorial position of the keto group relative to perfluorocyclohexyl rings as well as with conformation of the latter in the form of chair or bath.

Research of perfluorodialkyl ketones showed that like hexafluoroacetone they form hydrates in interaction with water. In particular, perfluoro-3-methylbutan-2-diol [hydrate (**VII**)] and perfluoro-3-methylpentane-2-diol [hydrate (**III**)] were identified by ^{19}F NMR spectra.

EXPERIMENTAL

For the analysis of the products of the reaction of perfluoroacyl fluorides with perfluoroolefins a Crystal 2000M chromatograph is typically used with thermal conductivity detector at 125°C on a column of diameter 3 mm and length of 2 m filled with 20% α,α,α-tris-(β-cyanoethyl)acetophenone on silochrome C-80 at 80°C (standard phase), carrier gas helium (flow 30 cm^3 min^{-1}). Perfluoropolyether PEF-5 (20%) on silochrome C-3 was used as a stationary phase for analysis of stereoisomers.

The resulting products mixture was separated into the laboratory glass column of 12 mm in diameter, 0.5 m height packed with 4 mm diameter coils with monitoring the composition of the probed fractions by GLC.

The products were identified by ^{19}F NMR spectra recorded at the frequency 470.6 MHz in a spectrometer Bruker Spectrospin HA-500 in the standard ampoules (5 mm) in 20% solution of deuterochloroform with hexafluorobenzene as internal standard.

Monomers containing not less than 99.9 vol % of tetrafluoroethylene (according to STP 044-39-2001) and hexafluoropropylene (TU 95-417-77), and also hexafluoropropylene epoxide (about 99.5%, TU 95-793-80) were used as initial perfluorinated products

Perfluoroacyl fluorides were prepared:

(a) pentafluoropropionyl fluoride (**II**): by passing HFPO through a tubular reactor heated to 110–120°C, filled with activated carbon BAU-A-2 (State standard GOST 6217-74) with 20 wt% cesium fluoride at a pressure of 0–0.25 MPa;

(b) pefluoro-(2-methyl-3-oxahexanoyl) fluoride (**IV**): by condensation of **II** with HFPO on potassium fluoride in environment of diethylene glycol dimethyl ether (diglyme) extracting by distillation the product with 98 wt% content;

(c) perfluorocyclohexane carbonyl fluoride (**VI**): by electrochemical fluorination of benzoyl chloride, separating it from electrolysis products by distillation with 93.5 wt% content.

Anhydrous sodium fluoride (GOST 4463-76, cesium fluoride (TU 6-09-04-254-85), calcium fluoride (TU 95-23-17-91), and potassium fluoride dihydrate (GOST 20848-75), which was dehydrated in a vacuum oven at 200°C, were used for obtaining catalysts. Catalysts on activated carbon BAU-A-2 was prepared by impregnating it by aqueous solutions of the corresponding fluorides in term of 15–20 wt %, followed by drying in an oven at 130–150°C for 3–5 hours

The catalyst was loaded into a metal-autoclave reactor of 100 cm^3 volume, made of steel 12Cr18Ni10Ti equipped with a pressure gauge, thermocouple, and a needle valve.

Immediately before the synthesis in the study of the catalytic activity the catalysts were finally dried in the reactor in a stream of dry nitrogen at 200°C for 12 hours with periodic evacuation at 2–5 mm Hg for 10 min. Then the reactor was cooled to –40°C and HFPO and HFP were sequentially condensed in it by 0.1 mol. The mixture in the reactor was heated to 65–180°C and maintained for 6–8 hours with checking the pressure, which did not exceed 1.1 MPa. Afterwards the reactor was cooled to room temperature, and the reaction products were fractionated and analyzed by GLC.

When studying the interaction of various perfluoroacyl fluorides with fluoromonomers, reagents were charged into the reactor successively by 0.1 mol per 30 g of catalyst: cesium fluoride (0.03 mol) in an amount of 20 wt% applied to activated carbon BAU-A-2, and then the synthesis was carried out as described above.

CONCLUSIONS

(1) A catalyst that enables high yield synthesis of perfluorinated ketones in the absence of solvent was developed.

(2) It is shown that interaction of fluorides with hexafluoropropylene leads to forming perfluoroisopropyl ketones of the significantly higher yield than by reaction of fluorides and tetrafluoroethylene with the formation of perfluoroethyl ketones.

(3) ^{19}F NMR spectroscopy of high resolution allowed the identification of stereoisomers in the products of addition of fluoroolefines to perfluoro-2-methyl-3-

oxahexanoyl fluoride and quantitative assessment of their ratio. Unlike perfluoroisopropyl ketones, which represent a racemic mixture, perfluoroethyl ketones differ in content of stereoisomers up to the ratio of 1 : 9.

(4) In the analysis of the composition of products of the addition of hexafluoropropene to perfluorocyclohexane carbonyl fluoride by ^{19}F NMR spectra manifestations of conformational isomerism was found.

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