Three-step regioselective synthesis of 2,3-difluorohalobenzenes using tetrafluoroethylene and buta-1,3-diene as starting building blocks*

N. V. Volchkov, M. B. Lipkind, O. M. Nefedov, and M. P. Egorov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 135 6390. E-mail: volchkov@ioc.ac.ru

The gas-phase copyrolysis of tetrafluoroethylene and buta-1,3-diene in a flow tube reactor at 490—510 °C gives 3,3,4,4-tetrafluorocyclohex-1-ene, which is selectively converted to 1-bromo- or 1-chloro-2,3-difluorobenzene *via* intermediate steps of halogenation and dehydrohalogenation.

Key words: tetrafluoroethylene, buta-1,3-diene, cycloaddition, tetrafluorocyclohexenes, halogenation, dihalotetrafluorocyclohexanes, dehydrohalogenation, 1-bromo-2,3-difluorobenzene, 1-chloro-2,3-difluorobenzene, 1-halo-5,5,6,6-tetrafluorocyclohexenes.

Fluorinated aromatic compounds are widely used in the synthesis of pharmaceuticals, agrochemicals, components of liquid crystals, and new technical materials stimulating the search and development of new efficient methods for fluoroarene synthesis.[1—14] Traditional approaches to the synthesis of these compounds accomplished in industry (technologies of dediazofluorination and fluorodechlorination) and the most part of described new laboratory methods are based on the reaction of nucleophilic or electrophilic substitution by the fluorine atom of hydrogen or appropriate functional groups that were preliminarily introduced into the aromatic ring using various fluorinating agents.[14—19] An alternative of these methods is the presently developed methodology of synthesis of fluoroarenes based on the synthetic assembling of fluorobenzoid structures from reactive fluorine-containing synthones (fluorinated carbenes, olefins, dienes, and acetylenes), which can simultaneously act as structure-forming blocks and carriers of fluorine bound to the C atom.[20—35] One of the efficient variants for the accomplishment of this synthetic methodology includes the formation of fluoroarene structures *via* thermal reactions of cycloaddition of polyfluoroolefins to buta-1,3-dienes and subsequent aromatization of the formed fluorinated carbocyclic adducts.[21—31] In this case, the necessary fluorinated C6-cyclic carbon skeleton is formed as a result of either [4+2] cycloaddition of fluoroalkenes to dienes, or *via* [2+2] cycloaddition and thermal rearrangement with ring expansion characteristic of vinylcyclobutanes. In particular, this method can efficiently be used for the synthesis of 1,2-difluorobenzene, difluoro- and trifluorotoluenes, and mixtures of isomeric dichlorofluorobenzenes *via* the cyclization of industrial fluoromonomers (tetrafluoro- or trichlorofluoroethylene) with buta-1,3-diene or its derivatives (isoprene, piperilene, fluoroisoprene, and chlorobuta-1,3-dienes).[24—31]

We developed a new variant of this method, the essence of which is that the processes of synthetic building of fluoroarene structures from fluoroalkene and 1,3-diene fragments are supplemented by the introduction into intermediate polyfluorocyclohexene structures of a functional group that is retained in the final fluoroarene product after the aromatization step. In the present work, we report the possibility of efficient using this modification of the method for the three-step regioselective synthesis of 1-bromo- and 1-chloro-2,3-difluorobenzenes from tetrafluoroethylene and buta-1,3-diene.

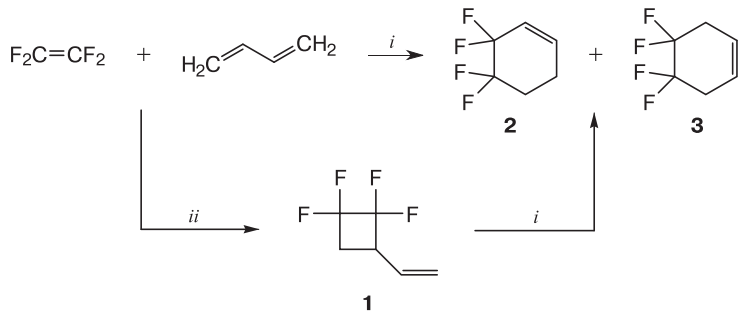
It is known[36—38] that tetrafluoroethylene, unlike ethylene, does not enter the Diels—Alder reaction but reacts with buta-1,3-diene under the thermolysis conditions according to the [2+2] cycloaddition type to selectively form 3-vinyl-1,1,2,2-tetrafluorocyclobutane (**1**). However, under the gas-phase pyrolysis conditions in a flow reactor at 470—710 °C, polyfluorocyclobutane **1** undergoes thermal rearrangement with ring expansion[23—25,39—41] and formation of 3,3,4,4-tetrafluorocyclohexene (**2**) and 4,4,5,5-tetrafluorocyclohexene (**3**) or aromatization[23—25,28—30] with the formation of 1,2-difluorobenzene (**4**). Thermal reactions of formation of cyclobutane **1** and its isomerization can be combined within one cycle of gas-phase pyrolysis to generate a mixture of tetrafluorocyclohexenes **2** and **3** in one step[25,42] (Scheme 1). The results of copyrolysis of tetrafluoroethylene and buta-1,3-diene at 425—535 °C presented in Table 1 show specific features of these processes.

* Dedicated to Academician of the Russian Academy of Sciences V. N. Charushin on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 925—932, May, 2021.

1066-5285/21/7005-0925 © 2021 Springer Science+Business Media LLC

Scheme 1



Conditions: *i*. 495—515 °C, flow tube reactor; *ii*. 425—445 °C, flow tube reactor.

Table 1. Compositions and yields of the products of gas-phase copyrolysis of tetrafluoroethylene and buta-1,3-diene under various temperature conditions[a]

T/°C	G[b]	Composition of pyrolyzate (wt.%)					Yield[c] (%)		
		1	**2**	**3**	**4**	Other products	**1**	**2**	**3**
425—430	36.2	87	4	1	—	8	59	—	—
440—445	43.9	81	9	2	—	8	67	5	—
475—480	41.8	46	35	7	1	11	32	21	3
495—500	37.9	19	56	11	2	12	9	34	5
505—510	36.8	14	60	12	2	12	7	37	5
510—515	35.7	12	57	11	5	15	5	31	2
530—535	31.3	9	48	8	12	23	—	24	—

[a] Conditions: flow tube reactor, flow rate of tetrafluoroethylene and buta-1,3-diene 0.33 mol h^{-1}.
[b] G is the amount of the mixture of the products (g h^{-1}) obtained after the distillation of the crude pyrolyzate with water vapor and drying.
[c] Preparative yield based on the starting reagents after product isolation from the mixture by fractional distillation.

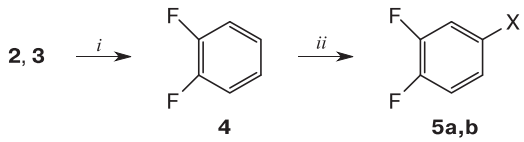
The copyrolysis at 425—445 °C occurs with the selective formation of tetrafluorocyclobutane **1** and a low amount of tetrafluorocyclohexenes **2** and **3**. The content of cyclobutane **1** in the pyrolyzate decreases because of an increase in the isomerization rate and the amount of formed tetrafluorocyclohexenes **2** and **3** increases with increasing temperature of the process. Under the optimum conditions at 490—510 °C, tetrafluorocyclohexene **2** can be obtained with a preparative yield of 34—37%. The yield of tetrafluorocyclohexene **3** is 5%. The further increase in the copyrolysis temperature leads to a decrease in the yield of tetrafluorocyclohexenes **2** and **3** because of an increase in the contribution of secondary fragmentation of tetrafluorocyclobutane **1**, aromatization of cyclohexenes, and resin formation processes. An alternative method for synthesis of tetrafluorocyclohexenes **2** and **3** from tetrafluoroethylene and buta-1,3-diene includes two steps: preliminary pyrolytic synthesis of tetrafluorocyclobutane **1** at 425—445 °C in 59—67% yield and its subsequent isomerization by pyrolysis at 505—510 °C, which occurs with a yield of tetrafluorocyclohexene **2** of 43%, whereas the yield of compound **3** is 6%.

It is found that tetrafluorocyclohexenes **2** and **3** can easily be transformed into 1,2-difluorobenzene (**4**) by water-alkaline dehydrohalogenation under the action of KOH in the presence of catalytic amounts of triethylbenzylammonium chloride (TEBAC) (~85% yield). Formed 1,2-difluorobenzene **4** is readily brominated or chlorinated in chloroform in the presence of $FeCl_3$ with the selective formation of 3,4-difluorobromobenzene (**5a**) or 3,4-difluorochlorobenzene (**5b**) (Scheme 2).

The transformations of tetrafluorocyclohexenes **2** and **3** for the same combination of dehydrohalogenation and halogenation reactions but with a change in their order lead to fundamentally different results.

The bromination and chlorination of 3,3,4,4-tetrafluorocyclohexene (**2**) result in the formation of dihalotetrafluorocyclohexanes **6a,b** in a yield of 78—83% (Scheme 3). Under the conditions of alkaline dehydrohalogenation by KOH or NaOH in the presence of TEBAC at 75—85 °C,

Scheme 2

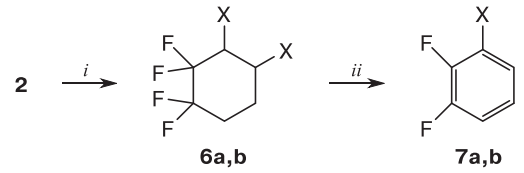


X = Br (**a**), Cl (**b**)

Reagents and conditions: *i*. KOH, H_2O, $BnEt_3NCl$ (cat.), 75—85 °C; *ii*. Br_2 or Cl_2, $CHCl_3$, $FeCl_3$ (cat.), 20—50 °C.

the latter undergo selective aromatization with the formation of 1-bromo- (**7a**) or 1-chloro-2,3-difluorobenzene (**7b**) in a preparative yield of 87—88%.

Scheme 3

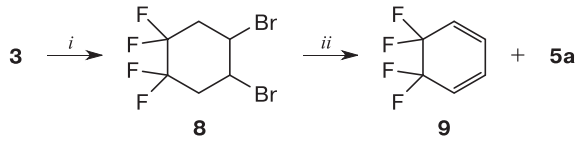


X = Br (**a**), Cl (**b**)

Reagents and conditions: *i*. Br_2 or Cl_2, $CHCl_3$, $FeCl_3$ (cat.), 20—50 °C; *ii*. KOH or NaOH, H_2O, $BnEt_3NCl$ (cat.), 75—85 °C.

At the same time, the bromination of 4,4,5,5-tetrafluorocyclohexene (**3**) affords dibromotetrafluorocyclohexane **8**, which converts to 5,5,6,6-tetrafluorocyclohexa-1,3-diene **9** (53% yield) and difluorobromobenzene **5a** (12% yield) under the action of aqueous KOH (Scheme 4).

Scheme 4



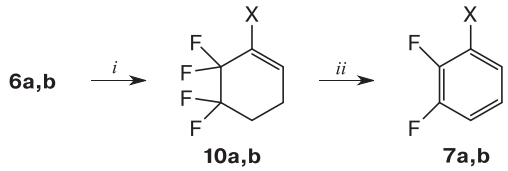
Reagents and conditions: *i*. Br_2, $CHCl_3$, $FeCl_3$ (cat.), 20—35 °C; *ii*. KOH, H_2O, $BnEt_3NCl$ (cat.), 60—65 °C.

The observed high selectivity of transformations of cyclohexanes **6a,b** into difluorohalobenzenes **7a,b** is unexpected, since the structure of dihalotetrafluorocyclohexanes **6a,b** assumes several possible competitive routes of dehydrohalogenation, which can lead to different products, including 4-halo-1,2-difluorobenzenes (**5a,b**). However, the latter were not observed in noticeable amounts upon the alkaline aromatization of dihalotetrafluorocyclohexanes **6a,b**. In addition, taking into account the results of dehydrohalogenation of dibromotetrafluorocyclohexane **8**, one could expect transformations of compounds **6a,b** to proceed with the elimination of both introduced bromine or chlorine atoms, since alkaline dehydrofluorination is usually much more difficult than dehydrochlorination or dehydrobromination.

In order to elucidate the mechanism of the found synthesis of difluorohalobenzenes **7a,b**, we carried out special studies of dehydrohalogenation processes of tetrafluorohalocyclohexanes **6a,b** with monitoring of a change in the composition of the reaction mixtures depending on the reaction time, temperature, and amount of added alkali.

It is found that the reaction of dihalotetrafluorocyclohexanes **6a,b** with KOH or NaOH (1.10 equiv.) in the presence of catalytic amounts of TEBAC at 20—25 °C affords a nearly quantitative amount of 1-halo-5,5,6,6-tetrafluorocyclohexenes (**10a,b)** at the 45—55% conversion of polyfluorocyclohexanes **6a**,**b** within 20—40 min and 95—99% conversion within 1.5—2 h. In this case, the content of difluorohalobenzenes **7a**,**b** in the reaction mixture did not exceed 0.5—2%. The addition of KOH or NaOH (3 equiv.) to the obtained reaction mixture results in the selective transformation of tetrafluorocyclohexenes **10a**,**b** into difluorohalobenzenes **7a**,**b**. The aromatization of tetrafluorocyclohexenes **10a,b** at 35—45 °C occurs slowly (conversion within 2 h does not exceed 25—35%) bus is significantly accelerated with increasing temperature to 75—85 °C (conversion 60—70% in 30 min and higher than 98% in 2 h) (Scheme 5).

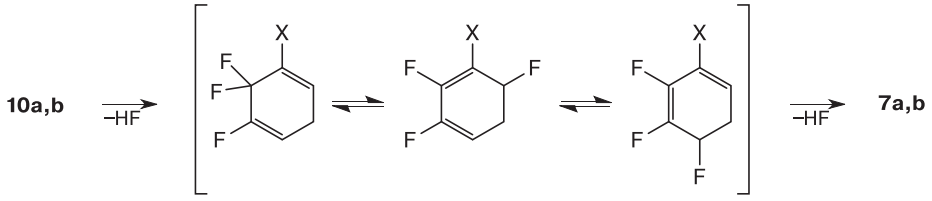
Scheme 5



Reagents and conditions: *i*. 1 equiv. KOH or NaOH, H_2O, $BnEt_3NCl$ (cat.), 20—35 °C; *ii*. 3 equiv. KOH or NaOH, H_2O, $BnEt_3NCl$ (cat.), 75—85 °C.

Thus, it was found that the alkaline aromatization of dihalotetrafluorocyclohexanes **6a,b** to 2,3-difluorohalobenzenes **7a,b** proceeded as a stepwise process including the primary step of easy dehydrohalogenation with the selective formation of halotetrafluorocyclohexenes **10a,b**, which are further transformed into difluorohalobenzenes **7a,b** due to double dehydrofluorination. The observed easiness and regiospecificity of transformation of cyclohexanes **6a,b** into cyclohexenes **10a,b** in the absence of appreciable amounts of products of possible competitive routes for their dehydrohalogenation are consistent with this process proceeding *via* the carbanionic mechanism E2 or E1cB. Evidently, the process can be explained by

Scheme 6



an increased acidity of the hydrogen atom bound to the carbon atom in position 3 of the starting 3,4-dihalo-1,1,2,2-tetrafluorocyclohexanes **6a,b** and efficient stabilization of the carbanionic intermediate formed upon deprotonation and caused by a significant electron-acceptor effect of four fluorine atoms in the β- and γ-positions of the carbon chain.

The transformations of halotetrafluorocyclohexenes **10a,b** into halodifluorobenzenes **7a,b** proceed probably *via* the primary dehydrofluorination to form cyclohexadienes, which are further converted into difluorohalobenzenes **7a,b** due to the subsequent elimination of HF through the simultaneous or preliminary rearrangement of multiple bonds *via* the allyl 1,3-shift of fluorine (see Scheme 6).

Unlike very easily proceeding transformations of cyclohexanes **6a,b** into halotetrafluorocyclohexenes **10a,b**, the aromatization of the latter involving the cleavage of the very strong C—F bond is much more energy-consuming and requires using substantially higher temperatures.

Thus, the simple three-step synthesis of 1-bromo- and 1-chloro-2,3-difluorobenzenes from commercially accessible industrial tetrafluoroethylene and butadiene monomers was accomplished. The formed products are convenient starting compounds for the introduction of 2,3-difluorophenyl fragments into various organic structures *via* cross-coupling reactions and are used in the synthesis of polycyclic liquid crystals, fluorinated heterocyclic structures, and new fluorine-containing biologically active compounds. It should be mentioned that the synthesis method was easily scaled and applied by us for the production of kilogram amount of difluorohalobenzenes under laboratory conditions, and the obtained difluorohalobenzenes were used for the synthesis of components of liquid crystals and development of new technologies for production of fluoroquinolone antibacterial drugs.

It can be assumed that the found method for regioselective synthesis of difluorohalobenzenes is general and can probably be applied for the generation of other similar fluoroarene structures with varied functional substituents, which are preliminarily introduced in polyfluorocyclohexene structures *via* diverse reactions of addition to the double bond and are retained in the final arene structure after aromatization.

Experimental

The following commercially accessible reagents were used as the starting compounds: tetrafluoroethylene (99.9%) (Poli-Traid, Russia), buta-1,3-diene (99%) (Sintez-Kauchuk, Russia), and gaseous chlorine (99%) (Kaustik, Russia). The following reagents (all Sigma-Aldrich) were also used as received: bromine (99%), $CHCl_3$ (98%), KOH (85%), NaOH (97%), Na_2SO_3 (98%), triethylbenzylammonium chloride (TEBAC) (98%), and $FeCl_3$ (97%).

GC analysis was carried out on a Kristall 2000M chromatograph (capillary column Macherey-Nagel OPTIMA-1, 30 m×0.25 mm, helium as carrier gas, flame-ionization detector). ^{1}H NMR spectra were recorded on Bruker AC-200 or Bruker AM 300 spectrometers (working frequencies 200.1 and 300.1 MHz, respectively). ^{13}C NMR spectra were recorded on Bruker AM 300, Bruker DRX-500, or Bruker AV-600 spectrometers (working frequencies 75.5, 125.8, and 150.9 MHz, respectively). ^{19}F NMR spectra were recorded on Bruker AC-200 or Bruker AM 300 spectrometers (working frequencies 183.3 and 282.4 MHz, respectively). Samples for NMR spectroscopy were prepared in $CDCl_3$. Chemical shifts for ^{1}H and ^{13}C are presented relative to Me_4Si as the internal standard (0.05%), and those for ^{19}F are presented relative to $CFCl_3$ (external standard). Mass spectra were detected on a Trace GC Ultra instrument equipped with a Finnigan MAT DSQII mass detector in the electron impact mode (ionization energy 70 eV, temperature of the system 200 °C, ionic trap as an ion source) and a Thermo TR-5ms SQC capillary chromatographic column (15 m×0.25 mm). Elemental analysis was carried out on a Perkin—Elmer Series II 2400 CHN Analyzer instrument.

Synthesis of tetrafluorocyclohexenes 2 and 3. ***A.*** The gas flows of tetrafluoroethylene and buta-1,3-diene with a constant flow rate of 0.33 mol h^{-1} for each reagent were passed through a quartz tube reactor (length 650 mm, internal diameter 22 mm) heated in a tubular furnace to 505—510 °C. The pyrolysis products coming from the reactor were condensed in a water reflux condenser and a trap cooled with an ice—water mixture. After 30 h of the continuous process, the formed liquid pyrolyzate (1188.0 g) was distilled with water vapor and dried with $CaCl_2$ to obtain a mixture (1104.3 g) of organic products containing, according to the GC data, tetrafluorocyclohexene **1** (14%), tetrafluorocyclohexene **2** (60%), tetrafluorocyclohexene **3** (12%), difluorobenzene **4** (2%), buta-1,3-diene (4%), and 8% (totally) of non-identified products. The fractional distillation of the mixture gave 106.6 g (7%) of tetrafluorocyclobutane **1** (b.p. 83—84 °C), 76.4 g (5%) of tetrafluorocyclohexene **3** (b.p. 53—54 °C, 90 Torr), and 563.3 g (37%) of tetrafluorocyclohexene **2** (b.p. 69—70 °C, 90 Torr).

B. Using procedure ***A*** (copyrolysis of tetrafluoroethylene and buta-1,3-diene at 440—445 °C and flow rate of 0.33 mol h^{-1} for each reactant for 10 h), the liquid mixture (439.1 g) of the products was obtained and contained, according to the GC data, tetrafluorocyclobutane **1** (81%), tetrafluorocyclohexene **2** (9%), tetrafluorocyclohexene **3** (2%), buta-1,3-diene (4%), and 4% (totally) of non-identified products. Tetrafluorocyclobutane **1** (339.2 g, 67%) was obtained after fractional distillation.

Tetrafluorocyclobutane **1** (138.6 g, 0.90 mol) with a constant flow rate of 0.77 g min^{-1} in a nitrogen flow (flow rate 120 mL min^{-1}) was passed through a tube reactor heated to 505—510 °C for 3 h. The pyrolysis products were condensed in a water reflux condenser, washed with water, and dried over $CaCl_2$. According to the GC data, the obtained mixture of products (100.3 g) contained tetrafluorocyclobutane **1** (11%), tetrafluorocyclohexene **2** (66%), and tetrafluorocyclohexene **3** (14%). Tetrafluorocyclohexene **3** (8.3 g, 6%) and tetrafluorocyclohexene **2** (59.2 g, 43%) were obtained after the fractional distillation of the mixture.

1,1,2,2-Tetrafluoro-3-vinylcyclobutane (1).[30,36] B.p. 83—84 °C. ^{1}H NMR ($CDCl_3$, 200.1 MHz), δ: 2.22—2.47 (m, 1 H, CH_2); 2.57—2.84 (m, 1 H, CH_2); 3.17—3.41 (m, 1 H, CH); 5.27 (d, 1 H, $=CH_2$, J = 17.5 Hz); 5.33 (d, 1 H, $=CH_2$, J = 10.5 Hz); 5.84 (ddd, 1 H, =CH, J = 17.5 Hz, J = 10.5 Hz, J = 7.5 Hz). ^{19}F NMR ($CDCl_3$, 188.3 MHz), δ: −109.5 and −128.2 (AB system, 2 F, CF_2, ^2J = 196.0 Hz); −110.2 and −117.7 (AB system, 2 F, CF_2, ^2J = 203.5 Hz). MS, m/z (I_{rel} (%)): 154 $[M]^+$ (17), 115 $[M - F - HF]^+$ (22), 100 $[M - C_4H_6]^+$ (11), 90 $[M - C_2H_2F_2]^+$ (100), 64 $[C_2H_2F_2]^+$ (37), 54 $[C_4H_6]^+$ (56), 39 (31).

3,3,4,4-Tetrafluorocyclohex-1-ene (2).[39,42] B.p. 69—70 °C (90 Torr). ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 2.20—2.36 (m, 2 H, CH_2); 2.38—2.50 (m, 2 H, CH_2); 5.75—5.87 (m, 1 H, =CH); 6,24 (dt, 1 H, =CH, J = 10.3 Hz, J = 3.5 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz), δ: 23.6 (tt, C(6), J = 5.2 Hz, J = 2.0 Hz); 28.4 (tt, C(5), J = 23.0 Hz, J = 1.0 Hz); 112.7 (tt, C(4), J = 273 Hz, J = 23.0 Hz); 117.0 (tt, C(3), J = 278 Hz, J = 25.0 Hz); 121.5 (tt, C(1), J = 27.0 Hz, J = 0.7 Hz); 137.6 (tt, C(2), J = 10.5 Hz, J = 1.0 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: −111.6 (m, 2 F, CF_2); −121.4 (m, 2 F, CF_2). MS, m/z (I_{rel} (%)): 154 $[M]^+$ (10), 115 $[M - F - HF]^+$ (11), 90 $[M - C_2H_2F_2]^+$ (100), 64 (27), 54 (2), 51 (14), 39 (26).

4,4,5,5-Tetrafluorocyclohex-1-ene (3).[30,39] B.p. 53—54 °C (90 Torr). ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 2.78 (ddd, 4 H, 2 CH_2, J = 17.0 Hz, J = 9.7 Hz, J = 7.4 Hz); 5.59—5.64 (m, 2 H, HC=CH). ^{19}F NMR ($CDCl_3$, 188.3 MHz), δ: −118.2 (m, 4 F, $2CF_2$). MS, m/z (I_{rel} (%)): 154 $[M]^+$ (23), 115 $[M - F - HF]^+$ (11), 90 $[M - C_2H_2F_2]^+$ (100), 64 (26), 54 (11), 51 (20), 39 (35).

Synthesis of 1,2-difluorobenzene 4. ***A.*** A 50% aqueous KOH (365 g, 3.13 mol) was added for 2 h to the stirred mixture of 3,3,4,4-tetrafluorocyclohexene (2) (154.1 g, 1 mol) and TEBAC (2.75 g, 12 mmol) maintaining temperature of the reaction at 70—80 °C. The reaction mixture was additionally stirred at 80—85 °C for 2 h, after which the organic product was distilled off with water vapor and dried over $CaCl_2$, and 1,2-difluorobenzene (**4**) (96.8 g, 84%) with b.p. 91—92 °C was isolated by distillation.

B. A 50% aqueous solution of KOH (36 g, 321 mol) was added at 60—70 °C for 30 min with stirring to a mixture of 4,4,5,5-tetrafluorocyclohexene (**3**) (15.4 g, 100 mmol) and TEBAC (0.23 g, 1 mmol). Then the reaction mixture was additionally stirred at 80—85 °C for 2 h and diluted with water, and the product was extracted with dichloromethane. The organic product was dried over $CaCl_2$ and distilled. 1,2-Difluorobenzene (**4**) was obtained in a yield of 9.71 g (85%).

1,2-Difluorobenzene (4).[26] B.p. 91—92 °C. ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 7.05—7.25 (m, 4 H, Ar). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: −137.5 (m, 2 F). MS, m/z (I_{rel} (%)): 114 $[M]^+$ (100), 95 (7), 88 (30), 63 (35), 56 (17), 50 (14).

Bromination of 1,2-difluorobenzene (4). A solution of Br_2 (110.2 g, 686 mmol) in $CHCl_3$ (100 mL) was added at 30—35 °C for 2 h to a solution of 1,2-difluorobenzene (**4**) (71.8 g, 630 mmol) in $CHCl_3$ (100 mL) containing $FeCl_3$ (2.0 g, 12 mmol), and the mixture was stirred at 35—45 °C for 4 h. The reaction mixture was washed with water and a 10% aqueous solution of Na_2SO_3. The organic product was dried over $CaCl_2$ and distilled. 4-Bromo-1,2-difluorobenzene (**5a**) (b.p. 151—152 °C) was obtained in a yield of 95.8 g (79%).

4-Bromo-1,2-difluorobenzene (5a).[43] B.p. 151—152 °C. ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 7.02—7.15 (m, 1 H, Ar); 7.20—7.29 (m, 1 H, Ar); 7.31—7.40 (m, 1 H, Ar). ^{13}C NMR ($CDCl_3$, 75.5 MHz), δ: 116.00 (dd, C(4), J = 7.3 Hz, J = 4.0 Hz); 118.60 (d, C(3), J = 18.3 Hz); 120.95 (d, C(6), J = 19.9 Hz); 127.69 (dd, C(5), J = 5.6 Hz, J = 3.9 Hz); 149.82 (dd, C(1), J = 248.9 Hz, J = 12.5 Hz); 150.43 (dd, C(2), J = 253.0 Hz, J = 13.6 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: −135.2 (m, 1 F), −139.9 (m, 1 F). MS, m/z (I_{rel} (%)): 194, 192 $[M]^+$ (100, 100), 113 $[M - Br]^+$ (88), 63 (35).

Chlorination of 1,2-difluorobenzene (4). Gaseous chlorine (29.8 g, 420 mmol) was bubbled at 35—40 °C for 6 h through a solution of 1,2-difluorobenzene (**4**) (45.6 g, 400 mmol) in $CHCl_3$ (100 mL) containing $FeCl_3$ (1.33 g, 8 mmol). Then the reaction mixture was stirred at 45—50 °C for 2 h. The resulting product was washed with water and a 10% aqueous solution of Na_2SO_3, dried over $CaCl_2$, and distilled. 4-Chloro-1,2-difluorobenzene (**5b**) (b.p. 127—128 °C) was obtained in a yield of 45.7 g (77%).

4-Chloro-1,2-difluorobenzene (5b).[44,45] B.p. 127—128 °C. ^{1}H NMR ($CDCl_3$, 200.1 MHz), δ: 7.23—7.45 (m, 3 H, Ar). ^{19}F NMR ($CDCl_3$, 188.3 MHz), δ: −134.3 (d, 1 F, Ar, J = 20.0 Hz); −139.5 (d, 1 F, Ar, J = 20.0 Hz). MS, m/z (I_{rel} (%)): 150, 148 $[M]^+$ (32, 100), 113 $[M - Cl]^+$ (23), 63 (13).

Bromination of tetrafluorocyclohexene 2. A solution of Br_2 (120.0 g, 750 mmol) in $CHCl_3$ (200 mL) was added at 25—30 °C for 3 h to a solution of 3,3,4,4-tetrafluorocyclohexene (**2**) (106.7 g, 693 mmol) in $CHCl_3$ (200 mL) containing $FeCl_3$ (2.5 g, 11 mmol). The reaction mixture was stirred at 30—35 °C for 2 h and then washed with a 10% aqueous solution of Na_2SO_3 and water. The organic product was dried over $CaCl_2$, and then the solvent $CHCl_3$ was distilled off on a rotary evaporator. The obtained residue was distilled under reduced pressure. 3,4-Dibromo-1,1,2,2-tetrafluorocyclohexane (**6a**) (b.p. 69—70 °C, 4 Torr) was obtained in a yield of 180.6 g (83%).

3,4-Dibromo-1,1,2,2-tetrafluorocyclohexane (6a). B.p. 69—70 °C (4 Torr). ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 1.98—2.43 (m, 3 H, C<u>H</u>$_2$—CH<u>H</u>); 2.44—2.70 (m, 1 H, C<u>H</u>H); 3.99—4.15 (m, 1 H, CHBr); 4.16—4.35 (m, 1 H, CHBr). ^{13}C NMR ($CDCl_3$, 125.8 MHz), δ: 30.26 (t, C(6), J = 22.1 Hz); 31.21 (br.s, C(5)); 47.53 (br.s, C(4)); 53.29 (t, C(3), J = 22.0 Hz); 112.53 (tt, C(1), J = 257.8 Hz, J = 27.6 Hz); 115.51 (tt, C(2), J = 254.8 Hz, J = 27.4 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: −117.6 and −119.3 (AB system, 2 F, CF_2, ^2J = 256.0 Hz, ^3J = 22.5 Hz); −119.9 and −121.1 (AB system, 2 F, CF_2, ^2J = 256.0 Hz). MS, m/z (I_{rel} (%)): 316, 314, 312 $[M]^+$ (5, 9, 4), 235, 233 $[M - Br]^+$

(25, 29), 153 [M – Br – HBr]$^+$ (100), 133 [M – Br – HBr – HF]$^+$ (90). Found (%): C, 22.91; H, 1.80. $C_6H_6Br_2F_4$. Calculated (%): C, 22.96; H, 1.93.

Chlorination of tetrafluorocyclohexene 2. Gaseous Cl_2 (79.5 g, 1.12 mol) was bubbled at 25—35 °C for 6 h with vigorous stirring through a solution of tetrafluorocyclohexene **2** (150.9 g, 980 mmol) in $CHCl_3$ (300 mL) containing $FeCl_3$ (4.0 g, 24 mmol). The reaction mixture was heated to 30—35 °C, kept for 2 h with stirring, and washed with a 10% aqueous solution of Na_2SO_3 and water. The organic product was washed over $CaCl_2$, then $CHCl_3$ was removed, and the residue was distilled on a rotary evaporator under reduced pressure. 3,4-Dichloro-1,1,2,2-tetrafluorocyclohexane (**6b**) (b.p. 60—62 °C, 13 Torr) was obtained in a yield of 173.1 g (78%).

3,4-Dichloro-1,1,2,2-tetrafluorocyclohexane (6b). B.p. 60—62 °C (13 Torr). ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 1.95—2.27 (m, 2 H, CH_2); 2.27—2.52 (m, 2 H, CH_2); 3.90—4.07 (m, 1 H, CHCl); 4.08—4.24 (m, 1 H, CHCl). ^{13}C NMR ($CDCl_3$, 75.5 MHz), δ: 29.03 (t, C(6), J = 22.2 Hz); 29.72 (d, C(5), J = 9.6 Hz); 57.71 (t, C(4), J = 2.4 Hz); 62.38 (td, C(3), J = 21.2 Hz, J = 2.2 Hz); 112.95 (tdd, C(1), J = 258.0 Hz, J = 32.5 Hz, J = 22.7 Hz); 116.23 (tt, C(2), J = 253.9 Hz, J = 26.6 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: –117.7 and –120.3 (AB system, 2 F, CF_2, ^2J = 257.0 Hz, ^3J = 29.5 Hz), –125.5 (m, 2 F, CF_2). MS, m/z (I_{rel} (%)): 228, 226, 224 [M]$^+$ (5, 28, 46), 191, 189 [M – Cl]$^+$ (43, 48), 190, 188 [M – HCl]$^+$ (12, 27), 171, 169 [M – HCl – F]$^+$ (2, 7), 153 [M – HCl – Cl]$^+$ (32), 133 (37), 125 (42), 111 (31), 90 (31), 77 (92), 75 (100), 64 (28), 51 (30), 39 (35). Found (%): C, 32.15; H, 2.46. $C_6H_6Cl_2F_4$. Calculated (%): C, 32.03; H, 2.69.

Bromination of tetrafluorocyclohexene 3. A solution of Br_2 (24.0 g, 150 mmol) in $CHCl_3$ (40 mL) was added by portions at 20—25 °C for 2 h to a solution of tetrafluorocyclohexene **3** (21.1 g, 137 mmol) in $CHCl_3$ (30 mL) containing $FeCl_3$ (0.15 g, 1 mmol), and the mixture was stirred at 25—30 °C for 2 h. The reaction mixture was washed with a 10% aqueous solution of Na_2SO_3 and water, and the obtained organic product was dried over $CaCl_2$ and distilled under reduced pressure. 4,5-Dibromo-1,1,2,2-tetrafluorocyclohexane (**8**) (b.p. 70—72 °C, 12 Torr) was obtained in a yield of 39.1 g (91%).

4,5-Dibromo-1,1,2,2-tetrafluorocyclohexane (8). B.p. 74—75 °C (12 Torr). ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 2.45—2.75 (m, 2 H, 2C<u>H</u>H); 2.88—3.08 (m, 2 H, 2CH<u>H</u>); 4.05—4.23 (m, 2 H, 2CHBr). ^{13}C NMR ($CDCl_3$, 125.8 MHz), δ: 40.36 (t, C(3) and C(6), J = 22.1 Hz); 46.48 (d, C(4) and C(5), J = 7.5 Hz); 114.32 (tdd, C(1) and C(2), J = 255 Hz, J = 31.4 Hz, J = 21.7 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: –116.6 and –123.2 (AB system, 4 F, 2CF_2, ^2J = 256.0 Hz). MS, m/z (I_{rel} (%)): 316, 314, 312 [M]$^+$ (6, 12, 6), 235, 233 [M – Br]$^+$ (88, 88), 154 [M – 2Br]$^+$ (6), 153 [M – Br – HBr]$^+$ (72), 133 [M – Br – HBr – HF]$^+$ (100), 89 (26). Found (%): C, 32.05; H, 2.66. $C_6H_6Br_2F_4$. Calculated (%): C, 32.03; H, 2.69.

Dehydrohalogenation of dibromotetrafluorocyclohexane 8. A 50% aqueous solution of KOH (45.0 g, 401 mmol) was added at 20—25 °C for 30 min to a mixture of 4,5-dibromo-1,1,2,2-tetrafluorocyclohexane **8** (37.14 g, 118 mmol) and TEBAC (0.23 g, 1 mmol), and the reaction mixture was stirred at 60—65 °C for 4 h. The obtained organic product was diluted with water, extracted with CH_2Cl_2, dried over $CaCl_2$, and distilled. 5,5,6,6-Tetrafluorocyclohexa-1,3-diene (**9**) (b.p. 54—56 °C, 150 Torr) was obtained in a yield of 9.57 g (53%), and the yield of 4-bromo-1,2-difluorobenzene (**5a**) was 2.82 g (12%).

5,5,6,6-Tetrafluorocyclohexa-1,3-diene (9).[46] B.p. 54—56 °C (150 Torr). ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ: 5.98—6.12 (m, 2 H, CH=CH); 6.22—6.35 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$, 125.8 MHz), δ: 112.24 (tt, C(5) and C(6), J = 249 Hz, J = 26.3 Hz); 124.47 (t, C(1) and C(4), J = 27.7 Hz); 128.96 (tt, C(2) and C(3), J = 12.9 Hz, J = 4.7 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: –122.8 (br.s, 4 F, 2 CF_2). MS, m/z (I_{rel} (%)): 152 [M]$^+$ (100), 132 [M – HF]$^+$ (44), 112 [M – 2HF]$^+$ (15), 101(30), 83 (31).

Synthesis of 1-bromo-2,3-difluorobenzene 7a by dehydrohalogenation of dibromotetrafluorocyclohexane 6a. A 50% aqueous solution of KOH (140.0 g, 1.25 mol) was added for 1.5 h to a mixture of 3,4-dibromo-1,1,2,2-tetrafluorocyclohexane (**6a**) (100.0 g, 318 mmol) and TEBAC (0.94 g, 4 mmol) maintaining temperature in a range of 20—30 °C. Then the reaction mixture was stirred at 80—85 °C for 2 h, after which the organic product was distilled off with water vapor, dried over $CaCl_2$, and distilled. 2,3-Difluorobromobenzene (**7a**) (b.p. 157—158 °C) was obtained in a yield of 54.1 g (88%).

1-Bromo-2,3-difluorobenzene (7a).[8] B.p. 157—158 °C. ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 7.00—7.16 (m, 1 H, Ar); 7.17—7.29 (m, 1 H, Ar); 7.34—7.47 (m, 1 H, Ar). ^{13}C NMR ($CDCl_3$, 75.5 MHz), δ: 110.40 (d, C(1), J = 17.5 Hz); 116.40 (d, C(4), J = 17.7 Hz); 124.70 (dd, C(5), J = 7.1 Hz, J = 5.0 Hz); 128.23 (d, C(6), J = 3.6 Hz); 148.10 (dd, C(2), J = 248.8 Hz, J = 14.3 Hz); 150.92 (dd, C(3), J = 251.9 Hz, J = 13.3 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: –130.9 (m, 1 F, Ar), –134.8 (m, 1 F, Ar). MS, m/z (I_{rel} (%)): 194, 192 [M]$^+$ (100, 99), 113 [M – Br]$^+$ (88), 63 (60). Found (%): C, 37.54; H, 1.50. $C_6H_3BrF_2$. Calculated (%): C, 37.34; H, 1.52.

Synthesis of 1-chloro-2,3-difluorobenzene 7b by dehydrohalogenation of dichlorotetrafluorocyclohexane 6b. A 50% aqueous solution of KOH (285.0 g, 2.54 mol) was added at 20—30 °C for 2 h to a mixture of 3,4-dichloro-1,1,2.2-tetrafluorocyclohexane (**6b**) (142.9 g, 635 mmol) and TEBAC (1.85 g, 8 mmol). The reaction mixture was stirred at 80—85 °C for 3 h. The obtained organic product was distilled with water vapor, dried over $CaCl_2$, and distilled. 2,3-Difluorochlorobenzene (**7b**) (b.p. 136—137 °C) was obtained in a yield of 82.1 g (87%).

1-Chloro-2,3-difluorobenzene (7b).[30] B.p. 136—137 °C. ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 7.00—7.25 (m, 3 H, Ar). ^{13}C NMR ($CDCl_3$, 125.8 MHz), δ: 115.71 (d, C(4), J = 17.5 Hz); 122.70 (d, C(1), J = 14.3 Hz); 124.02 (dd, C(5), J = 7.5 Hz, J = 5.1 Hz); 125.47 (d, C(6), J = 3.4 Hz); 147.21 (dd, C(2), J = 250.5 Hz, J = 14.4 Hz); 151.15 (dd, C(3), J = 251.0 Hz, J = 12.3 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: –134.7 (m, 1 F, Ar); –138.5 (d, 1 F, Ar, J = 19.5 Hz). MS, m/z (I_{rel} (%)): 150, 148 [M]$^+$ (34, 100), 113 [M – Cl]$^+$ (36), 63 (13). Found (%): C, 48.36; H, 2.08. $C_6H_3ClF_2$. Calculated (%): C, 48.52; H, 2.04.

Synthesis of halosubstituted tetrafluorocyclohexenes 10a,b. A 50% aqueous solution of KOH (11.80 g, 105 mmol) was added for 30 min with stirring to a mixture of dibromotetrafluorocyclohexane **6a** (30.2 g, 96 mmol) and TEBAC (0.23 g, 1 mmol) maintaining temperature of the reaction mixture at 15—20 °C, and then the mixture was kept at 25—30 °C with stirring for 2 h and diluted with water. The organic phase was washed with water, dried over $CaCl_2$, and distilled. 1-Bromo-5,5,6,6-tetrafluorocyclohex-1-ene (**10a**) (b.p. 80—81 °C, 52 Torr) was obtained in a yield of 20.56 g (92%).

1-Chloro-5,5,6,6-tetrafluorocyclohex-1-ene (**10b**) (b.p. 93—94 °C, 80 Torr) was synthesized in a yield of 17.1 g (91%) using a similar procedure by the dehydrochlorination of dichloro-

tetrafluorocyclohexane **6b** (22.5 g, 100 mmol) with a 50% aqueous solution of KOH (12.4 g, 110 mmol) in the presence of TEBAC (0.23 g, 1 mmol).

1-Bromo-5,5,6,6-tetrafluorocyclohex-1-ene (10a). B.p. 80—81 °C (52 Torr). ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 2.23—2.51 (m, 4 H, 2 CH_2); 6.58 (t, 1 H, =CH, J = 3.9 Hz). ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ: 24.82 (t, C(3), J = 5.0 Hz); 28.35 (t, C(4), J = 22.5 Hz); 110.46 (tt, C(5), J = 249 Hz, J = 27.0 Hz); 113.77 (t, C(1), J = 27.8 Hz); 116.28 (tt, C(6), J = 253 Hz, J = 25.1 Hz); 139.08 (t, C(2), J = 6.5 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: −113.7 (m, 2 F, CF_2), −119.8 (m, 2 F, CF_2). MS, m/z (I_{rel} (%)): 234, 232 $[M]^+$ (6, 6), 170, 168 $[M - C_2H_2F_2]^+$ (42, 41), 153 $[M - Br]^+$ (15), 133 $[M - Br - HF]^+$ (22), 39 (100). Found (%): C, 30.98; H, 2.06. $C_6H_5BrF_4$. Calculated (%): C, 30.93; H, 2.16.

1-Chloro-5,5,6,6-tetrafluorocyclohex-1-ene (10b).[39] B.p. 93—94 °C (80 Torr). ^{1}H NMR ($CDCl_3$, 300.1 MHz), δ: 2.21—2.52 (m, 4 H, 2 CH_2); 6.34 (t, 1 H,=CH, J = 4.1 Hz). ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ: 23.05 (t, C(3), J = 5.2 Hz); 28.29 (t, C(4), J = 22.5 Hz); 110.45 (tt, C(5), J = 250 Hz, J = 27.3 Hz); 116.65 (tt, C(6), J = 251 Hz, J = 25.0 Hz), 124.40 (t, C(1), J = 26.5 Hz); 134.58 (t, C(2), J = 6.1 Hz). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: −116.8 (m, 2 F, CF_2), −119.6 (m, 2 F, CF_2). MS, m/z (I_{rel} (%)): 190, 188 $[M]^+$ (5, 16), 171, 169 $[M - F]^+$ (3, 11), 153 $[M - Cl]^+$ (14), 133 $[M - Cl - HF]^+$ (42), 126, 124 $[M - C_2H_2F_2]^+$ (32, 87), 89 (53), 77 (56), 75 (67), 64 (40), 51 (56), 39 (100). Found (%): C, 37.98; H, 2.51. $C_6H_5ClF_4$. Calculated (%): C, 38.22; H, 2.67.

Dehydrohalogenation of bromotetrafluorocyclohexene 10a. A 50% aqueous solution of KOH (18.0 g, 160 mmol) was added at 30—35 °C for 30 min to a mixture of bromotetrafluorocyclohexane **10a** (11.65 g, 50 mmol) and TEBAC (0.15 g, 0.7 mmol). The reaction mixture was kept at 75—85 °C for 2 h and then cooled and diluted with water. The organic product was extracted with CH_2Cl_2, dried over $CaCl_2$, and distilled. 1-Bromo-2,3-difluorobenzene (**7a**) was obtained in a yield of 8.47 g (88%).

Dehydrohalogenation of chlorotetrafluorocyclohexene 10b. A 50% aqueous solution of NaOH (16 g, 200 mmol) was added at 20—25 °C for 30 min to a mixture of 1,2-dichloro-3,3,4,4-tetrafluorocyclohexane (**6b**) (45.0 g, 200 mmol) and TEBAC (0.45 g, 2 mmol). The reaction mixture was kept with stirring for 1.5 h. According to the GC data, the obtained organic product contained 3% of the starting dichlorotetrafluorocyclohexane **6b**, 95% of chlorotetrafluorocyclohexene **10b**, and 0.8% difluorochlorobenzene **7b**. A 50% aqueous solution of NaOH (48.0 g, 600 mmol) was added to the reaction mixture, and the latter was stirred at 75—85 °C for 3 h. The resulting product was washed with water, dried over $CaCl_2$, and distilled. 2,3-Difluorochlorobenzene (**7b**) was obtained in a yield of 26.2 g (88%).

The authors are grateful to the Program for Development of Scientific Schools of the N. D. Zelinsky Institute of Organic Chemistry (Russian Academy of Sciences) for financial support of the present studies (Project "New Methodologies of Organic and Organoelement Synthesis on the Basis of Detailed Study of Mechanisms and Intermediates of Chemical Reactions").

This work does not contain descriptions of studies on animals or humans.

The authors declare no competing interests.

References

1. *Organofluorine Compounds in Medical Chemistry and Biomedical Application*, Eds R. Filler, Y. Kobayashi, L. M. Yagupolskii, Elsevier, Amsterdam, 1993.
2. V. Prakash Reddy, *Organofluorine Compounds in Biology and Medicine*, Elsevier, Amsterdam, 2015.
3. D. O´Hagan, *J. Fluorine. Chem.*, 2010, **131**, 107.
4. E. P. Gillis, K. J. Eastman, M. D. Donnelly, N. A. Meanwell, *J. Med. Chem.*, 2015, **58**, 8315.
5. Y. Znou, J. Wang, Z. Gu, S. Wang, W. Zhu, J. L. Acena, V. A. Soloshonok, K. Izawa, H. Liu, *Chem. Rev.*, 2016, **116**, 422.
6. P. Kirsch, M. Bremer, *Angew. Chem., Int. Ed.*, 2000, **39**, 4216.
7. J. S. Gasovska, S. J. Cowling, M. C. R. Cockett, M. Hird, R. A. Levis, E. P. Raynes, J. W. Goodby, *J. Mater. Chem.*, 2010, **20**, 299.
8 I. A. Radini, M. Hird, *Liquid Crystals*, 2009, **36**, 1417.
9. W. K. Hagmann, *J. Med. Chem.*, 2008, **51**, 4358.
10. R. Berger, G. Resnati, P. Metrangolo, E. Weber, J. Hulliger, *Chem. Soc. Rev.*, 2011, **40**, 3496.
11. G. A. Selivanova, E. V. Tretyakov, *Russ. Chem. Bull.*, 2020, **69**, 838.
12. S. A. Prikhod´ko, A. Y. Shabalin, M. M. Shmakov, V. V. Bardin, N. Yu. Adonin, *Russ. Chem. Bull.*, 2020, **69**, 17.
13. P. Kirsch, *Modern Fluoroorganic Chemistry. Synthesis, Reactivity, Application*, Wiley-VCH, Weinheim, 2004.
14. V. Prakash Reddy, *Organofluorine Chemistry: Synthesis and Applications*, Elsevier, Amsterdam, 2020.
15. *Aromatic Fluorination*, Eds J. N. Clark, D. Wails, T. W. Bastock, CRC Press, Boca Raton, 1996.
16. P. A. Champagne, J. Desroches, J.-D. Hamel, M. Vandamme, J.-F. Paquin, *Chem. Rev.*, 2015, **115**, 9073.
17. A. J. Cresswell, S. G. Davies, R. M. Roberts, J. Thomson, *Chem. Rev.*, 2015, **115**, 566.
18. M. G. Campbell, T. Ritter, *Chem. Rev.*, 2015, **115**, 612.
19. L. V. Politanskaya, G. A. Selivanova, E. V. Panteleeva, E. V. Tretyakov, V. E. Platonov, P. V. Nikul´shin, A. S. Vinogradov, Ya. V. Zonov, V. M. Karpov, T. V. Mezhenkova, A. V. Vasilyev, A. B. Koldobskii, O. S. Shilova, S. M. Morozova, Ya. V. Burgart, E. V. Shchegolkov, V. I. Saloutin, V. B. Sokolov, A. Yu. Aksinenko, V. G. Nenajdenko, M. Yu. Moskalik, V. V. Astakhova, B. A. Shainyan, A. A. Tabolin, S. L. Ioffe, V. M. Muzalevskiy, E. S. Balenkova, A. V. Shastin, A. A. Tyutyunov, V. E. Boiko, S. M. Igumnov, A. D. Dilman, N. Yu. Adonin, V. V. Bardin, S. M. Masoud, D. V. Vorobyeva, S. N. Osipov, E. V. Nosova, G. N. Lipunova, V. N. Charushin, D. O. Prima, A. G. Makarov, A. V. Zibarev, B. A. Trofimov, L. N. Sobenina, K. V. Belyaeva, V. Ya. Sosnovskikh, D. L. Obydennov, S. A. Usachev, *Russ. Chem. Rev.*, 2019, **88**, 425; DOI: 10.1070/RCR4871.
20. W. J. Middleton, W. H. Sharkey, *J. Am. Chem. Soc.*, 1959, **81**, 803.
21. D. J. Barton, B. A. Link, *J. Fluorine Chem.*, 1983, **22**, 397.
22. P. D. Barlett, E. H. Gunter, A. S. Wallbillich, J. S. Swenton, L. K. Montgomery, B. D. Kramer, *J. Am. Chem. Soc.*, 1968, **90**, 2049.
23. O. M. Nefedov, N. V. Volchkov, in *Chemistry of Carbenes and Small-Sized Cyclic Compounds*, Ed. O. M. Nefedov, MIR Publisher, Moscow, 1989, p. 69.
24. O. M. Nefedov, N. V. Volchkov, *Russ. J. Org. Chem.*, 1994, **30**, 1181.

25. O. M. Nefedov, N. V. Volchkov, *Mendeleev Commun.*, 2006, 121.
26. N. V. Volchkov, M. B. Lipkind, O. M. Nefedov, *Russ. Chem. Bull.,* 2020, **69**, 68.
27. US Pat. 6008407.
28. O. M. Nefedov, S. F. Politanskii, A. A. Ivashenko, M. B. Lipkind, A. V. Strashnenko, V. N. Veremii, Authors′ Certificate USSR 869242, *Byul. Izobret.* [*Invention Bulletin*], 2000, 27 (in Russian).
29. US Pat. 4754084.
30. F. J. Weigert, R. F. Davis, *J. Fluorine Chem.*, 1993, **63**, 69.
31. F. J. Weigert, R. F. Davis, *J. Fluorine Chem.*, 1993, **63**, 59.
32. N. V. Volchkov, M. B. Lipkind, O. M. Nefedov, *Russ. Chem. Bull.*, 2019, **68**, 1232.
33. N. V. Volchkov, A. V. Zabolotskikh, A. V. Ignatenko, O. M. Nefedov, *Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1990, **39**, 1458.
34. N. V. Volchkov, A. V. Zabolotskikh, M. B. Lipkind, O. M. Nefedov, *Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1989, **38**, 1782.
35. N. V. Volchkov, M. B. Lipkind, O. M. Nefedov, *Russ. Chem. Bull.*, 2020, **69**, 270.
36. D. D. Coffman, P. L. Barrick, R. D. Cramer, M. S. Raasch, *J. Am. Chem. Soc.*, 1949, **71**, 490.
37. V. H. Sharkey, in *Fluorine Chemistry Reviews*, Ed. P. Tarrant, Marsel Dekker, New York, 1968, **2**, 1—54.
38. J. D. Roberts, C. M. Sharts, *Org. Reactions*, 1962, **12**, 1.
39. US Pat. 2861095.
40. M. B. Lipkind, N. V. Volchkov, A. I. Shipilov, V .F. Zabolotskikh, in *VI Vsesoyuzn. konf. po khimii ftororgan. soedinenii* [*VI All-Union Conference on Chemistry of Organofluorine Compounds*], Novosibirsk, June 26—28, 1990, 26 (in Russian).
41. A. I. Shipilov, V. F. Zabolotskikh, O. M. Nefedov, *Russ. J. Appl. Chem.*, 1994, **67**, 77.
42. Yu. V. Tomilov, D. N. Platonov, G. P. Okonnishnikova, R. A. Novikov, N. V. Volchkov, *Russ. Chem. Bull.*, 2012, **61**, 1138.
43. A. Roe, J. A. Montgomery, W. A. Yarnall, V. A. Hoyle, Jr., *J. Org. Chem.*, 1956, **21**, 28.
44. Z. Li, N. Huang, *Org. Prep. Proced. Int.*, 1996, **28**, 245.
45. G. C. Finger, M. J. Gortatowski, R. N. Shiley, R. N. White, *J. Am. Chem. Soc.*, 1959, **81**, 94.
46. A. Zweig, R. Fisher, J. E. Lancaster, *J. Org. Chem.*, 1980, **45**, 3597.

Received February 5, 2021;
in revised form March 17, 2021;
accepted March 19, 2021