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N-(Polyfluoroalkyl)imidazolium-2-carbodithioates

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Abstract—Chemical properties of carbenes derived from 1-methyl-3-polyfluoroalkylimidazolium salts were studied. These unstable intermediate products reacted with carbon disulfide to give the corresponding imidazolium-2-carbodithioates which were subjected to methylation at the sulfur atom.

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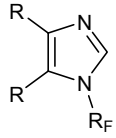
In the recent time, imidazolium carbenes have attracted attention due to their high stability and broad synthetic potential as complexing ligands and catalysts. Chemical properties of these compounds were reviewed in [1–3]. Imidazolium carbenes having bulky groups on the nitrogen atoms and aryl substituents in positions *4* and *5* of the imidazole ring are more stable. We previously studied imidazole derivatives having fluorinated substituents on the nitrogen [4]. It was found that such compounds are hydrolytically and thermally stable and that they relatively readily undergo quaternization despite the presence of an electron-withdrawing group on the nitrogen atom. The resulting quaternary salts were converted into the corresponding thioxo imidazolium salts through intermediate carbene species. The present work continues our studies on the chemical properties of *N*-polyfluoroalkylimidazolium carbenes. We tried to obtain stable fluorine-containing carbenes; for this purpose, we selected as starting compounds imidazole derivatives **Ia**–**Id** having no substituents in positions *4* and *5*, as well as 4,5-diphenylimidazoles **Ie**–**Ih** and benzimidazoles **Ii** and **Ij**. Difluoromethyl-substituted imidazole and benzimidazole **Ia** and **Ii** were reported in [5], while compounds **Ib**–**Id**, and **Ij** were synthesized by us previously [6, 7].



Ia–Ih

Ii, **Ij**

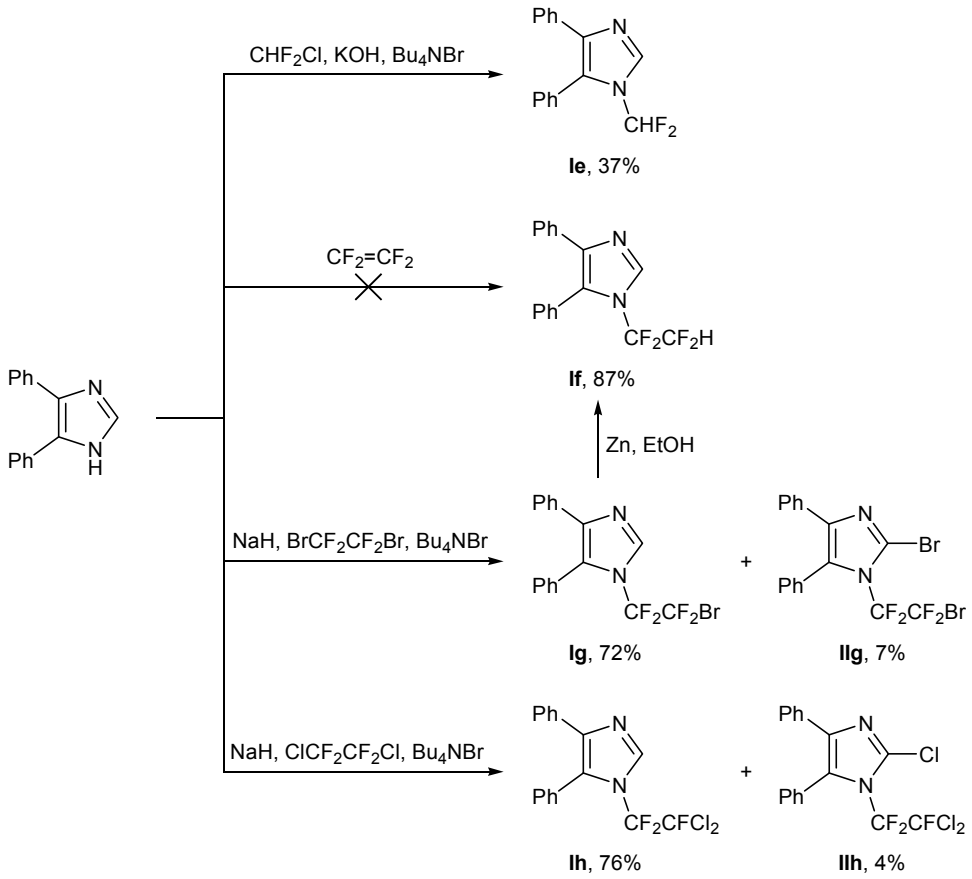
R = H, R_F = CHF_2 (**a**), HCF_2CF_2 (**b**), $BrCF_2CF_2$ (**c**), Cl_2CFCF_2 (**d**); R = Ph, R_F = CHF_2 (**e**), HCF_2CF_2 (**f**), $BrCF_2CF_2$ (**g**), Cl_2CFCF_2 (**h**); R_F = CF_2H (**i**), Cl_2CFCF_2 (**j**).

In the present work we examined alkylation of 4,5-diphenylimidazole with polyfluorohaloalkanes. Difluoromethylation of 4,5-diphenyl-1*H*-imidazole with chlorodifluoromethane (Freon 22) in alkaline medium, as difluoromethylation of pyrazole derivatives [8], is likely to be reversible; therefore, compound **Ie** is formed only under mild conditions in the presence of phase-transfer catalysis, tetrabutylammonium bromide (Scheme 1). The reaction of 4,5-diphenylimidazole with tetrafluoroethylene in the presence of a catalytic amount of potassium derivative of the former, unlike analogous reaction with 3,5-dimethylpyrazole [9], almost does not occur under atmospheric pressure, whereas the reaction of preliminary prepared 4,5-diphenylimidazole potassium salt with tetrafluoroethylene leads to a mixture of products, and the yield of **If** does not exceed 10%.

The reactions of sodium derivatives of 4,5-diphenylimidazole with 1,2-dibromotetrafluoroethane (Freon 114 B2) and 1,1,2-trichlorotrifluoroethane (Freon 113) in the presence of tetrabutylammonium bromide smoothly afforded the corresponding polyfluoroethyl-substituted imidazoles **Ig** and **Ih** in high yield (70–75%). These reactions were accompanied by side bromination (with 1,2-dibromotetrafluoroethane) or chlorination (with 1,1,2-trichlorotrifluoroethane) of the imidazole ring; compounds **IIa** and **IIb** were isolated by chromatography of the mother liquors in 4–7% yield. 2-Bromotetrafluoroethyl derivative **Ig** was read-

† Deceased.

Scheme 1.



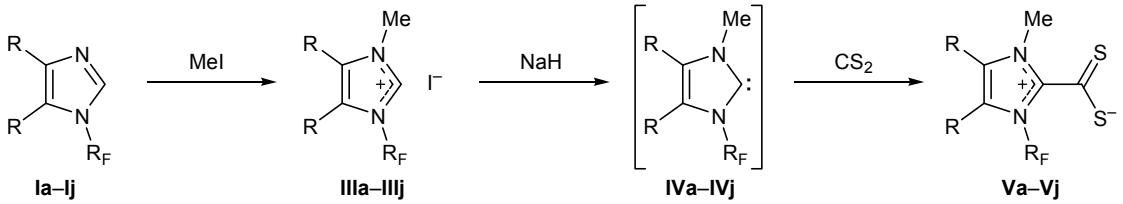
ily reduced to tetrafluoroethylimidazole **If** by the action of zinc in ethanol; therefore, this procedure for the synthesis of compound **If** may be regarded as preparative.

Compounds **Ia**–**Ij** were alkylated with methyl iodide by heating in anhydrous acetonitrile (reaction time ~10 h) to obtain the corresponding salts **IIIa**–**IIIj** in up to 90% yield. 4,5-Unsubstituted imidazole derivatives **IIIa**–**IIId** were isolated by evaporation of the reaction mixture and treatment of the residue with diethyl ether, whereas very poorly soluble benzimidazole and diphenylimidazole derivatives **IIIe**–**IIIj** crystallized during the process even from boiling acetonitrile (Scheme 2).

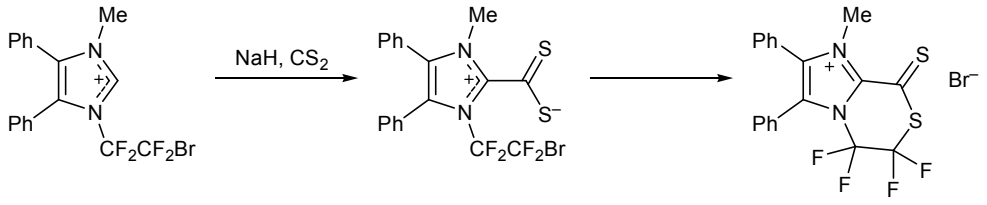
We made an attempt to obtain free imidazolium carbenes **IV** from salts **IIIf** and **IIIg** by reaction with sodium hydride in anhydrous tetrahydrofuran in the presence of potassium *tert*-butoxide as catalyst, by analogy with the known procedure [10]. However, tarring was observed even in the absence of catalyst, and salt **IIIf** reacted more rapidly (in 10–15 min) than did salt **IIIh** (in 2–3 ch). Presumably, intermediate imidazolium carbene reacts with the fluorinated fragment of the other molecule, which contains relatively acidic proton or labile halogen atom.

We tried to trap intermediate carbene species via reaction with carbon disulfide which is a reactive electrophile but inert toward sodium hydride. In the

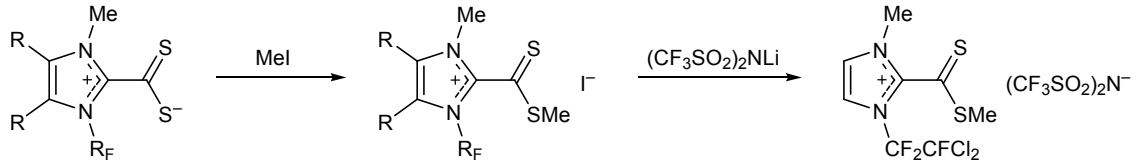
Scheme 2.



Scheme 3.



Scheme 4.



presence of excess carbon disulfide we obtained in high yield the corresponding zwitterionic imidazolium-2-carbodithioates **Va**–**Vf** from both 4,5-unsubstituted imidazolium salts and 4,5-diphenylimidazolium salts having difluoromethyl and tetrafluoroethyl groups. The reactions were carried out over a period of 10–30 min, and compounds with partly hydrogenated fluorine-containing substituents reacted at a higher rate than their exhaustively halogenated analogs. The yield of compounds **Va**–**Vf** was 65–80%. Imidazolium-2-carbodithioates **Vg** and **Vh** were formed at a lower rate (reaction time ~3 h). Benzimidazolium salts **IIIi** and **IIIj** were almost insoluble in tetrahydrofuran, and they reacted with sodium hydride very slowly; even after 12 h, the reaction was not complete, for final products **Vi** and **Vj** were also poorly soluble in THF. The target compounds were isolated in ~30% yield by chromatography (Scheme 2). When the reaction was carried out in more polar DMF, tarring was observed. Analogous imidazolium carbodithioates were reported previously only for nonaromatic 4,5-dihydroimidazole derivatives [11].

Compound **Vg** having a bromotetrafluoroethyl group was isolated by chromatography in ~35% yield. It underwent intramolecular condensation involving the dithiocarboxylate moiety and terminal bromine atom to give 20% of bicyclic compound **VI** (Scheme 3). The latter was isolated as yellow high-melting crystalline substance; it was eluted only with a polar solvent (acetone). The ^{19}F NMR spectrum of **VI** displayed two *AB* systems due to the presence of four nonequivalent fluorine atoms.

Imidazolium-2-carbodithioates **Va**–**Vj** readily undergo alkylation at the sulfur atom. Their reaction with methyl iodide in boiling acetonitrile was complete in 20 min. As a result, we isolated salts **VIIa**–**VIIj** in high yield (Scheme 4). Replacement of the iodide ion in compound **VIId** by bis(trifluoromethanesulfonyl)-imide, as with analogous nonfluorinated derivatives of 4,5-dihydroimidazole [12], gave a new ionic liquid, compound **VIIId**. It is liquid at room temperature, and its vitrification temperature is lower than 0°C.

To conclude, we have studied chemical properties of carbenes derived from 1-methyl-3-polyfluoroalkylimidazolium salts and obtained the corresponding carbodithioates and their methyl esters. The obtained compounds may be promising for the preparation of new ionic liquids.

EXPERIMENTAL

The syntheses of compounds **IIg**, **IIh**, and **Va**–**Vj** were performed in an inert atmosphere. The progress of reactions was monitored by thin-layer chromatography on Kieselgel 60 F/UV$_{254}$ plates (Merck). The products were purified by column chromatography on silica gel, 70–230 mesh, 60 Å (Aldrich). The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer (299.5 MHz) using tetramethylsilane as internal reference. The ^{19}F NMR spectra were measured on a Varian Gemini 200 instrument (188.14 MHz) using trichlorofluoromethane as internal reference. The melting points were determined in open capillaries using a Thiele melting point apparatus. The solvents used were dried and distilled prior to use.

1-Difluoromethyl-4,5-diphenyl-1*H*-imidazole (Ie). A solution of 30 g (0.53 mol) of potassium hydroxide in 50 ml of water and 0.5 g of tetrabutylam-

monium bromide was added under stirring to a mixture of 4.4 g (0.02 mol) of 4,5-diphenyl-1*H*-imidazole and 50 ml of 1,4-dioxane, and a stream of chlorodifluoromethane was passed over a period of 4 h at 30–35°C under vigorous stirring. The mixture was cooled, diluted with 50 ml of water, and extracted with diethyl ether (3×30 ml), the extract was washed with water (5×30 ml) and dried over $MgSO_4$, the solvent was distilled off to dryness, and the residue was recrystallized from hexane and dried in air. Yield 2 g (37%), mp 97–98°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.52 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz), 7.00–7.28 m (10H, H_{arom}), 7.83 s (1H 2-H). ^{19}F NMR spectrum ($CDCl_3$): δ_F –92.80 ppm, d (CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: C 71.25; H 4.56; F 14.12. $C_{16}H_{12}F_2N_2$. Calculated, %: C 71.11; H 4.48; F 14.06.

4,5-Diphenyl-1-(1,1,2,2-tetrafluoroethyl)-1*H*-imidazole (If). A solution of 0.5 g (1.2 mmol) of compound **Ig** in 10 ml of ethanol and 0.05 ml of concentrated hydrochloric acid were added to a suspension of 0.11 g (1.8 mmol) of zinc dust in 10 ml of ethanol. The mixture was heated for 4 h under reflux with vigorous stirring, the solvent was distilled off to dryness under reduced pressure, a mixture of 5 ml of hexane and 35 ml of 1% hydrochloric acid was added, and the mixture was stirred for 3 min and extracted with hexane (2×20 ml). The extract was washed with water (2×30 ml) and dried over $MgSO_4$, the solvent was distilled off to dryness, and the residue was recrystallized from hexane and dried in air. Yield 0.35 g (87%), mp 77–80°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.49 t.t (1H, CF_2H, $^2J_{HF}$ = 55, $^3J_{HF}$ = 5 Hz), 7.18–7.49 m (10H, H_{arom}), 7.94 s (1H 2-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –94.78 s (2F, NCF_2), –137.75 d (2F, CF_2H, $^2J_{FH}$ = 55 Hz). Found, %: C 63.37; H 3.63; F 23.61. $C_{17}H_{12}F_4N_2$. Calculated, %: C 63.75; H 3.78; F 23.73.

Reactions of 4,5-diphenyl-1*H*-imidazole with 1,2-dibromotetrafluoroethane and 1,2,2-trichlorotrifluoroethane (*general procedure*). A solution of 3.3 g (15 mmol) of 4,5-diphenyl-1*H*-imidazole in 20 ml of anhydrous DMF was added dropwise over a period of 30 min at room temperature to a suspension of 0.81 g (17 mmol) of 50% sodium hydride in 20 ml of anhydrous DMF. Tetrabutylammonium bromide, 0.05 g, was added, the mixture was stirred for 5 min, and 6.5 g (25 mmol) of 1,2-dibromotetrafluoroethane (in the synthesis of **Ig** and **IIg**) or 4.65 g (25 mmol) of 1,2,2-trichlorotrifluoroethane (in the synthesis of **Ih** and **IIh**) was added. The mixture was stirred for 2 h at a bath temperature of 55–60°C (**Ig**, **IIg**) or 75–80°C (**Ih**, **IIh**) and poured into 200 ml of water, the precipitate was filtered off and dissolved in 60–70 ml of hexane, the solution was heated under reflux with a small amount of silica gel, the sorbent was filtered off, and the solvent was distilled off from the filtrate. Compounds **Ig** and **Ih** were isolated by recrystallization of the residue from hexane and were dried in air. The mother liquor (after crystallization of **Ig** and **Ih**) was subjected to column chromatography using chloroform as eluent to isolate compounds **IIg** and **IIh**.

1-(2-Bromotetrafluoroethyl)-4,5-diphenyl-1*H*-imidazole (Ig). Yield 4.38 g (73%), mp 124–125°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.13–7.43 m (10H, H_{arom}), 7.95 s (1H, 2-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –66.72 s (2F, CF_2Br), –90.97 s (2F, NCF_2). Found, %: C 51.06; H 2.87; Br 20.27. $C_{17}H_{11}BrF_4N_2$. Calculated, %: C 51.15; H 2.78; Br 20.02.

2-Bromo-1-(2-bromotetrafluoroethyl)-4,5-diphenyl-1*H*-imidazole (IIg). Yield 0.48 g (7%), mp 151–153°C, R_f 0.6. ^{1}H NMR spectrum ($CDCl_3$): δ 7.07–7.40 ppm, m (10H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –64.28 s (2F, CF_2Br), –86.58 s (2F, NCF_2). Found, %: C 42.89; H 2.17; Br 33.25. $C_{17}H_{10}Br_2F_4N_2$. Calculated, %: C 42.71; H 2.11; Br 33.43.

1-(2,2-Dichlorotrifluoroethyl)-4,5-diphenyl-1*H*-imidazole (Ih). Yield 2.17 g (64%), mp 137–139°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.11–7.41 m (10H, H_{arom}), 7.93 s (1H, 2-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –72.63 s (1F, $CFCl_2$), –87.96 s (2F, NCF_2). Found, %: C 55.21; H 3.16; Cl 19.01. $C_{17}H_{11}Cl_2F_3N_2$. Calculated, %: C 55.00; H 2.96; Cl 19.10.

2-Chloro-1-(2,2-dichlorotrifluoroethyl)-4,5-diphenyl-1*H*-imidazole (IIh). Yield 0.19 g (4%), mp 134–136°C, R_f 0.5. ^{1}H NMR spectrum ($CDCl_3$): δ 7.09–7.39 ppm, m (10H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –70.01 s (1F, $CFCl_2$), –85.61 s (2F, NCF_2). Found, %: C 49.78; H 2.64; Cl 26.25. $C_{17}H_{10}Cl_3F_3N_2$. Calculated, %: C 50.34; H 2.47; Cl 26.22.

1-Methyl-3-polyfluoroalkylimidazolium iodides IIIa–IIIj (*general procedure*). A mixture of 0.01 mol of compound **Ia–Ij** and 2.13 g (15 mmol) of methyl iodide in 10 ml of anhydrous acetonitrile was heated for 10 h under reflux. The mixture was cooled to room temperature, and the solvent was distilled under reduced pressure (in the synthesis of **IIIa–IIId**). In the synthesis of **IIIe–IIIj**, the mixture was diluted with

5 ml of diethyl ether, and after 2 h the precipitate was filtered off, washed with diethyl ether, and dried in air.

3-Difluoromethyl-1-methyl-1*H*-imidazolium iodide (IIIa). Yield 2.32 g (90%), mp 120–121°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.93 s (3H, CH_3), 7.93 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz), 7.94 s (1H, 5-H), 8.23 s (1H, 4-H), 9.72 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6): δ_F –95.55 ppm, d (CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: I 48.90. $C_5H_7F_2IN_2$. Calculated, %: I 48.85.

1-Methyl-3-(1,1,2,2-tetrafluoroethyl)-1*H*-imidazolium iodide (IIIb). Yield 87%, mp 140–142°C; published data [4]: mp 140–142°C.

3-(2-Bromotetrafluoroethyl)-1-methyl-1*H*-imidazolium iodide (IIIc). Yield 3.56 g (92%), mp 144–145°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.96 s (3H, CH_3), 8.14 s (1H, 5-H), 8.46 s (1H, 4-H), 10.21 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –71.27 s (2F, CF_2Br), –95.40 s (2F, NCF_2). Found, %: I 32.57. $C_6H_6BrF_4IN_2$. Calculated, %: I 32.63.

3-(2,2-Dichlorotrifluoroethyl)-1-methyl-1*H*-imidazolium iodide (IIId). Yield 3.34 g (93%), mp 168–170°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.94 s (3H, CH_3), 7.14 s (1H, 5-H), 7.64 s (1H, 4-H), 10.41 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –68.72 s (1F, $CFCl_2$), –86.38 s (2F, NCF_2). Found, %: I 35.45. $C_6H_6Cl_2F_3IN_2$. Calculated, %: I 35.16.

3-Difluoromethyl-1-methyl-4,5-diphenyl-1*H*-imidazolium iodide (IIIe). Yield 3.62 g (88%), mp 180–182°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.59 s (3H, CH_3), 7.09 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz), 7.11–7.39 m (10H, H_{arom}), 10.61 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6): δ_F –94.49 ppm, d (CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: I 30.19. $C_{17}H_{15}F_2IN_2$. Calculated, %: I 30.79.

1-Methyl-3-(1,1,2,2-tetrafluoroethyl)-4,5-diphenyl-1*H*-imidazolium iodide (IIIf). Yield 4.0 g (87%), mp 233–235°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.60 s (3H, CH_3), 7.54 t.t (1H, CF_2H, $^2J_{HF}$ = 55, $^3J_{HF}$ = 5 Hz), 7.61–7.89 m (10H, H_{arom}), 10.61 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –95.08 s (2F, NCF_2), –136.45 d (2F, CF_2H, $^2J_{FH}$ = 55 Hz). Found, %: I 27.23. $C_{18}H_{15}F_4IN_2$. Calculated, %: I 27.45.

3-(2-Bromotetrafluoroethyl)-1-methyl-4,5-diphenyl-1*H*-imidazolium iodide (IIIg). Yield 4.81 g (89%), mp 243–244°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.80 s (3H, CH_3), 7.46 m (10H, H_{arom}), 10.44 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –69.85 s (2F, CF_2Br), –90.03 s (2F, NCF_2). Found, %: I 23.51. $C_{18}H_{14}BrF_4IN_2$. Calculated, %: I 23.45.

3-(2,2-Dichlorotrifluoroethyl)-1-methyl-4,5-diphenyl-1*H*-imidazolium iodide (IIIh). Yield 4.41 g (86%), mp 252–254°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.82 s (3H, CH_3), 7.45 m (10H, H_{arom}), 10.48 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –74.62 s (1F, $CFCl_2$), –88.22 s (2F, NCF_2). Found, %: Cl 13.89; I 25.67. $C_{18}H_{14}Cl_2IF_3N_2$. Calculated, %: Cl 13.82; I 24.73.

3-Difluoromethyl-1-methyl-1*H*-benzimidazolium iodide (IIIi). Yield 2.85 g (92%), mp 224–225°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.16 s (3H, CH_3), 7.80–8.18 m (4H, H_{arom}), 8.37 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz), 10.20 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6): δ_F –97.69 ppm, d (2F, CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: I 41.15. $C_9H_9F_2IN_2$. Calculated, %: I 40.93.

3-(2,2-Dichlorotrifluoroethyl)-1-methyl-1*H*-benzimidazolium iodide (IIIj). Yield 3.56 g (87%), mp 218–220°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.20 s (3H, CH_3), 7.28–8.22 m (4H, H_{arom}), 10.45 s (1H, 2-H). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –75.26 s (1F, $CFCl_2$), –92.25 s (2F, NCF_2). Found, %: I 31.06. $C_{10}H_8Cl_2F_3IN_2$. Calculated, %: I 30.90.

1-Methyl-3-polyfluoroalkyl-1*H*-imidazolium-2-carbodithioates Va–Vj (*general procedure*). Compound **IIIa**–**IIIj**, 5 mmol, was dispersed in 35 ml of anhydrous THF, 0.20 g (5.5 mmol) of 50% sodium hydride was added under stirring, the mixture was stirred for ~30–40 s (until its color began to change), 0.76 g (0.57 ml, 0.01 mol) of carbon disulfide was added, and the mixture was vigorously stirred at room temperature over a period of 2 (**IIIa**–**IIIe**), 4 (**IIIg**, **IIIh**), or 12 h (**IIIi**, **IIIj**). During the process, the mixture turned dark red. The solvent was distilled under reduced pressure, and the residue was subjected to chromatography to isolate compounds **Va**–**Vj** and **VI** which were purified by recrystallization from propan-2-ol–hexane (1:1).

3-Difluoromethyl-1-methyl-1*H*-imidazolium-2-carbodithioate (Va). Yield 0.58 g (56%), mp 145–147°C, R_f 0.4 (chloroform–acetone, 4:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.81 s (3H, NCH_3), 7.75 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz), 7.19 s (1H, 5-H), 7.33 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$): δ_F –95.18 ppm, d (CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: C 34.37; H 2.85; S 30.94. $C_6H_6F_2N_2S_2$. Calculated, %: C 34.61; H 2.90; S 30.79.

1-Methyl-3-(1,1,2,2-tetrafluoroethyl)-1*H*-imidazolium-2-carbodithioate (Vb). Yield 0.93 g (72%), mp 114–116°C, R_f 0.4 (chloroform–acetone, 4:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.82 s (3H, NCH_3), 6.99 t.t (1H, CF_2H, $^2J_{HF}$ = 55, $^3J_{HF}$ = 5 Hz), 7.10 s (1H 5-H), 7.17 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –91.52 d (2F, NCF_2), –135.73 d (2F, CF_2H, $^2J_{FH}$ = 55 Hz). Found, %: C 32.85; H 2.43; N 10.62; S 24.73. $C_7H_6F_4N_2S_2$. Calculated, %: C 32.56; H 2.34; N 10.85; S 24.81.

3-(2-Bromotetrafluoroethyl)-1-methyl-1*H*-imidazolium-2-carbodithioate (Vc). Yield 1.0 g (59%), mp 162–165°C (decomp.), R_f 0.5 (chloroform–acetone, 4:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.96 s (3H, NCH_3), 7.12 s (1H, 5-H), 7.16 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –65.89 s (2F, CF_2Br), –91.82 s (2F, NCF_2). Found, %: C 24.91; H 1.28; S 18.78. $C_7H_5BrF_4N_2S_2$. Calculated, %: C 24.94; H 1.49; S 19.02.

3-(2,2-Dichlorotrifluoroethyl)-1-methyl-1*H*-imidazolium-2-carbodithioate (Vd). Yield 1.28 g (83%), mp 158–159°C, R_f 0.5 (chloroform–acetone, 4:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.68 s (3H, NCH_3), 7.19 s (1H, 5-H), 7.26 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –70.72 s (1F, $CFCl_2$), –90.38 s (2F, NCF_2). Found, %: C 27.50; H 1.53; Cl 22.95; S 21.13. $C_7H_5Cl_2F_3N_2S_2$. Calculated, %: C 27.20; H 1.63; Cl 22.94; S 20.74.

3-Difluoromethyl-1-methyl-4,5-diphenyl-1*H*-imidazolium-2-carbodithioate (Ve). Yield 1.02 g (57%), mp 194–195°C (decomp.), R_f 0.6 (chloroform–acetone, 3:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.66 s (3H, NCH_3), 7.21–7.53 m (10H, H_{arom}), 7.61 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –94.61 ppm, d (CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: C 59.83; H 3.65; S 17.75. $C_{18}H_{14}F_2N_2S_2$. Calculated, %: C 60.00; H 3.89; S 17.79.

1-Methyl-3-(1,1,2,2-tetrafluoroethyl)-4,5-diphenyl-1*H*-imidazolium-2-carbodithioate (Vf). Yield 1.10 g (54%), mp 175–177°C (decomp.), R_f 0.6 (chloroform–acetone, 3:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.65 s (3H, NCH_3), 7.48–7.69 m (10H, H_{arom}), 7.97 t.t (1H, CF_2H, $^2J_{HF}$ = 55, $^3J_{HF}$ = 5 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –91.52 s (2F, NCF_2), –135.73 d (2F, CF_2H, $^2J_{FH}$ = 55 Hz). Found, %: C 56.06; H 3.52; S 15.63. $C_{19}H_{14}F_4N_2S_2$. Calculated, %: C 55.61; H 3.44; S 15.62.

3-(2-Bromotetrafluoroethyl)-1-methyl-4,5-diphenyl-1*H*-imidazolium-2-carbodithioate (Vg). Yield 0.86 g (36%), mp 177–179°C (decomp.), R_f 0.5 (chloroform–acetone, 3:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.61 s (3H, NCH_3), 7.14–7.32 m (10H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –63.68 s (2F, CF_2Br), –84.75 s (2F, NCF_2). Found, %: C 46.61; H 2.83; S 13.00. $C_{19}H_{13}BrF_4N_2S_2$. Calculated, %: C 46.64; H 2.68; S 13.09.

5,5,6,6-Tetrafluoro-1-methyl-2,3-diphenyl-8-thioxo-5,6-dihydro-8*H*-imidazo[2,1-*c*][1,4]thiazin-1-ium bromide (VI). Yield 0.48 g (20%), mp 199–200°C, R_f 0.2 (acetone). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.60 s (3H, NCH_3), 7.42–7.47 m (10H, H_{arom}). ^{19}F NMR spectrum, δ_F, ppm: –65.97 (2F, CF_2S, *AB* system), –84.85 (2F, NCF_2, *AB* system). Found, %: C 46.72; H 2.36; S 12.62. $C_{19}H_{13}BrF_4N_2S_2$. Calculated, %: C 46.62; H 2.66; S 13.09.

3-(2,2-Dichlorotrifluoroethyl)-1-methyl-4,5-diphenyl-1*H*-imidazolium-2-carbodithioate (Vh). Yield 1.42 g (62%), mp 193–195°C (decomp.), R_f 0.6 (chloroform–acetone, 3:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.54 s (3H, NCH_3), 7.34–8.51 m (10H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –68.52 s (1F, $CFCl_2$), –82.74 s (2F, NCF_2). Found, %: C 48.97; H 3.07; S 14.00. $C_{19}H_{13}Cl_2F_3N_2S_2$. Calculated, %: C 49.46; H 2.82; S 13.90.

3-Difluoromethyl-1-methyl-1*H*-benzimidazolium-2-carbodithioate (Vi). Yield 0.41 g (30%), mp 198–200°C (decomp.), R_f 0.6 (chloroform–acetone, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.92 s (3H, NCH_3), 7.71–8.05 m (4H, H_{arom}), 8.18 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –100.06 d (CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: C 46.97; H 3.07; S 24.70. $C_{10}H_8F_2N_2S_2$. Calculated, %: C 46.50; H 3.12; S 24.83.

3-(2,2-Dichlorotrifluoroethyl)-1-methyl-1*H*-benzimidazolium-2-carbodithioate (Vj). Yield 0.57 g (32%), mp 172–174°C (decomp.), R_f 0.6 (chloroform–acetone, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.95 s (3H, CH_3), 7.77–8.06 m (4H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –68.42 s (1F, $CFCl_2$), –87.38 s (2F, NCF_2). Found, %: C 36.57; H 1.64; S 17.77. $C_{11}H_7Cl_2F_3N_2S_2$. Calculated, %: C 36.77; H 1.95; S 17.85.

3-Methyl-2-[(methylsulfanyl)carbonothioyl]-1-polyfluoroalkyl-1*H*-imidazol-3-ium iodides VIIa–VIIj (*general procedure*). A mixture of 1 mmol of compound **Va–Vj**, 0.21 g (1.5 mmol) of methyl iodide, and 2 ml of anhydrous acetonitrile was heated for 20 min under reflux. The mixture was cooled to room temperature, diluted with 5 ml of diethyl ether, and left

to stand for 2 h, and the precipitate was filtered off, washed with diethyl ether, and dried in air.

1-Difluoromethyl-3-methyl-2-[(methylsulfanyl)-carbonothioyl]-1*H*-imidazol-3-ium iodide (VIIa). Yield 0.3 g (84%), mp 112–114°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.03 s (3H, SCH_3), 4.10 s (3H, NCH_3), 8.14 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz), 8.10 s (1H, 5-H), 8.33 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$): δ_F –94.17 ppm, d (CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: I 36.36; S 18.41. $C_7H_9F_2IN_2S_2$. Calculated, %: I 36.28; S 18.28.

3-Methyl-2-[(methylsulfanyl)carbonothioyl]-1-(1,1,2,2-tetrafluoroethyl)-1*H*-imidazol-3-ium iodide (VIIb). Yield 0.38 g (95%), mp 155–157°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 2.97 s (3H, SCH_3), 4.07 s (3H, NCH_3), 6.91 t.t (1H, CF_2H, $^2J_{HF}$ = 55, $^3J_{HF}$ = 5 Hz), 7.90 s (1H, 5-H), 8.51 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –96.97 s (2F, NCF_2), –135.17 d (2F, CF_2H, $^2J_{FH}$ = 55 Hz). Found, %: I 31.88; S 16.19. $C_8H_9F_4IN_2S_2$. Calculated, %: I 31.71; S 16.02.

1-(2-Bromotetrafluoroethyl)-3-methyl-2-[(methylsulfanyl)carbonothioyl]-1*H*-imidazol-3-ium iodide (VIIc). Yield 0.42 g (87%), mp 182–184°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.00 s (3H, SCH_3), 4.18 s (3H, NCH_3), 7.71 s (1H, 5-H), 8.62 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –67.60 s (2F, CF_2Br), –91.88 (2F, NCF_2, *AB* system). Found, %: I 26.11; S 13.17. $C_8H_8BrF_4IN_2S_2$. Calculated, %: I 26.49; S 13.39.

1-(2,2-Dichlorotrifluoroethyl)-3-methyl-2-[(methylsulfanyl)carbonothioyl]-1*H*-imidazol-3-ium iodide (VIId). Yield 0.4 g (90%), mp 182–183°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.00 s (3H, SCH_3), 4.19 s (3H, NCH_3), 7.80 s (1H, 5-H), 8.43 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –72.12 s (1F, $CFCl_2$), –87.96 (2F, CF_2, *AB* system). Found, %: I 28.40; S 14.27. $C_8H_8Cl_2F_3IN_2S_2$. Calculated, %: I 28.13; S 14.22.

1-Difluoromethyl-3-methyl-2-[(methylsulfanyl)-carbonothioyl]-4,5-diphenyl-1*H*-imidazol-3-ium iodide (VIIe). Yield 0.42 g (85%), mp 191–193°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.97 s (3H, SCH_3), 3.70 s (3H, NCH_3), 7.17 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz), 7.36–7.67 m (10H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –92.26 d (CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: I 25.08; S 13.06. $C_{19}H_{17}F_2IN_2S_2$. Calculated, %: I 25.26; S 12.76.

3-Methyl-2-[(methylsulfanyl)carbonothioyl]-4,5-diphenyl-1-(1,1,2,2-tetrafluoroethyl)-1*H*-imidazol-3-ium iodide (VIIf). Yield 0.5 g (90%), mp 178–179°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.95 s (3H, SCH_3), 3.78 s (3H, NCH_3), 7.29 t.t (1H, CF_2H, $^2J_{HF}$ = 55, $^3J_{HF}$ = 5 Hz), 7.36–7.67 m (10H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –95.65 s (2F, NCF_2), –135.36 d (2F, CF_2H, $^2J_{FH}$ = 55 Hz). Found, %: I 23.08; S 11.46. $C_{20}H_{17}F_4IN_2S_2$. Calculated, %: I 22.97; S 11.61.

1-(2-Bromotetrafluoroethyl)-3-methyl-2-[(methylsulfanyl)carbonothioyl]-4,5-diphenyl-1*H*-imidazol-3-ium iodide (VIIg). Yield 0.54 g (87%), mp 182–184°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.00 s (3H, SCH_3), 4.18 s (3H, NCH_3), 7.36–7.67 m (10H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –67.60 s (2F, CF_2Br), –91.88 s (2F, NCF_2). Found, %: I 19.81; S 10.17. $C_{20}H_{16}BrF_4IN_2S_2$. Calculated, %: I 20.10; S 10.16.

1-(2,2-Dichlorotrifluoroethyl)-3-methyl-2-[(methylsulfanyl)carbonothioyl]-4,5-diphenyl-1*H*-imidazol-3-ium iodide (VIIh). Yield 0.55 g (92%), mp 176–178°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.95 s (3H, SCH_3), 3.70 s (3H, NCH_3), 7.32–7.65 m (10H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –69.29 s (1F, $CFCl_2$), –82.17 s (2F, NCF_2). Found, %: I 21.48; S 11.17. $C_{20}H_{16}Cl_2F_3IN_2S_2$. Calculated, %: I 21.04; S 10.63.

1-Difluoromethyl-3-methyl-2-[(methylsulfanyl)-carbonothioyl]-1*H*-benzimidazol-3-ium iodide (VIIi). Yield 0.36 g (90%), mp 144–145°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.16 s (3H, SCH_3), 4.24 s (3H, NCH_3), 7.62–8.08 m (4H, H_{arom}), 8.26 t (1H, CF_2H, $^2J_{HF}$ = 60 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –97.23 ppm, d (2F, CF_2H, $^2J_{FH}$ = 60 Hz). Found, %: I 31.49; S 16.27. $C_{11}H_{11}F_2IN_2S_2$. Calculated, %: I 31.71; S 16.02.

1-(2,2-Dichlorotrifluoroethyl)-3-methyl-2-[(methylsulfanyl)carbonothioyl]-1*H*-benzimidazol-3-ium iodide (VIIj). Yield 0.45 g (90%), mp 172–174°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.10 s (3H, SCH_3), 4.21 s (3H, NCH_3), 7.56–8.11 m (4H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –69.74 s (1F, $CFCl_2$), –81.59 (2F, NCF_2, *AB* system). Found, %: I 25.49; S 13.27. $C_{12}H_{10}Cl_2F_3IN_2S_2$. Calculated, %: I 25.32; S 12.80.

1-(2,2-Dichlorotrifluoroethyl)-3-methyl-2-[(methylsulfanyl)carbonothioyl]-1*H*-imidazol-3-ium bis(trifluoromethylsulfonyl)imide (VIIId). A mixture of 0.41 g (0.9 mmol) of compound **VIId**, 0.29 g (1 mmol) of lithium bis(trifluoromethylsulfonyl)imide, 7 ml of water, and 5 ml of methylene chloride was vigorously stirred for 10 min at room temperature. The

organic phase was separated, the aqueous phase was extracted with 5 ml of methylene chloride, the organic extracts were mixed with 10 ml of benzene and evaporated to a volume of 2–3 ml (to remove residual water as azeotrope), and the remaining solvent was removed under reduced pressure (0.5 mm) at 50°C over a period of 1 h. Yield quantitative. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.88 s (3H, SCH_3), 3.80 s (3H, NCH_3), 7.82 s (1H, 5-H), 7.93 s (1H, 4-H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –73.38 s (1F, $CFCl_2$), –79.75 s (6F, SO_2CF_3), –89.25 (2F, CF_2, *AB* system). Found, %: I 0.12; N 6.87; S 21.07. $C_{10}H_8Cl_2F_9N_3O_4S_4$. Calculated, %: I 0.00; N 6.95; S 21.19.

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