

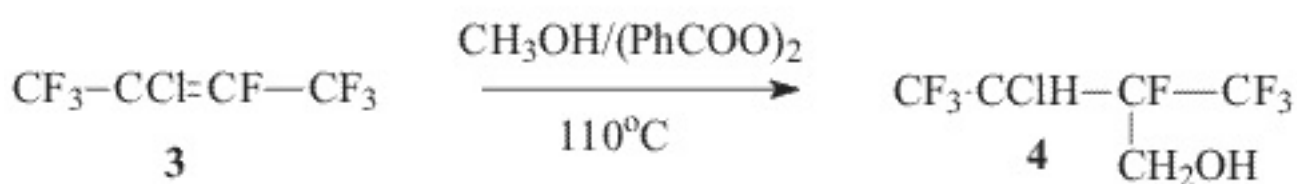
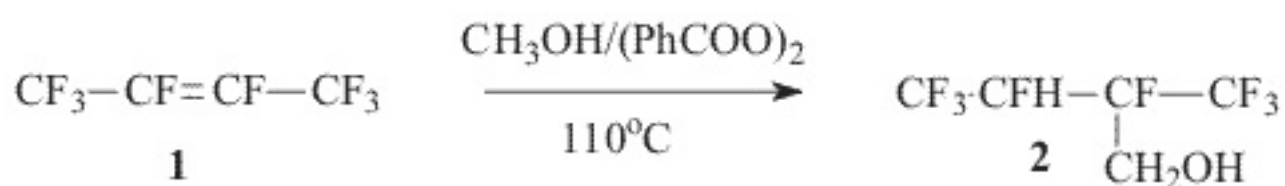
2-TRIFLUOROMETHYL-3,3,4,4,4-PENTAFLUOROBUTENE-1 SYNTHESIS

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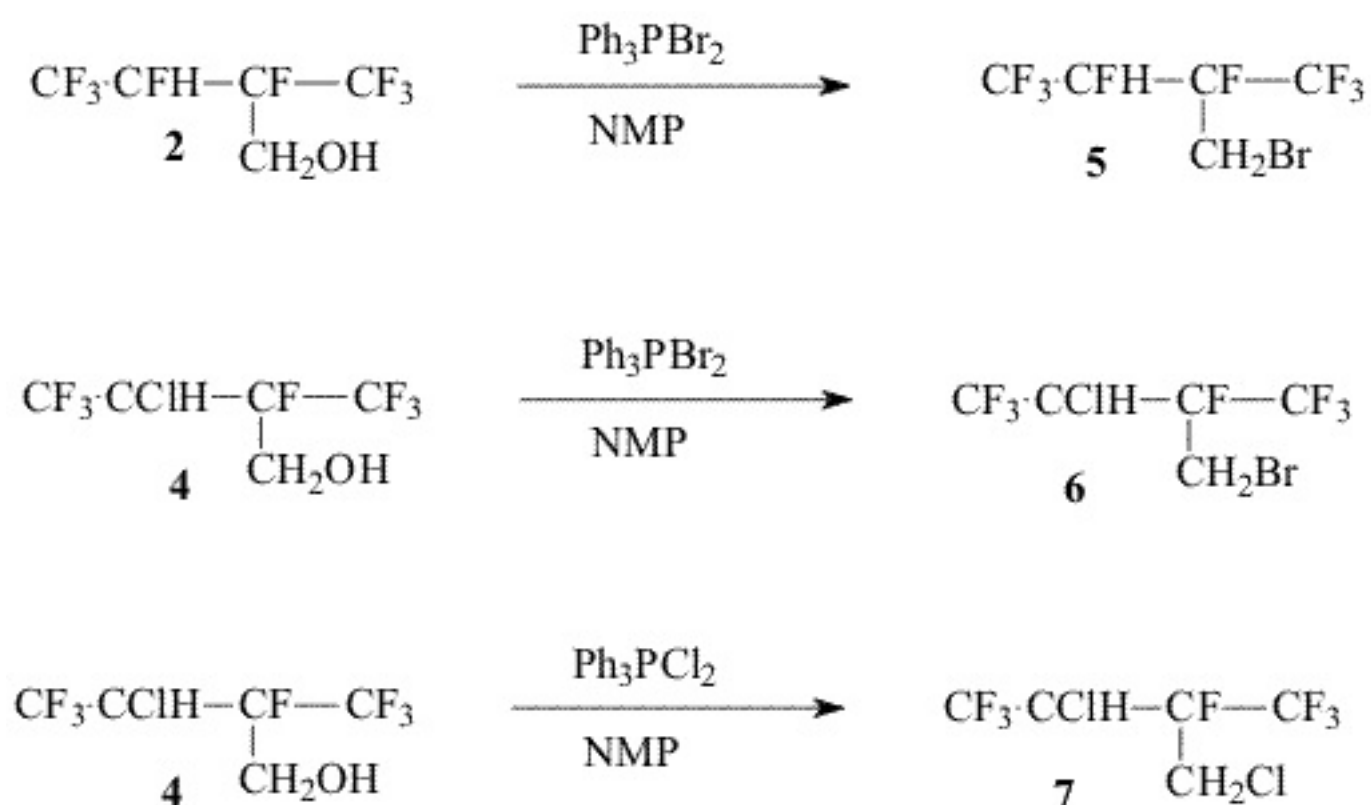
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Hexafluoroisobutylene and its derivatives are used for production of polymers. It is known that non-symmetrical hexafluoroisobutylene analogues are of interest for synthesis of amorphous polymers [1]. We have developed a new approach to the synthesis of its homologue, 2-trifluoromethyl-3,3,4,4,4-pentafluorobutene-1 (**8**), on the basis of available fluorobutenes including the following stages:.

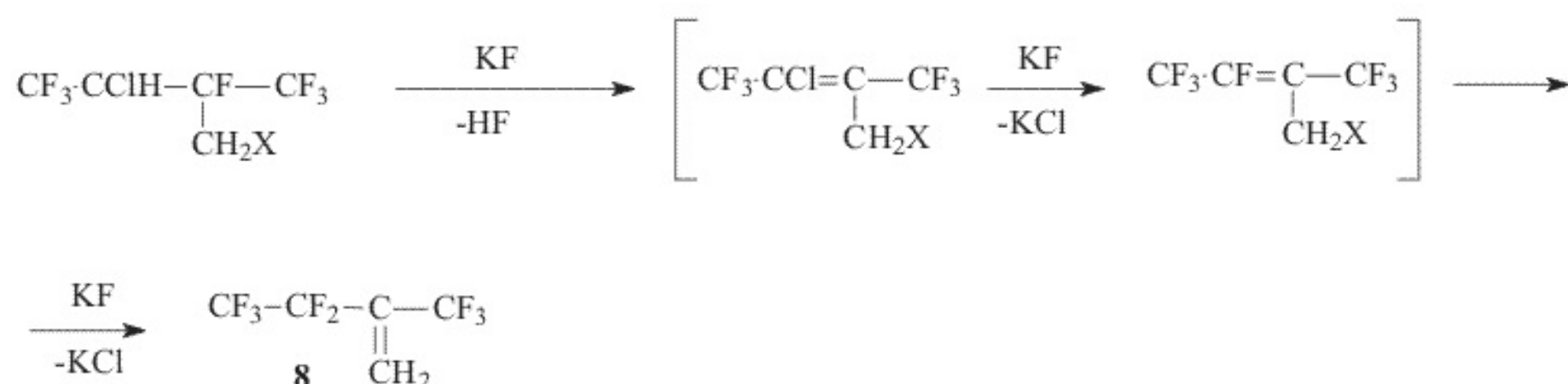
a) Radical addition of methanol to octafluorobutene-2 (**1**) or to heptafluoro-2-chlorobutene-2 (**3**) [2].



b) Replacement of the hydroxyl group for halogen



c) Treatment of the obtained halides (**5,6,7**) with potassium or cesium fluorides in a polar solvent at 100-150°C followed by dehydrohalogenation, substitution of the allyl chlorine or bromine for fluorine and isomerization of obtained olefin **8**.



Earlier [3] we proposed to convert alcohols (**2,4**) into corresponding chlorosulfites, but the reaction with thionyl chloride is accompanied by the formation of a considerable share of symmetrical dialkylsulfites that reduce significantly the total yield of target olefin **8**.

In the present work for exchange of the hydroxyl group for halogen we used either triphenylphosphine dichloride and triphenylphosphine bromide in dimethylformamide or N-methylpyrrolidone that made possible to afford chloride **7** and bromides **5,6** in a high yield.

Experimental

The ^{19}F NMR and ^1H NMR spectra were recorded on a "Bruker AC-200 X" instrument (200 Hz for ^1H and 188.3 Hz for ^{19}F accordingly, TMS and CF_3COOH standard, chemical shifts in ppm, spin-spin coupling constants in Hz).The mass-spectra were recorded on a V6-7070F instrument at ionizing irradiation energy of 70eV. For the reaction there were used dry N-methylpyrrolidone, CsF.

1,1,3-Trihydro-3-chloroperfluoro-2-methylbutanol-1 (**4**)

a.The mixture of 2-chloroperfluorobutene-2 (**3**)(28g, 0.12 mol) , methanol (30 mL) and benzoyl peroxide(BP) (0.8g) was heated in a steel autoclave at a temperature of 110°C for 10 hours. By distillation of the reaction mixture there was obtained 18.4 g of carbinol (**4**) with

the boiling temperature of 138-143°C (two diastereomers) Found: C 24.38; H 1.63%. $C_5H_4ClF_7O$. Calculated: C 24.14; H 1.61%. ^{19}F NMR: -8.1 m and -8.2 m (CF_3); -1.8 m and -2.0 m (CF); 99.2 v (CF).

b. The mixture of 2-chloroperfluorobutene-2 (22g, 0.1 mol), methanol (20 mL) and BP (0.3g) was heated at a temperature of 110°C for 6 hours in a sealed glass ampoule. After removal of BP residue and methanol excess, by distillation there was obtained 24.8 g (97%) of carbinol **4**.

2,4,4-Trihydro-4-bromoperfluoro-3-methylbutane (5)

Br_2 (8g, 0.05 mol) was added to triphenylphosphine (13.1g, 0.05 mol) in 15 mL of N-methylpyrrolidone. After completion of the exothermal reaction carbinol (2) (10g, 0.043mol) was added dropwise. The reaction mixture was heated at stirring at a temperature 120-140°C slowly distilling low-boiling products. There was obtained 7.8 g of bromide 5 with the boiling temperature of 97-98,5°C (two diastereomers).

The mass spectrum (m/z , rel. intensity, %): 294[M]⁺ 45; 274 [M-HF]⁺ 64; 255 [M-F-HF]⁺ 2; 225 [M- CF_3]⁺ 3; 213 [M-HBr]⁺ 4; 205 [M-HF- CF_3]⁺ 15; 195 [M-Br-HF]⁺ 55; 145 [$CF_2C(CF_3)=CF_2$]⁺ 73; 111[CBrHF]⁺ 32; 93 [CH_2Br]⁺ 100; 69 [CF_3]⁺ 92; 51 [CF_2H]⁺ 68..

^{19}F NMR: -2.5 m and -1.3 m (CF_3); 99.5 m and 100.8m (F 1); 136 m and 1366 m (F2)

1H NMR: 4.2 m (CH); 2.6 m (CH₂).

2,4,4-Trihydro-3-chloro-4-bromoperfluoro-3-methylbutane (6)

Bromide (6) was obtained similarly to bromide (5) from carbinol (4) as two diastereomers, T_b = 128-132°C, in 70% yield.

^{19}F NMR: -3.2m and -7.5m (CF_3); 90.2m (CF).

1H NMR: 3.6m (CH); 2.5m (CH₂).

2,4,4-Trihydro-3,4-dichloroperfluoro-3-methylbutane (7)

Chloride (7) was obtained similarly to bromide (6) by addition of carbinol (4) to the reaction mixture of equimolar quantities of triphenylphosphine, Cl_2 in N-methylpyrrolidone.

The mass spectrum (m/z , rel.intensity, %): 266[M]⁺ 5; 246 [M-HF]⁺ 32; 230 [M-HCl]⁺ 2; 211 [M-HF-Cl]⁺ 9; 197 [M- CF_3]⁺ 7; 177 [M- C_2F_5]⁺ 38; 69 [CF_3]⁺ 65; 49 [CH_2Cl]⁺ 100..

^{19}F NMR: -8.5m and -3.1m (CF_3);

1H NMR: 3.8m (CH); 2.4m (CH₂).

2-Trifluoromethyl-3,3,4,4,4-pentafluorobutene-1 (8)

Bromide (5) (7.8g, 0.025 mol) was added dropwise to the solution of CsF (8g, 0.05mol) in 15 mL of N-methylpyrrolidone. The reaction mixture was heated at stirring to 95-100°C, distilling olefin (8) into a cold trap connected to a water-jet pump (~100 mm Hg). By distillation there was produced 3.8g (71%) of olefin(8) identical to [3]. In a similar way olefin (8) was produced from bromide (6) and chloride (7).

Literature

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2. J. D. Lazerte, R. J. Koshar, *J. Am. Chem. Soc.*, 1955, 77, 910
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