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Reaction of substituted phenols and alcohols with (*E*)-1-chloro-3,3,3-trifluoropropene (HFCO-1233zd)

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ABSTRACT

Simple and convenient one-pot procedures for the preparation of $ArOCH=CHCF_3$, $ROCH=CHCF_3$ and $CF_3CH=CHOArOCH = CHCF_3$ starting from the industrial product HFCO-1233zd ($CF_3CH=CHCl$) are presented. These syntheses involve the reaction of 1233zd with phenols and alcohols in the presence of potassium hydroxide in DMF or pyridine solvent at elevated temperatures.

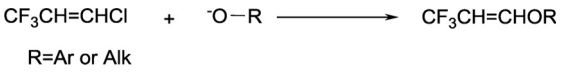
1. Introduction

(*E*)-1-Chloro-3,3,3-trifluoropropene (HFCO-1233zd) **1** belongs to the modern class of hydrofluorochloroolefins that has a low global warming potential (GWP) and no significant ozone depleting properties [1a, b], It is used as a blowing agent and a solvent. Literature describing the reaction chemistry of (*E*)-1-chloro-3,3,3-trifluoropropene is of limited scope and number of references. The existing patent literature is mostly focused on 1233zd use in applications. Some citations disclose reactions with hydroxy containing compounds [2–8], but there is no systematic description of the reaction of (*E*)-1-chloro-3,3,3-trifluoropropene **1** with O- and S- nucleophiles. An exception is the detailed procedure for the preparation of 3,3,3-trifluoropropanal dimethyl acetal from (*E*)-1-chloro-3,3,3-trifluoropropene and methanol in the presence of KOH at 70 (or 100) °C [9]. We decided to perform a systematic study on the reactions of **1** with phenols and aliphatic alcohols as representatives of O-nucleophiles.

2. Results and discussion

It is noteworthy to outline that the main mechanism of nucleophilic vinylic substitution via addition-elimination was investigated in details by Prof. Zvi Rappoport [10a,b] and suggests the stereoconversion or even retention of starting product configuration, especially upon action of the oxygen nucleophiles.

The reaction of (*E*)-1-chloro-3,3,3-trifluoropropene **1** with substituted phenols and alcohols is described by the following general scheme leading to form *Z*/*E* isomer mixtures:

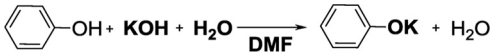


Due to the steric influence of bulky CF3 group (in contrast to chlorine atom) as well as to the electron withdrawing character of this group one can assume nucleophile attack to =CCl moiety.

An important consideration is the H_2O concentration in the reaction mixture, thus three methods of O-anion generation were employed that involve varying amount of water, as follows:

2.1. Method A. The treatment of substituted phenols with solid KOH in anhydrous N,N-dimethylformamide

2.2. Method B. The treatment of substituted phenols with aqueous KOH solution (25 %) in N,N-dimethylformamide



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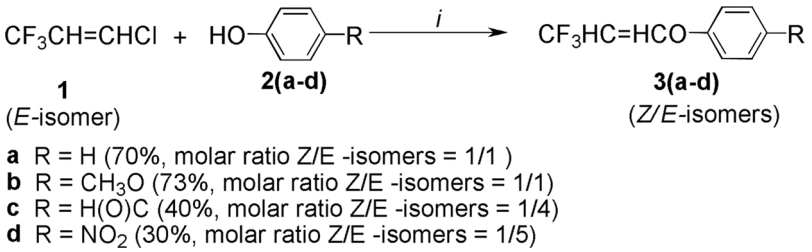


Scheme 1. The treatment of olefin **1** with substituted penols. *i*) 1 eq. KOH, DMF, 80 °C 8 h.

2.3. Method C. The treatment of substituted phenols and alcohol with NaH in anhydrous N,N-dimethylformamide

2.4. Examples of method A

Recently we showed that chloroperfluoro-containing olefin, such as 1,2-dichloro-1,2-difluoro ethene, was capable of reacting with phenols in the presence of potassium hydroxide. The reaction products constitute olefins with an aryloxy group replacing the chlorine atom. Reaction conditions were rather mild utilizing an open system at 80 °C in DMF [11].

It was found that the treatment of (*E*)-1-chloro-3,3,3-trifluoropropene (**1**) with substituted phenols **2** in the presence of 1 eq. potassium hydroxide at 80 °C for 8 h gave corresponding products **3** as a mixture of *Z/E* -isomers in various ratios depending on the phenol as expected on the basis of literature precedent [10a,b] (Scheme 1). A study devoted to the explanation of E/Z ratio of products formed is needed but falls outside the scope of the present study due to the specific character of experiments that establish reaction mechanism (thermodynamic or kinetic factors).

The (*E*)-1-chloro-3,3,3-trifluoropropene (**1**) also reacted with 2,2,3,3-tetrafluoropropan-1-ol in the presence of 1 eq. potassium hydroxide at 80 °C for 8 h to give (*Z/E*)-3,3,3-trifluoro-1-(2,2,3,3-tetrafluoropropoxy)propene **4** in 76 % yield (*Z/E*-ratio = 1/24) (Scheme 2).

The treatment of (*E*)-1-chloro-3,3,3-trifluoropropene (**1**) with dipotassium hydroquinolate (obtained from 1 eq. of hydroquinone and 2 eq. of potassium hydroxide) in DMF at 80 °C for 8 h gave 1,4-di(3,3,3-trifluoropropenyloxy)benzene **5** in only 10 % yield (molar ratio *Z/E*-isomers 1/5) (Scheme 3).

2.5. Examples of method B

This method was used for the reaction of (*E*)-1-chloro-3,3,3-trifluoropropene (**1**) with benzyl alcohol and aliphatic alcohols. In the reaction of (*E*)-1-chloro-3,3,3-trifluoropropene with benzyl alcohol in the presence of 1 eq. potassium hydroxide and 3 eq. of water at 80 °C for 8 h the product **6** was obtained in 50 % yield (*Z/E* ratio = 1/9) (Scheme 4).

The treatment of (*E*)-1-chloro-3,3,3-trifluoropropene (**1**) with 1 eq. of 2-methoxy-ethanol in a solution of potassium hydroxide in DMF and water (3 eq. water to 1 eq. KOH) in the presence 1 mol% Bu_4NCl gave product **7**, but olefin conversion after 10 h at 80 °C, according to ^{19}F NMR, was only 10 %. The product **7** was not isolated. (Scheme 5)

The interaction of aqueous potassium hydroxide solution in DMF and water (3 eq. water to 1 eq. KOH) with 0.5 eq. of the diethylene glycol, 1 mol% of Bu_4NCl and (*E*)-1-chloro-3,3,3-trifluoropropene after stirring 10 h at 80 °C gave product **8** in 20 % yield. When pyridine was used instead of DMF, the yield of product **8** increased to 40 %. In no case double addition was observed (Scheme 6).

2.6. Examples of method C

This method utilized the pregeneration of the O-anion in DMF by NaH treatment of the alcohols.

We investigated the reaction of (*E*)-1-chloro-3,3,3-trifluoropropene with benzyl alcohol under anhydrous conditions using NaH. The result was similar to that obtained by **Method B**, conversion of benzyl alcohol was 50 % (Scheme 7).

The reaction of olefin **1** with hydroquinone in anhydrous conditions under Argon using 2 eq. of sodium hydride at 80 °C after 10 h stirring gave the mixture of products **5** and **9** as the E-isomers only (Scheme 8).

The treatment of (*E*)-1-chloro-3,3,3-trifluoropropene (**1**) with 1 eq. of 2-methoxy-ethanol in DMF using 1 eq. of sodium hydride led to product **7** formation in 20 % yield with predominant formation of E-isomer (Scheme 9).

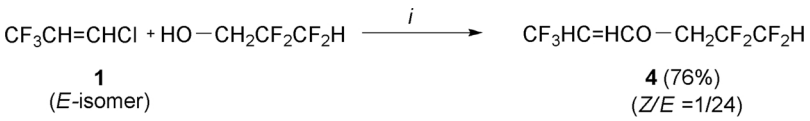
The reaction of olefin **1** with 2-(2-hydroxyethoxy)ethyl benzoate **10** was carried out using **Method C**. The sodium hydride was added to 2-(2-hydroxyethoxy)ethyl benzoate followed by addition of (*E*)-1-chloro-3,3,3-trifluoropropene. The reaction mixture was stirred 1 h at room temperature and 10 h at 80 °C. The product **11** was isolated in 10 % overall yield. E-isomer was the main product (*Z/E* = 1/13) (Scheme 10).

2.7. Reaction of (E)-1-chloro-3,3,3-trifluoropropene with 2-dimethylaminoethanole

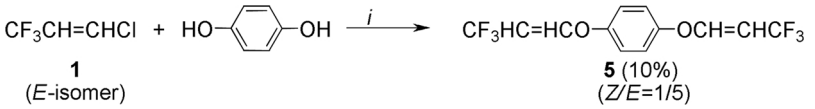
In the reaction of 1 eq. of olefin **1** with 2 eq. of 2-dimethylaminoethanol in open system with the addition of small amount DMF as a solvent for olefin, at 80 − 85 °C for 11 h the product **12** was isolated in 72 % yield (Scheme 11).

3. Conclusion

Systematic study on the reactivity of (*E*)-1-chloro-3,3,3-trifluoropropene (HFCO-1233zd) in the presence of base with *O*-nucleophiles such as substituted phenols and primary alcohols was described. This work proved 1233zd's ability to serve as promising starting material to construct olefins of general structure CF_3CH = CHOAr and CF_3CH = CHOR. The solvent of choice is DMF but in some instances pyridine is the preferred, reaction temperature around 80 °C was necessary to achieve reasonable yields. The alcohols investigated include polyols that are common ingredients in blowing agent formulations.



Scheme 2. The reaction of olefin **1** with telomere alcohol. *i*) 1 eq. KOH, DMF, 80 °C 8 h.



Scheme 3. The treatment of olefin **1** with hydroquinone; *i*) 2 eq. KOH, DMF, 80 °C 8 h.

4. Experimental

NMR spectra of compounds isolated were recorded on a Varian UNITY-Plus 400 (^{1}H, 399.98 MHz, ^{19}F, 376.49 MHz) and ^{13}C NMR-spectra were recorded on a Bruker AVANCE DRX 500 instrument at 125,71 MHz in $CDCl_3$. The chemical shifts are given in units of δ (ppm). External standards were used in all cases (^{1}H, ^{13}C: Me_4Si, ^{19}F: CCl_3F). Elemental analyses were carried out in the Analytical Laboratory of the Institute of Organic Chemistry, NAS of Ukraine, Kyiv. Purification of products by column chromatography was performed on Silica gel 70–230 mesh (Aldrich) with hexane: dichloromethane eluent (3:1 by volume).

Isomer structures were determined by NMR ^{1}H and ^{19}F data. Both isomers are characterized by chemical shift in NMR^{19}F as (-56÷-57 ppm) for Z-isomer and

(-59÷-61 ppm) for E-isomer; the most specific J-constants are presented in ^{1}H NMR spectra: $^3J_{HH} \approx 8$ Hz for Z-изомера и $^3J_{HH} \approx 12$ Hz for E-isomer.

4.1. The treatment of substituted phenols with KOH in anhydrous N,N-dimethylformamide – Method A

4.1.1. General procedure

A mixture of corresponding substituted phenol or telomere alcohol (40 mmol), of potassium hydroxide (40 mmol) and anhydrous DMF (30 ml) was stirred at room temperature till the entire potassium hydroxide was reacted with phenol. Then of of (*E*)-1-chloro-3,3,3-trifluoropropene (40 mmol) was added to solution and reaction mixture was stirred for 8 h at 80 − 90 °C. Reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with MTBE (methyl-*tert*-butyl ether), the extract was washed with 5 % aqueous potassium hydroxide, followed by water and dried over sodium sulfate. The solvent was evaporated under reduced pressure. The crude product was purified by distillation or column chromatography.

4.2. 1-Phenoxy-3,3,3-trifluoropropene 3a

Colorless liquid. Yield 70 %, b.p. 69 − 76 °C (16 mm Hg).

4.2.1. E-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 (m, 1H, *CH*=), 7.05 (d, 2H, $^3J_{HH}$ = 7.8 Hz, arom. H), 7.17 (m, 1H, arom. H), 7.25 (dd, 1H, $^3J_{HH}$ = 12 Hz, $^4J_{HF}$ = 1.6 Hz, *CH*=), 7.37 (m, 2H, arom. H); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 156.62 (arom. C), 151.92 (q, $^3J_{CF}$ = 8 Hz, *OCH*=), 130.01 (s, arom. C), 129.91 (arom. C,), 124.96 (arom. C), 124.8 (q, $^1J_{CF}$ = 269 Hz, *CF_3*), 117.99 (arom. C), 99.9 (q, $^2J_{CF}$ = 34 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -60.8 (dd, 3 F, $^3J_{HF}$ = 7.5 Hz, $^4J_{HF}$ = 1.6 Hz).

4.2.2. Z-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.9 (m, 1H, *CH*=), 6.74 (d, 1H, *CH*=, $^3J_{HH}$ = 6.7 Hz), 7.04 (d, 2H, J_{HH} = 8 Hz, arom. H), 7.17 (m, 1H, arom. H), 7.37 (m, 2H, arom. H); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 156.72 (arom. C), 149.17 (q, $^3J_{CF}$ = 5.5 Hz, *OCH*=), 130.01 (arom. C), 129.91 (arom. C), 124.63 (arom. C), 122.87 (q, $^1J_{CF}$ = 267 Hz, CF_3), 117.24 (arom. C), 99.21 (q, $^2J_{CF}$ = 35.6 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -58.4 (d, 3 F, $^3J_{HF}$ = 7 Hz).

Analysis: Found: %C 57.48; %H 3.53. $C_9H_7F_3O$. Calcd.: %C 57.45; % H 3.75.

4.3. 1-(4-Methoxyphenyl)-3,3,3-trifluoropropene 3b

Colorless liquid. Yield 73 %, b.p. 50 − 56 °C (0.4 mm Hg).

4.3.1. E-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, CH_3), 5.24 (m, 1H, *CH*=), 6.89 (d, 2H, $^3J_{HH}$ = 7.5 Hz, arom. H), 7.07 (d, 2H, $^3J_{HH}$ = 7.5 Hz, arom. H), 7.25 (dd, 1H, $^3J_{HH}$ = 12 Hz, $^4J_{HF}$ = 1.4 Hz, *CH*=); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 156.89 (arom. C), 153.17(q, $^3J_{CF}$ = 8.1 Hz, *OCH*=), 150.77 (arom. C), 124.8 (q, $^1J_{CF}$ = 267 Hz, *CF_3*), 119.5 (arom. C), 118.5 (arom. C), 114.96 (arom. C), 114.83 (arom. C), 99.8 (q, $^2J_{CF}$ = 34.5 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -60.25 (br.s, 3 F).

4.3.2. Z-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.8 (s, *CH_3*), 4.9 (m, 1H, *CH*=), 6.66 (m, 1H, *CH*=) 6.88 (d, 2H, $^3J_{HH}$ = 8 Hz, arom. H), 7.04 (d, 2H, $^3J_{HH}$ = 8 Hz, arom. H); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 156.62 (arom. C), 150.31(q, $^3J_{CF}$ = 5.9 Hz, *OCH*=), 149.31 (arom. C), 124.8 (q, $^1J_{CF}$ = 267 Hz, *CF_3*), 119.5 (arom. C), 118.5 (arom. C), 114.96 (arom. C), 114.83 (arom. C), 99.20 (q, $^2J_{CF}$ = 35.2 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -57.9 (br s, 3 F).

Analysis: Found: %C 54.8; %H 3.86. $C_{10}H_9F_3O_2$. Calcd.: %C 55.05; % H 4.16.

4.4. 4-(3,3,3-trifluoropropenyloxy)benzaldehyde 3c

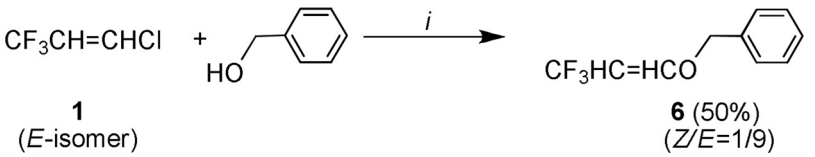
Yellow liquid. Yield 40 %, b.p. 74 − 78 °C (15 mm Hg).

4.4.1. E-isomer

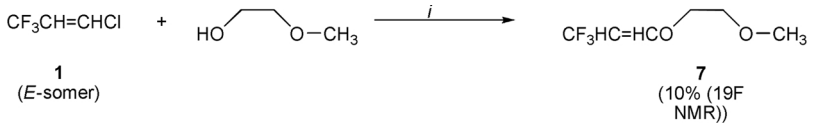
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.59 (m, 1 H), 7.17(d, 2H, $^3J_{HH}$ = 8 Hz, arom. H) 7.34 (dd, 1H, $^3J_{HH}$ = 12 Hz, $^4J_{HF}$ = 1.6), 7.93 (d, 2H, $^3J_{HH}$ = 8 Hz, arom. H), 9.97 (s, 1 H); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 190.56 (*CO*), 160.10 (arom. C), 149.69 (q, $^3J_{CF}$ =8.1 Hz, *OCH*=), 133.01 (arom. C), 132.03 (arom. C) 123.7 (q, $^1J_{CF}$ = 267 Hz, *CF_3*), 117.63 (arom. C), 102.65 (q, $^2J_{CF}$ = 34.5 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -61.3 (dd, 3 F, $^3J_{HF}$ = 7.6 Hz, $^4J_{HF}$ = 1.7 Hz).

4.4.2. Z-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.18 (m, 1 H), 6.84 (d, 1H, $^3J_{HH}$ = 6.8 Hz), 7.19 (d, 2H, $^3J_{HH}$ = 8 Hz, arom. H), 7.93 (d, 2H, $^3J_{HH}$ = 8 Hz, arom. H), 9.97 (s, 1 H); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 190.56 (*CO*), 159.64 (arom. C), 147.21 (q, $^3J_{CF}$ = 5.9 Hz, *OCH*=), 132.55 (arom. C), 131.99 (arom. C) 123.7 (q, $^1J_{CF}$ = 267 Hz, *CF_3*), 117.63 (arom. C), 102.65 (q, $^2J_{CF}$ = 35.2 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -58.6 (d, 3 F, $^3J_{HF}$ = 7.5 Hz).

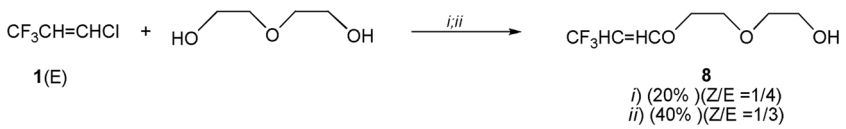


Scheme 4. The reaction of olefin **1** with benzyl alcohol; *i*) 1 eq. KOH, 3 eq. H_2O, DMF, 80 °C 8 h.



1 (*E*-somer) **7** (10% (19F NMR))

Scheme 5. The reaction of olefin **1** with 2-methoxy-ethanol; *i*) 1 eq.KOH, 3 eq. H_2O, DMF, 1 mol% Bu_4NCl, 80 °C, 10 h.



1(E) **8** *i*) (20%)(Z/E =1/4) *ii*) (40%)(Z/E =1/3)

Scheme 6. The reaction of olefin 1 in the aqueous potassium hydroxide solution in mixture solvent DMF and water; *i*) 2 eq. **1**, 2 eq. KOH, 3 eq.H_2O, DMF, 1 mol% Bu_4NCl, 80 °C, 10 h; *ii*) 2 eq. **1**, 2 eq. KOH, 3 eq. H_2O, Py, 1 mol% Bu_4NCl, 80 °C, 10 h.

Analysis: Found: %C 55.28; %H 3.30. $C_{10}H_7F_3O_2$. Calcd.: %C 55.57; % H 3.26.

4.5. 1-(4-nitrophenyl)-3,3,3-trifluoropropene 3d

Yellow oil (after flash chromatography (hexane/CH_2Cl_2: 75/25)). Yield 30 %.

4.5.1. E-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.6 (m, 1 H), 7.20(d, 2H, $^3J_{HH}$ = 8.1 Hz, arom. H) 7.34 (dd, 1H, $^3J_{HH}$ = 12.3 Hz, $^4J_{HF}$ = 1.8 Hz), 7.93 (d, 2H, $^3J_{HH}$ = 8.1 Hz, arom. H); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 164.10 (arom. C), 149.21 (q, $^3J_{CF}$ = 8 Hz, *OCH*=), 144.32 (arom. C), 126.09 (arom. C) 123.58 (q, $^1J_{CF}$-267 Hz, *CF_3*), 117.46 (arom. C), 103.55 (q, $^2J_{CF}$ = 34.1 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -60.5 (dd, 3 F, $^3J_{HF}$ = 6.76 Hz, $^4J_{HF}$ = 1.7 Hz).

4.5.2. Z-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (m, 1 H), 6.8 (d, 1H, $^3J_{HH}$ = 6.7 Hz), 6.95 (d, 2H, $^3J_{HH}$ = 8.5 Hz, arom. H), 7.93 (d, 2H, $^3J_{HH}$ = 8.5 Hz, arom. H); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 160.68 (arom. C), 146.74 (q, $^3J_{CF}$ = 5.5 Hz, *OCH*=), 141.27 (arom. C), 126.02 (arom. C) 125.58 (q, $^1J_{CF}$ = 267 Hz, CF_3), 117.06 (arom. C), 102.47 (q, $^2J_{CF}$ = 35.1 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -57.8 (d, 3 F, $^3J_{HF}$ = 8.5 Hz).

Analysis: Found: %C 46.64 %H 2.49; N 6.17. $C_9H_6F_3NO_3$. Calcd.: %C 46.37; % H 2.59;

N 6.01.

4.6. 1-(2,2,3,3-tetrafluoropropoxy)-3,3,3-trifluoro-propene 4

Colorless liquid. Yield 76 %, b.p. 120−122 °C

4.6.1. E-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (t, 2H, $^3J_{HH}$ = 11.8 Hz), 5.15(m, 1 H), 5.93 (dm, 1H, $^2J_{HF}$ = 52.9 Hz), 7.0 (d, 1H, $^3J_{HH}$ = 13.7 Hz); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 153.25 (q, $^3J_{CF}$ = 7.7 Hz, *OCH*=), 124.06 (q, $^1J_{CF}$ = 267 Hz, *CF_3*), 113.88 (tt, $^1J_{CF}$ = 250.5 Hz, $^2J_{CF}$ = 28.1 Hz), 108.94 (tt, $^1J_{CF}$ = 250 Hz, $^2J_{CF}$ = 35.6 Hz), 97.03 (q, $^2J_{CF}$ = 34.1 Hz, *CF_3CH*=) 66.63 ($^2J_{CF}$ = 29.6 Hz, *CH_2*); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -57.2 (d, 3 F, $^3J_{HF}$ = 4 Hz), -121.52 (s, 2 F), -135.4 (d, 2 F, J_{HF} = 52.9 Hz).

4.6.2. Z-isomer

^{1}H (400 MHz, $CDCl_3$): δ 3.9 (t, 2H, $^3J_{HH}$ = 11.4 Hz), 4.86 (m, 1 H), 5.96 (dm, 1H, $^2J_{HF}$ = 48.9 Hz), 6.9 (d, 1H, $^3J_{HH}$ = 11.6 Hz); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -55.1 (d, 3 F, $^3J_{HF}$ = 8 Hz), -124.2 (s, 2 F), -136.2 (d, 2 F, J_{HF} = 48.9 Hz).

Analysis: Found: %C 31.79 %H 2.34. $C_6H_7F_7O$. Calcd.: %C 31.87; % H 2.23.

4.7. (E)-4,4'-Di(3,3,3-trifluoropropenyloxy)benzene 5

Colorless oil. Yield 10 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 (m, 2 H), 7.2 (br s, 4H, arom. H), 7.24 (dm, 2H, $^3J_{HH}$ = 12.8 Hz); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 152.53 (arom. C.), 151.86 (q, $^3J_{CF}$ = 8.1 Hz, *OCH*=), 124.27 (q. $^1J_{CF}$ = 267 Hz, CF_3), 119.66 (arom. C), 100.39 (q $^2J_{CF}$ = 34.5 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -61.0 (dd, 6 F, $^3J_{HF}$ = 6.1 Hz, $^4J_{HF}$ = 1.6 Hz).

Analysis: Found: %C 48.35 %H 2.76. $C_{12}H_8F_6O_2$. Calcd.: %C 48.34; % H 2.7.

4.8. The treatment of alcohols with KOH solution (25 %) in N,N-dimethylformamide – method B

4.8.1. General procedure

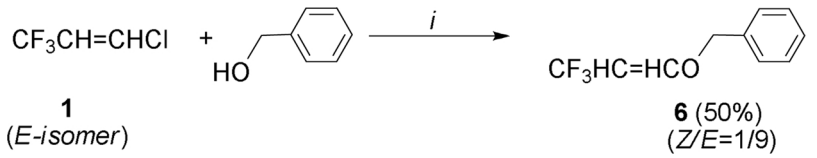
A mixture of corresponding alcohol (40 mmol), potassium hydroxide (80 mmol), in water (120 mmol) [in case 2-methoxy ethanol and diethylene glycol it was used 1 %-mol of Bu_4NCl as phase transfer] and DMF (30 mL) was mixed together and stirred at room temperature till the entire potassium hydroxide was dissolved. Then of of (*E*)-1-chloro-3,3,3-trifluoropropene (80 mmol) was added to solution and reaction mixture was stirred for 8 h at 80−90 °C. The reaction mixture was cooled to room temperature and poured into water. Organic layer was extracted with MTBE, the organic layer was washed with 5 % aqueous potassium hydroxide, followed by water and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified by distillation or column chromatography.

4.9. ((E)-(3,3,3-Trifluoropropenyloxy)methyl)benzene 6

Colorless liquid. Yield 50 %, b.p. 79−80 °C (14 mm Hg).

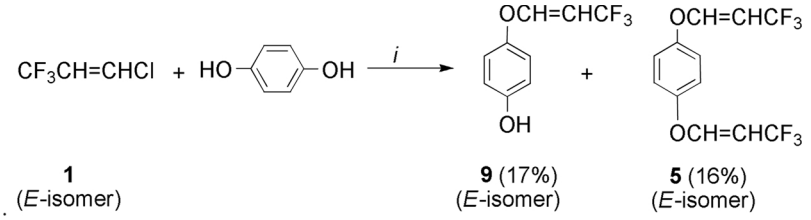
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.84 (s, 2 H), 5.1 (m, 1 H), 7.13 (dd, 1H, $^3J_{HH}$ = 12.6 Hz; $^4J_{HF}$ = 1.6 Hz), 7.38 (m, 5 H, arom. H); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 154.28 (q, $^3J_{CF}$ = 8.0 Hz, *OCH*=), 143.57 (arom. C), 128.76 (arom. C), 128.61 (arom. C), 127.7 (arom. C), 124.83 (q, $^1J_{CF}$ = 267 Hz, *CF_3*), 95.02 (q, $^2J_{CF}$ = 34.6 Hz, *CF_3CH*=); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -59.82 (d, 3 F, $^3J_{HF}$ = 6.3 Hz).

Analysis: Found: %C 59.14; %H 4.46. $C_{10}H_9F_3O$. Calcd.: %C 59.41; % H 4.41.

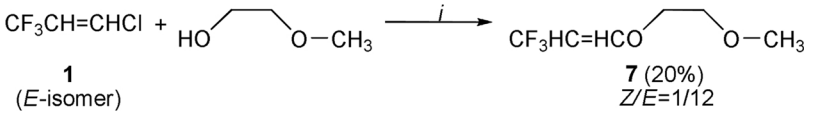


1 (*E-isomer*) **6** (50%) (*Z/E*=1/9)

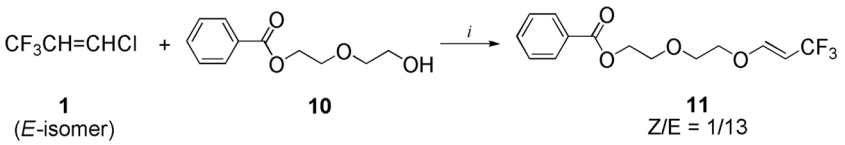
Scheme 7. The anhydrous condition of the reaction of olefin **1** with sodium benzylate; *i*) 1 eq. NaH, DMF, 80 °C 10 h.



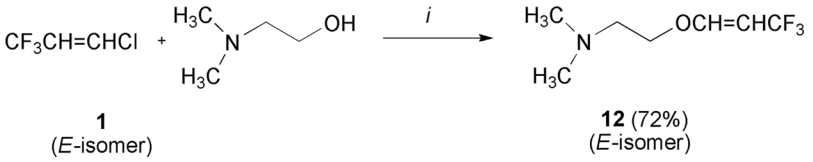
Scheme 8. The reaction of olefin **1** with hydroquinone under anhydrous condition; *i)* 2 eq. NaH, DMF, 80 °C 10 h.



Scheme 9. The interaction of olefin **1** with sodium 2-metoxy-ethylate; *i*) 1 eq. NaH, DMF, 80 °C 10 h.



Scheme 10. The method utilizing the pregeneration of the O-anion in DMF by NaH treatment of the alcohols.; *i*) 1 eq. NaH, DMF, 80 °C 10 h.



Scheme 11. The reaction of olefin **1** with 2-dimethylaminoethanole; *i)* 1 eq. of olefin **1** with 2 eq. of 2-dimethylaminoethanol, DMF, 80 °C 11 h.

4.10. 2-(2-(3,3,3-Trifluoroprop-1-enyloxy)ethoxy)ethanol 8

Colorless oil. Yield 20 % (reaction in the DMF); 40 % (reaction in pyridine);

4.10.1. E-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.1 (br s, 1 H), 3.6 (t, 2H, $^3J_{HH}$ = 4.3 Hz), 3.74 (m, 4 H), 3.93 (m, 2 H), 4.98 (m, 1 H), 7.5 (dd, 1H, $^3J_{HH}$ = 12.7, $^4J_{HF}$ = 1.6 Hz); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 154.58 (q, $^3J_{CF}$ = 8.0 Hz, *OCH*=), 124.74 (q. $^1J_{CF}$ = 266.3 Hz, CF_3), 94.5 (q $^2J_{CF}$ = 33.7 Hz, *CF_3CH*=), 72.61, 69.7, 69.09, 61.61; ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -59.9 (d, 3 F, $^3J_{HF}$ = 6.5 Hz).

4.10.2. Z-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.1 (brs, 1 H), 3.6 (t, 2H, $^3J_{HH}$ = 4.3 Hz), 3.74 (m, 4 H), 3.93 (m, 2 H), 4.63 (m, 1 H), 7.5 (m 1 H); ^{19}F (376.49 MHz, $CDCl_3$): δ -57.8 (d, 3 F, $^3J_{FH}$ = 6.5 Hz).

Analysis: Found: %C 42.25; %H 5.51. $C_7H_{11}F_3O_3$. Calcd.: %C 42.01; % H 5.54

4.11. The treatment of substituted phenols and alcohols with NaH in anhydrous N,N-dimethylformamide – method C

4.11.1. General procedure

To suspension of sodium hydride (40 mmol) in anhydrous DMF (30 mL) at ambient temperature under argon and stirring was slowly added corresponding alcohol (40 mmol). After observed termination of hydrogen evolution the reaction mixture was stirred for 10 min and of (*E*)-1-chloro-3,3,3-trifluoropropene (40 mmol) was added dropwise. The reaction mixture was then stirred for 10 h at 80 °C. After end of reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with MTBE, the extract was washed with 5 % aqueous potassium hydroxide, followed by water and dried over sodium sulfate. The solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography.

4.12. (E)-4,4'-di(3,3,3-trifluoropropenyloxy)benzene 5

Colorless oil. Yield 16 %.

4.13. ((E)-(3,3,3-Trifluoropropenyloxy)methyl)benzene 6

Colorless liquid. Yield 50 %, b.p. 79 − 80 °C (14 mm Hg).

4.14. 1-(2-methoxy-ethoxy)-3,3,3-Trifluoro-propene 7

Yellow oil. Yield 20 %.

4.14.1. E-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.4 (s, CH_3), 3.61 (t, 2H, $^3J_{HH}$ = 4.6 Hz), 3.92 (t, 2H, $^3J_{HH}$ = 4.6), 4.98 (m, 1 H), 7.07 (dm, 1H, $^3J_{HH}$ = 12.7, $^4J_{HF}$ = 1.6 Hz); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 154.6 (q, $^3J_{CF}$ = 8.1 Hz, *OCH*=), 124.78 (q, $^1J_{CF}$ = 266.3 Hz, *CF_3*), 94.42 (q, $^2J_{CF}$ = 33.7 Hz, *CF_3CH*=), 70.42, 69.64, 59.08; ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -59.86 (d 3 F, $^3J_{FH}$ = 5.8 Hz).

4.14.2. Z-isomer

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (s, CH_3), 3.64 (t, 2H, $^3J_{HH}$ = 4.3 Hz), 4.08 (t, 2H, $^3J_{HH}$ = 4.3), 4.62 (m, 1 H), 6.4 (d, 1H, $^3J_{HH}$ = 6.9 Hz); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -59.9 (d, 3 F, $^3J_{FH}$ = 8.5 Hz).

Analysis: Found: %C 42.45; %H 5.26. $C_6H_9F_3O_2$. Calcd.: %C 42.36; % H 5.33

4.15. (E)-4-(3,3,3-Trifluoro-propenyloxy)phenol 9

Dark red oil. Yield 17 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.07 (s, 1H-OH); 5.22 (m, 1 H); 6.81(d, 2H, $^3J_{HH}$ = 8.4 Hz, arom. H); 6.91 (d, 2H, $^3J_{HH}$ = 8.4 Hz, arom. H); 7.18 (d, 1H $^3J_{HH}$ 13.6 Hz); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -60.41 (d, 3 F, $^3J_{HF}$ = 7.8 Hz).

Analysis: Found: %C 52.96; %H 3.7. $C_9H_7F_3O_3$. Calcd.: %C 52.95; % H 3.46

4.16. 2-(2-Hydroxyethoxy)ethyl benzoate 10

To solution of diethylene glycol (30 mmol) and of triethyl amine (30 mmol) in anhydrous diethyl ether (20 mL) at 0 °C benzoyl chloride (30 mmol) was added slowly. Reaction mixture was stirred for 4 h then poured into water. Organic layer was extracted with diethyl ether, the extract was washed with 5 % aqueous potassium hydroxide, followed by water and dried over sodium sulfate. The solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography.

Colorless oil. Yield 80 %.

NMR ^{1}H (400 MHz, $CDCl_3$): δ 8.04 (m, 2H, arom. H); 7.54 (m, 1H, arom. H); 7.41 (m, 2H arom. H); 4.49 (t, 2H, CH_2, $^{3}J_{HH}$ = 4.8 Hz); 3.89 (t, OH, $^{3}J_{HH}$ = 4.8 Hz); 3.84 (t, 2H, CH_2, $^{3}J_{HH}$ = 4.8 Hz); 3.75 (t, 2H, CH_2, $^{3}J_{HH}$ = 4.4 Hz); 3.65 (t, 2H, CH_2, $^{3}J_{HH}$ = 4.4 Hz); ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 166.46 (COO), 132.96 (arom. C), 130.03 (arom. C), 129.63 (arom. C), 128.32 (arom. C), 69.16, 63.89.

Analysis: Found: %C 62.70; %H 6.72. $C_{11}H_{14}O_4$. Calcd.: %C 62.85; % H 6.71

4.17. (E)-2-(2-(3,3,3-Trifluoroprop-1-enyloxy)ethoxy)ethyl benzoate 11

Yellow oil. Yield 10 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (m, 2H, arom. H); 7.52 (m, 1H, arom. H); 7.37 (m, 2H, arom. H); 7.04 (d, 1H, *CH*=, $^{3}J_{HH}$ = 11 Hz); 4.95 (m, 1H, *CH*=) 4.47 (t, 2H, CH_2, $^{3}J_{HH}$ = 4.5 Hz); 3.85 (m, 6 H); ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -59.8 (d, 3 F, $^{3}J_{HH}$ = 5.8).

Analysis: Found: %C 55.30; %H 5.07. $C_{14}H_{15}F_3O_4$. Calcd.: %C 55.27; % H 4.97

4.18. N,N-Dimethyl-1-((E)-3,3,3-trifluoropropenyloxy)-ethylamine 12

A solution of 34 mmol of (*E*)-1-chloro-3,3,3-trifluoropropene with 68 mmol of 2-dimethylaminoethanole, and 50 ml of DMF in open system, was stirred for 11 h at 80 − 85 °C. The reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with MTBE, the extract was washed with water and dried over sodium sulfate. The solvent was evaporated under reduced pressure. The crude product was isolated by fractional distillation.

Colorless liquid. Yield 72 %, b.p. 86 − 88 °C (20 mm Hg):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, 1H, $^{3}J_{HH}$ 12.8 Hz,), 4.94 (m, 1 H), 3.83 (t, 2H, $^{3}J_{HH}$ = 5.4 Hz), 2.61 (t, 2H, $^{3}J_{HH}$ = 5.4 Hz), 2.27 (s, 6 H); ^{13}C NMR:154.41 (q, $^{3}J_{CF}$ = 7.5 Hz, *OCH*=), 124.77 (q. $^{1}J_{CF}$ = 266.7 Hz, CF_3), 94.04 (q $^{2}J_{CF}$ = 34.4 Hz, *CF₃CH*=), 67.90, 57.59, 45.48; ^{19}F NMR ($CDCl_3$, 376.49 MHz): δ -60.19 (d, 3 F, $^{3}J_{HF}$ = 7.8 Hz).

Analysis: Found: %C 45.88; %H 6.61; %N 7.64. $C_7H_{12}F_3NO$. Calcd.: %C 45.90; % H 6.60; N 7.65

Declaration of competing interest and authorship conformation form

- All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.
- This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.
- The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript

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