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A Convenient Access to 1,1-Difluoroethyl Triflate and Iodide†

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1,1-Difluoroethyl triflate obtained from 1,1-difluoroethylene and trifluoromethanesulfonic acid is converted into its corresponding iodide by the action of iodide anion in diethyl ketone.

The synthesis of compounds bearing two fluorine atoms on the same carbon is of great importance owing to their chemical and biological properties. However, few methods are known for the functionalization of RCF_2X compounds ($X = H$, halogen).[1]

1,1-Difluoro-1-iodoethane is currently prepared from 1,1-difluoroethylene and hydrogen iodide [eqn. (1)]. On a small scale, the reaction is very slow; however, it is very fast and exothermic on a larger scale but requires complex apparatus.[2–4]

$$CH_2{=}CF_2 + HI \longrightarrow CH_3CF_2I \qquad (1)$$

We report now a two-step procedure for its preparation using 1,1-difluoroethylene **1** and trifluoromethanesulfonic acid **2** (triflic acid) as starting materials [eqn. (2)].

$$\underset{\mathbf{1}}{CH_2{=}CF_2} + \underset{\mathbf{2}}{CF_3SO_3H} \longrightarrow \underset{\mathbf{3}}{CH_3CF_2OSO_2CF_3} \xrightarrow{NaI} \underset{\mathbf{4}}{CH_3CF_2I} \qquad (2)$$

It is known that the reaction of triflic acid with simple alkenes gives the adduct mixed with telomeric products.[5] In order to suppress such polymerization, a procedure avoiding the presence of an excess of olefin was chosen.

Thus, in the first step, the preparation of the 1,1-difluoroethyl trifluoromethanesulfonate was performed in a Parr apparatus. Trifluoromethanesulfonic acid was placed in a thick-walled glass bottle. Then, 1,1-difluoroethylene was introduced under pressure (3.9 to 1 bar). After shaking had continued for 3 h at room temperature, the product was obtained in 94% yield and was pure enough to be used as such. However, in order to check its stability, the product was distilled at atmospheric pressure at 70–72 °C. This compound has already been obtained as a secondary product from 1,1-difluoroethylene and chlorine trifluoromethanesulfonate in 5% yield.[6] Although nucleophilic additions to fluorinated olefins are possible,[7] the triflate anion is so poorly nucleophilic that the first step should be in fact the protonation of the double bond, as in additions to normal olefins. This addition is regioselective owing to the stabilization of the intermediate carbocation by the two geminal fluorine atoms [eqn. (3)].

$$\underset{\mathbf{1}}{CH_2{=}CF_2} \xrightarrow{H^+} CH_3CF_2^+ \xrightarrow{CF_3SO_3^-} \underset{\mathbf{3}}{CH_3CF_2OSO_2CF_3} \qquad (3)$$

Alkyl triflates are known to be powerful alkylating agents:[8] they are 10^4 times more reactive with iodide ion than alkyl toluene-*p*-sulfonates. However, an unusual behaviour of trifluoromethyl trifluoromethanesulfonate ($CF_3SO_3CF_3$) has been reported:[9,10] attack by the iodide anion did not occur at the carbon atom but at the sulfur atom. This behaviour could be related to the strong repulsive effect arising from the n orbitals of the fluorine atoms contained in the fluoroalkyl chain. The triflate CH_3CF_2OTf (**3**) has a structure intermediate between the usual alkyl triflate RCH_2OTf and trifluoromethyl triflate CF_3OTf. Its chemical reactivity has not yet been studied.[6]

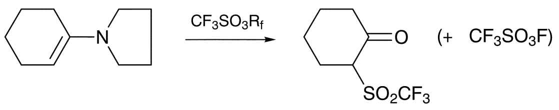
We performed the Finkenstein reaction with sodium iodide in diethyl ketone. 1,1-Difluoro-1-iodoethane **4** was obtained in 62% yield after atmospheric distillation at 45–48 °C. We chose diethyl ketone (bp 102 °C) instead of acetone (bp 56 °C) in order to separate more easily the product from the solvent.

$$\underset{\mathbf{3}}{CH_3CF_2OSO_2CF_3} \xrightarrow[Et_2CO]{NaI} \underset{\mathbf{4}}{CH_3CF_2I} \qquad (4)$$

A similar reaction was achieved in 3 days with sodium bromide. Analysis of the solution by ^{19}F NMR showed only the presence of 1-bromo-1,1-difluoroethane **5**. In contrast, chloride and acetate anions produced only difluoroethylene and traces of 1,1,1-trifluoroethane.

When we tried to condense the triflate **3** with phenyllithium and 1-pyrrolidinocyclohex-1-ene, in both cases we obtained only traces of trifluoromethylsulfonylbenzene and 2-trifluoromethylsulfonylcyclohexan-1-one respectively [eqns. (5) and (6)]. Major products were trifluoromethanesulfonyl fluoride and trifluoromethanesulfonic acid, the presence of difluoroethylene also being detected by ^{19}F NMR analysis. These results were similar to those of CF_3OTf reported in the literature[9–11] which can be explained by a primary nucleophilic attack occurring at the sulfur atom.

$$PhLi \xrightarrow{CF_3SO_3R_f} PhSO_2CF_3 \quad (+\ CF_3SO_3Li) \qquad (5)$$



(6)

$R_f = CF_3, CF_2CH_3$

It appears that the regioselectivity of the nucleophilic attack at the triflate **3** depends on the nature of the reagents. Formal substitution of the triflyl group was observed clearly with iodide and bromide anion in a ketonic solvent.

In order to check the reactivity of the iododifluoroethane **4**, we carried out its radical chain reaction with hex-1-ene **6** in boiling benzene in the presence of AIBN, when we obtained 2,2-difluoro-4-iodooctane **7** in 82% yield. The

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efficiency of this addition is in agreement with the known reactivity order $RCH_2CH_2\cdot < RCH_2CF_2\cdot < F_3C\cdot$.[12]

$$CH_3CF_2I + H_2C{=}CH{-}[CH_2]_3CH_3 \xrightarrow[\text{Benzene, heat}]{\text{AIBN}} CH_3CF_2CH_2CHI[CH_2]_3CH_3 \quad (7)$$

In conclusion, the iodide **4** can be prepared easily in a two-step procedure. This iodide is a useful synthon for the preparation of more elaborated fluorinated compounds.[4]

Experimental

^1H NMR spectra (δ_H) were recorded on a Bruker AM 300 spectrometer and are expressed in ppm downfield from tetramethylsilane (solvent: $CDCl_3$). ^{19}F NMR spectra (δ_F) were recorded in ppm downfield from chlorotrifluoromethane. We thank 3M for providing us with triflic acid and Atochem for 1,1-difluoroethylene.

1,1-*Difluoroethyl Trifluoromethanesulfonate* **3**.—A thick-walled glass bottle filled with trifluoromethanesulfonic acid **2** (24 g, 0.16 mol) was placed in a Parr apparatus. A 5 mbar vacuum was applied. The bottle was shaken for 3 h under 3.9 atm pressure of 1,1-difluoroethylene **1**. Then, the bottle was opened. ^{19}F and ^1H NMR analysis of the product **3** so obtained (32.2 g; 0.15 mol; 94%) showed that it was pure. Distillation gave a boiling point of 70–72 °C. δ_H 1.9 (t, J_{HF} 15 Hz); δ_F −75 (3 F, t, J_{FF} 5.9 Hz); −58 (2F, q*q).

1,1-*Difluoro*-1-*iodoethane* **4**.—Sodium iodide (15 g, 0.1 mol) and a catalytic amount of tetrabutylammonium bromide were stirred in pentan-3-one (25 mL) for 20 min. Then, 1,1-difluoroethyl trifluoromethanesulfonate (4.5 g, 0.021 mol) was added dropwise. The stirring was maintained for 12 h. After filtration, the organic phase was evaporated under vacuum and condensed in a dry ice–acetone-cooled trap. Then, distillation in a Fisher apparatus gave 1,1-difluoro-1-iodoethane **4** (2.48 g, 0.013 mol) in 62% yield. bp 45–48 °C (lit.,[4] 45 °C), δ_H 2.55 (t, J_{FH} 19.1 Hz), δ_F −26.5 (q, J_{FH} 19.1 Hz).

1-*Bromo*-1,1-*difluoroethane* **5**.—The same experiment was repeated with sodium bromide. The conversion rate was about 75%. The bp of 1-bromo-1,1-difluoroethane is 14 °C[3] but the major part of the product evaporated during the distillation. δ_H 2.22 (t); δ_F −38 (q, J_{FH} 15.9 Hz).

2,2-*Difluoro*-4-*iodooctane* **7**.—Hex-1-ene **6** (1.35 g, 0.016 mol), 1,1-difluoro-1-iodoethane **4** (1.5 g, 0.008 mol) and a catalytic amount of azobisisobutyronitrile (0.1 g) in benzene (5 mL) were stirred under reflux during 17 h. The solvent was evaporated and the compound was eluted with pentane on a silica gel thin-layer plate with pentane as eluent to give 2,2-difluoro-4-iodooctane **7** (1.8 g, 0.0065 mol) in 82% yield. δ_F −91.5 (1 F, d*quint*d, J_{FF} 241.3 Hz, F_A), −87 (1 F, d*d*q*d, F_B). δ_H 1.47 (CH_3CF_2, t, J 18.5 Hz), 2.71 ($CF_2CH_AH_B$, d*d*d*d, J_{HAFB} 20.2, J_{HAHB} 15.4, $J_{FAHA} = 13.4$, J_{HAH4} 6.0 Hz), 2.54 ($CF_2CH_AH_B$, d*d*d*d, J_{FAHB} 18.5, J_{HAHB} 15.4 Hz, J_{HBFB} 10.5 Hz, J_{HAH4} 6.0 Hz); 4.11 ($CH_{(4)}I$, q*d, J = 7 Hz, J_{HAH4} 6.0 Hz), 1.4–1 (6 H, m), 0.75 (3 H, m) (Found: C, 35.14; H, 5.71. $C_8H_{15}F_2I$ requires C, 34.8; H, 5.48%).

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