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Novel method for the synthesis of (trifluoromethyl)oxirane

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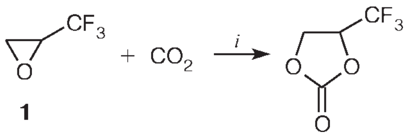
The reaction of 3,3,3-trifluoropropene with *N*-bromosuccinimide in acetic acid at 65—70 °C affords 3-acetoxy-2-bromo-1,1,1-trifluoropropane. When treated with an alkali, the latter is readily converted into (trifluoromethyl)oxirane.

Key words: (trifluoromethyl)oxirane, trifluoropropylene carbonate, *N*-bromosuccinimide, carbon dioxide.

(Trifluoromethyl)oxirane **1** is a key compound for the synthesis of trifluoropropylene carbonate, which is currently believed to be one of the most promising solvents for the production of lithium cells.[1—4]



i. Catalyst.

Oxirane **1** is generally prepared either from hexafluoropropylene oxide by laborious synthesis in many steps,[5] or by the reduction of difficultly accessible bromotrifluoroacetone followed by cyclization,[6,7] or by the reaction of 3,3,3-trifluoropropene with bromine in acetic acid in the presence of mercury salts with subsequent alkaline treatment of bromoacetates.[8,9] The latter method involves the dangerous and toxic starting reagents and hence is inconvenient. The reaction of trifluoroacetaldehyde with diazomethane, which affords oxirane **1** in low yield, has also been described.[10]

We found that 3,3,3-trifluoropropene easily reacts with *N*-bromosuccinimide in acetic acid at 65—70 °C in the presence of a catalytic amount of sulfuric acid to give 3-acetoxy-2-bromo-1,1,1-trifluoropropane **2** in good yield, and the latter is converted into oxirane **1**.

$$CF_3CH{=}CH_2 + AcOH + NBS \xrightarrow{H^+}$$

$$\longrightarrow \underset{\mathbf{2}}{CF_3CHBrCH_2OAc} \xrightarrow{OH^-/H_2O} \mathbf{1}$$

The reaction of trifluoropropene with *N*-bromosuccinimide does not occur without heating. Bromoacetate **2** isolated by distillation is admixed with isomeric 2-acetoxy-3-bromo-1,1,1-trifluoropropane $CF_3CH(OAc)CH_2Br$ **2´** (5—6%), which also undergoes cyclization into oxirane **1** under the action with hot alkali. Isomers **2** and **2´** are spectrally discernible; bands were assigned using general rules for electrophilic addition, on the assumption that an electrophilic species is the Br^+ ion or its equivalent (*e.g.*, protonated *N*-bromosuccinimide).

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker DPX-200 spectrometer (200 and 188 MHz, respectively) with TMS and CF_3COOH as external standards.

3-Acetoxy-2-bromo-1,1,1-trifluoropropane (2) and 2-acetoxy-3-bromo-1,1,1-trifluoropropane (2´). *N*-Bromosuccinimide (72 g, 0.4 mol), glacial acetic acid (300 mL), and conc. H_2SO_4 (2 mL) were placed in a 500-mL flask equipped with an inlet for a gas, a thermometer, and a reflux condenser. While stirring, the reaction mixture was heated to 65—70 °C (*N*-bromosuccinimide dissolved completely at this temperature), and CF_3—$CH{=}CH_2$ was passed at such a rate that it was absorbed virtually completely. After 10—12 h, the reaction mixture was cooled (which results in the formation of a white precipitate of succinimide) and poured into 2 L of water to dissolve this precipitate. An oily yellow liquid was separated; NaCl was added to the aqueous layer, and the product was extracted with ether. The combined organic layer was washed with aqueous soda and water and dried with $MgSO_4$. Distillation gave a mixture of bromoacetates **2** and **2´** (94 : 6) (59.7 g, 62.8%), b.p. 45—46 °C/10 Torr (*cf.* Ref. 8: b.p. 149 °C).

Compound 2. ^{19}F NMR ($CDCl_3$), δ: 7.05 (d, CF_3, ^3J = 6.1 Hz). ^1H NMR ($CDCl_3$), δ: 2.0 (s, 3 H, CH_3); 4.3—4.5 (m, 3 H, CH_2—CH). **Compound 2´.** ^{19}F NMR ($CDCl_3$), δ: 7.5 (d, CF_3, ^3J = 6.5 Hz).

(Trifluoromethyl)oxirane (1). Sodium hydroxide (170 g) and water (130 mL) were placed in a three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a Liebig condenser and heated in an oil bath to 120—130 °C. A mixture of bromoacetates **2** and **2´** (81.3 g, 0.346 mol) was added so rapidly

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that a mixture of oxirane **1** and water was promptly distilled off (vapor temperature 35—50 °C). The organic layer was separated, dried with K_2CO_3, and distilled over a small amount of potassium carbonate. The yield of oxirane **1** was 17.3 g (41%), b.p. 39—41 °C (*cf.* Ref. 9: b.p. 40 °C). ^{19}F NMR ($CDCl_3$), δ: 2.0 (d, J = 5 Hz). ^{1}H NMR ($CDCl_3$), δ: 3.0 (m, 2 H, CH_2); 3.4 (m, 1 H, CH).

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