Letters to the Editor

Fluorination of haloolefins with the XeF_2 -CF₃SO₃H system

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At present, fluorine-containing haloolefins are most commonly synthesized by fluorination of halogenated alkanes by the Swarts method with subsequent dehydrohalogenation or dehalogenation. However, the introduction of a fluorine atom in the α -position is difficult in the case of haloolefins containing two hydrogen atoms or a hydrogen atom and an alkyl group at the α -position.¹

The present communication describes a one-step method for synthesizing α -fluorohaloolefins using xenon difluoride. Mixing an equimolar amount of XeF₂ and trifluoromethanesulfonic acid in anhydrous CH₂Cl₂ followed by the introduction of a haloolefin of the general formula RCH=CCl₂ results in a product which formally results from substitution of the vinyl hydrogen atom by fluorine. Probably, this result can be described by the following reaction scheme:

$$CF_{3}SO_{3}H + XeF_{2} \xrightarrow{CH_{2}Cl_{2}} FXeOSO_{2}CF_{3} \xrightarrow{CHR = CCl_{2}} 1$$

$$\rightarrow [CHFR-CCl_{2}OSO_{2}CF_{3}] \xrightarrow{-HSO_{3}CF_{3}} CRF=CCl_{2}$$

$$2 \xrightarrow{3: R = H} 4: R = Me$$

$$5: R = Et$$

The addition of the fluorinating reagent (1) to a haloolefin proceeds according to Markovnikov's rule to give product 2. Elimination of trifluoromethanesulfonic acid from 2 to give fluorolefins 3-5 occurs spontaneously (which is probably due to the presence of the easily leaving triflate group in combination with other electronegative substituents at one carbon atom).

XeF₂ (1.69 g, 10 mmol) and CF₃SO₃H (1.49 g, 10 mmol) in anhydrous methylene dichloride were mixed at -50 to -30 °C. The mixture was stirred for 1 h at -30 °C and then for 0.5 h at 0 °C. The reaction mixture was cooled to -10 °C, and excess CH₂=CCl₂ (1.92 g, 20 mmol) was added. After the temperature reached ~20 °C, the mixture was treated with 3 % NaHCO₃ and washed with water. The organic layer was separated and dried with MgSO₄. The residue was distilled to give 0.74 g (65 %) of 2,2-dichloro-1-fluoroethylene (3), b.p. 39 °C. ¹H NMR (CDCl₃), δ : 6.8 d (J_{H-F} = 77 Hz, 1 H, CHF). ¹⁹F NMR (CDCl₃), δ : -45.1 d. MS (70 eV), *m/z*: 114, 118 [M]⁺.

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References

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