

Fluorinated Dioxolane Olefins and Epoxides^{1,2}

Ming-H. Hung,^{†,‡} Shlomo Rozen,^{†,‡}
Andrew E. Feiring,[‡] and Paul R. Resnick[†]

Du Pont Polymers and Du Pont Central Research & Development, Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

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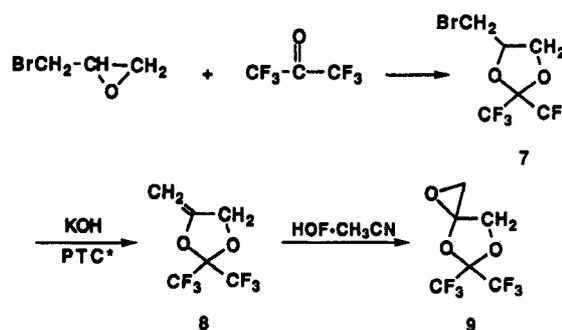
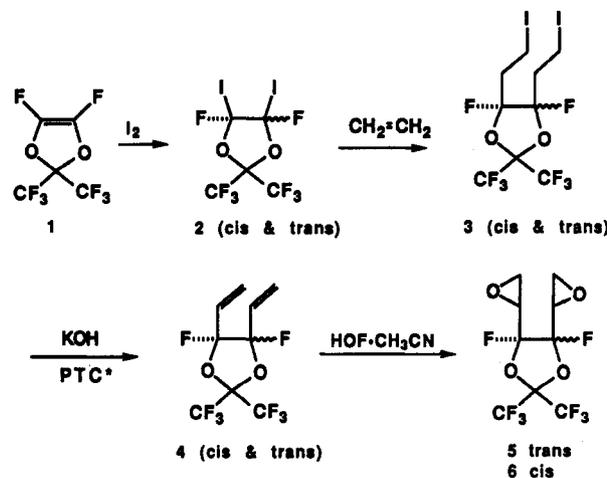
Perfluoro-2,2-dimethyl-1,3-dioxole³ (1) is a monomer for a new fluoropolymer, Teflon-AF,^{4,5} which exhibits outstanding thermal and chemical stability among other useful properties. Due to the unique features of this polymer with a fluorinated dioxolane group in its backbone, we are preparing derivatives of 1 with other functional groups as precursors to new polymers. Initially, epoxides have been targeted, since they are excellent substrates for polymerization, affording lubricants, thermostat resins, adhesive and coatings, and fluorinated epoxy resins which often have superior properties compared to their hydrocarbon counterparts.⁶ However, fluorine substituents also tend to deactivate double bonds toward electrophilic attack, and especially toward direct epoxidation, so the synthesis of fluorinated epoxides can be troublesome, requiring multistep reactions.⁷

Recently, we reported that the HOF·CH₃CN complex,⁸ generated in situ from fluorine and water, is a powerful oxidizing agent which reacts efficiently even with deactivated olefins.⁹ In addition, the complex does not involve peracids and does not create heavy-metal disposal problems as with many other oxidants do. We now report synthesis of novel fluorodioxolane mono- and bis-epoxides using the HOF·CH₃CN complex for the epoxidation steps.

The highly deactivated bis-olefin 4¹⁰ was prepared from 1. Direct iodination of 1 gave the diiodide 2 as a 5/1 trans/cis mixture. This mixture reacted with ethylene under high pressure and temperature to form 2,2-bis(trifluoromethyl)-4,5-difluoro-4,5-bis(2-iodoethyl)-1,3-dioxolane (3) in good yield.¹¹ (+)-Limonene was also added in this reaction to inhibit ethylene polymerization. Treat-

ment of 3 with base under phase transfer conditions gave 4 as a cis/trans mixture which could be separated by distillation. TLF-2370C,¹² an efficient phase-transfer agent for reactions involving fluorinated hydrocarbons, was used in this reaction.

Monoolefin 8 was prepared from epibromohydrin and hexafluoroacetone. The intermediate bromo dioxolane 7, formed in 95% yield, was treated with a base under phase-transfer conditions producing the exocyclic olefin 8.



For epoxidation reactions, the HOF·CH₃CN complex was prepared by passing nitrogen-diluted fluorine through an aqueous acetonitrile solution. The oxidizing agent was then allowed to react with trans and cis 4 forming the respective bis-epoxides 5 and 6 in 77% yield in 15 min at 0 °C. The epoxidation reaction does not affect the stereochemistry; only the trans epoxide 5 was formed from the trans olefin and only cis epoxide 6 was obtained from the cis-olefin. The monoolefin 8, which is not as deactivated as 4, could be epoxidized in 1-2 min at -10 °C forming the oxirane 9 in 95% yield, demonstrating the exceptional activity of the HOF·CH₃CN reagent.

Applications for these novel fluoro epoxides are being investigated.

Experimental Section

¹H NMR and ¹³C NMR spectra were recorded at 300 and 75.4 MHz, respectively, with CDCl₃ as solvent and Me₄Si as internal standard. The ¹³C NMR spectra are proton broad band decoupled

(12) TLF-2370C: {[CH₃CH(OH)CH₂]₂N(Bz)(C₁₂H₂₅)}Cl, a commercial product available from Du Pont Chemicals.

[†] Du Pont Polymers.

[‡] Du Pont Central Research & Development.

[§] Permanent address: School of Chemistry, Tel-Aviv University, Tel-Aviv, 69978, Israel.

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(2) The Chemistry of Fluorinated Dioxoles and Dioxolanes, Part 3. For earlier papers in this series, see: (a) Hung, M.-H.; Resnick, P. R. *J. Am. Chem. Soc.* 1990, 112, 9672. (b) Hung, M.-H. *J. Fluorine Chem.* 1991, 52, 159.

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(4) Trademark of E. I. du Pont Nemours and Company.

(5) (a) Resnick, P. R. *Polym. Prepr., ACS. Polym. Div. Polym. Chem.* 1990, 31, 312. (b) Hung, M.-H.; Resnick, P. R.; Squire, E. N. *Pacific Polymer Preprints* 1990, 1, 331.

(6) (a) Griffith, J. R. *Chemtech* 1982, 12, 290. (b) Griffith, J. R. U.S. Pat. 4,633,023, 1986.

(7) See for example: (a) *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley & Sons: New York, 1980; Vol. 9, p 166. (b) Tarrant, P., Ed. *Fluorine Chemistry Reviews*; Marcel Dekker, Inc.: New York, 1971; p 78.

(8) Rozen, S.; Kol, M. *J. Org. Chem.* 1990, 55, 5155.

(9) Hung, M.-H.; Smart, B. E.; Feiring, A. E.; Rozen, S. *J. Org. Chem.* 1991, 56, 3187. Deactivated fluorinated olefins gave very poor epoxidation results when traditional reagents, such as NaOCl or *m*-chloroperbenzoic acid, were used.

(10) Anton, D. R.; Farnham, W. B.; Hung, M.-H.; McKinney, R. J.; Resnick, P. R. Eur. PCT Pat. WO-91-09025, 1991.

(11) (a) Baum, K.; Bedford, C. D.; Hunadi, R. J. *J. Org. Chem.* 1982, 47, 2251. (b) Knunyants, I. L.; Khrlakyan, S. P.; Zeifman, Yu. V.; Shokina, V. V.; *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1964, 2, 384.

and only the C–F couplings were observed. The ^{19}F NMR spectra were recorded at 188.35 MHz and are reported in ppm upfield from CFCl_3 , which also served as internal standard.

General Procedure for Working with Fluorine. Fluorine is a strong oxidizer and a very corrosive material. An appropriate vacuum line made from copper or monel in a well-ventilated area should be constructed for work with this corrosive gas. The reactions themselves can be carried out in glass vessels. If elementary precautions are taken, work with fluorine is relatively simple.^{8,9}

General Procedure for Producing the HOF·CH₃CN Oxidizing System. Mixtures of 10–15% F₂ diluted with nitrogen were used in this work. The gas mixtures were prepared in a separate cylinder before the reaction was started. This gas mixture was then passed at a rate of about 300–400 mL/min through a cold (–10 °C) and mechanically stirred mixture of CH₃CN (400 mL) and H₂O (40 mL). The high gas flow rate is necessary because the lifetime of the HOF·CH₃CN complex is limited. The level of the oxidizing power was monitored by reacting aliquots with an acidic aqueous solution of KI. The liberated iodine was then titrated with thiosulfate. Concentrations of more than a mole/liter oxidizing reagent can be generated.

Representative Epoxidation Procedure. A solution of an appropriate amount of olefin (5–20 g) in CH₂Cl₂ (about 50 mL) was stirred and cooled at 0 °C and then added in one portion to the glass reaction vessel in which the oxidizing agent had been prepared. Except for reactions with the more reactive olefins, the cooling bath was removed and the reaction was stopped after 3 h by neutralization with saturated NaHCO₃ solution. Reactions can be left much longer, but most of the reagent decomposes after 3–4 h. The reaction mixture was then poured into 1500 mL of water, extracted with CFCl₃, and washed with aqueous NaHCO₃ and water until neutral. The organic layer was dried over MgSO₄, and the solvent was distilled through an efficient distillation column. The residue containing the crude product was usually distilled at either atmospheric or reduced pressure.

2,2-Bis(trifluoromethyl)-4,5-difluoro-4,5-diiodo-1,3-dioxolane (2). Perfluoro-2,2-dimethyl-1,3-dioxole (48.8 g, 0.2 mol) (1) was mixed with I₂ (70 g, 0.276 mol) in dry THF (20 mL). The reaction mixture was heated slowly to 70 °C. After a full conversion was achieved as monitored by gas chromatography, the product was distilled from the reaction mixture, washed with saturated thiosulfate, and distilled again under reduced pressure to give 69.4 g of 2, 70% yield, as a trans/cis mixture (mole ratio 5:1), bp 70 °C (45 mm). ^{19}F NMR: trans isomer –26.8 (m, 2 F), –78.6 (t, $J = 5.1$ Hz, 6 F); cis isomer –39.5 (m, 2 F), –77.8 (3 F), –79.0 (3 F).

Anal. Calcd for C₅F₈I₂O₂: C, 12.05; F, 30.53; I, 50.99. Found: C, 12.13; F, 30.64; I, 50.79.

2,2-Bis(trifluoromethyl)-4,5-difluoro-4,5-bis(2-iodoethyl)-1,3-dioxolane (3). A 400-mL stainless steel shaker tube contained (+)-limonene (2 g) was charged with compound 2 (199.2 g, 0.4 mol) and ethylene (60 g, 2.14 mol). The sealed tube was heated at 220 °C for 10 h. The tube was then cooled, and the product mixture was fractionally distilled to give 3 (115 g, 52% yield) as a pale yellow liquid, bp 105 °C (0.5 mm). ^{19}F NMR: –79.0 (m, 6 F), [–105.8 (m, trans), –108.0 (m, cis)] (2 F for both 2 signals). ^1H NMR: 3.69 (t, $J = 9.0$ Hz, 4 H), 3.10 (m, 4 H).

Anal. Calcd for C₉H₈F₈I₂O₂: C, 19.50; H, 1.46; F, 27.44; I, 45.83. Found: C, 19.19; H, 1.48; F, 27.52; I, 45.74.

2,2-Bis(trifluoromethyl)-4,5-difluoro-4,5-divinyl-1,3-dioxolane (4). Compound 3 (95 g, 0.17 mol), aqueous 10 M KOH (190 mL, 1.90 mol), and TLF-2370C¹² (24.6 g, as a 60% w/w

aqueous solution, 0.034 mol), a phase-transfer catalyst, were vigorously stirred at rt for 4 h. The lower organic layer was separated and further purified by distillation to give 25.3 g of olefins 4 (50% yield), bp 90 °C (200 mm). If desired, the cis and trans isomers could be separated by distillation with a spinning-band column. ^1H NMR: 5.90 (m, 2 H), 5.70 (m, 4 H) [trans]; 5.76 (m, 4 H), 5.58 (m, 2 H) [cis]; ^{19}F NMR: –80.2 (m, 6 F), –109.6 (m, 2 F) [trans]; –80.2 (m, 3 F), –81.0 (q, $J = 8.6$ Hz, 3 F), –109.3 (quintet, $J = 7.0$ Hz, 2 F) [cis]. Anal. Calcd for C₉H₈F₈O₂ (as isomeric mixture): C, 36.24; H, 2.03; F, 51.00. Found: C, 36.20; H, 2.00; F, 51.08.

Epoxidation of 4. Trans 4 (28.4 g, 95 mmol) was dissolved in CH₂Cl₂ (30 mL) and added to a solution containing HOF·CH₃CN (130 mmol). After 15 min the reaction was worked up as described above. After removal of the solvent the reaction mixture was distilled, bp 81 °C (5 mm), to give 24.1 g of 5 (clear oil), 77% yield. This product is a pair of diastereomer (mole ratio 1.0:0.6 determined by ^{19}F NMR). ^1H NMR: 3.42 (m, 2 H), 3.10–2.90 (m, 4 H). ^{19}F NMR: [–80.2, –80.4 (2 m, 6 F total)], [–121.9, –122.2 (2 m, 2 F total)]. MS m/e calcd for (M + H)⁺ 331.02166, found 331.02506.

Anal. Calcd for C₉H₈F₈O₄: C, 32.73; H, 1.83; F, 46.05. Found: C, 32.70; H, 1.61; F, 45.82.

Cis 4 (1 g, 3.36 mmol) was reacted as above to give 0.9 g of the bis-epoxide 6 (81% yield), also as a diastereomeric mixture (mole ratio 1.0:0.7). ^1H NMR: 3.60–3.40 (m, 2 H), 3.20–2.86 (m, 4 H). ^{19}F NMR: –80.3 (m, 3 F), –81.0 (m, 3 F), [–120.0, –121.9 (2 m, 1 F total)], –128.0 (m, 1 F). MS m/e calcd for (M)⁺ 330.0138, found 330.0124.

Anal. Calcd for C₉H₈F₈O₄: C, 32.73; H, 1.83; F, 46.05. Found: C, 32.59; H, 1.67; F, 45.72.

2,2-Bis(trifluoromethyl)-4-(bromomethyl)-1,3-dioxolane (7). Epibromohydrin (46 g, 0.326 mol), hexafluoroacetone (55.5 g, 0.334 mol), and catalytic amounts of Bu₄NBr (0.2 g) and water (~0.5 mL) were heated in a stainless steel tube at 125 °C for 5 h. Pure 7 was distilled at 56 °C (2 mm), 95% yield (clear oil). ^1H NMR: 4.88 (m, 1 H), 4.73 (t, $J = 7.5$ Hz, 1 H), 4.22 (t, $J = 7.5$ Hz, 1 H), 3.60 (m, 2 H). ^{19}F NMR: –80.5 (q, $J = 8.5$ Hz, 3 F), –81.0 (q, $J = 8.5$ Hz, 3 F).

Anal. Calcd for C₆H₈BrF₆O₂: C, 23.78; H, 1.66; Br, 26.37; F, 37.62. Found: C, 23.91; H, 1.64; Br, 26.87; F, 37.84.

2,2-Bis(trifluoromethyl)-4-methylene-1,3-dioxolane (8). Compound 7 (30.3 g), 10 M aqueous KOH (60 mL), and TLF-2370C¹² (7.13 g, as a 60% w/w aqueous solution, 0.034 mol), a phase-transfer catalyst, were vigorously stirred at rt for 4 h. The lower organic layer was separated and further purified by distillation. The yield of product 8 was 18 g (81% yield), bp 85 °C. ^1H NMR: 4.60 (m, 3 H), 4.10 (m, 1 H). ^{19}F NMR: –82.2 (s). ^{13}C NMR: 120.0 (q, $^1J_{\text{CF}} = 288$ Hz), 153.2 (C=CH₂), 101.5 (4° C), 83.9, 69.1.

Anal. Calcd for C₆H₄F₆O₂: C, 32.45; H, 1.82; F, 51.33. Found: C, 31.96; H, 1.81; F, 51.45.

Epoxidation of 8. Olefin 8 (19 g, 85 mmol) was dissolved in 40 mL of CH₂Cl₂ and added to HOF·CH₃CN (200 mmol). After 2 min the reaction was worked up as described above. After the distillation of the solvent, the reaction mixture was distilled and the main fraction was identified as the mono-epoxide 9, bp 55 °C (2 mm), yield 19 g (94%). ^1H NMR: 4.35 and 4.60 (AB, $J = 2.7$ Hz, 2 H), 3.42 and 3.04 (AB, $J = 2.7$ Hz, 2 H). ^{19}F NMR: –81.0 (q, $J = 8$ Hz, 3 F), –81.5 (q, $J = 8$ Hz, 3 F).

Anal. Calcd for C₆H₄F₆O₃: C, 30.27; H, 1.69; F, 47.88. Found: C, 30.08; H, 1.90; F, 47.55. MS m/e (M)⁺ calcd 238.0064, found 238.0098.