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FLUORODIOXOLANE-CONTAINING ALKYNES [1,2]

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SUMMARY

Novel fluorinated dioxolane-containing alkyne compounds **1** and **2** were synthesized from hexafluoroacetone and either 1,4-dibromo-2-butene or propargyl alcohol.

INTRODUCTION

Alkynes are interesting organic intermediates and also used as monomers for making semi-rigid polymers. Alkyne polymers have exhibited many useful properties as gas separation membranes, conducting polymers, thermosetting resins, etc [3]. Fluorinated alkynes are of special interest since they may provide additional chemical and thermal stability [4,5].

There are few reports on the synthesis of fluorinated alkynes other than simple trifluoromethyl-containing acetylene derivatives [4,6]. We now report the syntheses of two novel fluorinated alkynes **1** and **2** which contain the fluorodioxolane ring skeleton. This kind of structural unit is known to offer high chemical and thermal stability [7,8].

RESULTS AND DISCUSSION

Both molecules **1** and **2** are made from hexafluoroacetone (HFA). Oxidation of 1,4-dibromo-2-butene with m-chloroperbenzoic acid gave epoxide **3** in 85% yield. Molecule **3** was reacted with HFA at 180 °C for 6 hours in a sealed tube to afford **4** as a diastereomeric mixture in 76% yield. This reaction

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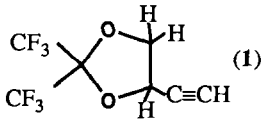
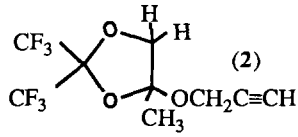
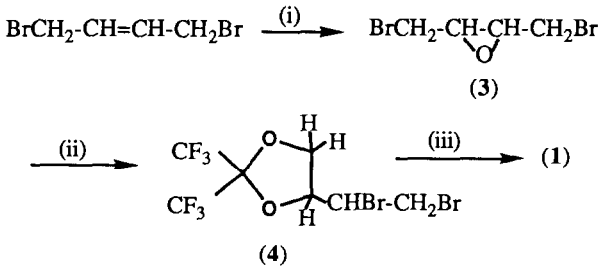


(1)



(2)

was catalyzed by trace amounts of tetrabutylammonium bromide. The bromide ion presumably first opened the epoxide ring and the resulting oxide added to the highly reactive HFA carbonyl group. Ring closure occurred with attack at the least hindered primary alkyl halide by an anionic oxygen intermediate **5** to give **4** as the sole product. The preference between the two primary centers was dictated by the more facile formation of a five-membered ring by internal S_N2 reaction. No six-membered ring or 2,2-bis(trifluoromethyl)-4,5-di(bromomethyl)-1,3-dioxolane was observed. Double hydrogen bromide elimination was accomplished with 10M KOH and 15% phase transfer catalyst $[CH_3CH(OH)CH_2]_2$-$N(CH_2C_6H_5)(C_{12}H_{25})Cl$. Compound **1** was characterized by proton NMR absorption at 2.68 ppm (C≡C-H) and the IR absorption at 3313 cm^{-1} (C≡C-H stretch) and 2142 cm^{-1} (C≡C stretch).

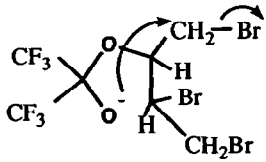


(3)

(4)

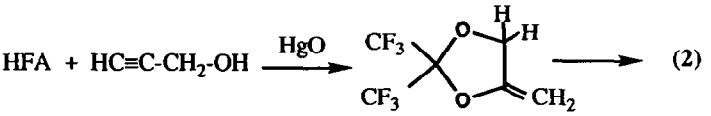
(i) MCPBA, $CHCl_3$, reflux, 85% (ii) HFA, nBu_4NBr Cat., 180 °C, 76%
(iii) 10M KOH, phase transfer catalyst, 65 °C, 35-40%

Molecule **2** was prepared by a one-pot, two-step addition across the triple bond of propargyl alcohol, catalyzed by mercuric oxide and BF_3. Propargyl alcohol had been reported to react with an equimolar amount of bis(chlorodifluoromethyl) ketone over two hours to give



(5)

2,2-bis(chlorodifluoromethyl)-4-methylene-1,3-dioxolane [7]. However, we found that with longer reaction time and in the presence of a small amount of Lewis acid ($BF_3.Et_2O$), HFA reacted with propargyl alcohol at ambient temperatures to yield the double addition product **2**. The intermediate **6**, 2,2-bis(trifluoromethyl)-4-methylene-1,3-dioxolane was observed during the reaction.



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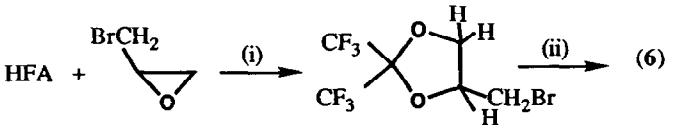

(7)

(i) HFA, nBu_4NBr Cat., 125 °C/5hrs, sealed tube, 95%
(ii) 10M KOH, phase transfer catalyst, RT, 16 hours, 80%

The structure of intermediate adduct **6** was confirmed by a separate synthesis shown above. Hexafluoroacetone was condensed with epibromohydrin under conditions similar to those above to give 2,2-bis(trifluoromethyl)-4-bromomethyl-1,3-dioxolane (**7**) in 95% yield.

Dehydrobromination of **7** generated **6** in high yield. The attempts to dehydrochlorinate the chloro analog of compound **7** failed to give pure **6**.

EXPERIMENTAL

Reaction of 1,4-dibromo-2,3-epoxybutane with HFA

1,4-Dibromo-2,3-epoxybutane (80.5 g) was charged into a stainless steel tube with tetrabutylammonium bromide (0,35 g) and water (0.35 g). The tube was sealed, cooled and evacuated and HFA (60 g) was transferred into the tube. The reaction mixture was heated with shaking at 80 °C for 1 hour, 100 °C for 1hour and 180 °C for 6 hours. The tube was cooled and the liquid product discharged was distilled to give a clear, colorless 1,3-dioxolane compound **4** as an diastereomeric liquid mixture (isomeric ratio 6.5:1); yield: 105 g (76%). Compound **4** has b.p. 60 °C/2 mm. ^{1}H NMR ($CDCl_3$): δ4.84 (m, 1H), 4.60 (m, 1H), 4.20 (m, 2H), 3.88 (m, 2H); ^{19}F NMR ($CDCl_3$): [-80.5 (q, J = 7.6 Hz, 3F), -80.8 (q, J = 7.7 Hz, 3F), major isomer], [-79.6 (q, J = 7.6 Hz, 3F), -80.8 (q, J = 7.6 Hz, 3F), minor isomer]. Anal. Calc. for $C_7H_6Br_2F_6O_2$: C: 21.24, H: 1.53, F: 40.36; Found: C: 21.26, H: 1.53, F: 40.33. Mass: [M-H]: 392.8560; Found: 392.8602; [M-CF_3] Calc. 324.8687; Found: 324.8691.

Synthesis of fluorinated alkyne **1**

Compound **4** obtained as above (39.6 g) was mixed with 10M KOH (100 ml) and $[CH_3CH(OH)CH_2]_2$-$N(CH_2C_6H_5)(C_{12}H_{25})Cl$ (60% w/w aqueous solution) (11.0 g) in a reaction flask (Complex products were formed in the absence of the phase transfer catalyst). The reaction mixture was vigorously stirred at 65 °C overnight. The bottom organic layer was separated, washed with water and distilled to give the alkyne product **1** as a clear, colorless liquid, yield: 8.5 g (36%). Compound **1** has b.p. 90 °C. ^{1}H NMR ($CDCl_3$): δ5.08 (m, 1H), 4.53 (t, J = 7.2 Hz,1H), 4.17 (t, J = 7.9 Hz, 1H), 2.68 (d, J = 1.6 Hz, 1H); ^{19}F NMR ($CDCl_3$): -80.4 (q, J = 7.7 Hz, 3F), -80.8 (q, J = 7.8 Hz, 3F). ^{13}C NMR ($CDCl_3$): 77.6, 76.0, 72.9, 69.7, 101.2 (4 °C), 120.3 (m, CF_3); Anal. Calc. for $C_7H_4F_6O_2$: C: 35.92, H: 1.72, F: 48.69; Found: C: 35.48, H: 1.47, F: 48.05. Mass: [M]: 234.0115; Found: 234.0085.

Synthesis of fluorinated alkyne **2**

In a typical experiment, HFA (99.6 g) was first condensed into a dry flask at -40 °C and propargyl alcohol (33.6 g) was added rapidly at -35 °C (ca. 15 minutes). The mixture was then warmed up to ambient temperature and mercuric oxide (yellow form, 2.0 g) was added followed by boron trifluoride etherate (1.0 ml). The reaction mixture was stirred overnight and the product was fractionally distilled to afford the desired product **2** as a clear, colorless liquid in 45-50% yield. Compound **2** has b.p. 172-173 °C. ^{1}H NMR ($CDCl_3$): δ4.36 (dd, J = 2 Hz, 9 Hz, 1H), 4.28 (m ,2H), 4.07 (d, J = 9 Hz, 1H), 2.43 (t, J = 2 Hz, 1H), 1.72 (s, 3H); ^{19}F NMR ($CDCl_3$): -80.1 (q, J = 8.6 Hz, 3F), -81.1 (q, J = 8.5 Hz, 3F). ^{13}C NMR ($CDCl_3$) (the peak assignments were based on off-resonance spectrum): 20.5 ($\underline{C}H_3$), 51.4 ($O\underline{C}H_2C{\equiv}CH$), 74.5 ($C{\equiv}\underline{C}H$), 79.0 ($O\underline{C}H_2C$), 79.5 ($\underline{C}{\equiv}CH$), 101.9 ($\underline{C}$-$(CF_3)_2$), 110.1 ($\underline{C}$-$CH_3$), 119.9 (m, J_{C-F} = 289 Hz, $\underline{C}F_3$); Anal. Calc. for $C_9H_8F_6O_3$: C: 38.86, H: 2.90, F: 40.98; Found: C: 38.02, H: 2.82, F: 40.54. Mass: [M+H]: 279.0459; Found: 279.0394; [M-CH_3]: 263.0143; Found: 263.0117. IR: 3300 cm^{-1} (C≡C-H stretch) and 2150 cm^{-1} (C≡C stretch).

Synthesis of 2,2-bis(trifluoromethyl)-4-bromomethyl-1,3-dioxolane **7**

This compound was prepared from epibromohydrin and HFA (1:1 mole ratio) in the presence of catalytic amounts of tetrabutylammonium bromide and water at 125 °C in 95% isolated yield. Compound **7** has b.p. 56 °C/2 mm. ^{1}H NMR (neat): δ4.88 (m, 1H), 4.73 (t, J = 7.5 Hz,1H), 4.22 (t, J = 7.5 Hz, 1H), 3.60 (m, 2H); ^{19}F NMR (neat): -80.5 (q, J = 8.5 Hz, 3F), -81.0 (q, J = 8.5 Hz, 3F). Anal. Calc. for $C_6H_5BrF_6O_2$: 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.

Synthesis of 2,2-bis(trifluoromethyl)-4-methylene-1,3-dioxolane **6**

Compound **6** could be isolated as a reaction intermediate from the reaction of HFA with propargyl alcohol. This molecule also could be prepared by dehydrobromination of compound **7**. Compound **7** obtained from above reaction (30.3 g) was mixed with 10M KOH (60 ml) and $[CH_3CH(OH)CH_2]_2$-$N(CH_2C_6H_5)(C_{12}H_{25})Cl$ (60% w/w aqueous solution) (7.13 g), stirred at

ambient temperature for 16 hours, the bottom organic layer was separated, washed with water and distilled to give **6** as a clear, colorless liquid; yield 18 g (81%). Compound **6** has b.p. 85 °C. ^{1}H NMR (neat): δ4.60 (m, 3H), 4.10 (m, 1H); ^{19}F NMR (neat): -82.2 (s). ^{13}C NMR ($CDCl_3$): 69.1, 83.9, 153.2 ($\underline{C}=CH_2$), 101.5 (4 °C), 120.0 (q, J_{C-F} = 288 Hz, CF_3); Anal. Calc. for $C_6H_4F_6O_2$: C: 32.45, H: 1.82, F: 51.33; Found: C: 31.96, H: 1.81, F: 51.45. IR: 1710 cm^{-1}, 1682 cm^{-1}, 840 cm^{-1}.

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