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Synthesis of (*E*)- and (*Z*)-2,3-Bis(trifluoromethyl)allyl Alcohols by γ-Ray Irradiation of Hexafluoro-2-butyne with Alcohols and Some Reactions

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Synopsis. Radiation-induced addition reaction of alcohols to hexafluoro-2-butyne provided (*E*)- and (*Z*)-2,3-bis(trifluoromethyl)allyl alcohols, which were dehydrated to afford 1,2-bis(trifluoromethyl)-1,3-butadienes. Thermal cyclization of 3-methyl-1,2-bis(trifluoromethyl)-1,3-butadiene afforded 1-methyl-2,3-bis(trifluoromethyl)cyclobutene.

Although radical addition is one of the most useful reactions to synthesize organic compounds,[1)] little is known on the reaction of polyfluoroalkynes. In our continuing series of studies on the radical addition reaction of polyfluoro compounds,[2—8)] the reaction of hexafluorobutyne with alcohols to give 1:1 adducts, 2,3-bis(trifluoromethyl)allyl alcohols, and a few reactions of the adducts have been examined in this investigation.

Irradiation of hexafluoro-2-butyne (**1**) with alcohols (**2**) in Freon 113 afforded (*E*)- and (*Z*)-2,3-bis(trifluoromethyl)allyl alcohols **3** (Table 1). The stereoisomers were identified based on the ^{19}F NMR spectroscopy (*E*: $J_{\mathrm{CF_3,CF_3}}=1$ Hz, *Z*: $J_{\mathrm{CF_3,CF_3}}=12$ Hz).[9)]

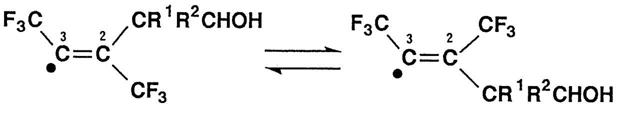
A reasonable reaction path for the formation of **3** is shown in Eqs. 1—3.

$$\mathrm{RR'CHOH}\ (\mathbf{2}) \xrightarrow{\gamma\text{-ray}} \mathrm{RR'\dot{C}OH}\ (\mathbf{4}) \tag{1}$$

$$\mathrm{RR'\dot{C}OH}\ (\mathbf{4}) + \mathrm{CF_3C{\equiv}CCF_3}\ (\mathbf{1}) \longrightarrow \mathrm{CF_3\dot{C}{=}C(CF_3)CRR'OH}\ (\mathbf{5}) \tag{2}$$

$$\mathrm{CF_3\dot{C}{=}C(CF_3)CRR'OH}\ (\mathbf{5}) + \mathrm{RR'CHOH}\ (\mathbf{2}) \longrightarrow \mathrm{CF_3CH{=}C(CF_3)CRR'OH}\ (\mathbf{3}) + \mathrm{RR'\dot{C}OH}\ (\mathbf{4}) \tag{3}$$

More stable 1-hydroxyalkyl radical **4** can give the products **3** in good yields (stability, primary<secondary<tertiary). Radical intermediate **5** is in equilibrium between *E*-**5** and *Z*-**5** (Scheme 1). Steric hindrance between the $\mathrm{CF_3}$ group at the 3-position and an alkyl group at the 2-position can control the product distribution, i.e., the bulky alkyl group at the 2-position may shift the equilibrium to *Z*-**5** to increase the yield of *Z*-**3**.

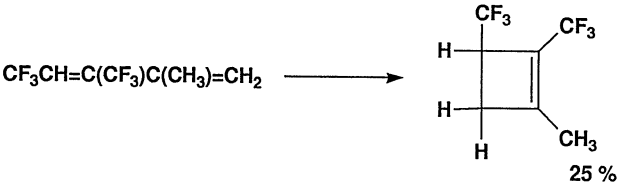


E-**5** *Z*-**5**

Scheme 1.

Dehydration of a mixture of *E*- and *Z*-**3** gave a mixture of *E*- and *Z*-**6** in 60—95 % yields (Table 2). In the case of **3b** and **3d**, the *E*/*Z* ratio of the products **6** concerning with the double bond with two $\mathrm{CF_3}$ groups was the same as that of starting materials, suggesting that *E*- and *Z*-**3** afforded the corresponding *E*- and *Z*-**6**, respectively. In the case of **3c**, the formation of four isomers was confirmed by gas chromatography.

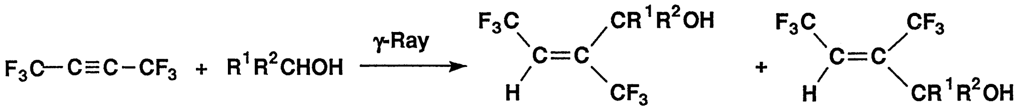
Thermal cyclization of **6d** gave 1-methyl-2,3-bis(trifluoromethyl)cyclobutene (**7d**) in 25% yield (Scheme 2).



6d **7d**

Scheme 2.

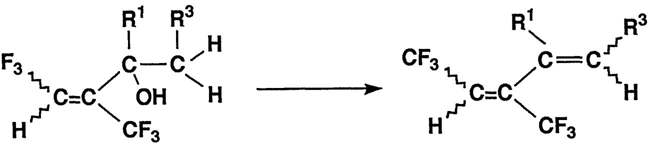
Table 1. Synthesis of 2,3-Bis(trifluoromethyl)allyl Alcohols



1 **2** *E*-**3** *Z*-**3**

Compd	$\mathrm{R^1}$	$\mathrm{R^2}$	Total irradiation Mrad	Yield of 3 %	*E*/*Z* Ratio
a	H	H	197	29	100/0
b	H	$\mathrm{CH_3}$	98	67	55/45
c	H	$\mathrm{C_2H_5}$	98	26	47/53
d	$\mathrm{CH_3}$	$\mathrm{CH_3}$	98	88	9/91

Table 2. Dehydration of 2,3-Bis(trifluoromethyl)allyl Alcohols



3 6

Compd	R¹	R³	Reaction time	Yield of **6**
			min	%
b	H	H	90	79
c	H	CH_3	50	60
d	CH_3	H	90	95

The structure of **7d** was confirmed by its ^1H NMR spectrum, i.e., δ values of methylene (5.01—5.23 ppm) and methine (5.95—6.14 ppm) protons of **6d** shifted to 2.57 and 3.90 ppm in **7d**, respectively. The same reaction of **6b** gave an amorphous polymer.

Experimental

Instruments. ^1H NMR spectra were measured with a Hitachi R-22 instrument (90 MHz) in carbon tetrachloride and chemical shifts were given as δ ppm relative to tetramethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were obtained with a Hitachi R-20B (56.45 MHz) in carbon tetrachloride and chemical shifts were given as δ ppm relative to trifluoroacetic acid as an external standard. The IR spectra were recorded on a Hitachi EPI-2 grating spectrometer.

General procedure for γ-Ray Irradiation of Hexafluoro-2-butyne with Alcohols. Hexafluoro-2-butyne (**1**, 16.28 g, 0.10 mol), ethanol (**2b**, 5.57 g, 0.12 mol), and Freon 113 (20.15 g, 0.11 mol) were placed in a glass ampoule (100 ml). The ampoule was degassed by a freeze-thaw cycle and was sealed under reduced pressure. The γ-ray irradiation was carried out at 6.2×10^4R h^{-1} by ^{60}Co for 158 h at ambient temperature (total irradiation, 98.2 Mrad). After the reaction, were evaporated the starting material, ethanol, and Freon 113. The residual liquid was distilled to give a mixture (14 g) of (*E*)- and (*Z*)-3,4-bis(trifluoromethyl)-3-buten-2-ol (*E*-**3b** and *Z*-**3b**), which were separated using a preparative gas chromatograph. The physical and spectral data are shown below.

(*E*)-2,3-Bis(trifluoromethyl)-2-propen-1-ol (*E*-3a): Bp 110 °C; d_4^{20} 1.501; n_D^{20} 1.3368; IR (neat) 1690 (C=C) cm^{-1}; ^1H NMR δ=3.58 (br s, 1H, OH), 4.42 (br s, 2H, CH_2), and 6.35 (qq, *J*=7.8 and 1.8 Hz, 1H, C=CH); ^{19}F NMR δ=11.1 (dq, *J*=2 and 1 Hz, 2-CF_3) and 20.8 (dq, *J*=8 and 1 Hz, 3-CF_3); Found: C, 31.06; H, 2.06 %. Calcd for $C_5H_4F_6O$: C, 30.95; H, 2.08 %.

(*E*)-3,4-Bis(trifluoromethyl)-3-buten-2-ol (*E*-3b): Bp 115 °C; d_4^{20} 1.408; n_D^{20} 1.3484; IR (neat) 1682 (C=C) cm^{-1}; ^1H NMR δ=1.49 (d, *J*=6.0 Hz, 3H, CH_3), 3.79 (br s, 1H, OH), 5.02 (q, *J*=6.0 Hz, 1H, 1-CH), and 6.22 (qq, *J*=8.4 and 1.2 Hz, 1H, 3-CH); ^{19}F NMR δ=15.6 (dq, *J*=1 and 1 Hz, 2-CF_3) and 21.6 (dq, *J*=8 and 1 Hz, 3-CF_3); Found: C, 34.57; H, 3.04 %. Calcd for $C_6H_6F_6O$: C, 34.63; H, 2.91%.

(*Z*)-3,4-Bis(trifluoromethyl)-3-buten-2-ol (*Z*-3b): Bp 128 °C; d_4^{20} 1.427; n_D^{20} 1.3500; IR (neat) 1691 (C=C) cm^{-1}; ^1H NMR δ=1.45 (d, *J*=6.0 Hz, 3H, CH_3), 3.23 (br s, 1H, OH), 4.58 (q, *J*=6.0 Hz, 1H, 1-CH), and 6.37 (q, *J*=8.4 Hz, 1H, 3-CH); ^{19}F NMR δ=18.0 (q, *J*=12 Hz, 2-CF_3) and 21.6 (dq, *J*=8 and 12 Hz, 3-CF_3); Found: C, 34.63; H, 2.66%. Calcd for $C_6H_6F_6O$: C, 34.63; H, 2.91%.

(*E*)-1,2-Bis(trifluoromethyl)-1-penten-3-ol (*E*-3c): Bp 126 °C; d_4^{20} 1.343; n_D^{20} 1.3579; IR (neat) 1678 (C=C) cm^{-1}; ^1H NMR δ=1.02 (t, *J*=6.6 Hz, 3H, CH_3), 1.67 (dq, *J*=6.6 and 6.0 Hz, 2H, CH_2), 3.63 (br s, 1H, OH), 4.74 (d, *J*=6.0 Hz, 1H, 1-CH), and 6.37 (q, *J*=7.8 Hz, 1H, 3-CH); ^{19}F NMR δ=16.8 (q, *J*=1 Hz, 2-CF_3) and 22.8 (dq, *J*=8 and 1 Hz, 3-CF_3); Found: C, 37.56; H, 3.80%. Calcd for $C_7H_8F_6O$: C, 37.70; H, 3.62%.

(*Z*)-1,2-Bis(trifluoromethyl)-1-penten-3-ol (*Z*-3c): Bp 139 °C; d_4^{20} 1.360; n_D^{20} 1.3589; IR (neat) 1687 (C=C) cm^{-1}; ^1H NMR δ=1.00 (t, *J*=6.6 Hz, 3H, CH_3), 1.62 (br, 2H, CH_2), 2.83 (br s, 1H, OH), 4.37 (br, 1H, 1-CH), and 6.34 (q, *J*=9.0 Hz, 1H, 3-CH); ^{19}F NMR δ=17.6 (q, *J*=12 Hz. 2-CF_3) and 20.4 (dq, *J*=9 and 12 Hz, 3-CF_3); Found: C, 37.85; H, 3.67%. Calcd for $C_7H_8F_6O$: C, 37.70; H, 3.62%.

(*E*)-3,4-Bis(trifluoromethyl)-2-methyl-3-buten-2-ol (*E*-3d): Bp 119 °C; d_4^{20} 1.360; n_D^{20} 1.3604; IR (neat) 1673 (C=C) cm^{-1}; ^1H NMR δ=1.58 (br s, 6H, CH_3), 2.86 (br s, 1H, OH), and 6.27 (qq, *J*=9.6 and 1.8 Hz, 1H, CH); ^{19}F NMR δ=14.8 (dq, *J*=2 and 2 Hz, 2-CF_3) and 24.8 (dq, *J*=10 and 2 Hz, 3-CF_3); Found: C, 37.73; H, 3.58%. Calcd for $C_7H_8F_6O$: C, 37.70; H, 3.62%.

(*Z*)-3,4-Bis(trifluoromethyl)-2-methyl-3-buten-2-ol (*Z*-3d): Bp 134 °C; d_4^{20} 1.356; n_D^{20} 1.3596; IR (neat) 1679 (C=C) cm^{-1}; ^1H NMR δ=1.52 (br s, 6H, CH_3), 2.61 (br s, 1H, OH), and 6.56 (q, *J*=8.4 Hz, 1H, CH); Found: C, 37.63; H, 3.62%. Calcd for $C_7H_8F_6O$: C, 37.70; H, 3.62%.

Dehydration of 2,3-Bis(trifluoromethyl)allyl Alcohols (3). In a flask (100 ml) equipped with a distillation apparatus, were placed a mixture of (*E*)- and (*Z*)-3,4-bis(trifluoromethyl)-3-buten-2-ol (**3b**, 12.3 g, 0.06 mol) and phosphorus pentaoxide (24 g, 0.17 mol). The mixture was heated at 100 °C. As the reaction proceeded, was distilled out a mixture of (*E*)- and (*Z*)-1,2-bis(trifluoromethyl)-1,3-butadiene (**6b**, 8.9 g), which were separated using a preparative gas chromatograph. The physical and spectral data are shown below.

(*E*)-1,2-Bis(trifluoromethyl)-1,3-butadiene (*E*-6b): Bp 53 °C; d_4^{20} 1.302; n_D^{20} 1.3321; IR (neat) 1613 and 1668 (C=C) cm^{-1}; ^1H NMR δ=5.4—6.7 (m, 3H, CH=CH_2) and 6.15 (q, *J*=9.0 Hz, 1H, CF_3CH); ^{19}F NMR δ=12.6 (d, *J*=1 Hz, 2-CF_3) and 19.4 (dq, *J*=9 and 1 Hz, 1-CF_3); Found: C, 37.86; H, 2.07%. Calcd for $C_6H_4F_6$: C, 37.91; H, 2.12%.

(*Z*)-Bis(trifluoromethyl)-1,3-butadiene (*Z*-6b): d_4^{20}1.350; n_D^{20} 1.3410; IR (neat) 1691 (C=C) cm^{-1}; ^1H NMR δ=5.3—6.7 (m, 3H, CH=CH_2) and 6.00 (q, *J*=7.8 Hz, 1H, CF_3CH); ^{19}F NMR δ=15.2 (q, *J*=11 Hz, 2-CF_3) and 19.7 (dq, *J*=8 and 11 Hz, 1-CF_3); Found: C, 37.49; H, 2.16%. Calcd for $C_6H_4F_6$: C, 37.91; H, 2.12%.

(*E*)-1,2-Bis(trifluoromethyl)-3-methyl-1,3-butadiene (*E*-6d): Bp 67.0 °C; d_4^{20} 1.221; n_D^{20} 1.3277; IR (neat) 1641 and 1681 (C=C) cm^{-1}; ^1H NMR δ=1.94 (br s, 3H, CH_3), 5.01 (br s, 1H, CH_2), 5.23 (q, *J*=1.2 Hz, 1H, CH_2), and 6.14 (qq, *J*=7.2 and 1.8 Hz, 1H, CH); ^{19}F NMR δ=9.7 (br s, 2-CF_3) and 18.3 (br d, 1-CF_3); Found: C, 40.67; H, 2.87%. Calcd for $C_7H_6F_6$: C, 41.19; H, 2.96%.

(*Z*)-1,2-Bis(trifluoromethyl)-3-methyl-1,3-butadiene (*Z*-6d): Bp 89 °C; d_4^{20}1.280; n_D^{20} 1.3441; IR (neat) 1648 and 1669 (C=C) cm^{-1}; ^1H NMR δ=1.96 (q, *J*=8.2 Hz, 3H, CH_3), 5.21 (br s, 2H, CH_2), and 5.95 (q, *J*=8.4 Hz, 1H, CH); ^{19}F NMR δ=17.0 (q, *J*=13 Hz, 2-CF_3) and 19.8 (dq, *J*=8 and 13 Hz, 1-CF_3); Found: C, 40.90; H, 2.92%, Calcd for $C_7H_6F_6$: C, 41.19; H, 2.96%.

Cyclization of 1,2-Bis(trifluoromethyl)-1,3-butadiene (6d). In a stainless steel autoclave (100 ml) was placed a mixture of (*E*)- and (*Z*)-1,2-bis(trifluoromethyl)-3-methyl-1,3-butadiene (**6d**, 5.9 g, 28.9 mmol) and *dl*-limonene (1.0 g, a polymerization inhibitor). After heating the reaction mixture at 200 °C for 24 h, the product was distilled and purified using a preparative gas chromatograph to afford 1-methyl-2,3-bis(trifluoromethyl)cyclobutene (**7d**, 1.5 g) in 25% yield.

1-Methyl-2,3-bis(trifluoromethyl)cyclobutene (7d): Mp 107 °C; d_4^{20} 1.305; n_D^{20} 1.3362; IR (neat) 1694 (C=C) cm^{-1}; ^{1}H NMR δ=1.90 (br s, 3H, CH_3), 2.57 (br s, 2H, CH_2), and 3.90 (br s, 1H, CH); ^{19}F NMR δ=5.7 (dq, J=8 and 2 Hz, CCF_3) and 13.8 (br, $CHCF_3$); Found: C, 40.90; H, 2.88%, Calcd for $C_7H_6F_6$: C, 41.19; H, 2.96%.

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