1 N $NaHCO_3$ (15 mL) under a hydrogen atmosphere for 10 h at room temperature. The catalyst was filtered off through Celite, and the filtrate was concentrated. To a cooled mixture of the residue in water (20 mL) was added dropwise 1 N NaOH (20 mL) at 0–5 °C, and the mixture was stirred for 3 h at room temperature. The mixture was carefully neutralized by the addition of cold 1 N AcOH to pH 7.5, and the insoluble material was filtered off with Celite. The filtrate was diluted to 250 mL, applied to a column of Dowex 1-X8 [HCO_2^-] (2 × 15 cm), and eluted with stepwise gradient of NH_4HCO_3, water (200 mL), 0.1 M NH_4HCO_3 (200 mL), 0.2 M NH_4HCO_3 (200 mL), and 0.3 M NH_4HCO_3 (200 mL). A trace amount of fucose was eluted out with water, and the desired **2** was eluted out between 0.2–0.3 M NH_4HCO_3. After removal of salt (NH_4HCO_3) by addition of Dowex 50W-X8 [H^+] into a solution of the residue, the resin was filtered off, and the filtrate was passed through a column of Dowex 50W-X8 [Na^+] (1 × 15 cm) with water. The appropriate fractions were pooled and lyophilized to give **2** (700 mg, 83%) concomitant with a small amount of NH_4HCO_3. The ^1H and ^{13}C NMR spectra were in good agreement with those reported.[6]

Preparation of 2 from 6 via Reaction of Tetrabutylammonium Dihydrogen Phosphate. A solution of tetrabutylammonium dihydrogen phosphate (1.29 g, 3.79 mmol) and 2,6-lutidine (814 mg, 7.6 mmol; 885 μL) in CH_2Cl_2 (5 mL) was added in one portion to a cooled solution of **6** (freshly prepared from **5** (2.0 g, 3.4 mmol) with HBr–AcOH (10 mL) in CH_2Cl_2 (30 mL) and Ac_2O (1 mL)) in CH_2Cl_2 (30 mL) at 0–5 °C, and the reaction mixture was stirred for 5 min at room temperature then cooled with an ice bath to 0–5 °C. To the cooled mixture was added water (20 mL) and 1 M NaOH (20 mL), and the reaction mixture was stirred for 5 h at room temperature. The mixture was neutralized with cold 1 M AcOH to pH 7.5. The organic phase was separated with a separatory funnel, and the aqueous layer contained fucose 1-phosphate. The products were purified as described for the preparation of **2** from **7** to give **2** in ~40% yield ($\alpha:\beta$ = 1:1 judged by ^1H NMR spectrum).

2,3,4-Tri-*O*-acetyl-L-fucose (9). A mixture of L-fucose (**4**) (3.0 g, 18.2 mmol) and anhydrous NaOAc (50 mg, 0.61 mmol) in Ac_2O (20 mL) was stirred for 2 h at room temperature and then heated for 2 h at 100 °C. After being cooled, the mixture was poured onto ice–water, stirred for 2 h, and extracted with $CHCl_3$. The extracts were successively washed with water, aqueous $NaHCO_3$, and water, dried over anhydrous $MgSO_4$, and concentrated. The residual syrup was chromatographed on silica gel, with toluene–EtOAc (10:1), to give 1,2,3,4-tetra-*O*-acetyl-L-fucose (**8**) (5.92 g, 98%) as a mixture of α and β (1:7 judged by ^1H NMR spectrum) anomers, H-1β 5.68 (8.29 Hz), H-1α 6.36 (2.19 Hz).

Chemical Method. A solution of **8** (3.0 g, 9.0 mmol) and $BnNH_2$[14] (1.45 g, 13.5 mmol; 1.47 mL) in THF (35 mL) was stirred for 1 day at room temperature. The mixture was diluted with $CHCl_3$ and successively washed with ice-cold dilute HCl, aqueous $NaHCO_3$, and water, dried over anhydrous $MgSO_4$, and concentrated. The residual syrup was chromatographed on silica gel, with toluene–EtOAc (1:1), to give **9** (2.40 g, 92%). Its ^1H NMR spectral data was in good agreement with that reported.[16]

Enzymatic Method.[16] A suspension of **8** (2.5 g, 7.5 mmol) and lipase (5.6 g) in 13% (v/v) DMF/phosphate buffer (50 mM, pH 7) was stirred for 5 days at room temperature, at which time the pH was adjusted by the addition of 1 N NaOH. The mixture was filtered, and the filtrate was extracted with EtOAc. The extracts were washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residual syrup was chromatographed on silica gel, with toluene–EtOAc (1:1), to give **9** (1.1 g, 48%) as a mixture of α and β (1:1 judged by ^1H NMR) anomers. The yield could be higher as the reaction was incomplete and the byproduct obtained was mainly the unreacted starting material.

Dibenzylphosphoryl 2,3,4-Tri-*O*-acetyl-L-fucoside (11). Dibenzyl *N,N*-diethylphosphoamidate[12] (2.7 g, 8.5 mmol) was added dropwise to a solution of **9** (1.0 g, 3.4 mmol) and 1,2,4,-triazole (1.0 g, 14.5 mmol) in THF (50 mL) under nitrogen atmosphere, and the mixture was stirred for 1 h at room temperature. Ether (50 mL) was added to the mixture, and the organic phase was successively washed with ice-cold dilute HCl, aqueous $NaHCO_3$, and water, dried over anhydrous $MgSO_4$, and concentrated. The residual syrup was chromatographed on silica gel, with hexane–EtOAc (4:1), to give **10** (1.43 g, 79%) as a mixture of α and β (1:10) anomers. β anomer: ^1H NMR ($CDCl_3$) δ 1.22 (3 H, d, *J* 6.50 Hz, 6-CH_3), 1.91, 1.99, 2.19 (3 H each, s, 3 × OAc), 3.85 (1 H, dq, *J* 1.00, 6.50 Hz, H-5), 4.82–4.96 (4 H, m, benzylic protons), 5.02–5.08 (2 H, m, H-2,3), 5.25 (1 H, dd, *J* 0.50, 3.50 Hz, H-4), 5.32 (1 H, dd, *J* 8.00, 10.50 Hz, H-1); H-1 for α anomer δ 5.82 (dd, *J* = 4.83, 8.62 Hz).

To a cooled solution of **10** (500 mg, 0.9 mmol) in THF (50 mL) was added 30% H_2O_2 (7 mL) in one portion, and the mixture was allowed to warm to room temperature and stirred for 1.5 h at room temperature. The mixture was diluted with ether and washed with ice-cold aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and water, dried over anhydrous $MgSO_4$, and concentrated to give **11** (420 mg, 81%) as a mixture of α and β (1:10) anomers. This was used for the next step without further purification. The ^1H NMR spectrum of the β anomer was in good agreement with that reported:[8] ^1H NMR ($CDCl_3$) δ 1.22 (3 H, d, *J* 7.5 Hz, 6-CH_3), 1.91, 1.99, 2.19 (3 H each, s, 3 × OAc), 3.90 (1 H, dq, *J* 6.50, 7.50 Hz, H-5), 5.00–5.03 (m, H-3, benzylic), 5.03–5.12 (m, benzylic), 5.26 (1 H, dd, *J* 1.00, 3.50 Hz, H-4), 5.27–5.33 (2 H, m, H-1,2); H-1 for α anomer δ 5.93 (dd, *J* = 3.68, 5.51 Hz); HRMS calcd for $C_{26}H_{31}O_{11}PCs$ (M + Cs^+) 683.0658, found 683.0658.

L-Fucose 1-Phosphate (2). Compound **11** (5.0 g, 9.1 mmol) was treated in the same manner as that for the preparation of **2** from **7** to give **2** (2.61 g) as a mixture of α and β anomers with some contamination of NH_4HCO_3 (78% yield) (1:10 judged by ^1H NMR, H-1α 5.33 (q); H-1β 4.86 (t). The ^1H and ^{13}C NMR data of the β anomer were in good agreement with those reported.[6]

GDP-fucose (1). GDP-Fuc was prepared following the procedure of Gokhale et al.[7] with some modifications. Anomerically pure compound **2** was first converted to its triethylammonium salt by passing through a column of Dowex 50W-X-8 [Et_3NH^+] form with water and lyophilized.[7] The lyophilized L-fucose 1-phosphate triethylammonium salt (300 mg, 0.83 mmol) and guanosine 5′-monophosphomorphalidate (600 mg, 0.83 mmol) were separately dried by coevaporating with pyridine twice. They were then combined in pyridine (20 mL), and the mixture was stirred for 5 days at room temperature and concentrated. The residual syrup was diluted to 50 mL with water and applied to a column of Dowex 1-X8 [HCO_2^-] (3 × 25 cm) and eluted with a gradient of NH_4HCO_3 (0–1 M NH_4HCO_3). The GDP-Fuc-containing fractions were pooled and lyophilized, and the product was further purified with a column of Sephadex G-25 (superfine) (3 × 65 cm) twice with water. The appropriate fractions were pooled and lyophilized. A solution of the lyophilized product in water was passed through a column of Dowex 50 W-X8 [Na^+] form with water. The fractions were pooled and lyophilized to give **1** (~300 mg) concomitant with a small amount of GMP (judged by ^1H NMR). The ^1H NMR spectral data were in good agreement with those reported.[6,7]

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Supplementary Material Available: ^1H-NMR spectra of compounds **2**, **7** and **11** (3 pages). Ordering information is given on any current masthead page.

Electrolytic Reactions of Fluoro Organic Compounds. 11.[1] Anodic Preparation and Synthetic Applications of β-Trifluoromethylated *O,S*-Acetals

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Introduction

Fluoro organic compounds, particularly partially fluorinated compounds, have attracted much interest in many

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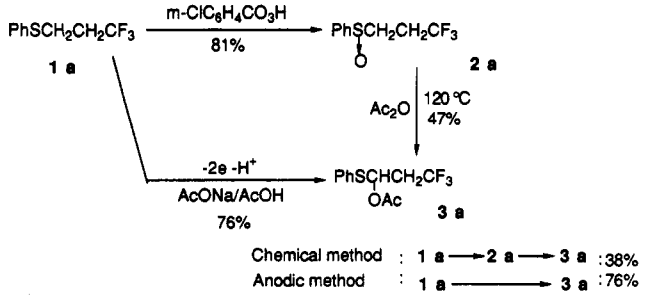
Scheme I



fields such as material science and medicinal chemistry.[1,2] Although many new methods for the preparation of such partially fluorinated compounds have been developed, there still remain many synthetic problems to be solved. For example, it is quite difficult to perform nucleophilic α-substitution adjacent to a trifluoromethyl group owing to its strong electron-withdrawing effect (eq 1, where Nu = C-, N-, and O-nucleophiles and X = leaving group).[4-6]

$$CF_3CH_2X + Nu^- \xrightarrow[-X^-]{\text{slow}} CF_3CH_2Nu \qquad (1)$$

In our previous papers,[1,7-12] we have shown that electrochemical techniques often provide a useful method to solve such problems.

Nucleophilic substitution at the β-position to a trifluoromethyl group is also generally difficult, except for sulfur nucleophiles owing to the predominant elimination to trifluoropropene as shown in eq 2.

$$CF_3CH_2CH_2X + Nu^- \xrightarrow[-X^-]{-NuH} CF_3CH{=}CH_2 \qquad (2)$$

Strongly basic carbon, oxygen, and nitrogen nucleophiles behave as proton-abstracting reagents in S_N2 reactions to give the corresponding olefins.[13,14] In the case of S_N1 reactions, facile deprotonation from the β-position of the cationic intermediate takes place prior to trapping with nucleophiles.[15,16] It is well-known that a sulfur atom generally stabilizes an adjacent carbocation. Therefore, it could be anticipated that the use of this stabilization effect would impede the deprotonation in S_N1 reactions. These considerations led us to prepare the β-trifluoromethylated *O,S*-acetals **3** by anodic acetoxylation and to investigate their alkylation reactions with various carbon nucleophiles as shown in eq 3.

Scheme II

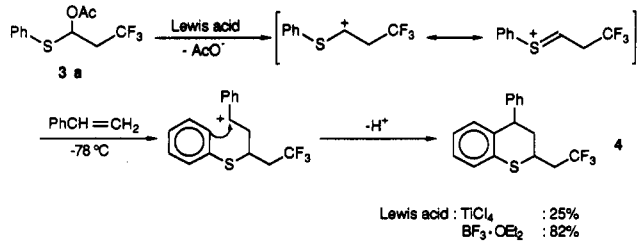
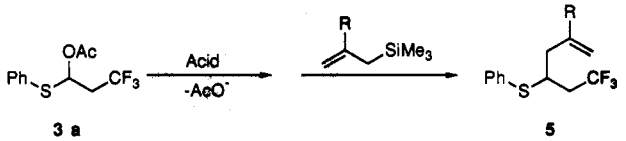


Table I. Allylation of 3a



R	acid	temp (°C)	product	yield (%)
H	$BF_3{\cdot}Et_2O$	reflux	5a	14[a]
H	$TiCl_4$	-78	5a	30
H	$AlCl_3$	rt	5a	0[b]
H	EGA	rt	5a	88
CH_3	EGA	rt	5b	82

[a] $PhSCH{=}CHCF_3$ (10%) was formed. [b] Many complicated products were formed.

$$RSCH_2CH_2CF_3 \xrightarrow{\text{acetoxylation}} \underset{\mathbf{3}}{RSC(OAc)HCH_2CF_3}$$

$$\xrightarrow[-AcO^-]{\text{acid}} [RS^+CHCH_2CF_3 \leftrightarrow RS{=}^+CHCH_2CF_3] \xrightarrow{Nu^-} RSC(Nu)HCH_2CF_3 \qquad (3)$$

Results and Discussion

The Pummerer rearrangement is a well-known method for the preparation of α-acetoxy sulfides from sulfoxides.[17] Therefore, we first attempted the preparation of α-acetoxy sulfide **3a** by the Pummerer rearrangement of sulfoxide **2a** derived from phenyl 3,3,3-trifluoropropyl sulfide (**1a**) as shown in Scheme I. However, sulfoxide **2a** provided **3a** in a low yield even after heating at 120 °C in acetic anhydride.

Then, we carried out anodic acetoxylation of **1a** in 0.2 M AcONa–AcOH solution in a manner similar to the case of 2,2,2-trifluoroethyl sulfides.[11] The reaction took place; however, the yield was also low (32%). Finally, it was found that this anodic acetoxylation proceeded smoothly to provide the α-acetoxy sulfide **3a** in good yield only when the concentrations of both substrate **1a** and the supporting electrolyte, AcONa, were extremely high (0.68 and 1.2 M, respectively). Thus, the electrochemical method for the preparation of **3a** is much superior to the conventional Pummerer reaction since the α-acetoxy sulfide was obtained in one step under mild conditions with much higher yield (Scheme I).

Next, this anodic acetoxylation was extended to an alkyl sulfide such as heptyl 3,3,3-trifluoropropyl sulfide (**1b**). The acetoxylation took place at both α-positions of the sulfide **1b**: however regioselectivity was not observed as shown in eq 4. Total yield: 33% (4.0 F/mol at low concentrations) and 57% (3.4 F/mol at high concentrations. Regioselectivity: **3b**:**3b′** = 52:48.) In this case, a similar

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$$\underset{\mathbf{1b}}{C_7H_{15}SCH_2CH_2CF_3} \xrightarrow[AcONa/AcOH]{-2e - H^+} \underset{\mathbf{3b}}{C_7H_{15}SC(OAc)HCH_2CF_3} + \underset{\mathbf{3b'}}{C_6H_{13}C(OAc)HSCH_2CH_2CF_3} \quad (4)$$

concentration effect on the efficiency for the acetoxylation was observed: the total yield of acetoxylated products **3b** and **3b'** at high concentrations was much higher than that at low concentrations.

α-Acetoxy sulfides **3a** and **3b** thus obtained have a β-trifluoromethylated acetal structure. It is well-known that Lewis acid-mediated reactions of acetals with carbon nucleophiles provide a versatile method for the construction of carbon–carbon bonds.[18] Accordingly, attempts were made to introduce various functional carbon nucleophiles into the β-position to the trifluoromethyl group of **3a**.

First, cationic polar cycloaddition of **3a** with styrene was attempted in dichloromethane at −78 °C in the presence of $TiCl_4$ and $BF_3{\cdot}OEt_2$. Although the reaction in the presence of $TiCl_4$ gave the expected thiochroman **4** in low yield (25%) due to the formation of many byproducts, the BF_3 etherate-induced annulation proceeded in 82% yield (Scheme II).

Allylation of **3a** with allylsilane was similarly conducted in the presence of various Lewis acids. As shown in Table I, the reaction in the presence of $BF_3{\cdot}OEt_2$ required heating and the yield was low owing to competing elimination leading to trifluoropropene. When a more reactive Lewis acid such as $TiCl_4$ was used, the yield increased somewhat. On the other hand, in the presence of the much more reactive Lewis acid, $AlCl_3$, no allylation product could be isolated from a reaction.

The allylation reaction was performed more efficiently by using electrogenerated acids (EGA) which have recently been shown to be useful for selective organic synthesis.[19] After constant current electrolysis was carried out at a platinum anode in a solution of dichloromethane containing equimolar amount of $LiClO_4$ and n-Bu_4NClO_4 using a divided cell, the resulting anolyte was used as the acid for the reaction. In this case, the allylation proceeded selectively to give the corresponding allylation product **5a** in excellent yield. The isobutenyl group was also similarly introduced in satisfactory yield.

Cyanation of **3a** with trimethylsilyl cyanide was also attempted. However, ordinary Lewis acids caused mainly cleavage of a carbon–sulfur bond, and the yield of cyanated product **6** was quite low. For example, the reaction in the presence of $TiCl_4$ gave dithioacetal **7** as the major product. It was found that the yield of **6** was remarkably increased by using EGA instead of the Lewis acids as shown in eq 5 (acid: $TiCl_4$, **6** (13%), **7** (22%); EGA, **6** (56%), **7** (0%)).

$$\mathbf{3a} \xrightarrow[-AcO^-]{acid} \xrightarrow{Me_3SiCN} \underset{\mathbf{6}}{PhSC(CN)HCH_2CF_3} + \underset{\mathbf{7}}{(PhS)_2CHCH_2CF_3} \quad (5)$$

Finally, we have attempted to introduce aryl groups onto **3a** using aromatic compounds as nucleophiles. The reaction with benzene was tried in the presence of various Lewis acids such as $BF_3{\cdot}OEt_2$, $SnCl_4$, and $FeCl_3$. However, the desired product **8** was not formed in any case and the dithioacetal **7** was formed as a major product in the presence of $BF_3{\cdot}OEt_2$ as shown in Scheme III. After many attempts, it was found that the reaction proceeded at 10 °C in the presence of $AlCl_3$ although the yield of **8** was not satisfactory. In this reaction, no bis-substituted benzene was formed.[20] Product **7** seems to be formed due to the cleavage of both carbon–sulfur and carbon–oxygen bonds as shown in Scheme III.

In summary, this work demonstrates a successful example of generation of a carbocation at the β-position to the trifluoromethyl group and its efficient trapping with functional carbon nucleophiles. Thus, the anodically prepared β-trifluoromethylated *O,S*-acetal is a highly useful synthetic fluoro building block.

Experimental Section

^{19}F NMR (40 MHz) spectra were recorded in $CDCl_3$. ^{19}F NMR chemical shifts are given in δ ppm upfield from external CF_3COOH. Electrolysis experiments were carried out using a Hokutodenko HA-501 Potentiostat/Galvanostat equipped with a Hokutodenko HF-201 digital coulombmeter.

Phenyl 3,3,3-Trifluoropropyl Sulfide (1a). The starting sulfide **1**[21] was prepared by the reaction of benzenethiol with 1,1,1-trifluoro-3-iodopropane in the presence of NaH in DMF at 0 °C. The yield was quantitative.

Heptyl 3,3,3-Trifluoropropyl Sulfide (1b). Sulfide **1b** was similarly prepared: 62% yield; bp 115–120 °C (35 Torr); ^1H NMR (60 MHz) δ 0.90 (t, 3 H, CH_3), 1.02–1.73 (m, 10 H, CH_2×5), 2.00–2.87 (m, 6 H, $CF_3CH_2CH_2SCH_2$); MS m/e 228 (M^+), 131 ($C_7H_{15}S^+$); calcd for $C_{10}H_{19}F_3S$ m/e 228.1165, found 228.1159.

Phenyl 3,3,3-Trifluoropropyl Sulfoxide (2a). To a stirred solution of 1.72 g (10 mmol) of m-CPBA in 45 mL of CH_2Cl_2 was added dropwise 2.06 g (10 mmol) of m-CPBA in 45 mL of CH_2Cl_2 was added dropwise 2.06 g (10 mmol) of phenyl 3,3,3-trifluoropropyl sulfide (**1a**) at 0 °C. After 1 h, the reaction mixture was mixed with water and extracted repeatedly with CH_2Cl_2. The extracts were washed with water and dried (Na_2SO_4). After evaporation, the residual solid was recrystallized from hexane to provide 1.80 g (81%) of pure sulfoxide **2a**: mp 49–50 °C; ^1H NMR δ 2.1–3.56 (m, 4 H, CH_2CH_2), 7.80 (s, 5 H, C_6H_5); ^{19}F NMR (60 MHz) δ −16.83 (t, J_{F-H} = 10 Hz); IR (CCl_4) 1055 cm^{-1} (SO); MS m/e 222 (M^+). Anal. Calcd for $C_9H_9F_3OS$: C, 48.64; H, 4.08. Found: C, 48.59; H, 4.13.

3,3,3-Trifluoro-1-(phenylthio)propyl Acetate (3a). Method A. Pummerer Rearrangement. A solution of 111 mg (0.5 mmol) of **2a** in 2 mL of acetic anhydride was stirred and heated at 120 °C for 1 h. The reaction mixture was poured into water, and the resulting solution was extracted repeatedly with ether and washed with aqueous K_2CO_3 and water. The solution was dried (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel (hexane–AcOEt (9:1)) to provide 62 mg (47%) of **3a** as a colorless oil: ^1H NMR (60 MHz) δ 2.03 (s, 3 H, CH_3), 2.56 (dq, 2 H, CH_2, J_{H-F} = 6 Hz, J_{H-H} = 2 Hz), 6.38 (t, 1 H, CH, J_{H-H} = 4 Hz), 7.2–7.7 (m, 5 H, Ph); ^{19}F NMR δ −13.75 (t, J_{F-H} = 10 Hz); IR 1770 cm^{-1} (C=O); MS m/e 264 (M^+), 205 (M^+ − AcO), 109 (PhS^+). Anal. Calcd for $C_{11}H_{11}F_3O_2S$: C, 50.00; H, 4.20. Found: C, 49.70; H, 4.40.

Method B. Anodic Acetoxylation of 1a at High Concentrations. Constant current (5 A/dm^2) electrolysis of 3.50 g (17 mmol) of **1a** was carried out at Pt electrodes (1 × 3 cm) in 1.2 M CH_3COONa–CH_3COOH (5 mL) using an undivided cylindrical cell (2.5 (i.d.) × 6 (H) cm) equipped with a magnetic stirrer. During the electrolysis, the temperature of the electrolytic solution was kept at ca. 50 °C. After passing 2.5 F/mol of electricity (monitoring unreacted **1a** by silica gel TLC), the electrolyte was mixed with water and extracted repeatedly with ether. The extracts were washed with aqueous $NaHCO_3$, water, and brine

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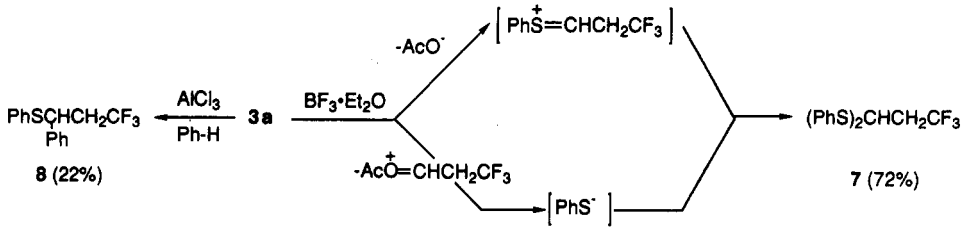
Scheme III



and then dried (Na_2SO_4). After evaporation of the solvent, the residue was chromatographed on silica gel (hexane–AcOEt (9:1)) to provide 3.41 g (76%) of α-acetoxy product **3a**.

At low concentrations, constant current (1.2 A/dm^2) was passed (3.6 F/mol) using Pt electrodes (2 × 3 cm) in 0.2 M AcONa–AcOH (30 mL) containing 0.41 g (2 mmol) of **1a**. The yield of **3a**: 32%.

Anodic acetoxylation of **1b** was carried out similarly, and the products **3b** and **3b'** were obtained as regioisomeric mixture in pure form by chromatography (hexane–AcOEt (10:1)). Anal. Calcd for $C_{12}H_{21}F_3O_2S$: C, 50.33; H, 7.39. Found: C, 50.04: H, 7.15. Each product was identified by GC–MS (OV-17 capillary column) and the following spectroscopic analyses. The product ratio was estimated by ^{19}F NMR spectra.

3,3,3-Trifluoro-1-(heptylthio)propyl acetate (3b): ^1H NMR (200 MHz) δ 1.11 (t, 3 H, CH_3), 1.20–1.45 (m, 8 H, $CH_3(CH_2)_4$), 1.50–1.70 (m, 2 H, CH_2CH_2S), 2.10 (s, 3 H, $OCOCH_3$), 2.55–2.82 (m, 4 H, $CH_2SCHCH_2CF_3$), 6.28 (dd, 1 H, SC*H*OAc); ^{19}F NMR δ −14.01 (t, J_{F-H} = 10 Hz); IR 1780 cm^{-1} (C=O); MS *m/e* 286 (M$^+$), 227 (M$^+$ − AcO), 226 (M$^+$ − AcOH).

1-[(3,3,3-Trifluoropropyl)thio]heptyl acetate (3b'): ^1H NMR (200 MHz) δ 1.11 (t, 3 H, CH_3), 1.21–1.45 (m, 8 H, $CH_3(CH_2)_4$), 1.72–1.88 (m, 2 H, CH_2CHS), 2.10 (s, 3 H, $OCOCH_3$), 2.3–2.5 (m, 2 H, CF_3CH_2), 2.55–2.82 (m, 2 H, SCH_2), 6.96 (t, 1 H, SC*H*OAc); ^{19}F NMR δ −11.87 (t, J_{F-H} = 10 Hz); IR 1780 cm^{-1} (C=O); MS *m/e* 286 (M$^+$), 227 (M$^+$ − AcO), 226 (M$^+$ − AcOH).

2-(2,2,2-Trifluoroethyl)-4-phenylthiochroman (4). To a stirred solution of 264 mg (1 mmol) of **3a** and 310 mg (3 mmol) of styrene in 8 mL of CH_2Cl_2 was added dropwise 0.2 mL (1.6 mmol) of BF_3·Et_2O at −78 °C. After 5 h of stirring, the solution was warmed to rt and 8 mL of water was added. The resulting solution was extracted repeatedly with ether and washed with aqueous $NaHCO_3$, water, and brine. The extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel (hexane–AcOEt (20:1)) to provide 253 mg (82%) of almost pure **4**, which was further purified by preparative GC (column: OV-17): yield 169 mg (55%); mp 38.7–41 °C; ^1H NMR (200 MHz) δ 2.08 (ddd, 1 H, PhCHC*H*, *J* = 11.8, 11.8, and 13.4 Hz), 2.43 (dq, 2 H, CF_3CH_2, *J* = 6.6 and 10.8 Hz), 2.53 (ddd, 1 H, PhCHC*H*, *J* = 3.6, 3.6, and 13.6 Hz), 3.80 (ddt, 1 H, SC*H*, *J* = 3.4, 7.4, and 10.6 Hz), 4.07 (dd, 1 H, PhC*H*, *J* = 4.0 and 12.0 Hz), 6.30–7.23 (m, 9 H, Ph and C_6H_4); ^{19}F NMR δ −14.5 (t, J_{F-H} = 11.0 Hz); IR (KBr) 3060, 3040, 2930, 2850 (CH_2), 1600, 1590 (C=C), 760 (Ar), 745, 700 cm^{-1} (Ph); MS *m/e* 308 (M$^+$), 225 (M$^+$ − CF_3CH_2), 197 ($SC_6H_4CPh^+$), 147 (M$^+$ − Ph − CF_3CH_2 − H); calcd for $C_{17}H_{15}F_3S$ *m/e* 308.0768, found 308.0841.

1-Allyl-3,3,3-trifluoropropyl Phenyl Sulfide (5a). EGA was generated as follows. Constant current (0.8 A/dm^2) electrolysis was carried out at a Pt anode and a graphite cathode in 33 mM $LiClO_4$/*n*-Bu_4NClO_4–CH_2Cl_2 (20 mL) using an undivided cell. After passing 0.35 F/mol (based on total amount of ClO_4^-), the resulting anolyte was used for the following reaction as an acid.

To a stirred solution of 1.6 mL (10 mmol) of allyltrimethylsilane and the above EGA (3 mL) in 1 mL of CH_2Cl_2 was added dropwise 264 mg (1 mmol) of **3a** at rt in an atmosphere of nitrogen. After 4 h of stirring, the solution was mixed with 7 mL of water and extracted with 15-mL portions of ether. The extracts were washed with aqueous $NaHCO_3$, water, and brine and then dried (Na_2SO_4). After evaporation of the solvent, the residue was chromatographed on silica gel (hexane–AcOEt (9:1)) to provide 216 mg (88%) of **5a** as a colorless oil: ^1H NMR (200 MHz) δ 2.2–2.6 (m, 4 H, CF_3CH_2 and CH_2=$CHCH_2$–), 3.40 (tt, 1 H, PhSC*H*, *J* = 6.2 and 6.2 Hz), 5.0–5.3 (m, 2 H, H_2C=CH–), 5.88 (ddt, 1 H, H_2C=C*H*–, *J* = 7.0, 10, and 17.5 Hz), 7.2–7.5 (m, 5 H, Ph): ^{19}F NMR δ −14.5 (t, J_{F-H} = 11.4 Hz); IR (neat) 3080, 3000, 2950 (CH_2), 1640, 1595 (C=C), 750, 690 CM^{-1} (Ph); MS *m/e* 246 (M$^+$), 205 (M$^+$ − CH_3), 110 (PhSH$^+$); calcd for $C_{12}H_{13}F_3S$ *m/e* 246.0643, found 246.0689.

1-Isobutenyl-3,3,3-trifluoropropyl Phenyl Sulfide (5b). The reaction was carried out using 1 mmol of **3a** and 640 mg (5 mmol) of isobutenyltrimethylsilane in a manner similar to the above procedure. The product **5b** (213 mg, 82%) was isolated as a colorless oil by silica gel chromatography (hexane–AcOEt (20:1): ^1H NMR (200 MHz) δ 1.75 (m, 3 H, CH_3), 2.25–2.52 (m, 4 H, CF_3CH_2 and H_2C=$CHCH_2$–), 3.45 (tt, 1 H, PhSC*H*, *J* = 7.1 and 7.1 Hz), 4.81 (dq, 1 H, H_2C=CCH_3–, *J* = 1 and 3 Hz), 4.90 (dq, 1 H, H_2C=CCH_3–, *J* = 1.6 and 3 Hz), 7.2–7.6 (m, 5 H, Ph); ^{19}F NMR δ −14.1 (t, J_{F-H} = 10.8 Hz); IR (neat) 3100, 2975, 2950 (CH_2), 1650, 1590 (C=C), 750, 690 cm^{-1} (Ph); MS *m/e* 260 (M$^+$), 245 (M$^+$ − CH_3), 110 (PhSH$^+$); calcd for $C_{13}H_{15}F_3S$ *m/e* 260.0846, found 260.0833.

1-Cyano-3,3,3-trifluoropropyl Phenyl Sulfide (6). The product **6** (130 mg, 56%) was obtained as a colorless oil by silica gel chromatography (hexane–AcOEt (9:1)) after the reaction was similarly performed using 1 mmol of **3a** and 1.2 mL (10 mmol) of cyanotrimethylsilane: ^1H NMR (200 MHz) δ 2.62 (ddq, CF_3CH_2, *J* = 6.8, 7.8, and 9.6 Hz), 3.91 (dd, 1 H, PhSC*H*, *J* = 6.8 and 7.8 Hz), 7.3–7.8 (m, 5 H, Ph); ^{19}F NMR δ −13.3 (dd, J_{F-H} = 9.0 and 9.0 Hz); IR (neat) 2250 cm^{-1} (C=N); MS *m/e* 231 (M$^+$), 205 (M$^+$ − CN), 148 (M$^+$ − CF_3CH_2), 109 (PhS$^+$); calcd for $C_{10}H_8F_3N$ MS *m/e* 231.0329, found 231.0244.

3,3,3-Trifluoro-1,1-bis(phenylthio)propane (7). To a stirred solution of 1 mmol of **3a** and 0.5 mL (5.3 mmol) of benzene in 6 mL of CH_2Cl_2 was added dropwise 0.14 mL (1.1 mmol) of BF_3·OEt_2 at −70 °C under a nitrogen atmosphere. After 5 h, the solution was stirred at −50 °C overnight. The solution was mixed with water and extracted with ether. The extracts were washed with $NaHCO_3$, water, and brine and then dried (Na_2SO_4). Evaporation of the solvent gave 283 mg of almost pure **7**, which was chromatographed on silica gel (hexane–AcOEt (9:1)) to provide 226 mg (72%) of **7** as a colorless oil: ^1H NMR (60 MHz) δ 2.5 (dq, 2 H, CF_3CH_2, *J* = 10 and 10 Hz), 4.4 (t, 1 H, PhC*H*, *J* = 6 Hz), 7.0–7.56 (m, 10 H, Ph); ^{19}F NMR δ −13.66 (t, J_{F-H} = 10 Hz); IR (neat) 3070, 2950 (CH_2), 1590 (C=C), 750, 695 cm^{-1} (Ph); MS *m/e* 314 (M$^+$), 205 (M$^+$ − PhS), 109 (PhS$^+$); calcd for $C_{15}H_{13}F_3S_2$ *m/e* 314.0411, found 314.0461.

Phenyl 3,3,3-Trifluoro-1-phenylpropyl Sulfide (8). To a stirred solution of 200 mg (1.5 mmol) of $AlCl_3$ in benzene (1.5 mL, 16 mmol) was added dropwise 1 mmol of **3a** at 10 °C under a nitrogen atmosphere. After 4 h of stirring, the reaction mixture was worked up in a manner similar to the above case. The crude product (360 mg) was chromatographed on silica gel (hexane–AcOEt (9:1)) to provide 62 mg (22%) of **8** as a colorless oil: ^1H NMR (60 MHz) δ 2.8 (dq, 2 H, CF_3CH_2, *J* = 10 and 10 Hz), 4.17 (t, 1 H, PhC*H*, *J* = 7 Hz), 6.8–7.7 (m, 10 H, Ph); IR (neat) 3080, 2940 (CH_2), 1580 (C=C), 740, 700 cm^{-1} (Ph); MS *m/e* 282 (M$^+$), 199 (M$^+$ − CF_3CH_2), 109 (PhS$^+$). Anal. Calcd for $C_{15}H_{13}F_3S$; C, 63.80; H, 4.46. Found: C, 64.02; H, 4.53.

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Registry No. **1a**, 102687-64-9; **1b**, 139758-52-4; **2a**, 139732-09-5; **3a**, 139732-10-8; **3b**, 139732-15-3; **3b'**, 139732-16-4; **4**, 139732-11-9; **5a**, 139732-12-0; **5b**, 139732-17-5; **6**, 139758-51-3; **7**, 139732-13-1; **8**, 139732-14-2; 1,1,1-trifluoro-3-iodopropane, 460-37-7; benzenethiol, 108-98-5; 1-mercaptoheptane, 1639-09-4; styrene, 100-42-5; allyltrimethylsilane, 762-72-1; isobutenyltrimethylsilane, 18292-38-1; cyanotrimethylsilane, 7677-24-9; benzene, 71-43-2.

Supplementary Material Available: ^{1}H NMR spectra for **1b**, **4**, **5a**, **5b**, **6**, and **7** (6 pages). ordering information is given on any current masthead page.

Direct Polynitroaliphatic Alcohol Addition to Alkenes. 2. One-Step Synthesis of β-Substituted Polynitroalkyl Vinyl Ethers via an Alternative Transetherification Pathway[1]

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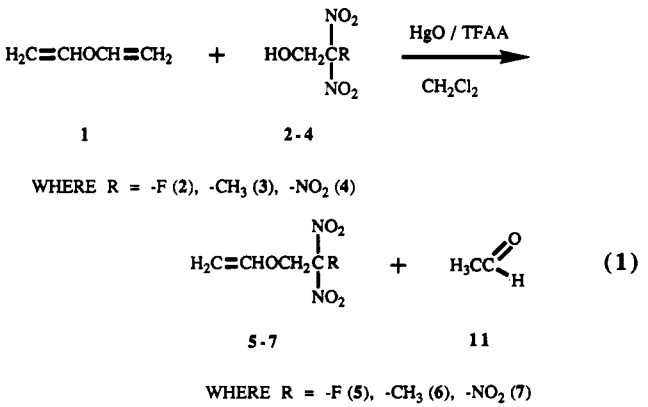
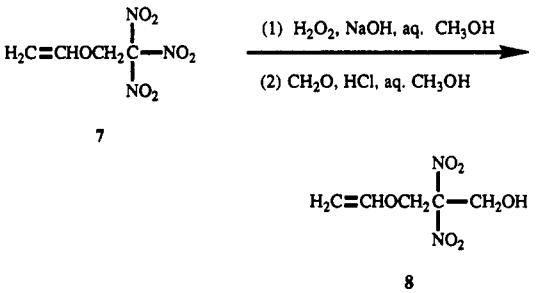
β-Substituted polynitroalkyl vinyl ether compounds represent monomeric polymer precursors which potentially could be useful chemical components in solid propellant or explosive formulations. Their preparation is limited by the inherent instability of the β-substituted polynitroalkyl structure in alkaline solution[2,3] and by the weak nucleophilic nature of the polynitroaliphatic alcohol precursors possessing either the geminal 2,2-dinitroalkyl or terminal 2,2,2-trinitroethyl structure.[3-6] This precludes using the common vinyl ether synthesis procedure where an alcohol and acetylene are reacted via base catalysis because these polynitroaliphatic alcohol reactants readily deformylate in alkaline solution forming formaldehyde plus their respective polynitroalkyl anion.[2,3] This paper reports our discovery of a novel reaction which permits the one-step, high-yield synthesis of β-substituted polynitroalkyl ethers under mild refluxing CH_2Cl_2 solvent conditions. Use of a mercury(II) oxide/trifluoroacetic acid (HgO/TFAA) cocatalyst and the divinyl ether (**1**) reactant with 2-fluoro-2,2-dinitroethanol (**2**), 2,2-dinitropropanol (**3**), and 2,2,2-trinitroethanol (**4**) produce their respective polynitroalkyl vinyl ethers through a nonreversible transetherification reaction (eq 1). While an inherent reversible



(1)

equilibrium in the transetherification reaction is responsible for the low (27–32%) yields obtained with more nucleophilic 2-nitroalkyl alcohols,[7] this particular transetherification reaction uniquely circumvents the equilibrium condition because the chemical structure of **1** does not permit formation of a conjugate alcohol. The 2-fluoro-2,2-dinitroethyl vinyl ether (**5**) and 2,2-dinitropropyl vinyl ether (**6**) compounds are known;[2,8] the 2,2,2-trinitroethyl vinyl ether (**7**) and its 3-hydroxy-2,2-dinitropropyl vinyl ether (**8**) derivative are reported for the first time (eq 2).



(2)

Results and Discussion

Two previous methods are reported which provide **5** and **6**.[2,8] The first reported synthesis produces **5** and **6** in 51 and 60% yields, respectively, and is achieved by heating **2** or **3** with vinyl acetate using mercury(II) acetate and concentrated H_2SO_4 in catalytic amounts.[8] A more recent procedure provides **5** in 88% yield and **6** in a 94% yield by heating their respective aldehyde bis[2,2-dinitroalkyl] acetal in the presence of anhydrous $NaHSO_4$.[2] While this pyrolysis reaction produces **2** or **3** as a recyclable byproduct for preparing more acetal reactant, the initial acetal preparation makes this a two-step process. The subject transetherification where **1** is reacted with either **2** or **3** in the presence of the HgO/TFAA cocatalyst produces vinyl ethers **5** and **6** in approximately 75–78% yields, respectively, prior to purification by vacuum distillation (eq 1). Reaction of **1** with **4** using the HgO/TFAA cocatalyst results in the first synthesis of **7** in a 26% yield which, in turn, is a precursor for the new compound **8** (eq 2). A one-pot procedure forms **8** via alkaline dinitrosation of **7** followed by an acidic formalation. Compound **8** represents a novel β-substituted 2,2-dinitroaliphatic structure since it possesses two different terminal functional reaction sites, a vinylic bond and a hydroxyl moiety.[10] Although the yield of **8** is not optimized, its formation demonstrates a synthetic strategy for obtaining a new type of difunctional polynitroaliphatic compound. Figure 1 compares the characteristic ^{1}H NMR spectra of the four vinyl ethers **5–8**

Table I. Comparison of Product 5, 9, and 10 Percentages as Function of Catalyst

DVE/FDNEOH reactant ratio	catalyst/cocatalyst	% 5	% 9	% 10
1.00	HgO/TFAA	90.5	0	9.5
1.00	$HgSO_4$/TFAA	11.0	5.3	83.7
1.00[3]	$HgSO_4$	3.7	35.1	61.2
2.00[3]	$HgSO_4$	5.6	73.4	21.0

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