Novel Perfluoroacyl Olefinations of Aldehydes Using *β*-Thio-Substituted Perfluoroalkyl Enol Ethers

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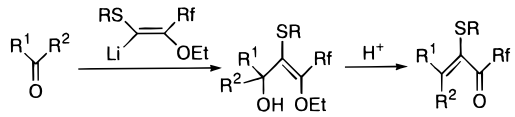
Received February 16, 1999

α-(Methylthio)- or α-(phenylthio)-substituted perfluoroacylolefinations of nonenolizable aldehydes using the *β*-lithio-*β*-thio-perfluoroalkyl enol ethers **1**−**4** stereoselectively proceeded to give (*Z*)-α,*β*-unsaturated perfluoroalkyl ketones **9a**−**e**, **10a**−**c**, **11a**−**c**, and **12a**. The α-(thio)-α,*β*-unsaturated trifluoromethyl ketones were easily converted to 3-(thio)-2-(trifluoromethyl)-1,3-butadienes **21a**−**c** and **22a**,**b** in moderate to high yields (41−85%).

Alkenyl trifluoromethyl ketones have been used as novel intermediates for the synthesis of biologically active fluorinated compounds.[1] Some methods for the preparation of the alkenyl ketones have been reported using the aldol condensation of the trifluoroacetone,[2] the Horner−Emmons reactions of the iminophosphonate,[3] the reactions of the boronate ester,[4] and the oxidation of the corresponding alcohols.[5] Especially, the iminophosphonate route is convenient from the viewpoint of its direct preparation from aldehydes. We have recently reported the tandem formyl olefinations of aldehydes and ketones using the α-lithio 2-ethoxyvinyl sulfide or selenide.[6] Lithium enol ethers are good candidates for the olefinations of carbonyl compounds;[7] however, it is difficult to generate the lithiated perfluoroalkyl enol ethers because the addition−elimination reaction of the fluorides easily occurs.[8] The transmetalation of the *β*-bromo perfluoroalkyl enol ethers is available as an alternative route.[9]

On the other hand, the vinyl sulfides are easily lithiated by treatment with strong base; therefore, the α-lithio vinyl sulfides easily react with electrophiles to give the adducts.[10] If the *β*-sulfur-substituted perfluoroalkyl enol ether could be prepared, *β*-lithio perfluoroalkyl enol ethers could easily be generated. Their lithium agents would react with aldehydes or ketones to gives allylic alcohols, whose isomerization afford the α,*β*-unsaturated perfluoroalkyl ketones (Scheme 1). We now report the novel perfluoroacylolefination of the aldehydes using *β*-lithio-*β*-thio-substituted perfluoroalkyl enol ethers.

Scheme 1



β-Sulfur-substituted fluoroalkyl enol ethers (*E*)-**1**−**4** were conveniently prepared under Wittig reaction conditions using phenylthio- or methylthiomethyltriphenylphosphorane and CF_3CO_2Et or $CF_3CF_2CO_2Et$.[11] We first examined the lithiation of (*E*)-2-ethoxy-1,1,1-trifluoro-3-(phenylthio)prop-2-ene (**1**) using *n*-BuLi at −78 °C, and the successive treatment with benzaldehyde afforded the allylic alcohol **5a** in 86% yield. The structure of **5a** was determined by the IR and ^1H, ^{13}C, and ^{19}F NMR spectra, MS, and elemental analysis. We also examined the reactions of **1** with other nonenolizable aldehydes, and these results are shown in Table 1 (entries 1−5). We then examined the isomerization of **5a** using various acids such as trimethylsilyl trifluoromethanesulfonate (TMSOTf), polyphosphoric acid trimethylsilyl ester (PPSE),[6] $BF_3{\cdot}Et_2O$, and other protic acids. *p*-Toluenesulfonic acid (TsOH) was suitable for the dehydration or the isomerization. The reaction of **5a** with 1 equiv of *p*-TsOH in $ClCH_2CH_2Cl$ gave 1,1,1-trifluoro-4-phenyl-3-(phenylthio)-but-3-en-2-one (**9a**) in 91% yield. *tert*-Butylaldehyde afforded the α,*β*-unsaturated trifluoromethyl ketone **9b** (entry 2). The structure of the product **9b** was mainly determined on the basis of the spectral data, showing the carbonyl absorption at ν 1730 cm^{-1} in the IR spectrum, revealing the olefinic absorption at δ 7.39 (s) ppm in the ^1H NMR, and exhibiting three quartets at δ 116.21 (J = 292 Hz) due to CF_3, 166.30 (J = 2 Hz) due to the 4-C, and 179.75 (J = 34 Hz) due to the carbonyl group in the ^{13}C NMR spectrum. The ^{19}F NMR spectrum also showed one singlet at δ −7.62 ppm. The other stereoisomers were not detected in the spectral data. Cinnamaldehyde stereoselectively gave (3*Z*,5*E*)-1,1,1-trifluoro-6-phenyl-3-(phenylthio)hexa-3,5-diene (**9c**) (entry 3). The trifluoromethyl enynyl ketone **9d** and the furyl derivative **9e** were also obtained; however, the reaction of *β*-lithio enol ether **1** with ketones such as acetone or cyclohexanone or enolizable aldehydes did not give the adduct and the enol ether **1** was recovered. 1,1,1,2,2-Pentafluoroethyl enol

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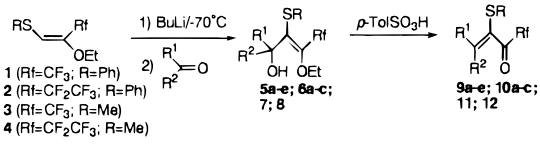
10.1021/jo990282p CCC: $18.00
Published on Web 06/17/1999

Table 1. α-Thiotrifluoroacetylolefinations of Aldehydes and Ketones



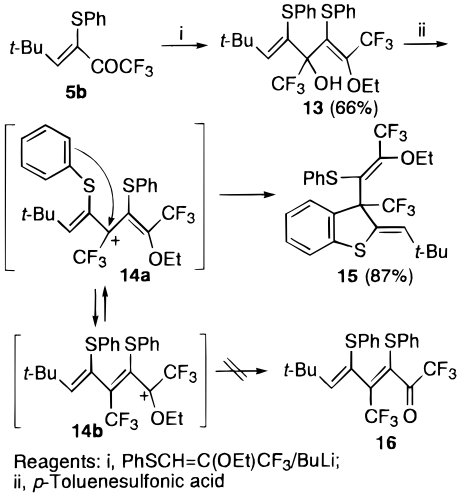
Entry	Enol	Electrophile	Product (%yield)	Product (%yield)
1	1	PhCHO	**5a** (86)	**9a** (91)
2	1	*t*-BuCHO	**5b** (76)	**9b** (88)
3	1	PhCH=CHCHO	**5c** (89)	**9c** (40)
4	1	*t*-Bu—≡—CHO	**5d** (58)	**9d** (78)
5	1	furan-CHO	**5e** (90)	**9e** (70)
6	2	*t*-BuCHO	**6a** (46)	**10a** (67)
7	2	PhCHO	**6b** (84)	**10b** (60)
8	2	Ph—≡—CHO	**6c** (57)	**10c** (85)
9	3	PhCHO	**7a** (79)	**11a** (90)
10	3	PhCH=CHCHO	**7b** (66)	**11b** (67)
11	3	furan-CHO	**7c** (71)	**11c** (55)
12	4	PhCHO	**8a** (44)	**12a** (72)
13	4	PhCH=CHCHO	**8b** (27)	—

ether **2** was also lithiated at −78 °C, and the treatments with almost the same aldehydes afforded (*Z*)-1,1,1,2,2-pentafluoro-4-(phenylthio)pent-4-en-3-ones (**10a**−**c**) in good yields (entries 6−8).

We next examined the lithiation and reaction of the MeS-substituted enol ether **3**. The reaction with benzaldehyde stereoselectively proceeded to give the allylic alcohol **7a**, and successive treatment with *p*-TsOH afforded the MeS-substituted trifluoromethyl ketone **11a** in high yield (entry 9). Other MeS-substituted ketones, **11b**−**c** and **12a**, were also obtained (entries 10−12); however, the dehydration of **8b** gave a complex mixture.

Recently, we reported that the tandem α-(phenylthio)- or α-(phenylseleno)-substituted formylolefinations of aldehydes and ketones stereoselectively proceeded to give the 2,4-bis(phenylthio)- or (phenylseleno)penta-2,4-dienals and 2,4,6-tris(phenylthio)hepta-2,4,6-trienal derivatives in good yields.[6] To examine the tandem α-(phenylthio)trifluoroacetylolefination of the aldehydes, we examined the second addition reaction of PhSCLi=C(OEt)CF_3 to the α,β-unsaturated trifluoromethyl ketone **5b** which proceeded to give octa-2,5-dien-4-ol **13** in 66% yield; however, the treatment of **13** with *p*-toluenesulfonic acid gave the dihydrobenzo[*b*]thiophene (**15**) via the intramolecular cyclization of **14a** and not 1,1,1-trifluoro-7,7-dimethyl-3,5-bis(phenylthio)-4-(trifluoromethyl)octa-3,5-dien-2-one (**16**) via the hydrolysis of **14b** (Scheme 2). The structure of the product **15** was elucidated by showing the existence of an ethoxy group at δ 1.09 (3H, t, J = 7 Hz, Me) and 3.39 (2H, q, J = 7 Hz, OCH_2) in the ^{1}H NMR spectrum, by exhibiting two singlets at δ 8.23 and 18.71 due to the CF_3 groups in the ^{19}F NMR spectrum, and by showing the ion peak assigned to the benzothiophene at m/z 518 (M^+), 449 ($M^+ - CF_3$), and 202 ($M^+ - (CF_3 + PhSC{=}CH(OEt)CF_3)$) in the MS spectrum.

Scheme 2



2-Sulfur- or 2-selenium-stabilized allylic cations have been reported to react with the soft nucleophiles to regioselectively afford the allylated compounds.[12] Trifluoromethyl-substituted allylic cations bearing the 2-sulfur atom are expected to be good electrophiles. Therefore, we examined the reactions of the α-trifluoromethyl-substituted allylic cations stabilized by the sulfur atom at the 2-position. The allylic alcohols **5a** and **7a** were converted to the acetals **17** and **18** by treatment with *p*-toluenesulfonic acid/$CH(OEt)_3$ at 78 °C. The reaction of **17** with allyltrimethylsilane in the presence of $SnCl_4$ was examined; however, it did not undergo the intermolecular allylation but exclusively formed 2-(benzylidene)-3-ethoxy-3-(trifluoromethyl)benzothiophene (**19**) via the intramolecular cyclization. The 3-(methylthio)-substituted **18** also gave the cyclized product **20** in good yield (Scheme 3).

We next investigated how to utilize the α,β-unsaturated trifluoromethyl ketones in the synthesis of other fluorinated compounds. Trifluoromethyl 1,3-dienes[13] or enynes[14] can be employed as useful intermediates for the synthesis of biologically active compounds. Most synthetic

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Scheme 3

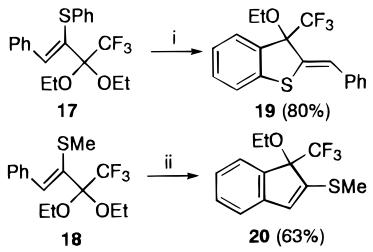
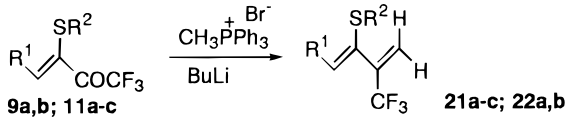


Table 2. Synthesis of 3-Trifluoromethyl-2-(thio)-1,3-butadienes



Entry	Ketone	R^1	R^2	Product (%yield)
1	**11a**	Ph	Me	**21a** (44)
2	**11b**	PhCH=CH	Me	**21b** (85)
3	**11c**	phenylethynyl	Me	**21c** (55)
4	**9a**	*t*-Bu	Ph	**22a** (65)
5	**9b**	Ph	Ph	**22b** (41)

methods for these compounds involve the well-known Wittig type reaction of trifluoromethyl ketones. We first examined the reaction of the enones **11a** with methylenetriphenylphosphorane at −78 °C, and 3-(methylthio)-2-(trifluoromethyl)buta-1,3-diene (**21a**) was obtained in 44% yield (Table 2, entry 1). The structure of **21a** was determined by its NMR spectrum. The ^{1}H NMR spectrum exhibited three olefinic absorptions at δ 5.83, 6.05, and 6.84 ppm. The ^{13}C NMR spectrum shows three carbons at δ 123.36 (t, $J_{C-F} = 5$ Hz) due to the CH_2 and at δ 137.97 (s, $J_{C-F} = 30$ Hz) due to the 2-C. The ^{19}F NMR also exhibited one singlet at δ −12.78 (CF_3). The reaction of cinnamaldehyde gave the triene **21b** in high yield (entry 2). Fluoroenyne **21c** was stereoselectively obtained (entry 3). The phenylthio derivatives **9a**,**b** also gave the dienes **22a**,**b** (entries 4 and 5).

In conclusion, we have reported a convenient method for the α-(thio)-substituted perfluoroacylolefination of nonenolizable aldehydes using the *β*-(thio)-perfluoroalkyl enol ethers. The tandem perfluoroacylolefination did not proceed; however, the α-(thio)-α,*β*-unsaturated trifluoromethyl ketones were steroselectively converted to the 3-(thio)-2-(trifluoromethyl)buta-1,3-dienes.

Experimental Section[12]

General. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard. The ^{19}F NMR (376.4 MHz) spectra were obtained in $CDCl_3$ with trifluoroacetic acid as the external standard. The stereochemistries of the products were determined by NOE experiments.

Preparation of (*E*)-2-Ethoxy-1,1,1-trifluoro-3-(phenylthio)-2-propene (1). Typical Procedure. BuLi was added dropwise to a THF (70 mL) solution of phenylthiomethyltriphenylphosphonium chloride[15] (8.40 g, 20.0 mmol) at −38 °C, and the reaction mixture was stirred for 30 min. Ethyl trifluoroacetate (5.60 g, 40.0 mmol) was added to it. The whole was stirred at room temperature for 3 days and poured into water (150 mL). The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was crystalized from pentane and filtered to remove Ph_3PO. The filtrate was evaporated, and the residue was purified by column chromatography on silica gel eluting with hexane to give the title compound (4.39 g, 88%) as a colorless oil.

(*E*)-2-Ethoxy-1,1,1-trifluoro-3-(phenylthio)prop-2-ene (1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (3H, t, $J = 7$ Hz), 4.11 (2H, q, $J = 7$ Hz), 6.48 (1H, d, $J = 1$ Hz), 7.27−7.36 (3H, m), 7.40−7.42 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.36 (q), 69.00 (t, $J_{C-F} = 3$ Hz, OCH_2), 117.75 (d, $J_{C-F} = 5$ Hz, 3-C), 120.41 (s, $J_{C-F} = 275$ Hz, CF_3), 127.83 (d), 129.40 (d × 2), 130.45 (d × 2), 133.61 (s), 139.95 (s, $J_{C-F} = 34$ Hz, 2-C); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −8.94 (3F, s, CF_3); MS *m*/*z* 171 (M^+ − Ph). Anal. Calcd for $C_{11}H_{11}F_3OS$: C, 53.22; H, 4.47. Found: C, 53.24; H, 4.50.

Preparation of Perfluoroalkyl Allylic Alcohols 5a−e, 6a−c, 7a−c, and 8a,b. Typical Procedure. BuLi (1.60 mL, 2.40 mmol) was added dropwise to a THF (6 mL) solution of 2-ethoxy-1,1,1-trifluoro-3-(phenylthio)-2-propene (0.50 g, 2.00 mmol) at −78 °C under an Ar atmosphere. A THF (2.0 mL) solution of benzaldehyde (0.26 g, 0.24 mmol) was added to the mixture. The reaction mixture was poured into water (100 mL), and the organic layer was separated. The aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by a preparative TLC on silica gel eluting with AcOEt−hexane (1:40) to give (*E*)-2-ethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylthio)-but-2-en-4-ol (**5a**) (0.65 g, 86%) as a pale yellow oil.

(2*E*,5*E*)-2-Ethoxy-1,1,1-trifluoro-6-phenyl-3-(phenylthio)hexa-2,5-dien-4-ol (5c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, t, $J = 7$ Hz), 2.59 (1H, d, $J = 9$ Hz), 3.83−4.00 (2H, m), 5.50 (1H, brt, $J = 7$ Hz), 6.18 (1H, dd, $J = 5$ and 15 Hz), 6.65 (1H, dd, $J = 1$ and 15 Hz), 7.17−7.32 (8H, m), 7.35−7.37 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.03 (q, $J_{C-F} = 4$ Hz, Me), 69.50 (t, $J_{C-F} = 4$ Hz, OCH_2), 69.62 (d, $J_{C-F} = 3$ Hz, 4-C), 121.02 (s, $J_{C-F} = 279$ Hz, CF_3), 126.67 (d × 2), 126.91 (d), 128.00 (d), 128.29 (s), 128.43 (d), 128.52 (d × 2), 129.01 (d × 2), 129.38 (d × 2), 131.95 (d), 132.76 (s), 136.17 (s), 145.99 (s, $J_{C-F} = 34$ Hz, 2-C); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −16.90 (3F, s, CF_3); MS *m*/*z* 380 (M^+). Anal. Calcd for $C_{20}H_{19}F_3O_2S$: C, 63.15; H, 5.03. Found: C, 63.26; H, 5.03.

(*E*)-2-Ethoxy-1,1,1-trifluoro-3-(methylthio)-4-phenylbut-2-en-4-ol (7a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (3H, t, $J = 7$ Hz), 2.23 (3H, s), 2.82 (1H, brd, $J = 9$ Hz), 4.01−4.14 (2H, m), 5.92 (1H, d, $J = 9$ Hz), 7.25−7.43 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.59 (q), 16.92 (q), 69.23 (t), 69.60 (d), 121.34 (s, $J_{C-F} = 278$ Hz, CF_3), 125.80 (d × 2), 127.87 (d), 128.53 (d × 2), 137.03 (s), 140.51 (s), 144.43 (s, $J_{C-F} = 34$ Hz, 2-C); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −17.48 (3F, s, CF_3); MS *m*/*z* 292 (M^+). Anal. Calcd for $C_{13}H_{15}F_3O_2S$: C, 53.42; H, 5.17. Found: C, 53.91; H, 5.21.

(*E*)-3-Ethoxy-1,1,1,2,2-pentafluoro-4-(methylthio)-5-phenylpent-3-en-5-ol (8a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (3H, t, $J = 7$ Hz), 2.22 (3H, s), 2.97 (1H, d, $J = 9$ Hz), 3.97−4.05 (1H, m), 4.19−4.26 (1H, m), 5.93 (1H, d, $J = 9$ Hz), 7.23−7.39 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.30 (q), 16.61 (q), 68.80 (d), 69.25 (t, $J_{C-F} = 4$ Hz, OCH_2), 112.98 (s, $J_{C-F} = 38$ and 259 Hz, CF_2), 118.73 (s, $J_{C-F} = 38$ and 287 Hz, CF_3), 125.65 (d × 2), 127.65 (d), 128.32 (d × 2), 139.61 (s), 140.37 (s), 143.14 (s, $J_{C-F} = 24$ Hz, 3-C); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −32.52 (1F, d, $J = 277$ Hz, CF_2), −30.74 (1F, d, $J = 2$ and 277 Hz, CF_2), −5.35 (3F, t, $J = 2$ Hz, CF_3); MS *m*/*z* 342 (M^+). Anal. Calcd for $C_{14}H_{15}F_5O_2S$: C, 49.12; H, 4.42. Found: C, 49.18; H, 4.49.

(2*E*,5*Z*)-2-Ethoxy-1,1,1-trifluoro-7,7-dimethyl-3,5-bis(phenylthio)-4-(trifluoromethyl)octa-2,5-dien-4-ol (13):

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^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (3H, s, J = 7 Hz), 1.20 (9H, s), 3.69−3.76 (2H, m), 4.31 (1H, brs), 6.95 (1H, brs), 7.16−7.31 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.17 (q), 30.22 (q × 3), 35.99 (s), 68.90 (t), 81.55 (s, J_{C-F} = 27 Hz, 4-C), 120.65 (s, J_{C-F} = 278 Hz, CF_3), 124.30 (s, J_{C-F} = 288 Hz, CF_3), 124.50 (s), 126.58 (d), 126.66 (d), 127.39 (d × 2), 127.58 (d × 2), 129.13 (d × 2), 129.40 (d × 2), 130.22 (s, J_{C-F} = 3 Hz), 135.06 (s), 135.93 (s), 151.17 (s, J_{C-F} = 36 Hz, 2-C), 159.42 (d); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ 6.67 (3F, q, J = 5 Hz, CF_3), 19.15 (3F, q, J = 15 Hz, CF_3); MS m/z 536 (M^+). Anal. Calcd for $C_{25}H_{26}F_6O_2S_2$: C, 55.95; H, 4.88. Found: C, 56.17; H, 4.86.

Isomerization Reactions of Allylic Alcohols by *p*-TsOH. Typical Procedure. A $ClCH_2CH_2Cl$ (13 mL) solution of (*E*)-2-ethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylthio)but-2-en-4-ol (**5a**) (1.33 g, 3.98 mmol) and *p*-TsOH (0.98 g, 5.17 mmol) was refluxed for 10 min. The reaction mixture was poured into a saturated $NaHCO_3$ (150 mL) solution, and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by a column chromatography on silica gel eluting with AcOEt−hexane (1:40) to give (*Z*)-1,1,1-trifluoro-4-phenyl-3-(phenylthio)but-3-en-2-one (**9a**) (1.11 g, 91%) as a yellow oil.

(*Z*)-1,1,1-Trifluoro-4-phenyl-3-(phenylthio)but-3-en-2-one (9a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.27 (5H, m), 7.37−7.48 (3H, m), 7.94−7.97 (2H, m), 8.09 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.69 (s, J_{C-F} = 292 Hz, CF_3), 127.02 (d × 2), 128.69 (d × 2), 129.31 (d × 2), 131.76 (d × 2), 131.77 (d × 2), 133.35 (s), 133.67 (s), 134.87 (s), 150.92 (d), 180.02 (s); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −7.07 (3F, s, CF_3); MS m/z 308 (M^+). Anal. Calcd for $C_{16}H_{11}F_3OS$: C, 62.13; H, 3.91. Found: C, 62.83; H, 3.75.

(*Z*)-1,1,1-Trifluoro-3-(methylthio)-4-phenylbut-3-en-2-one (11a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (3H, s), 7.46−7.51 (3H, m), 7.87 (1H, s), 7.89−7.92 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.22 (q), 116.73 (s, J_{C-F} = 293 Hz, CF_3), 128.80 (d × 2), 131.40 (d), 131.48 (s), 131.88 (d × 2), 133.86 (s), 148.22 (d), 179.53 (s, J_{C-F} = 34 Hz, CO); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −7.97 (3F, s, CF_3); MS m/z 246 (M^+). Anal. Calcd for $C_{11}H_9F_3OS$: C, 53.65; H, 3.68. Found: C, 53.72; H, 3.70.

(*Z*)-1,1,1,2,2-Pentafluoro-4-(methylthio)-5-phenylpent-4-en-3-one (12a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (3H, s), 7.43−7.50 (3H, m), 7.84 (1H, s), 7.84−7.90 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.88 (q), 108.43 (s, J_{C-F} = 36 and 271 Hz, CF_2), 118.06 (s, J_{C-F} = 34 and 288 Hz, CF_3), 128.60 (d × 2), 131.07 (d), 131.60 (d × 2), 132.35 (s), 133.69 (s), 146.98 (d, J_{C-F} = 5 Hz, 5-C), 181.90 (s, J_{C-F} = 34 Hz, CO); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −35.73 (2F, s, CF_2), −3.50 (3F, s, CF_3); MS m/z 296 (M^+). Anal. Calcd for $C_{12}H_9F_5OS$: C, 48.65; H, 3.06. Found: C, 48.66; H, 3.09.

Preparations of 1,1,1-Trifluoro-3-buten-2-one Diethyl Acetals 17 and 18. Typical Procedure. A dry EtOH (10.0 mL) solution of (*E*)-2-ethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylthio)but-2-en-4-ol (1.33 g, 3.75 mmol), ethyl orthoformate (2.78 g, 18.8 mmol), and *p*-TsOH (0.14 g, 0.75 mmol) was refluxed for 10 min. Et_3N (3 drops) was added to a reaction mixture. The workup procedure afforded the title compound (1.03 g, 71%) as a pale yellow oil.

(*Z*)-2,2-Diethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylthio)but-3-ene (17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (6H, t, J = 7 Hz), 3.59−3.61 (2H, m), 3.62−3.74 (2H, m), 6.98−7.02 (1H, m), 7.06−7.16 (2H, m), 7.17−7.23 (5H, m), 7.56 (1H, s), 7.65−7.67 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.15 (qx2), 59.29 (tx2), 100.02 (s, J_{C-F} = 30 Hz, 2-C), 122.78 (s, J_{C-F} = 292 Hz, CF_3), 125.66 (d), 127.34 (s), 128.17 (d × 4), 128.64 (d × 2), 128.89 (d), 130.03 (d × 2), 135.04 (s), 135.69 (s), 142.37 (d); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −2.59 (3F, s, CF_3); MS m/z 382. Anal. Calcd for $C_{20}H_{21}F_3O_2S$: C, 62.81; H, 5.53. Found: C, 62.83; H, 5.49.

(*Z*)-2,2-Diethoxy-1,1,1-trifluoro-3-(methylthio)-4-phenylbut-3-ene (18): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (6H, t, J = 7 Hz), 2.08 (3H, s), 3.63−3.77 (4H, m), 7.25−7.39 (4H, m), 7.75−7.77 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.29 (q × 2), 18.55 (q), 59.33 (t × 2, J_{C-F} = 1 Hz), 100.16 (s, J_{C-F} = 30 Hz, 2-C), 120.49 (s, J_{C-F} = 292 Hz, CF_3), 128.44 (d), 128.50 (d × 2), 129.70 (d × 2), 132.40 (s), 135.90 (s), 138.97 (d, J_{C-F} = 1 Hz, 4-C); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −1.40 (3F, s, CF_3); MS m/z 320. Anal. Calcd for $C_{15}H_{19}F_3O_2S$: C, 56.24; H, 5.98. Found: C, 56.43; H, 5.84.

(*Z*)-2-(Benzylidene)-3-ethoxy-3-(trifluoromethyl)-3*H*-benzo[*b*]thiophene (19): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, J = 7 Hz), 3.08−3.15 (1H, m), 3.42−3.49 (1H, m), 6.07 (1H, s), 6.95 (1H, brd, J = 7 Hz), 7.10−7.19 (1H, m), 7.23−7.27 (1H, m), 7.44−7.47 (4H, m), 7.61−7.62 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.44 (q), 60.24 (t), 120.28 (d), 124.02 (s, J_{C-F} = 285 Hz, CF_3), 124.95 (d), 125.44 (d), 129.55 (d), 129.64 (d), 129.92 (d × 2), 130.61 (d), 131.01 (s), 135.10 (d × 2), 138.34 (s), 143.61 (s), 145.01 (s); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ 0.78 (3F, s, CF_3); MS m/z 336 (M^+). Anal. Calcd for $C_{18}H_{15}F_3OS$: C, 64.27; H, 4.50. Found: C, 64.38; H, 4.58.

1-Ethoxy-2-(methylthio)-1-(trifluoromethyl)indene (20): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (3H, t, J = 7 Hz), 2.48 (3H, s), 3.03−3.10 (1H, m), 3.27−3.35 (1H, m), 6.41 (1H, s), 7.11−7.16 (2H, m), 7.30−7.34 (1H, m), 7.46 (1H, brd, J = 7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −11.12 (q), 15.09 (q), 59.87 (t), 89.74 (s, J_{C-F} = 30 Hz), 119.72 (d), 123.74 (s, J_{C-F} = 285 Hz, CF_3), 124.68 (d), 124.92 (d), 126.22 (d), 130.43 (d), 137.90 (s), 143.73 (s), 144.95 (s); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −1.37 (3F, s, CF_3); MS m/z 227 (M^+ − OEt). Anal. Calcd for $C_{13}H_{13}F_3OS$: C, 56.92; H, 4.78. Found: C, 56.80; H, 4.85.

Syntheses of 3-(Methylthio)- or 3-(Phenylthio)-2-(trifluoromethyl)-1,3-butadienes 21a−c and 22a−b. Typical Procedure. Under an Ar atmosphere, BuLi (1.30 mL, 2.00 mmol) was added to a THF (5 mL) solution of methyltriphenylphosphonium bromide (0.71 g, 2.00 mmol) at −30 °C. The mixture was stirred for 30 min and then cooled to −78 °C. A THF (1 mL) solution of (*Z*)-1,1,1-trifluoro-3-(methylthio)-4-phenylbut-3-en-2-one (**11a**) (0.25 g, 1.00 mmol) was added dropwise to the mixture. The whole was stirred overnight at room temperature. The workup procedure afforded (*Z*)-3-(methylthio)-4-phenyl-2-(trifluoromethyl)buta-1,3-diene (**21a**) (0.11 g, 44%) as a yellow oil.

(*Z*)-5,5-Dimethyl-3-(phenylthio)-2-(trifluoromethyl)-hexa-1,3-diene (22a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (9H, s), 5.65 (1H, s), 5.73 (1H, d, J = 2 Hz), 6.45 (1H, s), 7.12−7.26 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.60 (q × 3), 30.76 (s), 122.54 (t, J_{C-F} = 5 Hz, 1-C), 123.19 (s, J_{C-F} = 275 Hz, CF_3), 125.97 (s), 126.48 (d), 129.12 (d × 2), 129.37 (d × 2), 135.15 (s), 137.87 (s, J_{C-F} = 29 Hz, 2-C), 152.90 (d); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −14.37 (3F, s, CF_3); MS m/z 286 (M^+). Anal. Calcd for $C_{15}H_{17}F_3S$: C, 62.92; H, 5.98. Found: C, 62.74; H, 6.04.

Acknowledgment. The support of a part of this work by the Ministry of Education, Science and Culture, Japan, is gratefully acknowledged.

Supporting Information Available: Characterization data for the products **2−4, 5a−c, 5e, 6a−c, 7b−c, 8b, 9b−e, 10a−c, 11b−c, 15, 21a−c,** and **22b** and ^{1}H NMR spectra, complete with peak assignments of other products and full lists of the IR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990282P