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# New [4+1]-cycloadditions to trifluorinated dienes [1]

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**Abstract**

2,2-Bis(trifluoromethyl)-4-methyl-2,5-dihydrothiophene (**5**), 2,2-bis(trifluoromethyl)-4-methyl-2,5-dihydroselenophene (**6**), 2-trifluoromethyl-2,4-dimethyl-2,5-dihydrothiophene (**7**) and 2-trifluoromethyl-2,4-dimethyl-2,5-dihydroselenophene (**8**) were prepared from 5,5,5-trifluoro-4-trifluoromethyl-2-methyl-penta-1,3-diene and 5,5,5-trifluoro-2,4-dimethyl-penta-1,3-diene by reaction with elemental sulphur or selenium. 5,5,5-Trifluoro-4-trifluoromethyl-pent-3-en-2-one and 5,5,5-trifluoro-4-methyl-pent-3-en-2-one were treated with bromine and HBr. The 1,4-dibrominated products isolated did not undergo a metathesis reaction with $K_2S$. © 1997 Elsevier Science S.A.

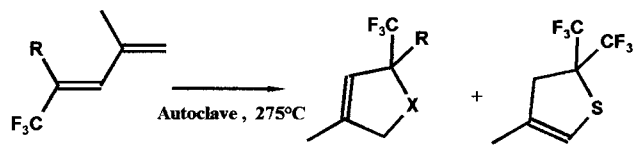
*Keywords:* Addition of HBr; Chalcogenophenes; [4+1]-Cycloadditions; Radical bromination; Trifluoromethylated dienes

## 1. Introduction, results and discussion

There are a limited number of literature references describing the preparation of chalcogenophenes by the [4+1]-cycloaddition of elemental chalcogens to trifluoromethylated conjugated dienes. The 4,4-bistrifluoromethylated 1,3-heterodienes are among the most reactive conjugated dienes [1]. Thus the reaction of 4,4-bis(trifluoromethyl)-1-thio-3-aza-buta-1,3-dienes with elemental sulphur or selenium in boiling toluene under reflux conditions leads to the corresponding heterocyclic systems [2].

[4+1]-Cycloadditions to trifluorohomodienes have not previously been studied. Some new trifluorinated homodienes, suitable for cyclization, were synthesized by treatment of 1-triphenylphosphoranyliden-2-propanone with hexa- or tri-fluoroacetone giving 5,5,5-trifluoro-4-trifluoromethyl-penta-3-en-2-one (**1**) and 5,5,5-trifluoro-4-methyl-penta-3-en-2-one (**2**). These products were methylated using the Grignard reagent $CH_3MgI$, and subsequently dehydrated with concentrated sulphuric acid yielding 5,5,5-trifluoro-4-trifluoromethyl-2-methyl-penta-1,3-diene [3] (**3**) and 5,5,5-trifluoro-2,4-dimethyl-penta-1,3-diene (**4**). The product from the reaction of **2** with $CH_3MgI$, 5,5,5-trifluoro-2,4-dimethyl-pent-3-ene-2-ole (**2a**), could be isolated and was fully characterized.

Compounds **3** and **4** were reacted with elemental sulphur or selenium in an autoclave without a solvent and in the presence of anhydrous trifluoroacetic acid anhydride (TFAA) as catalyst. The corresponding chalcogenophene derivatives were formed from **3** and **4** according to Scheme 1. The products from the reaction of **4** could only be identified by GC/MS analysis. The reaction of **3** with sulphur gave two stable products. In addition to the 2,5-dihydro derivative (**5**), it was possible to isolate 2,2-bis(trifluoromethyl)-4-methyl-2,3-dihydrothiophene (**9**) (see Scheme 1).

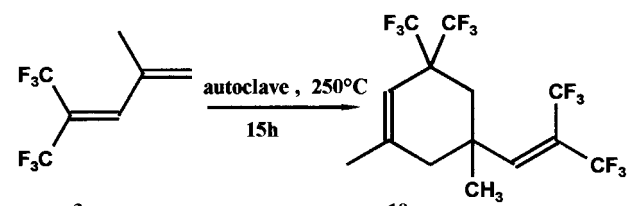



R = $CF_3$ (3), X = S (5), X = Se (6) 9

R = $CH_3$ (4), X = S (7), X = Se (8)

Scheme 1.

In each autoclave reaction a dimer of **3** was obtained, namely 1,1-bis(trifluoromethyl)-3-(1,1,1,4,4,4-hexafluoro-but-2-en-3-yl)-3,5-dimethyl-cyclohex-5-ene (**10**) (see Scheme 2).




3 10

Scheme 2.

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[1] Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday.


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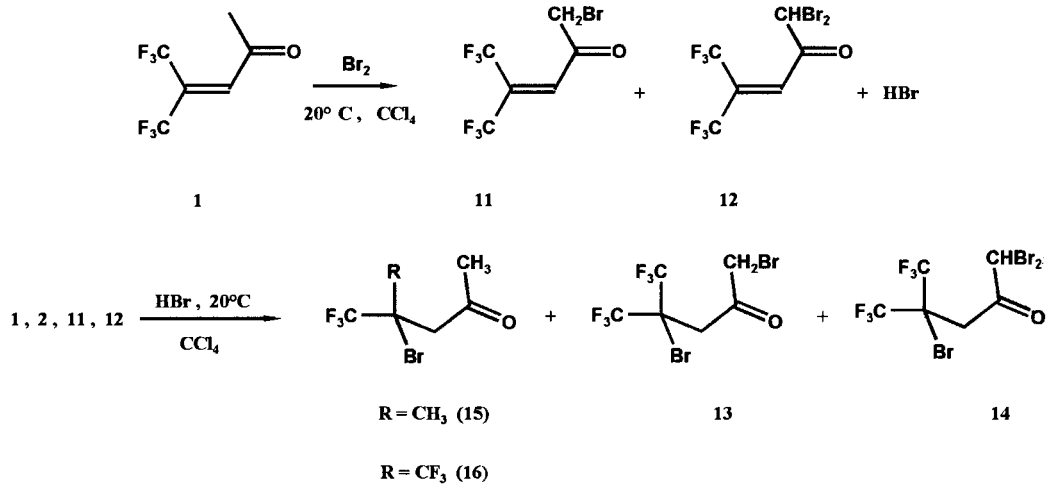


Scheme 3.

It is known that chalcogenophene derivatives can be prepared from 1,4-dihalogenated species. Thus **1** and **2** were treated with elemental bromine in $CCl_4$. Whilst **2** yielded a wide variety of unidentified products, four species were isolated in the reaction of **1**, as shown in Scheme 3, namely 5,5,5-trifluoro-4-trifluoromethyl-1-bromo-penta-3-ene-2-one (**11**), 5,5,5-trifluoro-4-trifluoromethyl-1,1-dibromo-penta-3-ene-2-one (**12**), 5,5,5-trifluoro-4-trifluoromethyl-1,4-dibromo-pentane-2-one (**13**) and 5,5,5-trifluoro-4-trifluoromethyl-1,1,4-tribromo-pentane-2-one (**14**). The formation of **13** and **14** can be explained by the Markovnikov addition of HBr to **11** and **12**. During the bromination of **1** to synthesize **11** and **12**, HBr is formed by radical H substitution in the methyl group (see Scheme 3).

The pure compounds **11** and **12** reacted readily with HBr forming **13** and **14**. In the same way, **1** and **2** were treated with HBr to prepare 5,5,5-trifluoro-4-trifluoromethyl-4-bromo-pentane-2-one (**15**) and 5,5,5-trifluoro-4-methyl-4-bromo-pentane-2-one (**16**).

All attempts to obtain the chalcogenophenes by reacting compounds **13** and **14** with nucleophiles, e.g. $K_2S$, in polar solvents at various temperatures failed. This can probably be attributed to the reduced stability of the bistrifluoromethylated carbocation formed during the substitution.

## 2. Experimental details

Volatile compounds were handled in a vacuum line and air-sensitive solids in a glove box (Co. M. Braun GmbH, München). Solvents were distilled before use and dried according to published procedures [4]. Deuterated solvents were dried and transferred from activated molecular sieves (4 Å). Microanalyses were performed using a Carlo-Erba elemental analyser model 1106. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ solution using a Bruker WM 250 PFT (internal standards, $Si(CH_3)_4$ ($^1H$, $^{13}C$); $CFCl_3$ ($^{19}F$)). IR spectra were recorded using a Bruker FT-IR IFS 85 (4000–400 $cm^{-1}$) (solids as KBr pellets and liquids as capillary films). Very weak bands and shoulders were not reported. Mass spectrometry (MS) was performed using a Varian MAT CH7 (70 eV). Gas chromatography/mass spectrometry (GC/MS) was performed using a Hewlett Packard 5989 A combined with a Hewlett Packard 5890 (12.5 m capillary column covered with OV1; 70 eV; CI: methane). Analytical gas chromatography was performed using a Hewlett Packard 5890 Series III and Varian Aerograph 920 (stationary phase: OV1, OV17, OV101 and Carbowax 20 M). Preparative gas chromatography was performed using a Perkin–Elmer F 21 (stationary phase: OV17 and OV1).

Starting materials, such as sulphur and selenium, were commercially available and were used without further purification. The compounds **1** and **2** were prepared by published methods [3,5].

### *2.1. 5,5,5-Trifluoro-2,4-dimethyl-pent-3-ene-2-ole (**2a**)*

In a 100 ml three-necked flask, equipped with a magnetic stirring bar, a reflux condenser and a dropping funnel, 1.22 g (50 mmol) of magnesium for the Grignard reaction and a small amount of Mg powder were added to 60 ml of dried diethylether. In an argon atmosphere, an equimolar amount of methyl iodide (7.11 g) in 20 ml of ether was added dropwise with stirring. When all the Mg had reacted, 6.08 g (40 mmol) of **2** was added over a period of 1 h. After stirring for a further 3 h, the reaction mixture was hydrolysed with 15 ml of ice–water. The water layer was extracted three times with ice-cooled ether and the organic layer was dried with $MgSO_4$. The mixture was fractionally distilled and, after removal of the solvent, pure **2a** was obtained. Yield, 5.58 g (83%). B.p., 129.5 °C. IR (film) ($cm^{-1}$): 3200–3300 (OH), 2979 (CH), 1679 (C=C), 1112–1367 (CF). $^1H$ NMR $\delta$: 1.35 (s, $CH_3$), 1.95 (m, $CH_3$), 2.25 (s, OH), 6.05 (m, C=C–H). $^{13}C$ NMR $\delta$: 11.0 (dq, $^1J(HC) = 129.7$ Hz, $^3J(HC) = 7.6$ Hz, $CH_3$),

30.4 (q, $^1J$(CH) = 127.2 Hz, $CH_3$), 70.8 (d, $^2J$(**C**–O**H**) = 3.8 Hz), 124.3 (q, $^1J$(CF) = 265.1 Hz, $CF_3$), 125.8 (m), 138.6 (d, $^1J$(CH) = 152.6 Hz). $^{19}$F NMR $\delta$: −70.5 (s). MS, $m/z$ (%): 168 (1) [$M^+$], 153 (97) [$M^+ - CH_3$], 148 (40) [$M^+ - HF$], 105 (100) [$C_5H_7F_2^+$]. $C_7H_{11}F_3O$ (168.2): calculated: C, 49.9%; H, 6.6%; found: C, 49.5%; H, 6.7%.

### 2.2. 5,5,5-Trifluoro-2,4-dimethyl-penta-1,3-diene (4)

Compound **2a** (3.43 g, 20.4 mmol) was added dropwise at 22 °C with stirring to 20 ml of concentrated sulphuric acid in a 100 ml two-necked flask. After 1 h, the reaction was complete and pure **4** was isolated by fractional distillation using a 10 cm vigreux column. Yield, 2.80 g (91%). B.p., 84.5 °C. IR (film) (cm$^{-1}$): 1633 (C=C), 1114–1363 (CF). $^1$H NMR $\delta$: 1.88 (m, $CH_3$), 1.92 (m, $CH_3$), 5.0–5.2 (m, C=$CH_2$), 6.40 (m, C=C–H). $^{13}$C NMR $\delta$: 11.6 (dq, $^1J$(HC) = 129.1 Hz, $^3J$(HC) = 7.5 Hz, $CH_3$), 22.2 (q, $^1J$(HC) = 125.9 Hz), 112.6 (q, $^1J$(CF) = 272.8 Hz, $CF_3$), 118.4 (t, $^1J$(HC) = 157.4 Hz, C=**C**$H_2$), 125.1 (q, $^2J$(CF) = 28.6 Hz), 132.8 (d, $^1J$(CH) = 154.5 Hz, C=**C**–H), 139.3 (m, C2). $^{19}$F NMR $\delta$: −70.1 (s). MS, $m/z$ (%): 150 (95) [$M^+$], 135 (25) [$M^+ - CH_3$], 81 (100) [$M^+ - CF_3$]. $C_7H_9F_3$ (150.1): calculated: C, 56.0%; H, 6.0%; found: C, 55.2%; H, 5.9%.

### 2.3. General procedure for the synthesis of compounds 5–9

Equimolar amounts of the enones and the chalcogens, 1 g of hydroquinone and 200 mg of TFAA as catalyst were placed in a 50 ml stainless autoclave which was then cooled to −196 °C. The air in the autoclave was changed to 0.8 bar of Ar and the mixture was heated for about 7 h at 275 °C. The liquid products were distilled into a glass trap cooled to −196 °C. The products were further purified by preparative gas chromatography (OV 17, 120 °C).

#### 2.3.1. 2,2-Bis(trifluoromethyl)-4-methyl-2,5-dihydrothiophene (5)

Compound **1** (5 g, 25 mmol) and sulphur (0.8 g, 25 mmol). Yield, 4.2 g (71%). IR (film) (cm$^{-1}$): 1650 (C=C), 1102–1358 (CF). $^1$H NMR $\delta$: 1.95 (s, $CH_3$), 3.80 (s, $CH_2$), 5.40 (s, C=C–H). $^{13}$C NMR $\delta$: 16.6 (s, DEPT $CH_3$), 42.2 (s, DEPT $CH_2$), 72.0 (m, **C**$(CF_3)_2$), 116.3 (s, DEPT CH), 134.5 (q, $^1J$(CF) = 281.7 Hz), 149.3 (s, DEPT C). $^{19}$F NMR $\delta$: −71.6 (s). MS, $m/z$ (%): 236 (33) [$M^+$], 167 (100) [$M^+ - CF_3$]. $C_7H_6F_6S$ (236.2): calculated: C, 35.6%; H, 2.6%; S, 13.6%; found: C, 36.1%; H, 2.4%; S, 13.4%.

#### 2.3.2. 2,2-Bis(trifluoromethyl)-4-methyl-2,5-dihydroselenophene (6)

Compound **1** (5 g, 25 mmol) and selenium (2.0 g, 25 mmol). Yield, 4.83 g (68%). IR (film) (cm$^{-1}$): 1676 (C=C), 1093–1355 (CF). $^1$H NMR $\delta$: 1.95 (s, $CH_3$), 3.85 (s, $CH_2$), 5.40 (s, C=C–H). $^{13}$C NMR $\delta$: 18.3 (s, DEPT $CH_3$), 34.9 (s, DEPT $CH_2$), 117.8 (s, DEPT CH), 150.7 (s, DEPT C). $^{19}$F NMR $\delta$: −68.8 (s). MS, $m/z$ (%): 284 (57) [$M^+$], 215 (100) [$M^+ - CF_3$]. $C_7H_6F_6Se$ (283.1): calculated: C, 29.7%; H, 2.1%; found: C, 29.5%; H, 2.3%.

#### 2.3.3. 2-Trifluoromethyl-2,4-dimethyl-2,5-dihydrothiophene (7)

Compound **2** (3.7 g, 25 mmol) and sulphur (0.8 g, 25 mmol). Characterized only by GC/MS analysis. MS, $m/z$ (%): 182 (65) [$M^+$], 113 (100) [$M^+ - CF_3$].

#### 2.3.4. 2-Trifluoromethyl-2,4-dimethyl-2,5-dihydroselenophene (8)

Compound **2** (3.7 g, 25 mmol) and selenium (2.0 g, 25 mmol). Characterized only by GC/MS analysis. MS, $m/z$ ($^{80}$Se, %): 230 (58) [$M^+$], 161 (100) [$M^+ - CF_3$].

#### 2.3.5. 2,2-Bis(trifluoromethyl)-4-methyl-2,3-dihydrothiophene (9)

MS, $m/z$ (%): 236 (38) [$M^+$], 167 (100) [$M^+ - CF_3$]. $C_7H_6F_6S$ (236.2).

### 2.4. 1,1-Bis(trifluoromethyl)-3-(1,1,1,4,4,4-hexafluoro-but-2-en-3-yl)-3,5-dimethyl-cyclohex-5-ene (10)

Compound **1** (3 g, 14.6 mmol) and 200 mg TFAA as catalyst were placed in a 50 ml stainless autoclave and cooled to −196 °C. The air in the autoclave was changed to 0.8 bar of Ar. The reaction mixture was heated for about 15 h at 250 °C. The liquid products were distilled into a glass trap cooled to −196 °C. The product was purified by preparative gas chromatography (OV 17, 135 °C). Yield, 2.16 g (72%). B.p., 88.5 °C at 20 mbar. IR (film) (cm$^{-1}$): 1640–1658 (C=C), 1096–1304 (CF). $^1$H NMR $\delta$: 1.5 (s, $CH_3$), 1.7 (s, $CH_3$), 2.1 (m, $CH_2$), 2.2 (m, $CH_2$), 5.3 (s, C=C–H), 7.2 (s, C=C–H). $^{13}$C NMR $\delta$: 20.7 (s, DEPT $CH_3$), 23.5 (s, DEPT $CH_3$), 26.3 (s, DEPT $CH_2$), 31.8 (s, DEPT $CH_2$), 40.9 (s, DEPT C), 58.8 (q, $^2J$(CF) = 23.1 Hz), 111.2 (s, DEPT CH), 142.6 (s, DEPT CH), 147.9 (s, DEPT C). $^{19}$F NMR $\delta$: −63.9 (s), −53.4 (q, $^4J$(CF) = 9 Hz, $CF_3$), −64.6 (q, $^4J$(CF) = 9 Hz, $CF_3$). MS, $m/z$ (%): 408 (12) [$M^+$], 339 (7) [$M^+ - CF_3$], 204 (100) [$C_7H_6F_6^+$] (retro Diels–Alder). $C_{14}H_{12}F_{12}$ (408.2): calculated: C, 41.2%; H, 3.0%; found: C, 41.6%; H, 3.1%.

### 2.5. General procedure for the synthesis of compounds 11–14

A solution of 6 g of $Br_2$ in 20 ml of $CCl_4$ was added dropwise at 0 °C over a period of 1.5 h to a stirred solution of 6 g (29.1 mmol) of the enone **1** in 50 ml of $CCl_4$ in a 250 ml three-necked flask. All the compounds were purified by preparative gas chromatography (OV 17, 138 °C and 172 °C).

*2.5.1. 5,5,5-Trifluoro-4-trifluoromethyl-1-bromo-pent-3-en-2-one (**11**)*

Yield, 4.00 g (48%). IR (film) ($cm^{-1}$): 3030 (CH), 1723 (CO), 1678 (C=C), 1174–1382 (CF). $^1$H NMR $\delta$: 4.1 (s, $CH_2Br$), 7.2 (s, C=C–H). $^{13}$C NMR $\delta$: 32.7 (t, $^1J$(CH) = 153.5 Hz, $CH_2Br$), 119.7 (dq, $^1J$(CF) = 275.3 Hz, $^3J$(CH) = 13.4 Hz, $CF_3$), 120.0 (dq, $^1J$(CF) = 274.0 Hz, $^3J$(CH) = 7.6 Hz, $CF_3$), 126.6 (dqq, $^2J$(CF) = 34.3 Hz, $^2J$(CF) = 34.3 Hz, $^2J$(CH) = 3.8 Hz, $(CF_3)_2$**C**=C), 138.0 (d, $^1J$(CH) = 164.0 Hz), 190.4 (s, CO). $^{19}$F NMR $\delta$: −61.1 (q, $^4J$(FF) = 6.7 Hz, E-$CF_3$), −66.1 (q, $^4J$(FF) = 6.7 Hz, Z-$CF_3$). MS, PCI, $m/z$ (%, $^{79}$Br): 285 (100) [$M^+ + 1$], 265 (29) [$M^+ - F$], 191 (8) [$M^+ - CH_2Br$]. $C_6H_3F_6BrO$ (284.8): calculated: C, 25.26%; H, 1.1%; found: C, 25.1%; H, 1.1%.

*2.5.2. 5,5,5-Trifluoro-4-trifluoromethyl-1,1-dibromo-pent-3-en-2-one (**12**)*

Yield, 2.5 g (24%). IR (film) ($cm^{-1}$): 3024 (CH), 1732 (CO), 1673 (C=C), 1178–1382 (CF). $^1$H NMR $\delta$: 5.9 (s, $CHBr_2$), 7.6 (s, C=C–H). $^{13}$C NMR $\delta$: 39.5 (d, $^1J$(CH) = 181.2 Hz, $CHBr_2$), 119.7 (dq, $^1J$(CF) = 275.3 Hz, $^3J$(CH) = 11.4 Hz, Z-$CF_3$), 120.3 (dq, $^1J$(CF) = 275.9 Hz, $^3J$(CH) = 7.6 Hz, E-$CF_3$), 130.1 (dqq, $^2J$(CF) = 34.3 Hz, $^2J$(CF) = 34.3 Hz, $^2J$(CH) = 3.8 Hz, $(CF_3)_2$**C**=C), 133.6 (d, $^1J$(CH) = 163.1 Hz), 183.7 (s, CO). $^{19}$F NMR $\delta$: −61.3 (q, $^4J$(FF) = 6.9 Hz, E-$CF_3$), −66.1 (q, $^4J$(FF) = 6.7 Hz, Z-$CF_3$). MS, PCI, $m/z$ (%, $^{79}$Br): 363 (51) [$M^+ + 1$], 343 (22) [$M^+ - F$], 191 (37) [$M^+ - CHBr_2$]. $C_6H_2F_6Br_2O$ (363.9): calculated: C, 19.8%; H, 0.6%; found: C, 19.8%; H, 0.5%.

*2.5.3. 5,5,5-Trifluoro-4-trifluoromethyl-1,4-dibromo-pentane-2-one (**13**)*

Yield, 1.3 g (12%). IR (film) ($cm^{-1}$): 2946 (CH), 1744 (CO), 1087–1383 (CF). $^1$H NMR $\delta$: 3.5 (s, $CH_2$), 4.0 (s, $CH_2Br$). $^{13}$C NMR $\delta$: 34.5 (t, $^1J$(CH) = 152.6 Hz, $CH_2Br$), 39.9 (t, $^1J$(CH) = 132.6 Hz, $CH_2$), 55.3 (esep, $^2J$(CF) = 31.5 Hz, $^2J$(CH) = 4.8 Hz, **C**$(CF_3)_2$Br), 121.8 (q, $^1J$(CF) = 286.1 Hz, $CF_3$), 192.4 (m, CO). $^{19}$F NMR $\delta$: −70.7 (s). MS, PCI, $m/z$ (%, $^{79}$Br): 365 (51) [$M^+ + 1$], 344 (5.5) [$M^+ - F$]. $C_6H_4F_6Br_2O$ (366.0): calculated: C, 19.7%; H, 1.1%; found: C, 19.9%; H, 1.2%.

*2.5.4. 5,5,5-Trifluoro-4-trifluoromethyl-1,1,4-tribromo-pentane-2-one (**14**)*

Yield, 1.3 g (10%). IR (film) ($cm^{-1}$): 1746 (CO), 1085–1380 (CF). $^1$H NMR $\delta$: 3.9 (s, $CH_2$), 5.9 (s, $CHBr_2$). $^{13}$C NMR $\delta$: 36.2 (t, $^1J$(CH) = 132.6 Hz, $CH_2$), 41.9 (d, $^1J$(CH) = 179.3 Hz, $CHBr_2$), 54.9 (tsep, $^2J$(CF) = 31.5 Hz, $^2J$(CH) = 4.8 Hz, **C**$(CF_3)_2$Br), 121.8 (q, $^1J$(CF) = 284.1 Hz, $CF_3$), 186.4 (m, CO). $^{19}$F NMR $\delta$: −70.7 (s). MS, PCI, $m/z$ (%, $^{79}$Br): 443 (37) [$M^+ + 1$], 423 (4) [$M^+ - F$], 271 (52) [$M^+ - CHBr_2$]. $C_6H_3F_6Br_3O$ (444.8): calculated: C, 16.2%; H, 0.7%; found: C, 16.4%; H, 0.6%.

*2.6. General procedure for the synthesis of compounds **15** and **16***

The enone (48.5 mmol, 10 g of **1** or 7.3 g of **2**) was placed in a 100 ml Carius tube with a Teflon-stemmed glass Young valve, and cooled to −196 °C. An equimolar amount of HBr (3.92 g) was added in vacuo. After warming to 20 °C, the reaction mixture was stirred for 1 h. The products were purified by vacuum distillation into a −60 °C trap. The excess of HBr condensed in a liquid-nitrogen-cooled trap.

*2.6.1. 5,5,5-Trifluoro-4-trifluoromethyl-4-bromo-pentane-2-one (**15**)*

Yield, 13.7 g (99%). IR (film) ($cm^{-1}$): 1727 (CO), 1069–1364 (CF). $^1$H NMR $\delta$: 2.2 (s, $CH_3$), 3.1 (s, $CH_2$). $^{13}$C NMR $\delta$: 31.6 (q, $^1J$(CH) = 128.4 Hz, $CH_3$), 43.7 (t, $^1J$(CH) = 131.6 Hz, $CH_2$), 55.5 (tsep, $^2J$(CF) = 31.5 Hz, $^2J$(CH) = 4.8 Hz, **C**$(CF_3)_2$Br), 121.9 (q, $^1J$(CF) = 283.6 Hz, $CF_3$), 198.9 (s, CO). $^{19}$F NMR $\delta$: −70.4 (s). MS, $m/z$ (%, $^{79}$Br): 286 (3) [$M^+$], 243 (30) [$M^+ - C(O)CH_3$], 69 (100) [$CF_3$]. $C_6H_5F_6BrO$ (286.9): calculated: C, 25.1%; H, 1.7%; found: C, 26.0%; H, 1.8%.

*2.6.2. 5,5,5-Trifluoro-4-methyl-4-bromo-pentane-2-one (**16**)*

Yield, 11.1 g (98%). IR (film) ($cm^{-1}$): 1726 (CO), 1096–1383 (CF). $^1$H NMR $\delta$: 1.8 (s, $CH_3$), 2.1 (s, $CH_3$), 2.9 (m, $CH_2$). $^{13}$C NMR $\delta$: 23.5 (qq, $^1J$(CH) = 131.7 Hz, $^4J$(CF) = 1.3 Hz, $CH_3$), 31.7 (q, $^1J$(CH) = 127.8 Hz, $CH_3$), 48.0 (t, $^1J$(CH) = 128.7 Hz, $CH_2$), 55.3 (q, $^2J$(CF) = 30.5 Hz, **C**$(CF_3)(CH_3)$Br), 124.6 (q, $^1J$(CF) = 279.1 Hz, $CF_3$), 201.9 (s, CO). $^{19}$F NMR $\delta$: −78.5 (s). MS, $m/z$ (%, $^{79}$Br): 232 (3) [$M^+$], 189 (14) [$M^+ - C(O)CH_3$], 153 (100) [$M^+ - Br$], 69 (42) [$CF_3$]. $C_6H_8F_3BrO$ (232.9): calculated: C, 30.9%; H, 3.4%; found: C, 31.4%; H, 3.6%.

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