

# Synthesis and reaction of $\beta,\beta$ -di(trifluoroacetyl)ethylene derivatives, $(\text{CF}_3\text{CO})_2\text{C}=\text{CR}_1\text{R}_2$

ShiZheng Zhu \*, Bin Xu, Jie Zhang

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 LingLing Lu, Shanghai 200032, People's Republic of China

Received 25 August 1994; accepted 14 May 1995

## Abstract

Reaction of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione with aromatic aldehydes, alkyl formate and *N,N*-dialkyl amides in acetic acid anhydride gave  $\beta,\beta$ -di(trifluoroacetyl)ethylene derivatives,  $(\text{CF}_3\text{CO})_2\text{C}=\text{CR}_1\text{R}_2$ , which reacted readily with some nucleophiles containing reactive hydrogen such as  $\text{ArSH}$ ,  $\text{HP}(\text{O})(\text{OR})_2$  giving the corresponding addition product. When treated with 3,4-dihydro-2*H*-pyran, a cycloaddition product was formed.

**Keywords:** Condensation; Hexafluoro-2,4-pentanedione; Carbonyl compounds; Di(trifluoroacetyl)ethylene derivatives; Nucleophilic addition; NMR/IR spectroscopy

## 1. Introduction

In recent years much research has been carried out on the reactions of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione,  $\text{CF}_3\text{COCH}_2\text{COCF}_3$  (**1**), which is now commercially available. In this work, compound **1** was mainly used to prepare heterocycles containing the trifluoroacetyl or trifluoromethyl group by the reactions with hydrazine, aminothiols, aminopyrazol and some aniline derivatives [1–6]. However, other chemical transformations of **1** have rarely been studied. Recently, Pashkevich et al. reported that treatment of **1** with aldehydes under basic conditions gave  $\alpha,\beta$ -unsaturated ketones [7], thus:

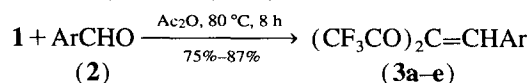


In this paper, we wish to report the condensation reactions of **1** with some carbonyl compounds such as  $\text{ArCHO}$ ,  $\text{HCOOR}$  and  $\text{RCONR}_2$ . From these reactions,  $\beta,\beta$ -di(trifluoroacetyl)ethylene derivatives,  $(\text{CF}_3\text{CO})_2\text{C}=\text{CR}_1\text{R}_2$  (**3**), were prepared. The polar carbon–carbon double bond caused by the electron-withdrawing group  $\text{CF}_3\text{CO}$ – was easily saturated by some nucleophiles containing reactive hydrogen,  $\text{NuH}$ .


## 2. Results and discussion

In our previous work, 1-aryl-2,2-di(perfluoroalkanesulfonyl)alkenes,  $(\text{R}_f\text{SO}_2)_2\text{C}=\text{CHAr}$ , were prepared from

the reactions of  $(\text{R}_f\text{SO}_2)_2\text{CH}_2$  with the corresponding aromatic aldehydes [8,9]. As an extension of this work, we found that this synthetic method can also be applied to prepare 1-aryl-2,2-di(trifluoroacetyl)alkenes,  $(\text{CF}_3\text{CO})_2\text{C}=\text{CHAr}$  (**3**). Heating a 1:1 mixture of **1** and the aromatic aldehydes in  $\text{Ac}_2\text{O}$  gave **3** in good yield:



$\text{Ar} = \text{C}_6\text{H}_5$  (**2a**); 4- $\text{CH}_3\text{C}_6\text{H}_4$  (**2b**); 4- $\text{CH}_3\text{OC}_6\text{H}_4$  (**2c**);

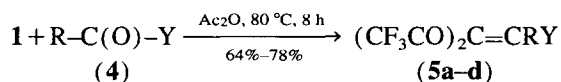
4- $\text{ClC}_6\text{H}_4$  (**2d**);  (**2e**)

The products **3** are yellowish liquids which are purified by vacuum distillation. The structure of all these new compounds are fully supported by their spectroscopic data and microanalyses. The  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR spectra indicate that the two trifluoroacetyl groups in compounds **3** are chemically unequal. For example, the  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR of compound **3c** are  $\delta_{\text{F}} -5.5; 0.0$  ppm (TFA as an external standard and upfield as positive);  $\delta_{\text{C}} 186.8$  (q);  $178.8$  (q);  $116.6$  (q);  $115.6$  (q) ppm for two different  $\text{CF}_3\text{CO}$  groups. They are chemically nonequivalent: one is *trans* to hydrogen and the other is *trans* to the aryl group. The large chemical shifts between the two carbonyl carbons ( $\Delta\delta = 8$  ppm) may be due to the carbons *cis* to the aryl group lying in the shielding cone of the aromatic ring. The  $\text{CF}_3\text{CO}$  group, which is on the same side as the hydrogen atom, has upfield chemical shifts (i.e.

\* Corresponding author.

$\delta_F$  – 76.8 ppm;  $\delta_C$  178.8; 115.6 ppm). Recently, the hydrocarbon analogues  $Y_2C=CHAr$  [ $Y=RCO, ROC(O)$ ] have been prepared by a two-step reaction [10]. In our case, compounds **3** are obtained more conveniently.

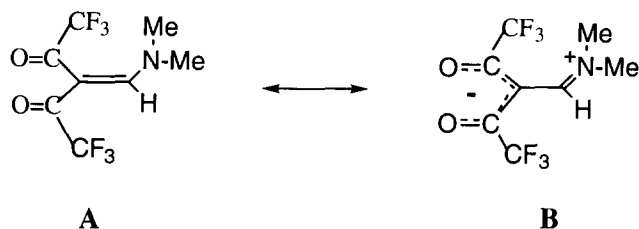
Extension of this reaction to other carbonyl compounds such as *N,N*-dialkyl amides and diethyl formate  $HCONR_2$ ,  $CH_3CONR_2$ ,  $HCOOEt$  are successful. Under the same reaction conditions, several  $\beta,\beta$ -di(trifluoroacetyl)ethylene derivatives are prepared:



$R=H$ ,  $Y=NMe_2$  (**4a**);  $R=H$ ,  $Y=NEt_2$  (**4b**);  $R=CH_3$ ,  $Y=NMe_2$  (**4c**);  $R=H$ ,  $Y=OEt$  (**4d**)

The compounds **5b** and **5d** were first reported by Schreiber [11] and Hojo et al. [12]. They were synthesized by treatment of  $(CF_3CO)_2O$  with  $Et_3N$  and  $EtOCH=CH_2$ , respectively.

In contrast to compound **3**, the NMR spectra of **5** show that the two  $CF_3CO$  groups are apparently equivalent due to the electron donation of the  $-NR_2$  or  $-OR$  group:



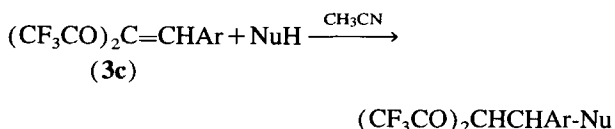
The true nature of the bonding and the  $\pi$ -electron distribution is probably closer to canonical form **B** than it is to canonical form **A**. This phenomenon is known in other 'push-pull' alkenes, although the present case shows the effect to an extreme extent.

The  $^{13}C$  NMR spectra of compounds **3** and **5** appear to support this. For example, the chemical shift of  $(CF_3CO)_2C=$  in compound **3c** is 115.6 ppm and it is only 101.0 ppm in compound **5a**.

Attempts to prepare di(trifluoroacetyl)ketene dimethyl acetal,  $(CF_3CO)_2C=C(OMe)_2$ , by similar treatment of **1** with  $(MeO)_2C=O$  failed.

All these results are summarized in Table 1.

Recently we found that the dialkyl phosphite  $HP(O)(OR)_2$  (**6**) is readily added to polar double bonds. For example, both  $(R_FSO_2)_2C=CHAr$  and  $R_FSO_2N=CHAr$  reacted smoothly with **6** at room temperature. Similarly, treatment of **6** with **3** gave an addition product in high yield. Thiophenol reacted with **3** in the same way:



$Ar=4-MeOC_6H_4$ ;  $Nu=P(O)(OCH_3)_2$  (**7**),  $C_6H_5S$  (**8**)

Table 1  
Preparations of compounds **3** and **5**

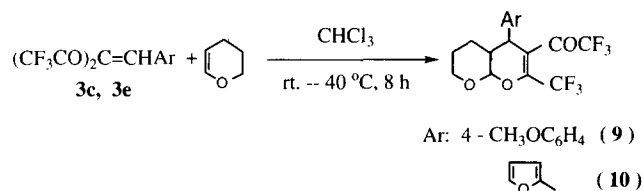
Entry No.	Reactant 2 or 4	Product 3 or 5	B.p. ( $^\circ C$ /Torr)	Yield (%) <sup>a</sup>
1	<b>2a</b>	<b>3a</b>	78/2	76
2	<b>2b</b>	<b>3b</b>	94/2	80
3	<b>2c</b>	<b>3c</b>	120/2	85
4	<b>2d</b>	<b>3d</b>	98–100/2	75
5	<b>2e</b>	<b>3e</b>	58–60/2	87
6	<b>4a</b>	<b>5a</b>	80/3	72
7	<b>4b</b>	<b>5b</b> <sup>b</sup>	40–42/3	64
8	<b>4c</b>	<b>5c</b>	83/3	78
9	<b>4d</b>	<b>5d</b> <sup>b</sup>	61–63/3	70

<sup>a</sup> Isolated yield based on **1**.

<sup>b</sup> Known compounds; cf. Refs. [11] and [12].

However, heating **3** with phenol or ethanol did not give the corresponding nucleophilic addition products. When **3** were treated with the alcohol containing some water, the hydrolysis products  $(CF_3CO)_2CH_2$  and  $ArCHO$  were formed readily.

Diels–Alder reactions between 2-aryl-1-(perfluoroalkanesulfonyl) acrylonitriles,  $R_FSO_2C(CN)=CHAr$ , and dienes have been reported by Hanack et al. [13]. Astonishingly, in our case push-pull dienophiles such as **3b**, **3c** and **5** did not react with cycloaddienes or isopentadiene. However, compound **3** reacted readily with 3,4-dihydro-2*H*-pyran giving a bicyclic addition product:



It is obvious that in this reaction 3,4-dihydro-2*H*-pyran acted as a dienophile [12]. Other alkenes such as cyclopentene or cyclohexene failed to form similar cycloaddition products.

A complete study on the condensation reaction of **1** with carbonyl compounds and the use of these condensation products is under investigation.

In summary, we have synthesized a new and reactive class of ethylene derivatives, their polar  $C=C$  double bonds being subject to nucleophilic addition.

### 3. Experimental details

Melting points were measured on a Thiele apparatus and all were uncorrected. Boiling points were uncorrected.  $^1H$  NMR and  $^{19}F$  NMR spectra were recorded on a Varian 360L instrument with  $Me_4Si$  and TFA as an internal and external standard, respectively, and the  $^{19}F$  NMR spectra were converted to  $\delta_{CFCl_3}$ .  $^{13}C$  NMR and  $^{31}P$  NMR spectra were recorded on a Bruker AM-300 instrument with TMS and  $H_3PO_4$  (85%) as external standards, respectively. IR spectra

were obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution mass spectra were obtained on a Finnigan GC-MS 4021 instrument. Elemental analyses were performed by this Institute. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione was commercially available from PCR Co. Other reagents and solvents were dried before use.

### 3.1. General procedure for the preparation of 3

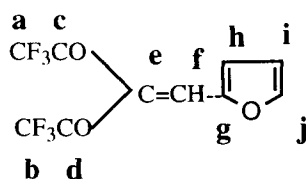
A mixture of **1** (2.08 g, 10 mmol), **2b** (1.20 g, 10 mmol) and acetic acid anhydride (10 ml) in a 25 ml flask, equipped with a reflux condenser, drying tube and magnetic stirring bar, was heated at 80 °C for 8 h. Ac<sub>2</sub>O and the AcOH formed were removed by distillation, the residue being distilled under vacuum to give (CF<sub>3</sub>CO)<sub>2</sub>C=CHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4 (**3b**) (2.48 g, 80%).

(CF<sub>3</sub>CO)<sub>2</sub>C=CHC<sub>6</sub>H<sub>5</sub> (**3a**): IR (film)  $\nu_{\max}$  (cm<sup>-1</sup>): 1754, 1693 (C=O); 1600 (C=C). <sup>1</sup>H NMR  $\delta$ : 7.40 (s, C=CH); 6.51–7.15 (ArH, 5H) ppm. <sup>19</sup>F NMR  $\delta$ : -71.3 (s, CF<sub>3</sub>); -76.8 (s, CF<sub>3</sub>) ppm. MS (*m/z*, %): 297 (3.09, M<sup>+</sup>H); 296 (24.20, M<sup>+</sup>); 69 (100.00, CF<sub>3</sub><sup>+</sup>). Analysis: Calc. for C<sub>12</sub>H<sub>6</sub>O<sub>2</sub>F<sub>6</sub>: C, 48.65; H, 2.03; F, 38.51%. Found: C, 48.78; H, 2.15; F, 38.62%.

(CF<sub>3</sub>CO)<sub>2</sub>C=CHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4 (**3b**): IR (film)  $\nu_{\max}$  (cm<sup>-1</sup>): 1750, 1690 (C=O); 1600, 1570 (C=C). <sup>1</sup>H NMR  $\delta$ : 7.46 (s, C=CH); 6.43–7.03 (AA'BB', 4H); 1.73 (s, CH<sub>3</sub>) ppm. <sup>19</sup>F NMR  $\delta$ : -71.3 (s, CF<sub>3</sub>); -76.8 (s, CF<sub>3</sub>) ppm. MS (*m/z*, %): 310 (41.38, M<sup>+</sup>); 119 (100.00, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sup>+</sup>). Analysis: Calc. for C<sub>13</sub>H<sub>8</sub>O<sub>2</sub>F<sub>6</sub>: C, 50.32; H, 2.58; F, 36.77%. Found: C, 50.11; H, 2.85; F, 36.90%.

(CF<sub>3</sub>CO)<sub>2</sub>C=CHC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-4 (**3c**): IR (film)  $\nu_{\max}$  (cm<sup>-1</sup>): 1750, 1690 (C=O); 1590, 1560 (C=C). <sup>1</sup>H NMR  $\delta$ : 7.43 (s, C=CH); 6.72–6.15 (AA'BB', 4H); 3.16 (s, OCH<sub>3</sub>) ppm. <sup>19</sup>F NMR  $\delta$ : -71.3 (s, CF<sub>3</sub>); -76.8 (s, CF<sub>3</sub>) ppm. <sup>13</sup>C NMR  $\delta$ : 55.9 (OCH<sub>3</sub>); 165.1 (C=CH); 115.6 [(CF<sub>3</sub>CO)<sub>2</sub>C]; 124.0, 125.5, 134.3, 152.2 (C<sub>6</sub>H<sub>4</sub>); 178.8 [CF<sub>3</sub>C(O)C=CH]; 186.8 [CF<sub>3</sub>C(O)C=CH] ppm; <sup>2</sup>J<sub>C-F</sub> = 40.5, 116.6 (CF<sub>3</sub>), 115.6 (CF<sub>3</sub>); <sup>1</sup>J<sub>C-F</sub> = 292 Hz. MS (*m/z*, %): 327 (6.02, M<sup>+</sup>H); 326 (37.60, M<sup>+</sup>); 257 (100.00, M<sup>+</sup> - CF<sub>3</sub>). Analysis: Calc. for C<sub>13</sub>H<sub>8</sub>O<sub>3</sub>F<sub>6</sub>: C, 47.85; H, 2.45; F, 34.97%. Found: C, 47.74; H, 2.52; F, 35.03%.

(CF<sub>3</sub>CO)<sub>2</sub>C=CHC<sub>6</sub>H<sub>4</sub>Cl-4 (**3d**): IR (film)  $\nu_{\max}$  (cm<sup>-1</sup>): 1750, 1690 (C=O); 1600, 1575 (C=C). <sup>1</sup>H NMR  $\delta$ : 7.40 (s, C=CH); 6.50–7.13 (ArH, 4H) ppm. <sup>19</sup>F NMR  $\delta$ : -71.2 (s, CF<sub>3</sub>); -76.8 (s, CF<sub>3</sub>) ppm. MS (*m/z*, %): 332/330 (13.52/40.60, M<sup>+</sup>); 263/261 (33.34/100.00, M<sup>+</sup> - CF<sub>3</sub>). Analysis: Calc. for C<sub>12</sub>H<sub>5</sub>ClO<sub>2</sub>F<sub>6</sub>: C, 43.57; H, 1.51; F, 34.49%. Found: C, 43.65; H, 1.65; F, 34.64%.



(**3c**): IR (film)  $\nu_{\max}$  (cm<sup>-1</sup>) 1750, 1690 (C=O); 1600 (C=C). <sup>1</sup>H NMR  $\delta$ : 7.30 (s, C=CH); 7.13 (s, 1H); 6.67 (d, 1H); 6.10 (d, 1H) ppm. <sup>19</sup>F NMR  $\delta$ : -71.3 (s, CF<sub>3</sub>); -76.8 (s, CF<sub>3</sub>) ppm. <sup>13</sup>C NMR  $\delta$ : 185.04 (q, d); 178.30 (q, c, <sup>2</sup>J<sub>C-F</sub> = 40.5 Hz); 150.72 (s, f); 148.23 (s, g); 134.78 (s, j); 126.14 (s, i); 123.42 (s, e); 115.29 (s, h); 116.74 (q, b); 115.83 (q, a, <sup>1</sup>J<sub>C-F</sub> = 292.5 Hz) ppm. MS (*m/z*, %): 286 (34.85, M<sup>+</sup>); 217 (100.00, M<sup>+</sup> - CF<sub>3</sub>). Analysis: Calc. for C<sub>10</sub>H<sub>4</sub>O<sub>3</sub>F<sub>6</sub>: C, 41.96; H, 1.40; F, 39.86%. Found: C, 42.11; H, 1.55; F, 40.01%.

Similar treatment of **1** with **4(a-d)** gave **5(a-d)** respectively. Yields and boiling points are shown in Table 1. Compounds **5b** and **5d** are known compounds. Their NMR spectra are confirmed by the literature values [10,11].

(CF<sub>3</sub>CO)<sub>2</sub>C=CHNMe<sub>2</sub> (**5a**): IR (film)  $\nu_{\max}$  (cm<sup>-1</sup>): 1770, 1690 (C=O); 1660, 1595 (C=C). <sup>1</sup>H NMR  $\delta$ : 7.63 (s, C=CH); 3.33 (s, CH<sub>3</sub>); 2.93 (s, CH<sub>3</sub>) ppm. <sup>19</sup>F NMR  $\delta$ : -72.3 (s, CF<sub>3</sub>) ppm. <sup>13</sup>C NMR  $\delta$ : 179.2 (q, CF<sub>3</sub>C(O), <sup>2</sup>J<sub>C-F</sub> = 36.0 Hz); 157.8 (s, CH=C); 115.3 (q, CF<sub>3</sub>, <sup>1</sup>J<sub>C-F</sub> = 292.5 Hz); 101.0 (s, C=CH); 48.5 (s, CH<sub>3</sub>); 45.3 (s, CH<sub>3</sub>) ppm. MS (*m/z*, %): 263 (25.8, M<sup>+</sup>); 194 (100.00, M<sup>+</sup> - CF<sub>3</sub>). Analysis: Calc. for C<sub>8</sub>H<sub>7</sub>F<sub>6</sub>NO<sub>2</sub>: C, 36.50; H, 2.66; F, 43.35; N, 5.32%. Found: C, 36.78; H, 2.53; F, 43.46; N, 5.26%.

(CF<sub>3</sub>CO)<sub>2</sub>C=C(CH<sub>3</sub>)NMe<sub>2</sub> (**5c**): IR (film)  $\nu_{\max}$  (cm<sup>-1</sup>): 1765, 1690 (C=O); 1658, 1590 (C=C). <sup>1</sup>H NMR  $\delta$ : 2.80 (s, CH<sub>3</sub>C=); 2.93 (s, CH<sub>3</sub>N); 3.50 (s, CH<sub>3</sub>N) ppm. <sup>19</sup>F NMR  $\delta$ : -72.5 (s, CF<sub>3</sub>) ppm. MS (*m/z*, %): 277 (10.33, M<sup>+</sup>); 208 (100.00, M<sup>+</sup> - CF<sub>3</sub>). Analysis: Calc. for C<sub>9</sub>H<sub>9</sub>F<sub>6</sub>NO<sub>2</sub>: C, 38.99; H, 3.25; F, 41.16; N, 5.05%. Found: C, 40.08; H, 3.12; F, 41.08; N, 5.16%.

### 3.2. Reactions of 3 with dialkyl phosphite and thiophenol

A mixture of **3c** (1.6 g, 5 mmol), dimethyl phosphite (0.6 g, 5.5 mmol) and dry CH<sub>3</sub>CN (5 ml) was stirred at room temperature for 4 h, then at 40 °C for another 2 h. After removing the solvent, the residue was distilled under vacuum to give **7** (2.0 g, 90%), b.p. 142–145 °C/2 Torr.

(CF<sub>3</sub>CO)<sub>2</sub>CHCH(Ar)-P(O)(OCH<sub>3</sub>)<sub>2</sub> (**7**): IR (film)  $\nu_{\max}$  (cm<sup>-1</sup>): 1780 (s, C=O); 1590, 1500 (ArH); 1250 (s, P=O); 1200–1110 (s, C-F); 1020 (m, P-O-C). <sup>1</sup>H NMR  $\delta$ : 7.66 (AA'BB', 2 ArH, <sup>2</sup>J<sub>HH</sub> = 9 Hz); 7.06 (AA'BB', 2 ArH); 6.02 [broad, (CF<sub>3</sub>CO)<sub>2</sub>CH]; 5.02 [d, CHP(O), <sup>2</sup>J<sub>PH</sub> = 23 Hz]; 3.70 (d, POCH<sub>3</sub>, <sup>2</sup>J<sub>PH</sub> = 10 Hz); 3.50 (d, POCH<sub>3</sub>); 2.67 (s, OCH<sub>3</sub>) ppm. <sup>19</sup>F NMR  $\delta$ : -77.1 (s, 2 × CF<sub>3</sub>) ppm. <sup>31</sup>P NMR  $\delta$ : 11.3 [s, P(O)(OMe)<sub>2</sub>] ppm. <sup>13</sup>C NMR  $\delta$ : 184.97 (CF<sub>3</sub>CO); 161.39, 134.37, 131.75, 131.21 (Ar); 114.92 [(CF<sub>3</sub>CO)<sub>2</sub>CH]; 98.71 (4-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>CH); 55.01 (4-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>); 42.37, 40.73 [P(O)(OCH<sub>3</sub>)<sub>2</sub>]; 123.61 (q, CF<sub>3</sub>, <sup>2</sup>J<sub>C-F</sub> = 40 Hz) ppm. MS (*m/z*, %): 436 (4.2, M<sup>+</sup>); 367 (1.7, M<sup>+</sup> - CF<sub>3</sub>); 339 (11.77, M<sup>+</sup> - CF<sub>3</sub>CO); 307 (100.00, M<sup>+</sup> - CF<sub>3</sub>CO - 2O); 293 (5.83, M<sup>+</sup> - CF<sub>3</sub>CO - CH<sub>3</sub> - OCH<sub>3</sub>); 229 (12.5, M<sup>+</sup> - (CF<sub>3</sub>CO)<sub>2</sub>CH); 213 (28.33, ArCHP(O)(OCH<sub>3</sub>)<sub>2</sub><sup>+</sup>); 161 (39.17, M<sup>+</sup> - CF<sub>3</sub>CO - CF<sub>3</sub> - P(O)(OCH<sub>3</sub>)<sub>2</sub>); 133 [10.83,

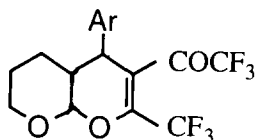
$M^+ - (CF_3CO)_2 - P(O)(OCH_3)_2$ ; 69 (4.2,  $CF_3^+$ ). Analysis: Calc. for  $C_{15}H_{15}O_6F_6P$ : C, 41.28; H, 3.44%. Found: C, 41.56; H, 3.81%.

Similar treatment of **3c** with  $C_6H_5SH$  gave compound **8**. Yield, 75%; m.p. 76 °C.

$(CF_3CO)_2CHCH(Ar)-SC_6H_5$  (**8**): IR (KBr)  $\nu_{max}$  ( $cm^{-1}$ ): 1780 (s, C=O); 1598, 1490 (ArH); 1210–1120 (s, C–F).  $^1H$  NMR  $\delta$ : 6.4–7.3 (ArH, 9H); 6.23 [s,  $(CF_3CO)_2CH$ ]; 5.23 (s, ArCH); 2.9 (s,  $CH_3$ ) ppm.  $^{19}F$  NMR  $\delta$ : –76.3 (s,  $2 \times CF_3$ ) ppm. MS ( $m/z$ , %): 368 (4.2,  $M^+H - CF_3$ ); 353 (2.5,  $M^+H - CF_3 - CH_3$ ); 339 (2.5,  $M^+ - CF_3CO$ ); 313 (5.5,  $M^+H - SC_6H_5 - CH_3$ ); 285 (2.4,  $M^+H - SC_6H_5 - CH_3 - CO$ ); 264 (2.5,  $M^+H - C_6H_4 - CF_3CO$ ); 239 (5.2,  $M^+ - CF_3CO - CF_3 - OCH_3$ ); 236 (5.0,  $M^+H - C_6H_4 - CF_3CO - CO$ ); 185 (4.2,  $M^+ - (CF_3CO)_2 - CHCH - OCH_3$ ); 109 (15.0,  $SC_6H_5^+$ ); 97 (32.5,  $CF_3CO^+$ ). Analysis: Calc. for  $C_{19}H_{14}F_6SO_3$ : C, 52.29; H, 3.21; F, 26.15%. Found: C, 52.48; H, 3.12; F, 26.43%.

### 3.3. Cycloaddition reactions of **3** with 3,4-dihydro-2H-pyran

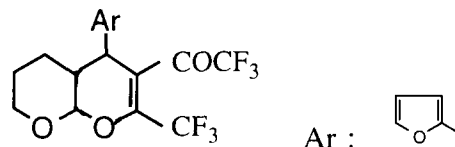
A mixture of **3c** (1.6 g, 5 mmol) and 3,4-dihydro-2H-pyran (5 ml) was stirred at room temperature for 24 h. After removing the excess 3,4-dihydro-2H-pyran, the residue was distilled under vacuum giving **9** (1.6 g, 77%); b.p. 140–143 °C/2 Torr.



(Ar = 4- $CH_3OC_6H_4$  (**9**)): IR (film)  $\nu_{max}$  ( $cm^{-1}$ ): 1750 (s, C=O); 1655 (C=C); 1590, 1495 (ArH); 1210–1120 (s, C–F).  $^1H$  NMR  $\delta$ : 6.83–7.78 (AA'BB', 4 ArH); 5.34 (s, –O–CH–O); 4.13–4.26 (m, CHAr); 3.63 (s,  $OCH_2$ ); 3.00 (s,  $OCH_3$ ); 1.93–2.40 (broad, 5H) ppm.  $^{19}F$  NMR  $\delta$ : –74.8 (s,  $CF_3$ ); –66.8 (s,  $CF_3$ ) ppm. MS ( $m/z$ , %): 410 (3.3,  $M^+$ ); 392 (4.1,  $M^+H - F$ ); 326 (5.1,  $M^+ - C_5H_8O$ ); 307 (2.5,  $M^+ - C_5H_8O - F$ ); 295 (6.6,  $M^+H - CF_3CO - F$ ); 257 (25.6,  $M^+ - C_5H_8O - CF_3$ ); 207 (17.4,  $M^+H - ArCH - C_5H_8O$ ); 166 (4.1,  $CF_3CO - CF_3^+$ ); 137 (2.4,  $M^+ - Ar - CF_3CO - CF_3$ ); 107 (7.5,  $C_6H_4OCH_3^+$ ); 84 (100.00,  $C_5H_8O^+$ ); 69 (35.3,  $CF_3^+$ ). Analysis: Calc. for  $C_{18}H_{16}F_6O_4$ :

C, 52.68; H, 3.90; F, 27.80%. Found: C, 52.92; H, 3.68; F, 27.42%.

Treatment of **3e** with 3,4-dihydro-2H-pyran gave **10**. Yield, 70%; b.p. 120–125 °C/2 Torr.



(**10**): IR (film)  $\nu_{max}$  ( $cm^{-1}$ ): 1760 (s, C=O); 1660, 1650 (C=C).  $^1H$  NMR  $\delta$ : 7.03 (s, 1H); 6.60 (d, 1H); 6.03 (d, 1H); 5.43 (s, 1H, O–CH–O); 5.30 (m, CHAr); 3.60 (m, 2H,  $OCH_2$ ); 2.43–1.23 (m, 5H) ppm.  $^{19}F$  NMR  $\delta$ : –75.3 (s,  $CF_3$ ); –66.5 (s,  $CF_3$ ) ppm. MS ( $m/z$ , %): 370 (5.9,  $M^+$ ); 353 (4.74,  $M^+ - H - O$ ); 352 (28.42,  $M^+H - F$ ); 296 (15.2,  $M^+H - O - O - F - CO$ ); 286 (17.57,  $M^+ - C_5H_8O$ ); 267 (9.5,  $M^+ - F - C_5H_8O$ ); 217 (74.41,  $M^+ - CF_3 - C_5H_8O$ ); 97 (2.8,  $CF_3CO^+$ ); 84 (100.00,  $C_5H_8O^+$ ); 69 (28.61,  $CF_3^+$ ); 67 (4.1,  $C_4H_8O^+$ ); 55 (19.8,  $C_4H_7^+$ ). Analysis: Calc. for  $C_{15}H_{12}F_6O_4$ : C, 48.65; H, 3.24; F, 30.81%. Found: C, 48.43; H, 3.52; F, 30.66%.

### Acknowledgement

The authors thank the National Natural Science Foundation of China (NNFSC No. 29472071) for financial support.

### References

- [1] M.D. Threadgill, A.K. Heer and B.G. Jones, *J. Fluorine Chem.*, 65 (1993) 21.
- [2] J. Elguero and G.I. Yranzo, *J. Chem. Res. Synop.*, 4 (1990) 120.
- [3] G. Meazza, G. Zanardi and P. Piccardi, *J. Heterocycl. Chem.*, 30 (1993) 365.
- [4] R. Balicki, *Pol. J. Chem.*, 55 (1981) 1995.
- [5] H.W.R. Williams and C.S. Rooney, US Pat. 3 962 262, [*Chem. Abs.*, 86 (1977) 5433d].
- [6] R.P. Soni and M.L. Jain, *Tetrahedron Lett.*, 21 (1980) 3795.
- [7] K.I. Pashkevich, R.R. Latypov and V.I. Filyakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1986) 2576.
- [8] ShiZheng Zhu, *Chin. Chem. Lett.*, 3 (1992) 601.
- [9] ShiZheng Zhu, *Synthesis*, (1994) 261.
- [10] ZhangLin Zhou, LiLan Shi and YaoZeng Huang, *Synth. Commun.*, 21 (1991) 1027.
- [11] S.L. Schreiber, *Tetrahedron Lett.*, 21 (1980) 1027.
- [12] M. Hojo, R. Masuda and E. Okada, *Synthesis*, (1990) 347.
- [13] M. Hanack, G. Bailer, J. Hackenberg and L.R. Subramaniam, *Synthesis*, (1991) 1205.