

# Convenient syntheses of 4-perfluoroalkyl-6-( $\alpha$ -thienyl)-2-pyranones and methyl 4-( $\alpha$ -thienacyl)-3-perfluoroalkyl-3-butenates

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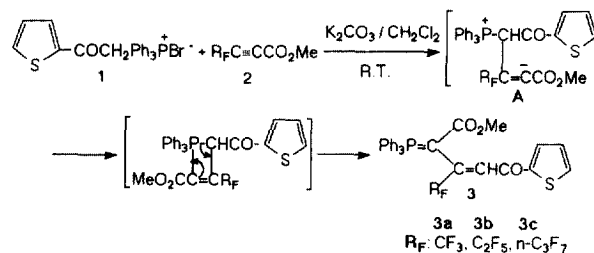
## Abstract

In the presence of  $K_2CO_3$ , reaction of ( $\alpha$ -thienacyl)methyltriphenyl phosphonium bromide (**1**) with methyl 2-perfluoroalkynoates (**2**) in  $CH_2Cl_2$  at room temperature gave methyl 4-( $\alpha$ -thienacyl)-2-triphenylphosphoranylidene-3-perfluoroalkyl-3-butenates (**3**) in excellent yields. 4-Perfluoroalkyl-6-( $\alpha$ -thienyl)-6-pyranones (**4**) and methyl 4-( $\alpha$ -thienacyl)-3-perfluoroalkyl-3-butenates (**5**) were obtained in high yield by hydrolysis of these methylene phosphoranates (**3**) with hot aqueous methanol. The butenoates (**5**) were isolated chromatographically as mixtures of *Z* and *E* isomers, the ratios of which were estimated by  $^1H$  NMR. Reaction mechanisms are proposed to account for the formation of products **3**, **4** and **5**. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Methyl 2-perfluoroalkynoates; 4-perfluoroalkyl-6-( $\alpha$ -thienyl)-2-pyranones; Methyl 4-( $\alpha$ -thienacyl)-3-perfluoroalkyl-3-butenates

## 1. Introduction

Fluorinated organic compounds are of interest because of their unique properties [1–3]. In previous papers, we reported the synthesis of fluorinated methyl (*Z*)-3-butenates [4–8] and 2-pyranones [9,10]; in continuation of that work, we now describe a convenient synthesis of 4-perfluoroalkyl-6-( $\alpha$ -thienyl)-6-pyranones (**4**) and methyl 4-( $\alpha$ -thienacyl)-3-perfluoroalkyl-3-butenates (**5**).



Scheme 1.

## 2. Results and discussion

The reaction of ( $\alpha$ -thienacyl)methyltriphenylphosphonium bromide (**1**) with methyl 2-perfluoroalkynoates (**2**) in the presence of  $K_2CO_3$  in methylene chloride at room temperature afforded methyl 4-( $\alpha$ -thienacyl)-2-triphenylphosphoranylidene-3-perfluoroalkyl-3-butenates (**3**) in excellent yield (Table 1), presumably according to Scheme 1. Hydrolysis of these products (**3**) in aqueous methanol in sealed tubes at  $180^\circ C$  or  $140^\circ C$  for 3–30 h gave mixtures of the corresponding 4-perfluoroalkyl-6-( $\alpha$ -thienyl)-6-pyranones (**4**) and methyl 4-( $\alpha$ -thienacyl)-3-perfluoroalkyl-3-

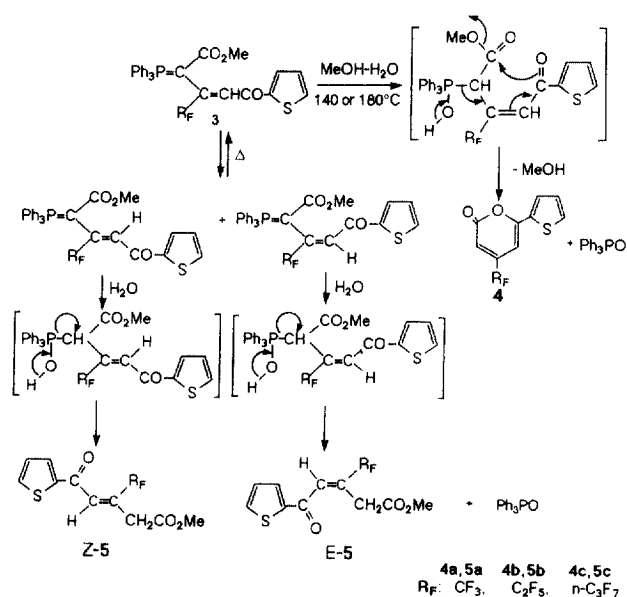
butenoates (**5**) in high yields, plus triphenylphosphine oxide (see Scheme 2 and Table 1). Compounds **4** and **5** were separated by column chromatography. The *Z* and *E* isomer pairs of the butenoates (**5**) could not be separated by column chromatography, however the *Z/E* ratios for each pair could be estimated by  $^1H$  NMR (Table 1). In the NMR spectra of compound **5**, pairs of absorptions are seen corresponding to pairs of *Z* and *E* isomers, the olefinic proton signal of each *E* isomer appearing as a singlet at 6.65 ppm, which is about 0.8 ppm upfield from that exhibited by the *Z* isomers (7.42 ppm); this can be attributed to the ester carbonyl group of *Z* isomers giving a downfield shift to the olefinic proton of *Z* isomers. The signals for the methylene protons of the *E* isomers appear 0.65 ppm downfield from those of the *Z* isomers; this can be

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Table 1  
Preparation of phosphoranes **3**, pyranones **4** and butenoates **5**

Product	Conditions	Yield (%) <sup>a</sup>	Z-5:E-5	m.p. (°C)	Micro found	Analyses calculated	MS (M <sup>+</sup> )	IR (cm <sup>-1</sup> )
<b>3a</b>	25°C, 24 h	94		165–166	C: 64.69 H: 4.02	C: 64.68 H: 4.12	539	1632, 1609
<b>3b</b>	25°C, 24 h	96		102–103	C: 61.23 H: 3.80	C: 61.23 H: 3.77	589	1654, 1618
<b>3c</b>	25°C, 30 h	93		134–135	C: 58.27 H: 3.37	C: 58.31 H: 3.47	639	1647, 1618
<b>4a</b>	140°C, 12 h	43		86–87	C: 48.58 H: 2.19	C: 48.79 H: 2.05	246	1750
<b>4a</b>	180°C, 3 h	60						
<b>4b</b>	140°C, 16 h	49		90–91	C: 44.58 H: 1.69	C: 44.61 H: 1.70	296	1746
<b>4b</b>	180°C, 6 h	53						
<b>4c</b>	140°C, 30 h	52		83–84	C: 41.84 H: 1.56	C: 41.63 H: 1.46	346	1735
<b>4c</b>	180°C, 12 h	56						
<b>5a</b>	140°C, 12 h	55	3:2	58–59	C: 47.52 H: 3.30	C: 47.48 H: 3.26	278	1750, 1671
<b>5a</b>	180°C, 3 h	34	3:2					
<b>5b</b>	140°C, 16 h	44	4:3	oil	C: 43.70 H: 2.72	C: 43.91 H: 2.76	328	1734, 1664
<b>5b</b>	180°C, 6 h	40	4:3					
<b>5c</b>	140°C, 30 h	38	1:1	oil	C: 41.19 H: 2.31	C: 41.28 H: 2.40	378	1748, 1670
<b>5c</b>	180°C, 12 h	36	1:1					

<sup>a</sup> Based on isolated product.



Scheme 2.

attributed to the deshielding effect of carbonyl group of *E* isomers making the methylene protons downfield.

Increasing the hydrolysis temperature of **3** from 140°C to 180°C, shortened the reaction time considerably and the ratio of **4** to **5** increased; however, no significant changes occurred in the total yield of **4** and **5** or the *Z/E* ratios for **5** (Table 1). The structures of products **3**, **4** and **5** were confirmed by IR,

MS, (Table 1) <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR (Table 2) and microanalysis.



















### 3. Experimental

Melting and boiling points are uncorrected. IR spectra were recorded on a 7400 spectrophotometer (Shanghai Analytical Instrument Factory, China) solid samples being examined as KBr discs and oils as liquid films. NMR spectra were determined with an AC-100SC spectrometer, using solutions in CDCl<sub>3</sub> with tetramethylsilane and CDCl<sub>3</sub> as the internal standard for <sup>1</sup>H and <sup>13</sup>C nuclei, respectively, and trifluoroacetic acid as the external reference for <sup>19</sup>F. Mass spectra were run on a HP 5989A spectrometer. Microanalyses were performed with a Foss Heraeus CHN-O-RAPID element analysis instrument. Petroleum ether refers to the fraction boiling in the range 60–90°C.

#### 3.1. Methyl 4-( $\alpha$ -thienacyl)-2-triphenylphosphoranylidene-3-perfluoroalkyl-3-butenoates (**3a–c**); general procedure

To a suspension of **1** [11] (2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added methyl 2-perfluoroalkynoates (**2a–c**) [12] (2.4 mmol) and K<sub>2</sub>CO<sub>3</sub> (3 mmol), and the mixture was stirred at room temperature for 24–30 h (see Table 1). After product mixtures had been filtered to remove insoluble material, the solvent was removed under reduced pressure and the residue was separated on a silica gel column with EtOAc/petroleum

Table 2  
<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectral data for phosphoranones 3, pyranones 4 and butenoates 5

Product	<sup>1</sup> H NMR (CDCl <sub>3</sub> /TMS) δ (ppm)	<sup>13</sup> C NMR (CDCl <sub>3</sub> /TMS) δ (ppm) (C=O)	<sup>19</sup> F NMR(CDCl <sub>3</sub> ) δ (ppm)(TFA ref.)
3 a	3.38(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 6.62(s, 1H, =CH), 7.07(m, 1H,  )	169.0(s, -CO <sub>2</sub> -), 183.3(s, -CO-)	11.2(s, CF <sub>3</sub> )
	15H <sub>arom</sub> + 		
3 b	3.24(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 6.97(s, 1H, =CH), 7.12(m, 1H,  )	169.0(s, -CO <sub>2</sub> -), 184.4(s, -CO-)	-6.3(t, 3F, CF <sub>3</sub> ), -36.0(q, 2F, CF <sub>2</sub> )
	15H <sub>arom</sub> + 		
3 c	3.22(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 6.97(s, 1H, =CH), 7.08(m, 1H,  )	168.6(s, -CO <sub>2</sub> -), 184.3(s, -CO-)	-3.7(t, 3F, CF <sub>3</sub> ), -32.2(m, 2F, CF <sub>2</sub> )
	15H <sub>arom</sub> + 		
4 a	6.47(s, 1H,  )	159.3(s, -CO <sub>2</sub> -)	8.3(s, CF <sub>3</sub> )
	7.15(m, 1H,  )		
4 b	6.48(s, 1H,  )	159.3(s, -CO <sub>2</sub> -)	-7.5(t, 3F, CF <sub>3</sub> )
	7.16(m, 1H,  )		
4 c	6.47(s, 1H,  )	159.3(s, -CO <sub>2</sub> -)	-3.5(t, 3F, CF <sub>3</sub> )
	7.16(m, 1H,  )		
Z-5 a	3.72(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 3.77(s, 2H, CH <sub>2</sub> ), 7.11-7.22(m, 3H,  )	164.6(s, -CO <sub>2</sub> -), 181.6(s, -CO-)	6.4(s, CF <sub>3</sub> )
E-5 a	3.73(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 4.40(s, 2H, CH <sub>2</sub> ), 6.65(s, 1H, =CH), 7.66-7.82(m, 3H,  )	168.6(s, -CO <sub>2</sub> -), 185.4(s, -CO-)	6.2(s, CF <sub>3</sub> )
Z-5 b	3.72(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 3.77(s, 2H, CH <sub>2</sub> ), 7.11-7.23(m, 3H,  )	164.6(s, -CO <sub>2</sub> -), 181.4(s, -CO-)	-7.0(t, 3F, CF <sub>3</sub> )
E-5 b	3.73(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 4.42(s, 2H, CH <sub>2</sub> ), 6.63(s, 1H, =CH), 7.24-7.82(m, 3H,  )	168.5(s, -CO <sub>2</sub> -), 186.8(s, -CO-)	-41.5(q, 2F, CF <sub>2</sub> ), -6.9(t, 3F, CF <sub>3</sub> )
Z-5 c	3.73(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 3.78(s, 2H, CH <sub>2</sub> ), 7.11-7.23(m, 3H,  )	164.6(s, -CO <sub>2</sub> -), 181.4(s, -CO-)	-3.8(t, 3F, CF <sub>3</sub> )
E-5 c	3.74(s, 3H, CO <sub>2</sub> CH <sub>3</sub> ), 4.43(s, 2H, CH <sub>2</sub> ), 6.63(s, 1H, =CH), 7.44-7.81(m, 3H,  )	168.8(s, -CO <sub>2</sub> -), 185.3(s, -CO-)	-38.5(m, 2F, CF <sub>2</sub> ), -48.6(s, 2F, CF <sub>2</sub> )
			-3.7(t, 3F, CF <sub>3</sub> ), -38.5(m, 2F, CF <sub>2</sub> )
			-48.5(s, 2F, CF <sub>2</sub> )

ether (2:8 v/v) as eluent to give red solids (**3a–c**). Further purification was carried out by careful recrystallization from EtOAc/petroleum ether to give analytically pure red crystalline samples of each butenoates (**3a–c**).

### 3.2. 4-Perfluoroalkyl-6-( $\alpha$ -thienyl)-6-pyranones (**4a–c**) and methyl 4-( $\alpha$ -thienacyl)-3-perfluoroalkyl-3-butenoates (**5a–c**); typical procedure

A solution of **3a–c** (1.5 mmol) in aqueous methanol (9 MeOH: 1 H<sub>2</sub>O) (10 ml) was heated in a sealed glass tube at 140°C for 12–30 h or at 180°C for 3–12 h. After the reaction mixtures had cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was passed through a silica gel column (GF<sub>254</sub>, 15 cm) and eluted with EtOAc/petroleum ether (2:98–10:90 v/v) to separate the products **4a–c** and **5a–c** from triphenylphosphine oxide, respectively. Products **4a–c** (yellow) and **5a** (colourless) were further purified by recrystallization from light petroleum to give crystalline specimens. Products **5b** and **5c** (colourless oils) were purified by vacuum distillation (140–160°C/1 mm Hg).

### Acknowledgements

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### References

- [1] R.E. Banks (Ed.), *Organofluorine Chemicals and their Industry Application*, Ellis Harwood, 1979.
- [2] J.T. Welch, *Tetrahedron* 43 (1987) 3123.
- [3] Mann, *J. Chem. Soc. Rev.* 16 (1987) 381.
- [4] W.Y. Ding, J.Q. Pu, X.Q. Kong, *Acta Chim. Sin.* 44 (1986) 62.
- [5] W.Y. Ding, J.Q. Pu, P.S. Zhang, *Acta Chim. Sin.* 45 (1987) 47.
- [6] W.Y. Ding, J.Q. Pu, C.M. Zhang, *Acta Chim. Sin.* 49 (1991) 284.
- [7] W.Y. Ding, J.Q. Pu, C.M. Zhang, W.G. Cao, *J. Chem. Soc. Perkin Trans. 1* (1991) 1369.
- [8] W.Y. Ding, W.G. Cao, D.K. Zhu, W.Q. Tong, *Chen. Res. Chin. Univ.* 8 (1992) 224.
- [9] W.Y. Ding, J.Q. Pu, X.Q. Kong, *Acta Chim. Sin.* 44 (1986) 255.
- [10] W.Y. Ding, J.Q. Pu, P.S. Zhang, *Youji Huaxue* (1987) 435.
- [11] W.T. Tao, H.F. Pu, *Youji Huaxue* (1983) 129.
- [12] Y.Z. Huang, Y.C. Shen, G.D. Chen, S.Q. Wang, *Acta Chim. Sin.* 37 (1979) 47.