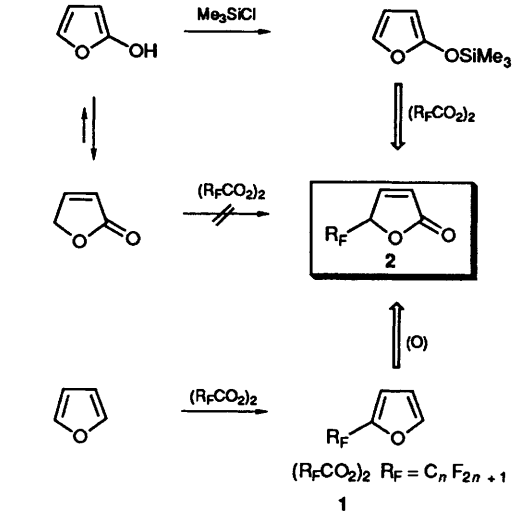
Convenient Preparations and Michael Reactions of 4-Fluoroalkylated But-2-en-4-olides

Masato Yoshida,* Rihoko Imai, Yuji Komatsu, Yoshihiro Morinaga, Nobumasa Kamigata and Masahiko Iyoda
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-Ohsawa, Hachioji, Tokyo 192-03, Japan

Trifluoromethyl, heptafluoropropyl and chlorodifluoromethyl substituted but-2-en-4-olides have been prepared both from 2-trimethylsiloxyfuran by fluoroalkylation with the corresponding bis(fluoroalkanoyl) peroxide and from 2-fluoroalkylfuran by oxidation with *m*-nitrobenzenesulfonyl peroxide. 4-Difluoromethylbut-2-en-4-olide was also prepared by chlorodifluoromethylation of 2-methoxyfuran followed by reduction of the chlorine. The 4-trifluoromethylated butenolide, thus prepared, could be readily converted into the anion by treatment with weak base. The anion so formed then reacted with electron-deficient olefins to give 4,4-disubstituted butenolides.

In recent years, considerable interest has been focussed on the synthesis of organofluorine compounds because of their unique physical properties and enhanced biological activities.[1] However, because of the many limitations on the synthesis of organofluorine compounds,[2-4] we have been exploring a novel method for the perfluoroalkylation of heteroaromatic compounds such as furans, thiophenes or pyrroles with bis(perfluoroalkanoyl) peroxides **1**, the latter being readily prepared from the corresponding acid chloride or acid anhydride.[5] In the course of our study, we found a convenient method for the preparation of 4-fluoroalkyl substituted but-2-en-4-olides **2** using the peroxide **1**. Since butenolides are known to have diverse biological activities and to be versatile building blocks in the synthesis of natural products,[6] we have investigated the potential of the but-2-en-4-olide **2** for the synthesis of fluorine-modified natural products.



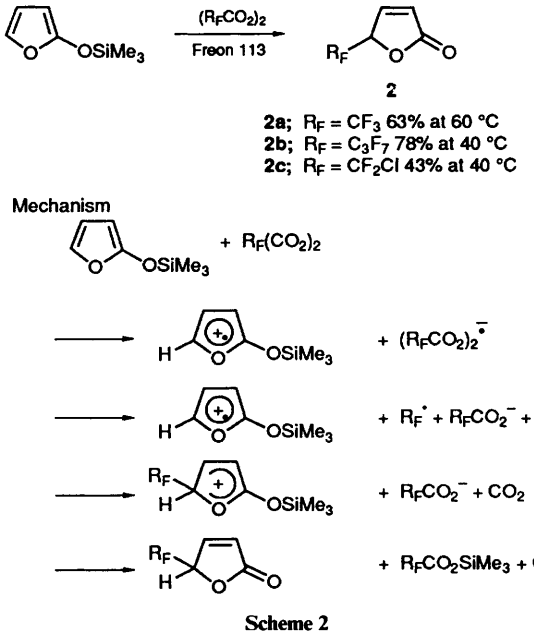
Scheme 1

Results and Discussion

Synthesis of 4-Fluoroalkylbut-2-en-4-olides using the Peroxide **1**.—Since the fluoroalkylation with the peroxide **1** proceeds by way of electron transfer from the substrate to the peroxide,[4] the method could not be applied to the fluoroalkylation of electron-poor substrates, such as but-2-en-4-olide. Thus, we examined two other approaches to the synthesis of 4-fluoroalkylbut-2-en-4-olide **2** (see Scheme 1); one is the fluoroalkylation of 2-trimethylsiloxyfuran with **1** and the other is oxidation of 2-fluoroalkylfuran to **2**.

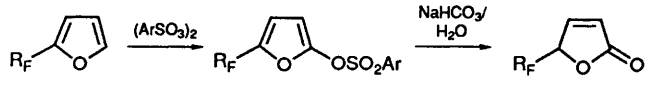
Although butenolide exists as a tautomer of 2-hydroxyfuran, the latter being expected to react with the peroxide **1**, the equilibrium greatly favours the butenolide (Scheme 1).[7] However, 2-trimethylsiloxyfuran retains the furan skeleton and is a masked butenolide.[8] Reaction of 2-trimethylsiloxyfuran (2 mol equiv.) with **1a** ($R_F = CF_3$), **1b** ($R_F = C_3F_7$) and **1c** ($R_F = CF_2Cl$) (each 1 mol equiv.) in Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) at 40–60 °C for 4 h gave trifluoromethyl, heptafluoropropyl and chlorodifluoromethyl substituted but-2-en-4-olides **2a–c** in good to moderate yields (see Scheme 2). The peroxide **1** was prepared from the corresponding acid chloride or acid anhydride in Freon 113 and was used as a solution in Freon 113 without isolation.

Since as reported in our earlier paper, furan can be readily fluoroalkylated with the peroxide **1**,[5] we have investigated the conversion of 2-fluoroalkylfurans into 4-fluoroalkylbut-2-en-4-olides. Fluoroalkylated butenolides **2a–c** were obtained by the sulfonyloxylation of 2-fluoroalkylfuran with *m*-nitrobenzene-



Scheme 2

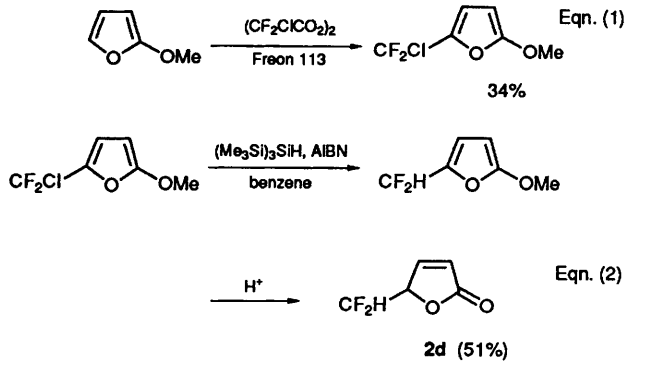
sulfonyl peroxide (*m*-NBSP) followed by hydrolysis under basic conditions (Scheme 3). *m*-NBSP is known to be a good reagent for nitrobenzenesulfonyloxylations of benzene rings.[9] The sulfonyloxylation was applied to 2-fluoroalkylfurans.



2a 24% at reflux
2b 40% at room temp.
2c 24% at room temp.

Scheme 3

Recently, we found that on treatment of $ArCF_2Cl$ with tributyltin hydride under radical conditions[10] ready displacement of chlorine by hydrogen occurred. The reduction of **2c** by tributyltin hydride or tris(trimethylsilyl)silane was, therefore, studied in order to prepare 4-difluoromethylbut-2-en-4-olide **2d**. However, such reactions gave unidentified polymeric products, not the reduction product **2d**. Difluoromethylated butenolide **2d** was obtained, however, by the synthetic routes shown in Scheme 4. 5-Chlorodifluoromethyl-2-methoxyfuran, obtained by the chlorodifluoromethylation of 2-methoxyfuran with the peroxide **1c** [Scheme 4, Eqn. (1)], was reduced with tris(trimethylsilyl)silane under radical conditions to 2-difluoromethyl-5-methoxyfuran, subsequent conversion of the latter into the butenolide **2d** being achieved by the addition of trifluoroacetic acid to the reaction mixture [Scheme 4, Eqn. (2)].

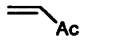
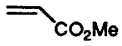
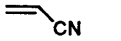
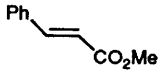
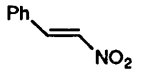
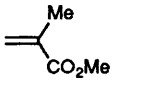


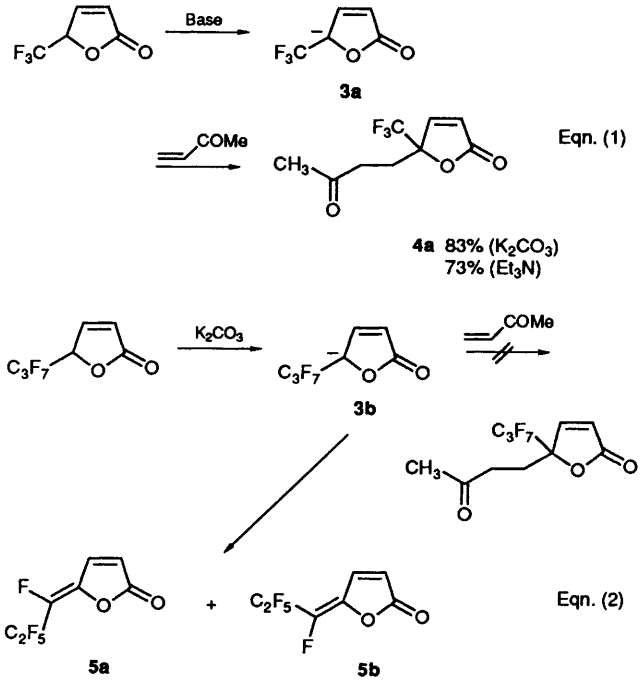
Scheme 4

Reactions of 4-Trifluoromethylbut-2-en-4-olide.—The butenolide **2a** on treatment with weak base such as potassium carbonate or triethylamine at room temperature was readily converted into the anion **3a** which when trapped by methyl vinyl ketone gave the Michael adduct **4a** [Scheme 5, Eqn. (1)]. The unfluoroalkylated but-2-en-4-olide failed under similar conditions to give such a Michael adduct, starting material being recovered. It is known, however, that a strong base, such as LDA, is necessary to prepare the anion of but-2-en-4-olide.[11] The trifluoromethyl group of **2a** should facilitate the formation of the anion as a result of its strong electron-withdrawing effect. Methyl vinyl ketone failed to trap the anion **3b** which, instead, preferentially eliminated fluoride ion to give **5a** and **5b** [Scheme 5, Eqn. (2)].

Carbanions bearing a trifluoromethyl group are usually not available for organic synthesis because of their facile defluorination[12] and a solution to this problem has been the focus of much attention.[13,14] The Michael addition of the anion **3a** to methyl vinyl ketone without defluorination is, therefore, very interesting. Probably, in anion **3a**, the delocalization of the unpaired electrons to the butenolide framework (see Scheme 6) prevents the elimination. We further investigated the reactions of the anion **3a** with various Michael acceptors in order to introduce other functional groups into the 4-position, with the results shown in Table 1. Nucleophilic attack of the anion **3a** to the added olefin [Scheme 7, Eqn. (1)] competed with that to the butenolide **2a** itself [Scheme 7, Eqn. (2)]. In the reactions of **3a** with methyl acrylate, acrylonitrile, and β-nitrostyrene, Michael adducts **4b**, **4c** and **4d** were obtained, respectively (Table 1, runs 2, 3 and 5). In the reactions with methyl methacrylate and methyl cinnamate, however, the dimer **6** was produced in yields of >80%, the corresponding Michael adducts **4** not being obtained under these conditions (Table 1, runs 4 and 6).

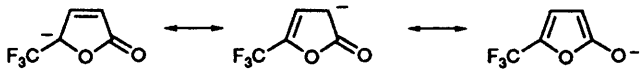
Table 1 Reactions of **2a** (1 mol equiv.) with olefins (5 mol equiv.) in the presence of potassium carbonate

Run	Olefin	Yields (%) 4	6
1		84	Trace
2		76	Trace
3		25	32
4		0	87
5		38	Trace
6		0	83



Scheme 5

The reactions with methyl methacrylate were investigated

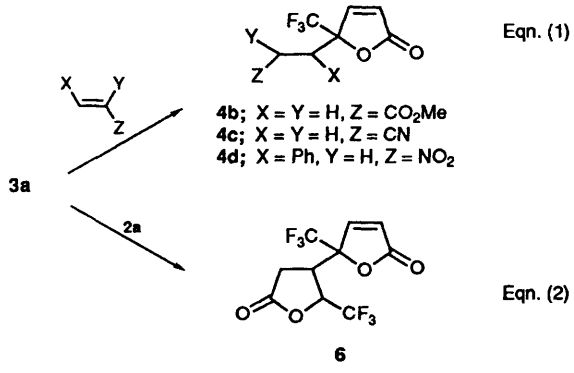


Scheme 6

Table 2 The reactions of **2a** with methyl methacrylate under a variety of conditions[a]

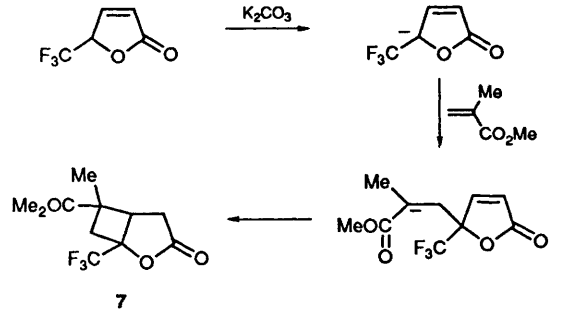
Run	Temp	Olefin (mmol)	Addition time	Yields (%) 7	6
1	Room temp.	5	20 min	1	83
2	50 °C	5	20 min	0	76
3	Room temp	20	1 h	8	73
4	Room temp.	100	7 h	82	Trace

[a] Butenolide **2a** (1 mmol) dissolved in acetonitrile (5 cm^3) was added to a solution of methyl methacrylate in acetonitrile (10 cm^3) in the presence of K_2CO_3.



Scheme 7

under various conditions in order to prevent the formation of dimer **6**. Thus, when a solution of **2a** (1 mmol) in acetonitrile (5 cm^3) was added to a solution of methyl methacrylate (100 mmol) in acetonitrile (10 cm^3) in the presence of K_2CO_3 over 7 h, no dimer **6** was formed. Interestingly, in this reaction the Michael adduct **4** also failed to form; the bicyclic compound **7**, however, was obtained (82%) as a result of intramolecular tandem Michael addition (see Scheme 8). The results obtained under various conditions are shown in Table 2.



Scheme 8

In conclusion, various 4-fluoroalkylated but-2-en-4-olides have been conveniently prepared from furan, 2-trimethylsiloxyfuran, and 2-methoxyfuran. The butenolide **2a** thus prepared was found to act as good Michael donor and acceptor. Therefore, **2a** is expected to be a useful building block for the synthesis of trifluoromethyl-modified natural products. Under basic conditions the butenolide **2b** eliminated fluoride ion to give perfluoroalkylidenebutenolide.

Experimental

^1H NMR spectra were taken with a JEOL JNM PMX60SI (60 MHz) or JNM EX400 (400 MHz) spectrometers. ^{13}C and ^{19}F NMR spectra were taken with a JEOL JNM FX90Q or JNM Ex400 spectrometer. Fluorine chemical shifts are given in ppm from external CF_3CO_2H; J values are recorded in Hz. IR spectra were recorded on a Hitachi 260-10 spectrometer. Gas chromatography was performed by a Hitachi G-3000 gas chromatograph with a SE-30 (10%) 2 m stainless column. Gel-permeation chromatography (GPC) was performed by means of a JAI Model LC-08 liquid chromatograph equipped with two JAIGEL-1H columns (20 mm × 600 mm) with chloroform as eluent. Mass spectra were obtained with a JEOL JMS AX-505 spectrometer by an electron-impact (EI) ionization technique at 70 eV.

Materials.—Bis(trifluoroacetyl) peroxide **1a** and bis(chlorodifluoroacetyl) peroxide **1c** were prepared from the corresponding acetic anhydrides and 30% hydrogen peroxide in Freon 113–water as was described in our previous papers.[5,10] Bis(heptafluorobutyryl) peroxide **1b** was prepared from heptafluorobutyryl chloride in Freon 113–water according to the literature.[15] These peroxides were not isolated but used as solutions in Freon 113; the concentrations of the peroxides were determined by iodometry. *m*-Nitrobenzenesulfonyl peroxide was prepared according to the literature.[9] 2-Trimethylsiloxy- and 2-methoxy-furan were obtained from Aldrich Chemical Co. Inc. and distilled prior to use.

General Procedure for the Preparations of **2a–c**.—(i) To a solution of **1a** in Freon 113 (0.1 mol dm^{-3}) was added 2-trimethylsiloxyfuran (2.0 mol equiv.), and the resulting solution was degassed by freeze–pump–thaw cycles, sealed in an ampoule, and heated at 60 °C for 4 h. The butenolide **2a** was obtained from the reaction mixture by distillation (100–105 °C/30 mmHg), and further purified by GPC. Similarly, the butenolides **2b** and **2c** were obtained.

(ii) To a solution of the furan (2 mmol) in dichloromethane (10 cm^3) was added **1a** (1 mmol) in Freon 113, and the resulting solution was degassed by freeze–pump–thaw cycles, sealed in an ampoule, and kept at 60 °C for 4 h. The reaction mixture was washed twice with 5% aqueous $NaHCO_3$ and then water, and then dried ($MgSO_4$). To this solution solid *m*-NBSP (1.0 mol equiv.) was added at 0 °C, and the reaction mixture then heated under reflux for 20 h. It was then quickly washed with 5% aqueous $NaHCO_3$, and dried ($MgSO_4$) and evaporated; the residue provided the butenolide **2a** by GPC.

4-Trifluoromethylbut-2-en-4-olide **2a**; $\delta_H(CDCl_3)$ 5.28 (q, m, J_{HF} 5.7, 1 H, 2-H), 6.35 (d, m, J_{HH} 6.0, 1 H, 4-H), 7.37 (dd, J_{HH} 6.0 and 2.0, 1 H, 3-H); $\delta_C(CDCl_3)$ 78.7 (q, J_{CCF} 35.4), 125.7, 147.1 and 170.4; ν_{max}(neat)/cm^{-1} 1800 (C=O) and 1360 (CF_3); *m*/*z* 152 (M^+) (Found: M^+, 152.0175. Calc. for $C_5H_3F_3O_2$: *M*, 152.0164).

4-Heptafluoropropylbut-2-en-4-olide **2b**; $\delta_H(CDCl_3)$ 5.48 (d, d, J_{HF} 13.2 and 6.6, 1 H, 4-H), 6.47 (d, J_{HH} 5.7, 1 H, 2-H), 7.56 (d, J_{HH} 5.7, 1 H, 3-H); $\delta_C(CDCl_3)$ 77.8 (dd, J_{CCF} 30.5 and 25.6), 125.9, 146.9 and 170.1; ν_{max}(neat)/cm^{-1} 1800 (C=O), 1340 (CF_3) and 1220 (CF_2); *m*/*z* 252 (M^+) (Found: M^+, 251.9962. Calc. for $C_7H_3F_7O_2$: *M*, 252.0021).

4-Chlorodifluoromethylbut-2-en-4-olide **2c**; $\delta_H(CDCl_3)$ 5.36 (t, m, J_{HF} 5.4, 1 H, 4-H), 6.43 (d, m, J_{HH} 6.0, 1 H, 2-H) and 7.45 (dd, 6.0 and 2.0, 1 H, 3-H); $\delta_C(CDCl_3)$ 82.7 (t, J_{CCF} 31.7), 125.9, 147.6 and 170.1; ν_{max}(neat)/cm^{-1} 1800 (C=O); *m*/*z* 168 (M^+) and 133 (M − Cl) (Found: M^+ − Cl, 133.0085. Calc. for $C_5H_3F_2O_2$: M^+ − Cl, 133.0102).

Synthesis of 4-*Difluoromethylbut*-2-*en*-4-*olide* **2d**.—2-Methoxyfuran (5.0 mmol) was treated with the peroxide **1c** (3.0 mmol) in Freon 113 at 20 °C for 10 min under degassed conditions. The reaction mixture was washed with 5% aqueous $NaHCO_3$ (30 cm^3) and water (30 cm^3) and then dried ($MgSO_4$) and evaporated. The residual oil was distilled to give 2-

chlorodifluoro-5-methoxyfuran (34%), b.p. 60 °C/24 mmHg. A solution of 2-chlorodifluoromethyl-5-methoxyfuran (0.61 mmol), tris(trimethylsilyl)silane (0.91 mmol), and catalytic amount of AIBN in benzene (25 cm^3) was refluxed for 3 h. Trifluoroacetic acid (0.61 mmol) was added to the reaction mixture, which was then stirred at room temperature for 1 day after which it was evaporated. 4-Difluoromethylbut-2-en-4-olide (51%) was isolated by GPC from the residue.

4-Difluoromethylbut-2-en-4-olide **2d**; $\delta_H(CDCl_3)$ 5.19 (m, 1 H, 4-H), 5.57 (d, t, J 3.9, J_{HF} 54.7, 1 H, CHF_2), 6.37 (d, J 5.9, 1 H, 2-H) and 7.52 (d, J 5.9, 1 H, 3-H); $\delta_C(CDCl_3)$ 80.3 (t, J_{CCF} 28), 112.1 (t, J_{CF} 246), 125.1, 148.7 and 171.1; ν_{max}(neat)/cm^{-1} 1790 and 1760 (C=O); m/z 134 (M^+) (Found: M, 134.0236. Calc. for $C_5H_4F_2O_2$: M, 134.0179).

Michael Reactions of **2a**.—The butenolide **2a** (1.0 mmol) dissolved in acetonitrile (5 cm^3) was added to a solution of the olefin (5 mmol) in acetonitrile (10 cm^3) in the presence of potassium carbonate, and the reaction mixture was stirred at room temperature for 2 h. It was then evaporated and the residual oil was dissolved in ether (20 cm^3) and the solution washed with water (20 cm^3 × 2), dried ($MgSO_4$), and evaporated. The products were separated by GPC. The butenolide derivatives so obtained, **4a–d**, **6** and **7**, were identified by spectroscopic analysis.

4a; $\delta_H(CDCl_3)$ 2.11 (3 H, s, CH_3), 2.41 (4 H, s, CH_2CH_2), 6.29 and 7.31 (ABq, J 6.0, 2 H); $\delta_C(CDCl_3)$ 23.9, 29.8, 35.6, 87.0 (q, J_{CCF} 31), 122.9 (q, J_{CF} 284), 125.0, 151.1, 170.0 and 205.6; $\delta_F(CDCl_3)$ −2.34; ν_{max}(neat)/cm^{-1} 1790 (C=O) and 1715 (C=O); m/z 222 (M^+) (Found: M, 222.0527. Calc. for $C_9H_9F_3O_3$: M, 222.0503).

4b; $\delta_H(CDCl_3)$ 2.37 (m, 4 H, CH_2CH_2), 3.64 (s, 3 H, OCH_3), 6.35 and 7.39 (ABq, J 6.0, 2 H); $\delta_C(CDCl_3)$ 25.5, 26.7, 52.1, 86.6 (q, J_{CCF} 30), 122.9 (q, J_{CF} 284), 125.6, 150.5, 169.8 and 172.2; $\delta_F(CDCl_3)$ −2.49; ν_{max}(neat)/cm^{-1} 1805 (C=O) and 1745 (C=O) cm^{-1}; m/z 238 (M^+) (Found: M, 238.0417. Calc. for $C_9H_9F_3O_4$: M, 238.0453).

4c; $\delta_H(CDCl_3)$ 2.43 (s, br, 4 H, CH_2CH_2), 6.45 and 7.43 (ABq, J 6.0, 2 H); $\delta_C(CDCl_3)$ 11.1, 26.8, 86.0 (q, J_{CCF} 32), 117.9, 122.5 (q, J_{CF} 284), 126.7, 149.6 and 169.2; ν_{max}(neat)/cm^{-1} 2250 (C≡N) and 1800 (C=O); m/z 206 (M^+ + 1) (Found: M + 1, 206.0424. Calc. for $C_8H_7F_3NO_2$: M + 1, 206.0428).

4d; $\delta_H(CDCl_3)$ 4.42 (dd, J 9.8, 5.0, 1 H, CPh*H*), 4.91 (dd, J 13.7, 9.8, 1 H, CH_2NO_2), 5.40 (dd, J 13.7, 5.0, 1 H), 6.06 (d, J 5.9, 1 H), 7.18 (m, 3 H) and 7.31 (m, 3 H); $\delta_C(CDCl_3)$ 44.8, 74.9, 87.2 (q, J_{CCF} 29), 122.6 (J_{CF} 285), 125.0, 128.3, 129.4, 129.5, 132.2, 150.1 and 169.3; m/z 301 (M^+) (Found: M, 301.0474. Calc. for $C_{13}H_{10}F_3NO_4$: M, 301.0562).

6; Although four isomeric products are possible from the reaction of the anion **3a** with **2a**, only two of them actually formed, the major one being isolated in pure form as colourless crystals; m.p. 93–95 °C (from hexane); $\delta_H(CDCl_3)$ 2.83 (dd, J 19.0, 5.0 1 H, CH_2CO), 2.98 (dd, J 19.0, 10.0, 1 H, CH_2CO), 3.04 (t, d, J 10.0, 5.0, 1 H, CH_2CH), 4.48 (d, t, J 10.0, J_{HF} 5.9, 1 H, $CHCF_3$), 6.61 and 7.36 (ABq, J 5.9, 2 H); $\delta_C(CDCl_3)$ 28.1, 36.6, 74.4 (q, J_{CCF} 34), 86.5 (q, J_{CCF} 29), 122.4 (q, J_{CF} 284), 122.9 (q, J_{CF} 281), 128.0, 148.1, 168.0, 171.6; $\delta_F(CDCl_3)$ 0.76 (s), −3.06 (d, J_{HF} 5.9); ν_{max}(neat)/cm^{-1} 1805 (C=O) (Found: C, 39.5; H, 1.9%. Calc. for $C_{10}H_6F_6O_4$: C, 39.49; H, 1.99%).

7; $\delta_H(CDCl_3)$ 1.41 (s, 3 H, CH_3), 2.74 (d, J 5.4, 2 H, CH_2CO), 2.21 and 3.16 (ABq, J 14.4, 2 H, CH_2CCF_3), 3.72 (t, J 5.4, 1 H, CH_2CH) and 3.76 (s, 3 H, OCH_3); $\delta_C(CDCl_3)$ 19.5, 29.0, 37.1, 40.1, 52.8, 174.9 and 175.3; $\delta_F(CDCl_3)$ −6.38; m/z 252 (M^+) (Found: 252.0586. Calc. for $C_{10}H_{11}F_3O_4$; M, 252.0608).

The reaction of the butenolide **2b** (0.5 mmol) with methyl vinyl ketone was carried out under similar conditions. The reaction mixture (80 mg) was subjected to column chromatography on Wakogel C-200 (hexane–ethyl acetate, 1 : 1 as eluent) to remove polymeric by-products. Fluoroalkylidenebutenolides (44 mg) were obtained as a mixture of the stereoisomers, **5a** and **5b**, the corresponding Michael adduct **4** not being produced. The isomers could be separated from each other by GPC (major product 28 mg and minor product 12 mg). We tentatively assigned the structure of the major product as **5a** and that of the minor product as **5b**, since the small *exo* substituent usually prefers to be *cis* to the ring hydrogen at 3-position in alkylidenebutenolides.[16]

5a; $\delta_H(CDCl_3)$ 6.46 (d, J 5.4, 1 H), 7.22 (d, J 5.4, 1 H); $\delta_C(CDCl_3)$ 123.2 (d, J_{CF} 11), 131.7 (d, t, J_{C-F} 276, J_{CCF} 30), 139.7, 141.5 (d, J_{CCF} 11) and 165.6; $\delta_F(CDCl_3)$ −59.4 (t, J 17, 1 F), −43.5 (d, J 17, 2 F) and −8.69 (s, 3 F); ν_{max}(neat)/cm^{-1} 1800 (C=O); m/z 232 (M^+) (Found: M^+, 231.9993. Calc. for $C_7H_2F_6O_2$: M, 231.9959).

5b; $\delta_H(CDCl_3)$ 6.48 (d, J 5.4, 1 H) and 7.87 (d, J 5.4, 1 H); $\delta_C(CDCl_3)$ 122.7 (d, J_{C-F} 5), 133.0 (d, t, J_{CF} 261, J_{CCF} 31), 139.1 and 143.6 (d, J_{CCF} 40), 166.5; $\delta_F(CDCl_3)$ −81.2 (t, J 17, 1 F), −44.7 (d, J 17, 2 F) and −8.54 (s, 3 F); ν_{max}(neat)/cm^{-1} 1808 (C=O); m/z 232 (M^+) (Found: M^+, 231.9991. Calc. for $C_7H_2F_6O_2$: M, 231.9959).

References

1 R. Filler and Y. Kobayashi, *Biomedical Aspects of Fluorine Chemistry*, Kodansha Ltd., Tokyo, 1982.
2 T. Fuchigami, *Yuki Gosei Kagaku Kyokaishi*, 1984, **42**, 775; *Synthesis of Fluorine Compounds*, ed. by I.L. Knunyants and G. G. Yakobson, Springer-Verlag, New York, 1985; J. T. Welch, *Tetrahedron*, 1987, **43**, 3123; T. Yamazaki and T. Kitazume, *Yuki Gousei Kagaku Kyokaishi*, 1991, **49**, 721.
3 K. Uneyama, *Yuki Gousei Kagaku Kyokaishi*, 1991, **49**, 612; M. A. McClinton and D. A. McClinton, *Tetrahedron*, 1992, **48**, 6555.
4 M. Yoshida, N. Kamigata, H. Sawada and M. Nakayama, *J. Fluorine Chem.*, 1990, **49**, 1.
5 H. Sawada, M. Yoshida, H. Hagii, K. Aoshima and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 215; M. Yoshida, T. Yoshida, N. Kamigata and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3594; M. Yoshida, T. Yoshida, M. Kobayashi and N. Kamigata, *J. Chem. Soc., Perkin Trans. 1*, 1989, 909; H, Sawada, M. Nakayama, M. Yoshida, T. Yoshida and N. Kamigata, *J. Fluorine Chem.*, 1990, **46**, 423.
6 C. W. Jefford, D. Jaggi, A. W. Seledeski and J. Boukouvalas, *Studies in Natural Products Chemistry*, ed. by Atta-ur-Rahman, Elsevier, Amsterdam, vol. 3, p. 157 (1989).
7 N. Bordor, M. J. S. Dewar and A. J. Harget, *J. Am. Chem. Soc.*, 1970, **92**, 2929.
8 M. Asaoka, N. Sugimura and H. Takei, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1953; C. W. Jefford, A. W. Seledeski and J. Boukouvalas, *J. Chem. Soc., Chem. Commun.*, 1988, 364.
9 R. L. Dannley, J. E. Gagn and O. J. Stewart, *J. Org. Chem.*, 1970, **35**, 3076.
10 M. Yoshida, Y. Morinaga, M. Ueda, N. Kamigata and M. Iyoda, *Chem. Lett.*, 1992, 227.
11 G. A. Kraus and B. Roth, *Tetrahedron Lett.*, 1977, 3129; B. Cederlund, A. Jesporson and A.-B. Hornfeldt, *Acta Chem. Scand.*, 1971, **25**, 3656; D. R. Gedge and G. Pattenden, *Tetrahedron Lett.*, 1977, 4443.
12 T. Nakai, K. Tanaka, H. Setoi and N. Ishikawa, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 3069.
13 T. Yokozawa, T. Nakai and N. Ishikawa, *Tetrahedron Lett.*, 1984, 3987 and 3991; T. Fuchigami and Y. Nakagawa, *J. Org. Chem.*, 1987, **52**, 5276; K. Uneyama and M. Momota, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 3378; C.-P. Qiun and T. Nakai, *Tetrahedron Lett.*, 1990, **31**, 7043; M. Kuroboshi and T. Ishihara, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1191.
14 T. Ishihara, *Yuki Gousei Kagaku Kyokaishi*, 1992, **50**, 347.
15 C. Zhao, R. Zhou, H. Pan, X. Jin, Y. Qu, C. Wu and X. Jiang, *J. Org. Chem.*, 1982, **47**, 2009.
16 G. A. Kraus and H. Sugimoto, *J. Chem. Soc., Chem. Commun.*, 1978, 30.

Paper 2/04629F
Received 27*th August* 1992
Accepted 6*th November* 1992