Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Fluorine Chemistry 126 (2005) 63–67
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Synthesis of α,α-difluoro-γ-butyrolactones via ethyl iododifluoroacetate

Fanhua Xiao[a], Fanhong Wu[a,b,*], Yongjia Shen[a], Lifang Zhou[a]

[a]*College of Chemistry and Pharmaceutics, East China University of Science and Technology, Box 422, 130 Meilong Road, Shanghai 200237, China*
[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

Received 9 June 2004; received in revised form 13 September 2004; accepted 16 October 2004
Available online 2 December 2004

Abstract

A novel synthesis of α,α-difluoro-γ-butyrolactones was realized by the alkaline hydrolysis of the adducts of ethyl iododifluoroacetate and alkenes. Ethyl iododifluoroacetate reacted with alkenes in the presence of sodium dithionite to give the addition products in 62–78% yields. The products were hydrolyzed in 10% aqueous sodium carbonate solution to give α,α-difluoro-γ-butyrolactones in 93–98% yields.

Keywords: Synthesis; α,α-Difluoro-γ-butyrolactone; Ethyl iododifluoroacetate; Sodium dithionite

1. Introduction

Partially fluorinated analogues of biologically important compounds bring about dramatic changes and distinctive modifications in their biological activities; this makes it more necessary to establish the efficient methods for the synthesis of selectively fluorinated compounds [1]. We are interested in the synthesis of fluorinated γ-lactones, which are important synthons that display more unique biologically active properties in organic chemistry [2]. We have reported some polyfluoroalkyl-γ-butyrolactones synthesized by the reaction of 4-pentenoic acids and polyfluoroalkyl iodides [3]. In addition, since it is believed that difluoromethylene moiety acts similar to ether-oxygen in vivo and interesting biological activity is anticipated for analogues of α,α-difluorinated biomolecules [4], several works have been reported on the methods to introduce the CF_2 group into organic molecules [5–7]. In this paper, we wish to report the synthesis of α,α-difluoro-γ-butyrolactones through the hydrolysis of the adduct **3** by the reaction of alkenes (**1**) with ethyl iododifluoroacetate (**2**) initiated by sodium dithionite.

2. Results and discussion

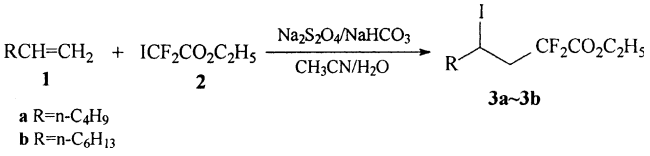
2.1. The addition reaction between alkenes and ethyl iododifluoroacetate

The addition reaction between alkenes and ethyl iododifluoroacetate was first reported by copper powder (10–20 mol%) in 65–83% yield at 50–60 °C [8]. The reaction of iododifluoroacetates with alkenes and zinc in the presence of catalytic amounts of nickel dichloride hexahydrate produced α,α-difluoro functionalized esters in good yields [6,9]. A single electron transfer initiated radical mechanism was proposed and confirmed by direct evidence of free radical as transient intermediates by spin trapping [10].

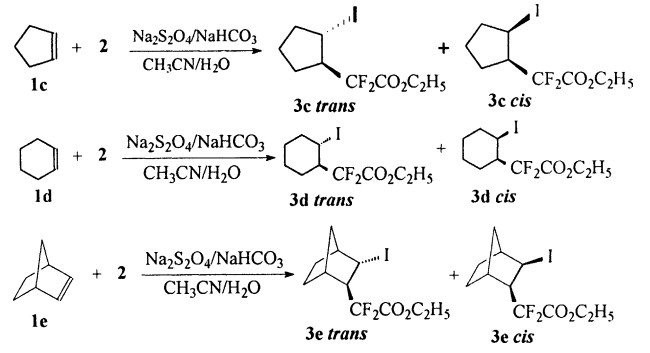
Studies on the sulfinatodehalogenation reaction showed that sodium dithionite was able to initiate the addition of perfluoroalkyl iodides to olefins effectively [11].

* Corresponding author. Fax: +86 21 64253074.
E-mail address: wfh@ecust.edu.cn (F. Wu).

0022-1139/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2004.10.009



Scheme 1.



Scheme 2.

Therefore, we tried the reaction of ethyl iododifluoroacetate (**2**) with alkenes in the presence of sodium dithionite in aqueous acetonitrile solution. It showed that the reaction took place readily at room temperature and completed within 4 h. The volume ratio of acetonitrile as cosolvents used to improve the mutual solubility of various reactants to water was 3:1.

The addition of **2** to terminal alkenes in the presence of sodium dithionite gave the corresponding products at room temperature. For example, in the case of the reaction of **2** with 1-hexene and sodium dithionite, ethyl-2,2-difluoro-4-iodooctanoate (**3a**) was isolated in 76% yield (Scheme 1).

The addition reaction could be successfully applied to internal alkenes. Upon reaction of **2** with cyclopentene (**1c**) and sodium dithionite, adduct *cis*-**3c** was isolated in 75% yield. The reaction of cyclohexene (**1d**) gave the corresponding *trans*- and *cis*-isomers in a 1.6:1 ratio. In the reaction with norbornene (**1e**), *trans*-**3e** was separated by column chromatography eluting with petroleum ether and ethyl acetate in 67% yield from the mixture of *trans*/*cis*-isomers in a 4:1 ratio. The structures of the isomers were assigned based on their ^{19}F NMR, ^{1}H NMR and ^{13}C NMR data (Scheme 2).

Previous reports by Huang et al. [12–14] documented that the addition of perfluoroalkyl iodides to alkenes can be initiated by sodium dithionite. A free radical chain involving a single electron transfer mechanism has been proposed in the addition reaction [15]. Accordingly, we propose that reaction of **2** with alkenes may also involve a single electron transfer (SET) process for the anion radical (Fig. 1).

In the addition to bicyclo-alkene norbornene (**1e**), the initial attack by free radical R_F could be from both the endo side and the exo side. Since the attack from the endo side was less-hindered, so the R_F-endo products were the only products.

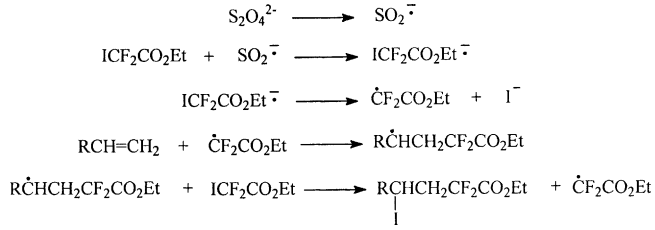


Fig. 1. The reaction mechanism of ethyl iododifluoroacetate with alkenes initiated by sodium dithionite.

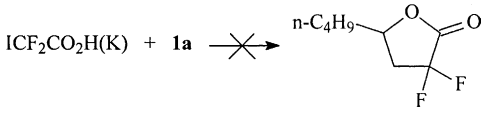


Fig. 2. The reaction of iododifluoroacetic acid with 1-hexene.

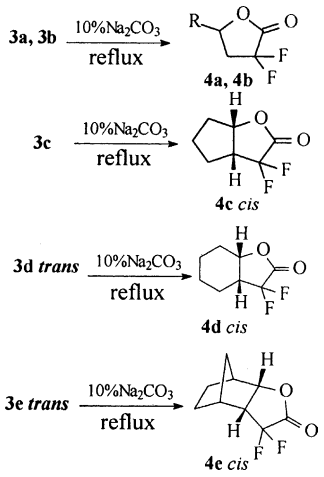
2.2. Hydrolysis of the adducts

Several examples were reported to provide α,α-difluoro-γ-lactones. Systematic synthesis of multifluorinated-α,α-difluoro-γ-lactones was accomplished through intramolecular radical cyclization as a key reaction of *O*-(trimethylsilyl)-α-bromo-α,α-difluoroacetate. The efforts failed to synthesize the lactones via radical cyclization directly of allyl-α,α-difluoro-α-iodoacetate [4]. The addition product of *N*,*N*-diethyl iododifluoroacetamide with alkenes could be converted into α,α-difluoro-γ-lactones by column chromatography on silica gel, which was considered that the amide groups were hydrolyzed on the surface of silica gel and subsequently cyclized to form γ-lactones [7].

In order to synthesize the lactones, we tried the reaction of iododifluoroacetic acid or the sodium salt with alkenes in the presence of sodium dithionite. However, no desired product was obtained (Fig. 2).

When the addition product **3a** was treated with 3% aqueous sodium hydroxide solution at room temperature for 1 h, γ-lactone (**4a**) was also obtained in 82% yield. Several by-products were found in the crude product determined by GC and GC–MS analysis which were difficult to separate by column chromatography. When the products **3a–e** were treated with 10% aqueous sodium carbonate solution, α,α-difluoro-γ-butyrolactones **4a–e** was produced in 93–98% yields (Scheme 3). For example, the addition product **3a** and 10% aqueous sodium carbonate were refluxed for 4 h to give the corresponding lactone (**4a**) in 93% yield after usual workup. Under similar conditions, the adduct **3c** was hydrolyzed to give the cyclization product **4c** in 93% yield.

It was not surprising that the NOESY spectra data of lactone (**4c**) suggested the configuration of **4c** was *cis*. The formation of lactones was supposed to be through the intramolecular neucleophilic substitution of the hydrolyzed products of the adducts. May be the *cis*-isomers of the five or six membered ring fused lactones were more stable than the *trans*-isomers.



Scheme 3.

In summary, a novel and efficient synthesis method of α,α-difluoro-γ-butyrolactones was realized by the hydrolysis of the addition products of alkenes with ethyl iododifluoroacetate initiated by sodium dithionite in aqueous sodium carbonate solution under mild conditions in high yields (Tables 1 and 2).

3. Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AC-500 (500 MHz) spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. ^{19}F NMR spectra were recorded with Bruker AC-500 (500 MHz) spectrometer with $CDCl_3$ as the solvent and TFA as the external standard. Infrared spectra were measured using a Nicolet Magna IR-550 instrument. High-resolution mass spectra were obtained on Finnigan GC-MS-4021 spectrometers. GC was measured by using Shimadzu GC-14B instrument. The configurations of **3c–e** and **4c–e** were confirmed by two-dimensional NMR (COSY, NOESY, HMQC and HMBC).

3.1. General method for the synthesis of adduct *3*

In a typical experiment, alkene (10 mmol) and ethyl iododifluoroacetate (12 mmol) were dissolved in the solution of water (10 ml) and acetonitrile (10 ml). Sodium dithionite (3.7 g) and sodium bicarbonate (1.85 g) was added to the solution. The mixture was stirred at ambient temperature for 6 h. When the reaction accomplished, the reactant was treated with water (ca. 50 ml). The mixture was extracted with ether of 3× 20 ml. The combined organic layer was washed with saturated brine and dried over anhydrous sodium sulfate. After the evaporation of ether, the crude product was purified by column chromatography or distillation under reduced pressure to give **3a–e**.

Table 1
The addition reaction between alkenes and ethyl iododifluoroacetate

Entry	Alkenes	Products	Isolated yield (%)	*Cis*	*Trans*
1	**1a**	**3a**	76	–	–
2	**1b**	**3b**	78	–	–
3	**1c**	**3c**	75	Trace	100
4	**1d**	**3d**	62	1	1.6
5	**1e**	**3e**	67	1	4

Table 2
Synthesis of α,α-difluoro-γ-butyrolactones

Entry	Adducts	Lactones	Isolated yield (%)	Configuration
1	**3a**	**4a**	93	–
2	**3b**	**4b**	96	–
3	**3c**	**4c**	93	*Cis*
4	**3d**	**4d**	98	*Cis*
5	**3e**	**4e**	96	*Cis*

3.1.1. Ethyl-2,2-difluoro-4-iodooctanoate (*3a*)

The product was isolated in 76% yield by distillation at reduced pressure, bp 103–105 °C, 3–4 mmHg; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 0.93 (3H, t, H-8), 1.38 (3H, t, J = 7.1 Hz, CH_3CH_2O), 1.38 (2H, m, H-7), 146 (2H, m, H-6), 1.80 (2H, m, H-5), 2.87 (2H, m, H-3), 4.22 (1H, m, H-4), 4.35 (2H, q, J = 7.1 Hz, CH_2O); ^{19}F NMR (470 MHz, $CDCl_3$), δ: 107.90 (dt, 1F, $J_{F,F}$ = 258.5 Hz, $J_{F,H}$ = 18.8 Hz), −103.18 (ddd, 1F, $J_{F,F}$ = 263.2 Hz, $J_{F,H}$ = 18.8 Hz, $J_{F,H}$ = 9.4 Hz); in accordance with Ref. [6].

3.1.2. Ethyl-2,2-difluoro-4-iododecanoate (*3b*)

The product was isolated in 76% yield by distillation at reduced pressure; bp 108–110 °C, 2–3 mmHg; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 0.89 (3H, t, H-10), 1.29 (6H, m, H-7, 8, 9), 1.38 (3H, t, J = 7.1, CH_3CH_2O), 1.50 (2H, m, H-6), 1.81 (2H, m, H-5), 2.86 (2H, m, H-3), 4.22 (1H, m, H-4), 4.35 (2H, q, J = 7.1 Hz, CH_2O); ^{19}F NMR (470 MHz, $CDCl_3$), δ: 107.91 (dt, $J_{F,F}$ = 258.5 Hz, $J_{F,H}$ = 18.8 Hz, 1F), −103.16 (ddd, $J_{F,F}$ = 263.2 Hz, $J_{F,H}$ = 18.8 Hz, $J_{F,H}$ = 14.1 Hz, 1F); in accordance with Ref. [6].

3.1.3. Ethyl-α,α-difluoro-(2-iodocyclopentanyl)acetate (*trans-3c*)

The product was isolated in 75% yield by column chromatography eluting with petroleum ether and ethyl acetate (10:1). IR (film), ν (cm^{-1}): 2980, 1780 (γ-lactone), 1300, 1220, 720; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 1.39 (3H, t, J = 7.1 Hz, CH_3CH_2O, H-10), 1.73 (2H, m, H-4), 1.89 (2H, m, H-5), 2.17 (2H, m, H-3), 3.13 (1H, m, H-1), 4.31 (1H, m, H-2), 4.37 (2H, q, J = 7.1 Hz, CH_2O); ^{19}F NMR (470 MHz, $CDCl_3$), δ: 114.21 (dd, $J_{F,F}$ = 258.5 Hz, $J_{F,H}$ = 14.1 Hz, 1F), −111.95 (dd, $J_{F,F}$ = 258.5 Hz, $J_{F,H}$ = 14.1 Hz, 1F); ^{13}C NMR (125.8 MHz, $CDCl_3$): 14.7 (s, CH_3), 20.2 (s, C-5), 26.2 (s, C-2), 26.0 (S, C-4), 41.9 (s, C-3), 55.9 (t, C-1), 63.8 (s, CH_2O), 116.7 (t, CF_2), 164.2 (s, C=O); HRMS calcd. for $C_9H_{13}O_2F_2I$ 318.1012, found 318.1015.

*3.1.4. Ethyl-α,α-difluoro-(2-iodocyclohexanyl)acetate (trans-**3d**)*

The pure *trans*-isomer was isolated from a mixture of *trans*- and *cis*-isomers by column chromatography eluting with petroleum ether and ethyl acetate (100:1). *Trans*-isomer: IR (film), ν (cm^{-1}): 2980, 1780 (γ-lactone), 1300, 1220, 720; ^1H NMR (500 MHz, $CDCl_3$), δ: 1.38 (3H, t, $J = 7.1$, CH_3CH_2O), 1.45 (3H, m, H-4,5,6), 1.63 (1H, m, H-4), 1.80 (1H, m, H-5), 2.06 (2H, m, H-3 and H-6), 2.35 (1H, m, H-3), 2.73 (1H, m, H-1), 4.35 (1H, m, H-2), 4.36 (2H, q, $J = 7.1$ Hz, CH_2O); ^{19}F NMR (470 MHz, $CDCl_3$), δ: −112.37 (dd, $J_{F,F} = 258.5$ Hz, $J_{F,H} = 14.1$ Hz, 1F), −106.67 (dd, $J_{F,F} = 258.5$ Hz, $J_{F,H} = 14.1$ Hz, 1F); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ: 13.8 (s, CH_3), 24.0 (s, C-5), 25.0 (s, C-6), 26.0 (s, C-2), 27.0 (s, C-4), 39.7 (s, C-3), 48.8 (t, C-1), 63.8 (s, OCH_2), 164.5–163.9 (t, C=O), 117.0 (t, CF_2); HRMS calcd. for $C_{10}H_{15}O_2F_2I$ 332.0085, found 332.0078.

*3.1.5. Ethyl-α,α-difluoro-(3-iodobicyclo[2,2,1]hept-2-yl)acetate (**3e**)*

The product was isolated in 67% yield by column chromatography eluting with petroleum ether and ethyl acetate (80:1). IR (film), ν (cm^{-1}): 2980, 2900, 1770 (γ-lactone), 1450, 1310, 1080, 850, 780; ^1H NMR (500 MHz, $CDCl_3$), δ: 1.27 (1H, m, H-7), 1.31 (1H, m, H-6), 1.38 (3H, t, $J = 7.1$ Hz, CH_3), 1.61 (1H, m, H-6), 1.64 (1H, m, H-5), 1.69 (1H, m, H-7), 1.83 (1H, m, H-5), 2.29 (1H, m, H-2), 2.35 (1H, s, H-1), 2.47 (1H, s, H-4), 4.22 (IH, m, H-3), 4.37 (2H, q, $J = 7.1$ Hz, OCH_2); ^{19}F NMR (470 MHz, $CDCl_3$), δ: 116.22 (dd, $J_{F,F} = 253.8$ Hz, $J_{F,H} = 18.8$ Hz, 1F), −110.14 (dd, $J_{F,F} = 253.8$ Hz, $J_{F,H} = 14.1$ Hz, 1F); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ: 14.6 (s, CH_3), 27.9 (s, C-5), 27.9 (s, C-3), 30.6 (s, C-6), 35.6 (s, C-7), 38.0 (s, C-1), 456 (s, C-4), 58.3 (t, C-2), 63.9 (s, OCH_2), 116.2 (t, CF_2), 164.3 (t, C=O); HRMS calcd. for $C_{11}H_{15}O_2F_2I$ 344.0085, found 344.0080.

*3.2. General method for the synthesis of α,α-difluoro-γ-lactones (**4**)*

A mixture of the adduct **3a**–**e** (1 g) and 10% Na_2CO_3 aqueous solution (10 ml) was refluxed for 4 h. The mixture was acidified and extracted with ether, washed with saturated brine and dried over anhydrous sodium sulfate. After concentrated, the crude product was purified by column chromatography to give lactones **4a**–**e**.

*3.2.1. 3,3-Difluoro-5-butyldihydrofuran-2-one (**4a**)*

The product was isolated in 93% yield by column chromatography eluting with petroleum ether and ethyl acetate (10:1). IR (film), ν (cm^{-1}): 2980, 1810 (γ-lactone), 1480, 1420, 1320, 1260, 1100, 1000, 740; ^1H NMR (500 MHz, $CDCl_3$), δ: 0.93 (3H, t, $J = 7.1$ Hz, H-9), 1.83–1.81 (m, 1H), 1.44 (m, 4H, m, H-7 and H-8), 1.76 (2H, m, C-6), 2.32 (1H, m, H-4), 2.83 (1H, m, H-4), 4.62 (1H, m, H-5); ^{19}F NMR (470 MHz, $CDCl_3$), δ: 108.75 (ddd, $J_{F,F} = 277.3$ Hz, $J_{F,H} = 14.1$ Hz, $J_{F,H} = 4.7$ Hz, 1F), −107.35 (ddd, $J_{F,F} = 277.3$ Hz, $J_{F,H} = 23.5$ Hz, $J_{F,H} = 18.8$ Hz, 1F); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ: 13.8 (s, C-9), 22.3 (s, C-8), 26.8 (s, C-7), 34.9 (s, C-6), 37.6 (t, C-4), 115.7 (t, C-3), 76.8 (s, C-5), 165.2 (t, C-2); HRMS calcd. for $C_8H_{11}O_2F_2$ ($M - 1$) 177.0727, found 177.0732.

*3.2.2. 3,3-Difluoro-5-hexyldihydrofuran-2-one (**4b**)*

The product was isolated in 96% yield by column chromatography eluting with petroleum ether and ethyl acetate (10:1). IR (film), ν (cm^{-1}): 2960, 2900, 1810 (γ-lactone), 1480, 1420, 1320, 1260, 1100, 760; ^1H NMR (500 MHz, $CDCl_3$), δ: 0.89 (3H, t, $J = 7.1$ Hz, H-11), 1.45 (8H, m, H-7,8,9,10), 1.71 (1H, m, H-6), 1.81 (1H, m, H-6), 2.33 (1H, m, H-4), 2.84 (1H, m, H-4), 4.62 (1H, m, H-5); ^{19}F NMR (470 MHz, $CDCl_3$), δ: 108.78 (ddd, $J_{F,F} = 277.3$ Hz, $J_{F,H} = 14.1$ Hz, $J_{F,H} = 4.7$ Hz, 1F), −107.44 (ddd, $J_{F,F} = 282$ Hz, $J_{F,H} = 21.2$ Hz, $J_{F,H} = 16.5$ Hz, 1F); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ: 13.9 (s, C-11), 22.4 (s, C-10), 24.5 (s, C-9), 28.6 (s, C-8), 31.4 (s, C-7), 35.1 (s, C-6), 37.4 (t, C-4), 76.8 (s, C-5), 115.6 (t, C-3), 165.2 (t, C-2); HRMS calcd. for $C_{10}H_{16}O_2F_2$ 206.1118, found 206.1114.

*3.2.3. 3,3-Difluorohexahydrocyclopenta[b]furan-2-one (**4c**)*

The product was isolated in 93% yield by column chromatography eluting with petroleum ether and ethyl acetate (10:1). IR (film), ν (cm^{-1}): 2990, 1810 (γ-lactone), 1460, 1340, 1260, 1220, 1160, 760; ^1H NMR (500 MHz, $CDCl_3$), δ: 1.65 (1H, m, H-7), 1.86 (3H, m, H-7 and H-8), 2.00 (1H, m, H-6), 2.17 (1H, m, H-6), 3.09 (1H, m, H-5), 5.13 (1H, t, $J_{F,H} = 5.1$ Hz, H-1); ^{19}F NMR (470 MHz, $CDCl_3$), δ: −116.76 (d, $J_{F,F} = 282$ Hz, 1F), −99.73 (dd, $J_{F,F} = 282$ Hz, $J_{F,H} = 18.8$ Hz, 1F); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ: 23.5 (s, C-7), 24.9–24.8 (t, C-6), 33.4 (s, C-8), 45.9 (t, C-5), 83.9 (d, C-1), 116.5 (dd, C-4), 165.9 (dd, C-3), HRMS calcd. for $C_7H_8O_2F_2$ 162.0492, found 162.0500.

*3.2.4. 3,3-Difluorohexahydrocyclohexyl[b]furan-2-one (**4d**)*

The product was isolated in 98% yield by column chromatography eluting with petroleum ether and ethyl acetate (10:1). IR (film), ν (cm^{-1}): 2990, 1810 (γ-lactone), 1460, 1340, 1260, 1220, 1160, 760; ^1H NMR (500 MHz, $CDCl_3$), δ: 1.30 (1H, m, H-8), 1.35 (1H, m, H-6), 1.44 (1H, m, H-8), 1.56 (1H, m, H-7), 1.76 (2H, m, H-7 and H-9), 1.85 (1H, m, H-6), 2.15 (1H, m, H-9), 2.66 (1H, m, H-5), 4.73 (1H, q, $J = 4.1$ Hz, H-1); ^{19}F NMR (470 MHz, $CDCl_3$), δ: 125.26 (d, $J_{F,F} = 267.9$ Hz, 1F), −111.87 (dd, $J_{F,F} = 272.6$ Hz, $J_{F,H} = 14.1$ Hz, 1F); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ: 19.8 (s, C-7), 20.7 (s, C-8), 22.7 (s, C-6), 28.1 (s, C-9), 41.8 (t, C-5), 76.1 (d, C-1), 118.1 (dd, C-4), 166.7 (t, C-3); HRMS calcd. for $C_8H_{10}O_2F_2$ 176.1618, found 176.1621.

*3.2.5. 5,5-Difluoro-3-oxatricyclo[5.2.1.$0^{2,6}$]decanone (**4e**)*

The product was isolated in 96% yield by column chromatography eluting with petroleum ether and ethyl

acetate (10:1). IR (film), ν (cm^{-1}): 2980, 2900, 1810 (γ-lactone), 1470, 1300, 1250, 1100, 810, 780; ^1H NMR (500 MHz, $CDCl_3$), δ: 1.20 (1H, m, H-9), 1.26 (1H, m, H-8), 1.35 (2H, m, H-10), 1.65 (1H, m, H-8), 1.71 (1H, m, H-9), 2.57 (1H, dd, $J_{F,H}$ = 24.7 Hz, $J_{H,H}$ = 6.3 Hz, H-6), 2.62 (2H, s, H-1 and H-7), 4.65 (1H, dd, $J_{F,H}$ = 6.2 Hz, $J_{H,H}$ = 1.2 Hz, H-2); ^{19}F NMR (470 MHz, $CDCl_3$), δ: −117.37 (d, $J_{F,F}$ = 286.7 Hz, 1F), −95.80 (dd, $J_{F,F}$ = 286.7 Hz, $J_{F,H}$ = 23.5 Hz, 1F); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ: 22.6 (s, C-9), 27.4 (s, C-8), 32.8 (s, C-10), 36.1 (t, C-7), 40.6 (s, C-1), 48.9 (t, C-6), 83.1 (s, C-2), 115.1 (dd, C-5), 166.4 (t, C-4); HRMS calcd. for $C_9H_{10}O_2F_2$ 188.0649, found 188.0627. HRMS calcd. for $C_8H_{10}F_2$ ($M - CO_2$) 144.0751, found 144.0747. Anal. calcd. for $C_9H_{10}O_2F_2$: C, 57.45; H, 5.36; F, 20.19. Found C, 57.03; H, 5.33; F, 20.26.

Acknowledgments

This research work was supported by the National Natural Science Foundation of China (Grant No. 29902001) and Shanghai Science and Technology Committee (03QB14012).

References

[1] P.V. Ramachandran, K.J. Padiya, V. Rauniyar, M.V.R. Reddy, H.C. Rrown, Tetrahedron Lett. 45 (2004) 1015–1017.
[2] Y. Komatsu, F. Sasaki, S. Takei, T. Kitazume, J. Org. Chem. 63 (1998) 8058–8061.
[3] X.W. Zou, F.H. Wu, Chin. Chem. Lett. 13 (2002) 410–411.
[4] T. Itoh, K. Sakabe, K. Kudo, H. Ohara, Y. Tagagi, H. Kihara, P. Zagatti, M. Renou, J. Org. Chem. 64 (1999) 252–265.
[5] K. Sato, S. Nakazato, H. Enko, H. Tsujita, K. Fujita, T. Yamamoto, M. Omote, A. Ando, I. Kumadaki, J. Fluorine Chem. 121 (2003) 105–107.
[6] Z.Y. Yang, D.J. Burton, J. Org. Chem. 56 (1991) 5125–5132.
[7] W.Y. Huang, L. Lu, Y.F. Zhang, Chin. J. Chem. 8 (1990) 68–74.
[8] Z.Y. Yang, D.J. Burton, J. Fluorine Chem. 45 (1989) 435–439.
[9] Z.Y. Yang, D.J. Burton, J. Chem. Soc., Chem. Commun. 57 (1992) 233–234.
[10] L. Julia, M.P. Bosch, S. Rodriguez, A. Guerrero, J. Org. Chem. 65 (2000) 5098–5103.
[11] W.Y. Huang, W. Wang, B.N. Huang, Acta Chim. Sinica (Chin. Ed.) 43 (1985) 409–410.
[12] W.Y. Huang, W. Wang, B.N. Huang, Acta Chim. Sinica (1986) 178–184.
[13] F.H. Wu, W.Y. Huang, Youji Huaxue 17 (1997) 106–125.
[14] W.Y. Huang, F.H. Wu, Israel J. Chem. 39 (1999) 167–170.
[15] B.N. Huang, F.H. Wu, C.M. Zhou, J. Fluorine Chem. 75 (1995) 1–5.