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Electrolytic partial fluorination of organic compounds. Part 15 ☆. Stereochemical study of the anodic monofluorination of α-phenylsulfenyl acetates

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Abstract

The diastereoselective anodic fluorination of α-phenylsulfenyl esters by intramolecular asymmetry-induction has been studied using chiral auxiliaries such as phenethyl, bornyl, isobornyl, menthyl and 8-phenylmenthyl groups. Of these chiral auxiliaries, the 8-phenylmenthyl group gave the best diastereoselectivity. The diastereoselectivity was also affected by supporting electrolytes and it was found that $Et_4NF \cdot 3HF$ showed better selectivity in comparison to $Et_3N \cdot 3HF$ and $Et_3N \cdot 2HF$.

Keywords: Electrolytic partial fluorination; Organic compounds; α-phenylsulfenyl acetates; Diastereoselectivity; Chiral fluorocompounds

1. Introduction

Efficient methods for the selective partial fluorination of organic compounds are becoming increasingly important in order to develop new types of medicines [2], agricultural chemical [3] and functional materials [4]. In particular, the development of synthetic routes to optically active fluorinated organic molecules is one of the goals in modern organofluorine chemistry because it is highly useful for biological applications. Although several papers dealing with the stereoselective anodic partial fluorination have been published, only one example of diastereoselective anodic partial fluorination using intramolecular asymmetry-induction has been reported so far by Kabore et al. [5].

Recently, we have found that sulfides bearing electron-withdrawing groups undergo regioselective anodic fluorination quite efficiently [6–8], and we have also achieved the regioselective anodic monofluorination of simple alkyl phenyl sulfides [7]. These findings have prompted us to attempt the diastereoselective anodic monofluorination of sulfides bearing chiral auxiliaries.

In this paper, we wish to report a stereochemical study of the anodic monofluorination of α-phenylsulfenyl acetates (**1**) having an ester group as a chiral auxiliary.

2. Results and discussion

2.1. Anodic monofluorination of α-phenylsulfenyl acetates having various chiral auxiliaries

The anodic monofluorination of α-phenylsulfenyl acetates having various chiral auxiliaries **1** was first performed. Anodic oxidation of **1** was carried out using an undivided cell at a constant potential in acetonitrile containing $Et_3N \cdot 3HF$ as a supporting electrolyte and a fluoride ion source. As shown in Table 1, highly regioselective anodic monofluorination proceeded smoothly to provide the desired α-fluorinated acetates **2** in good yield. However, in the cases of menthyl derivatives (Runs 4 and 5), the yields decreased slightly since considerable amounts of difluorinated products **3** were formed as by-products.

Asymmetric fluorination took place except for **1a** (Run 1); however, diastereomeric excess (*d.e.*) values were extremely low in most cases except for the 8-phenylmenthyl ester derivative **1e** (Run 5). The difference between the configuration (*endo* and *exo* form) of the bornyl and isobornyl esters slightly affected the diastereoselectivity (Runs 2 and 3). It should be noted that the existence of a phenyl group in the 8-position of the menthyl group led to a considerable increase in the *d.e.* value. One of the possible reasons for such a low efficiency with respect to asymmetric induction

☆ For Part 14, see Ref. [1].

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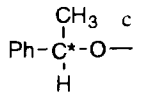
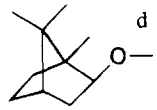
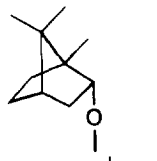
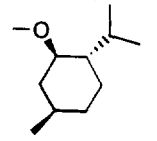
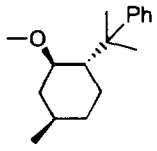
Table 1
Anodic monofluorination of α-phenylsulfenyl acetates **1**

$$\underset{(1)}{PhSCH_2CO-R^*} \xrightarrow[Et_3\cdot 3HF/MeCN]{-2e,\ -H^+} \underset{F\ (2)}{PhSC^*HCO-R^*} + \underset{(3)}{PhSCF_2CO-R^*}$$

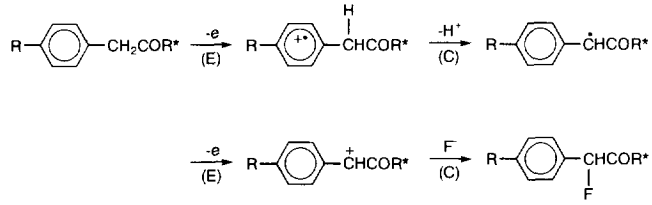
Run No.	Starting compounds	R*	Anodic potential (V vs. SSCE)	Charge passed (F mol^{-1})	Product yield[a] (%)		*d.e.* of **2**[b] (%)
					2	**3**	
1	**1a**		1.8	2.5	62 (50)	0	0
2	**1b**		1.8	2.9	66 (65)	trace	2
3	**1c**		1.6	2.5	69 (67)	trace	8
4	**1d**		1.9	4.0	56 (49)	15 (11)	4
5	**1e**		1.8	3.9	54 (45)	13 (10)	20

[a] ^{19}F NMR yields. The values in parentheses are isolated yields.
[b] From ^{19}F NMR analysis of the crude product.
[c] (±)-Phenylethyl ester was used.
[d] (±)-Isobornyl ester was used.

seems to be mainly the considerable separation between the chiral center of the auxiliaries and the reaction site. In other words, these are 1,4-asymmetric inductive reactions.

In contrast, Kabore et al. have reported diastereoselective anodic monofluorination at the benzylic position of α-(*p*-methoxyphenyl) acetates bearing chiral auxiliaries [5]. Although their anodic fluorination leads to 1,4-asymmetric inductive reaction, relatively high *d.e.* values have been obtained in the cases of menthyl and 8-phenylmenthyl esters (20% and 60% *d.e.*, respectively). Such a big difference may be partly attributable to differences in the reaction mechanisms. Laurent et al. have reported that anodic fluorination at the benzylic position of α-(*p*-substituted phenyl) acetates proceeds via a typical ECEC mechanism (Scheme 1) [9].

In contrast, we have recently established that the anodic fluorination of sulfides proceeds by a Pummerer-type mechanism (Scheme 2) [6]. This difference in the

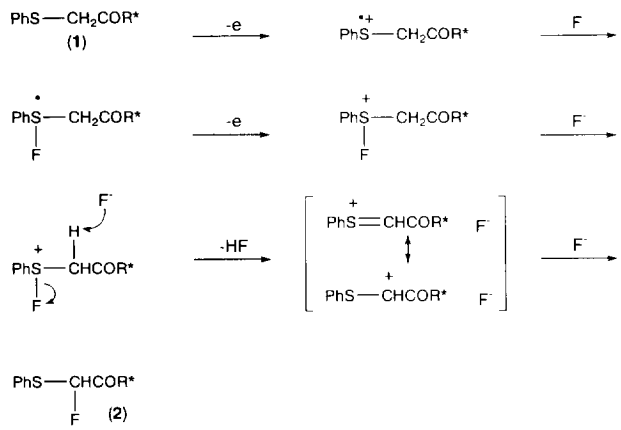


Scheme 1.

mechanism may affect the magnitude of the *d.e.* values quite considerably.

2.2. Effects of electrolytic conditions on the anodic fluorination of (−)-8-phenylmenthyl α-phenylsulfenyl acetate (1e)

Since the 8-phenylmenthyl ester **1e** gave the best result, anodic monofluorination of **1e** was investigated in detail under various electrolytic conditions.



Scheme 2.

First, solvent effects were investigated (Table 2, Runs 5–7). Of the various solvents investigated, the most polar solvent, MeCN, gave the best result for diastereoselectivity. In contrast, less polar solvents such as CH_2Cl_2 and dimethoxyethane (DME) caused a considerable decrease in the chemical yields and diastereoselectivities. Next, electrolysis was carried out at a low temperature (0 °C) (Run 8). In general, it is known that stereoselectivity often increases in asymmetric inductive reactions at a low temperature. However, in this case, the diastereoselectivity decreased slightly although the chemical yield and the current efficiency both increased appreciably. Of the fluorinating reagents used (Runs 5, 9 and 10), $Et_4NF \cdot 3HF$ was the most effective for obtaining higher diastereoselectivity, although the yield was not satisfactory due to the formation of a large amount of difluorinated **1e** (Run 9). It should be noted that $Et_4NF \cdot 2HF$ has a structure somewhat similar to $Et_4NF \cdot 3HF$, but despite this the diastereoselectivity was much lower. This result may suggest that the number of HF molecules in the quaternary ammonium fluoride salts plays an important role in the diastereoselectivity of the fluorination.

2.3. The most stable conformation of the cationic intermediate as proposed by MM2 calculations

8-Phenylmenthol is known to be an excellent chiral auxiliary and many examples of highly stereoselective intramolecular asymmetric induction using 8-phenylmenthyl esters have been reported in both electrophilic and nucleophilic substitution reactions [10]. In most cases, interaction between the carbonyl group of the esters and the phenyl ring at the 8-position of a menthyl group has been proposed as being involved in the transition state of the reaction. Hence, in order to obtain more information regarding the present diastereoselective fluorination, MM2 calculations [1] were carried out for the cation radical intermediate of **1e** when it was found that the most stable conformer is **4e** as shown in Fig. 1.

It is not unreasonable to assume that fluoride ions would predominantly attack the sulfinyl cation of **4e** from the *si* face because the phenyl group should block the attack from the *re* face. Thus, the absolute configuration of the major diastereomer of **2e** would be the *S*-form (Scheme 3). However, we have not established the absolute configuration of the products **2** at the present time [2].

2.4. Chemical fluorination of 1e

For comparison with our electrolytic results, a reaction was attempted using a chemical fluorinating reagent. Hitherto, known methods for the preparation of α-

[1] Calculations were performed by MM2 implemented by the CAChe Worksystem (SONY/Tektronix Corporation).

[2] Recently, Beguin et al. [11] have determined the absolute configuration of the major diastereomer of 8-phenylmenthyl α-fluoro-α-(*p*-methoxyphenyl) acetate, which was initially prepared by Kabore et al. [5], as being the *R*-form as indicated by ^{19}F NMR chemical shifts. The absolute configuration of our products could be determined similarly.

Table 2
Anodic monofluorination of (−)-8-phenylmenthyl α-phenylsulfenyl acetate (**1e**)

Run No.	Temp. (°C)	Solvent	Supporting electrolyte	Anodic potential (V vs. SSCE)	Charge passed (F mol^{-1})	Product yield [a] (%)		*d.e.* of **2** [b] (%)
						2e	**3e**	
5	R.T.	MeCN	$Et_3N \cdot 3HF$ [c]	1.8	3.9	54 (45)	13 (10)	20
6	R.T.	CH_2Cl_2	$Et_3N \cdot 3HF$ [c]	2.0	3.6	43	0	4
7	R.T.	DME	$Et_3N \cdot 3HF$ [c]	1.8	2.5	12	0	2
8	0	MeCN	$Et_3N \cdot 3HF$ [c]	1.8	2.6	69	0	16
9	R.T.	MeCN	$Et_4NF \cdot 3HF$ [d]	1.5	3.7	37	26	28
10	R.T.	MeCN	$Et_4NF \cdot 2HF$ [e]	1.6	3.6	55	17	18

[a] ^{19}F NMR yields. The values in parentheses are isolated yields.
[b] From ^{19}F NMR analysis of the crude product.
[c] 0.37 M $Et_3N \cdot 3HF$/solvent.
[d] 0.37 M $Et_4NF \cdot 3HF$/MeCN.
[e] 0.56 M $Et_4NF \cdot 2HF$/MeCN.

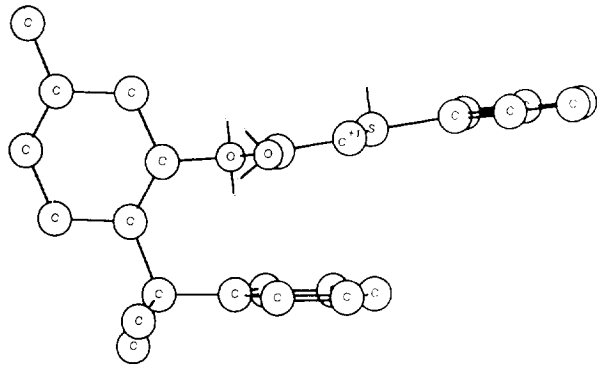
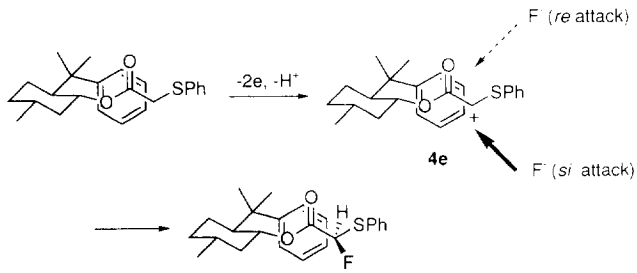
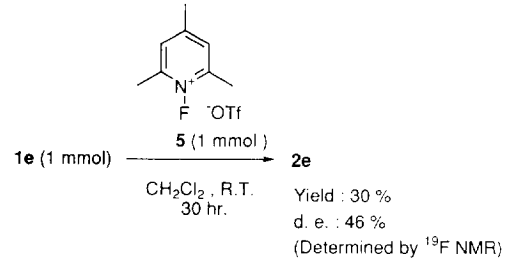


Fig. 1. The most stable conformation of the cationic intermediate **4e** proposed by the MM2 calculation.



Scheme 3.



Scheme 4.

fluorosulfides have required expensive, unstable and dangerous reagents such as xenon difluoride [12] or DAST [13]. Recently, *N*-fluoropyridinium triflates have also been shown to be effective fluorination reagents [14]. We carried out the first study of the stereochemical aspects of the chemical fluorinations with an *N*-fluoropyridinium triflate using **1e** as a model compound. Fluorination of **1e** with *N*-fluoro-2,4,6-trimethylpyridinium triflate (**5**) gave **2e** in poor yield but with a much higher diastereoselectivity (Scheme 4).

It is interesting that, even in the same solvent (CH_2Cl_2), the diastereoselectivity was much higher in a homogeneous chemical reaction system than in a heterogeneous electrochemical reaction system. However, the reason for this difference is not clear at the present time. The most stable conformer **4e** should be present as a major component in the homogeneous chemical fluorination reaction and this may contribute to the higher diastereoselectivity. In contrast, however, interaction between the cationic intermediate including **4e** and the anode would decrease the diastereoselectivity in the case of a heterogeneous electrochemical fluorination.

3. Experimental details

3.1. Apparatus

^1H NMR and ^{19}F NMR spectra were recorded at 270 MHz on JEOL EX270 or JEOL GX270 or at 60 MHz on Hitachi R-1200F NMR spectrometers. $CDCl_3$ was used as a solvent. The chemical shifts for ^1H and ^{19}F NMR are given in δ ppm downfield from internal Me_4Si and upfield from external CF_3COOH, respectively. IR spectra were obtained with a Hitachi 295 infrared spectrometer. Mass spectra and high-resolution mass spectra were obtained with a JEOL JMS-D100 or Hitachi M-80B GC–mass spectrometer. Preparative electrolysis experiments were carried out using a Hokutodenko HA-501 potentiostat/galvanostat equipped with a Hokutodenko HF-201 digital coulometer and a Hokutodenko HB-104 function generator.

3.2. Starting materials

(±)-1-Phenethyl α-phenylsulfenyl acetate (**1a**) was prepared as follows. To a stirred solution consisting of 1.22 g (10 mmol) of (±)-1-phenethyl alcohol in 5 ml of CH_2Cl_2 was added dropwise 2.80 g (15 mmol) of α-phenylsulphenyl acetyl chloride in 5 ml of CH_2Cl_2 at 0 °C. To the resulting solution was then added dropwise 1.58 g (20 mmol) of pyridine in 10 ml of CH_2Cl_2 at 0 °C. After stirring for 3 h at ambient temperature, the solution was mixed with water and extracted repeatedly with CH_2Cl_2. The extracts were washed with water and dried ($MgSO_4$). After evaporation, the residue was chromatographed on silica gel (hexane/CH_2Cl_2 = 1:1) to provide 2.24 g (79%) of **1a** as colorless oil. ^1H NMR δ: 1.48 [d, 3H, CH(CH_3)Ph, J = 6.60 Hz]; 3.63 (s, 2H, PhSCH_2); 5.87 [q, 1H, CH(CH$_3$)Ph, J = 6.60 Hz]; 7.16–7.37 (m, 10H, aromatic H) ppm. IR (cm^{-1}): 3060; 3040; 2900; 1750; 1740; 1585; 1480; 1440; 1265; 1130; 1060; 740. MS *m/z*: 272 (M^+); 228; 168; 137; 123; 105; 91; 77; 58. Calc. for $C_{16}H_{16}O_2S$: *m/z* 272.0869. Found: *m/z* 272.0868.

(±)-Isobornyl α-phenylsulfenyl acetate (**1b**) was similarly prepared in 61% yield as a colorless oil. ^1H NMR δ: 0.78 (s, 3H, CH_3); 0.81 (s, 3H, CH_3); 0.90 (s, 3H, CH_3); 1.03–1.13 (m, 2H); 1.52–1.77 (m, 5H); 3.62 (s, 2H, PhSCH_2); 4.66–4.69 (m, 1H, COOCH); 7.20–7.31 (m, 3H, aromatic H); 7.36–7.40 (m, 2H, aromatic H) ppm. IR (cm^{-1}): 3060; 2980; 2960; 2880; 1760; 1750; 1740; 1585; 1480; 1440; 1390; 1275; 1050; 735. MS *m/z*: 304 (M^+); 168; 137; 123; 109; 81. Calc. for $C_{18}H_{24}O_2S$: *m/z* 304.1496. Found: *m/z* 304.1496.

(−)-Bornyl α-phenylsulfenyl acetate (**1c**) was similarly prepared in 71% yield as a colorless oil. ^{1}H NMR δ: 0.75 (s, 3H, CH_3); 0.84 (s, 3H, CH_3); 0.87 (s, 3H, CH_3); 1.07–1.28 (m, 2H); 1.53–1.87 (m, 4H); 2.25–2.36 (m, 1H); 3.66 (s, 2H, PhSCH_2); 4.66–4.91 (m, 1H, COOC*H*); 7.18–7.32 (m, 3H, aromatic H); 7.37–7.43 (m, 2H, aromatic H) ppm. IR (cm^{-1}): 3075; 2970; 2900; 2340; 1750; 1730; 1590; 1480; 1450; 1440; 1395; 1300; 1280; 1135; 1115; 1020; 995; 740. MS *m/z*: 304 (M^+); 194; 168; 137; 123; 109; 95; 81. Calc. for $C_{18}H_{24}O_2S$: *m/z* 304.1496. Found: *m/z* 304.1458.

(−)-Menthyl α-phenylsufenyl acetate (**1d**) was similarly prepared in 70% yield as a colorless oil. ^{1}H NMR δ: 0.67 (d, 3H, CH_3, J=6.92 Hz); 0.83 [d, 3H, CH(CH_3)$_2$, J=6.92 Hz]; 0.88 [d, 3H, CH(CH_3)$_2$, J=6.60 Hz]; 0.74–2.02 (m, 9H); 3.63 (s, 2H, PhSCH_2); 4.68 (td, 1H, COOC*H*, J=10.89 Hz, J=4.62 Hz); 7.18–7.31 (m, 3H, aromatic H); 7.38–7.42 (m, 2H, aromatic H) ppm. IR (cm^{-1}): 3060; 2960; 2875; 1750; 1740; 1580; 1480; 1460; 1450; 1440; 1385; 1370; 1280; 1260; 1165; 1130; 980; 730. MS *m/z*: 306 (M^+); 168; 123; 83; 69; 55. Analysis: Calc. for $C_{18}H_{26}O_2S$: C, 70.55; H, 8.55; S, 10.46%. Found: C, 70.31; H, 8.63; S, 10.27.

(−)-8-Phenylmenthyl α-phenylsulfenylacetate (**1e**) was similarly prepared in 77% yield as a colorless oil. ^{1}H NMR δ: 0.84 (d, 3H, CH_3, J=6.59 Hz); 1.18 [s, 3H, C(CH_3)$_2$Ph]; 1.28 [s, 3H, C(CH_3)$_2$Ph]; 0.86–2.07 (m, 8H); 2.88 (s, 2H, PhSCH_2); 4.80 (td, 1H, COOC*H*, J=10.55 Hz, J=4.29 Hz); 7.10–7.30 (m, 10H, aromatic H) ppm. IR (cm^{-1}): 3070; 3040; 2970; 2940; 2880; 1760; 1740; 1600; 1590; 1495; 1480; 1440; 1390; 1290; 1280; 1170; 1130; 1090; 990; 760; 740. MS *m/z*: 382 (M^+); 264; 214; 168; 119; 105; 91; 77. Calc. for $C_{24}H_{30}O_2S$: *m/z* 382.1964. Found: *m/z* 382.1928.

3.3. Electrolytic procedure and product analysis

A typical electrolysis was performed potentiostatically in an undivided cell using a platinum anode and cathode (2×2 cm) in 0.37 M $Et_3N \cdot 3HF$/MeCN (15 ml) containing 1.5 mmol of the substrate. In order to avoid deposition of polymerized products on the electrodes, pulse electrolysis [applied potential (90 s)/0.0 V (10 s)] was performed. The electrolysis was performed at ambient temperature. After the starting material **1** had been consumed completely (monitoring by TLC and/or GC–MS), the electrolysis solution was passed through a short column of silica gel (CH_2Cl_2). After evaporation, the NMR yields and diastereomeric excess (*d.e.*) of the monofluorinated products **2** were estimated from their ^{19}F NMR spectra using C_6H_5F as an internal standard. The products **2** were then isolated by column chromatography (silica gel, hexane/CH_2Cl_2=1:1).

(±)-1-Phenethyl α-fluoro-α-phenylsulfenyl acetate (**2a**): isomeric mixture, colorless oil. ^{1}H NMR δ: 1.43 [d, 1.5H, CH(CH_3)Ph, J=6.60 Hz]; 1.49 [d, 1.5H, CH(CH_3)Ph, J=6.60 Hz]; 5.79–5.88 [m, 1H, C*H*(CH$_3$)Ph]; 6.047 [d, 0.50H, PhSC*H*F, J(H–F)=51.14 Hz]; 6.054 [d, 0.50H, PhSC*H*F, J(H–F)=51.80 Hz]; 7.22–7.56 (m, 10H, aromatic H) ppm. ^{19}F NMR δ: −82.27 [d, 0.50F, J(H–F)=50.86 Hz, isomer A]; −81.25 [d, 0.50F, J(H–F)=50.49 Hz, isomer B] ppm. IR (cm^{-1}): 3060; 3040; 2990; 2940; 1760; 1580; 1490; 1475; 1450; 1440; 1335; 1310; 1265; 1245; 1170; 1055; 1020; 740. MS *m/z*: 290 (M^+); 218; 137; 121; 105. Calc. for $C_{16}H_{15}FO_2S$: *m/z* 290.0776. Found: *m/z* 290.0777.

(±)-Isobornyl α-fluoro-α-phenylsulfenyl acetate (**2b**): isomeric mixture, colorless oil. ^{1}H NMR δ: 0.74–1.16 (m, 11H); 1.50–1.81 (m, 5H); 4.61–4.68 (m, 1H, COOC*H*); 6.019 [d, 0.49H, PhSC*H*F, J(H–F)=52.50 Hz, minor]; 6.025 [d, 0.51H, PhSC*H*F, J(H–F)=52.50 Hz, major]; 7.30–7.37 (m, 3H, aromatic H); 7.51–7.57 (m, 2H, aromatic H) ppm. ^{19}F NMR δ: −81.28 [d, 0.49F, J(H–F)=52.10 Hz, minor]; −81.08 [d, 0.51F, J(H–F)=52.10 Hz, major] ppm. IR (cm^{-1}); 3060; 2950; 2880; 1765; 1580; 1475; 1450; 1440; 1390; 1370; 1320; 1270; 1240; 1170; 1045; 1020; 1000; 975; 740. MS *m/z*: 322 (M^+); 181; 137; 121; 109. Calc. for $C_{18}H_{23}FO_2S$: *m/z* 322.1401. Found: *m/z* 322.1403.

(−)-Bornyl α-fluoro-α-phenylsulfenyl acetate (**2c**): isomeric mixture, colorless oil. ^{1}H NMR δ: 0.72–1.33 (m, 11H); 1.55–1.93 (m, 4H); 2.19–2.32 (m, 1H, C*H*); 4.79–4.89 (m, 1H, COOC*H*); 6.072 [d, 0.46H, PhSC*H*F, J(H–F)=51.79 Hz, minor]; 6.087 [d, 0.54H, PhSC*H*F, J(H–F)=51.79 Hz, major]; 7.31–7.38 (m, 3H, aromatic H); 7.48–7.58 (m, 2H, aromatic H) ppm. ^{19}F NMR δ: −81.05 [d, 0.54F, J(H–F)=51.49 Hz, major]; −80.91 [d, 0.46F, J(H–F)=51.48 Hz, minor] ppm. IR (cm^{-1}): 3060; 2955; 2875; 1765; 1740; 1470; 1450; 1440; 1310; 1300; 1280; 1020; 990; 975; 740. MS *m/z*: 322 (M^+); 181; 137; 121; 110. Calc. for $C_{18}H_{23}FO_2S$: *m/z* 322.1401. Found: *m/z* 322.1397.

(−)-Menthyl α-fluoro-α-phenylsulfenyl acetate (**2d**): isomeric mixture, colorless oil. ^{1}H NMR δ: 0.69 [d, 1.44H, CH_3, J=6.92 Hz, minor]; 0.70 [d, 1.56H, CH_3, J=6.93 Hz, major]; 0.75–1.08 (m, 9H); 1.33–1.50 (m, 2H); 1.64–1.90 (m, 4H); 4.62–4.76 (m, 1H, COOC*H*); 6.03 [d, 0.48H, PhSC*H*F, J(H–F)=52.13 Hz, minor]; 6.05 [d, 0.52H, PhSC*H*F, J(H–F)=52.13 Hz, major]; 7.30–7.37 (m, 3H, aromatic H); 7.53–7.58 (m, 2H, aromatic H) ppm. ^{19}F NMR δ: −80.79 [d, 0.48F, J(H–F)=52.11 Hz, minor]; −80.72 [d, 0.52F, J(H–F)=52.10 Hz, major] ppm. IR (cm^{-1}): 3060; 2950; 2870; 1765; 1580; 1450; 1440; 1385; 1365; 1315; 1270; 1245; 1170; 1030; 975; 735. MS *m/z*: 324 (M^+); 186; 83; 69; 55. Calc. for $C_{18}H_{25}FO_2S$: *m/z* 324.1557. Found: *m/z* 324.1537.

(−)-Menthyl α,α-difluoro-α-phenylsulfenyl acetate (**3d**): the difluorinated product **3d** was obtained as a colorless oil from higher fractions than **2d**. ^{1}H NMR δ: 0.75 (d, 3H, CH_3, J=7.26 Hz); 0.89 [d, 3H, CH(CH_3)$_2$, J=6.93 Hz]; 0.91 [d, 3H, CH(CH_3)$_2$, J=6.27 Hz];

0.84–1.96 (m, 9H); 4.77 (td, 1H, COOC*H*, J=10.88 Hz, J=4.29 Hz); 7.35–7.48 (m, 3H, aromatic H); 7.62–7.63 (m, 2H, aromatic H) ppm. ^{19}F NMR δ: −5.04 (s, 1F); −4.99 (s, 1F) ppm. IR (cm^{-1}): 3060; 2960; 2930; 2875; 1770; 1470; 1450; 1440; 1290; 1135; 1105; 1060; 1005; 980; 940; 820; 745. MS m/z: 342 (M^+); 323; 183; 139; 123; 109; 95; 81; 58. Calc. for $C_{18}H_{24}F_2O_2S$: m/z 342.1463. Found: m/z 342.1472.

(−)-8-Phenylmenthyl α-fluoro-α-phenylsulfenyl acetate (**2e**): isomeric mixture, colorless oil. ^{1}H NMR δ: 0.79 [d, 1.20H, CH_3, J=6.59 Hz, minor]; 0.85 [d, 1.80H, CH_3, J=6.60 Hz, major]; 1.17 [s, 1.80H, C(CH_3)$_2$Ph, major]; 1.23 [s, 1.20H, C(CH_3)$_2$Ph, minor]; 1.27 [s, 1.80H, C(CH_3)$_2$Ph, major]; 1.34 [s, 1.20H, C(CH_3)$_2$Ph, minor]; 0.67–2.13 (m, 8H); 4.69 [d, 0.60H, PhSC*H*F, J(H–F)=51.44 Hz, major]; 4.73–4.86 (m, 1H, COOC*H*); 5.63 [d, 0.40H, PhSC*H*F, J(H–F)=52.43 Hz, minor]; 7.04–7.53 (m, 10H, aromatic H) ppm. ^{19}F NMR δ: −82.03 [d, 0.60F, J(H–F)=51.48 Hz, major]; −80.25 [d, 0.40F, J(H–F)=52.73 Hz, minor] ppm. IR (cm^{-1}): 3060; 3030; 2960; 2930; 2880; 1765; 1600; 1580; 1490; 1480; 1455; 1400; 1390; 1370; 1320; 1270; 1255; 1175; 1115; 1030; 975; 760; 740. MS m/z: 400 (M^+); 282; 214; 119; 105; 91; 77; 58. Calc. for $C_{24}H_{29}FO_2S$: m/z 400.1871. Found: m/z 400.1872.

(−)-8-Phenylmenthyl α,α-difluoro-α-phenylsulfenyl acetate (**3e**): the difluorinated product **3e** was obtained as a colorless oil from higher fractions than **2e**. ^{1}H NMR δ: 0.85 (d, 3H, CH_3, J=6.26 Hz); 1.27 [s, 3H, C(CH_3)$_2$Ph]; 1.33 [s, 3H, C(CH_3)$_2$Ph]; 0.73–1.57 (m, 6H); 1.77–2.00 (m, 2H); 4.86 (td, 1H, COOC*H*, J=10.56 Hz, J=4.29 Hz); 7.13–7.48 (m, 8H, aromatic H); 7.59–7.62 (m, 2H, aromatic H) ppm. ^{19}F NMR δ: −5.17 (s, 1F); −5.14 (s, 1F) ppm. IR (cm^{-1}): 3075; 2950; 2890; 1780; 1605; 1585; 1495; 1480; 1445; 1395; 1375; 1300. MS m/z: 418 (M^+); 300; 218; 185; 168; 154; 137; 119; 105. Calc. for $C_{24}H_{28}FO_2S$: m/z 418.1776. Found: m/z 418.1753.

3.4. Chemical fluorination

The procedure was almost the same as that described earlier [14], except that N_2 gas was used instead of Ar gas. The yield and diastereomeric excess of **2e** were determined by ^{19}F NMR spectrometry. The spectral characteristics of the product were identical to those of **2e** described above.

4. Conclusions

Of the α-phenylsulfenyl acetates having various chiral auxiliaries, (−)-8-phenylmenthyl α-phenylsulfenyl acetate (**1e**) gave the best results in diastereoselective anodic monofluorination. From previous work [10] and MM2 calculations, it was proposed that the most stable calculated conformation of **1e**, i.e. **4e**, contributes to the reasonable diastereoselectivity observed. Of the various electrolytic conditions, MeCN gave the best results for chemical yield and diastereoselectivity. At low temperature, the chemical yield and current efficiency increased but the diastereoselectivity unexpectedly fell. $Et_3N\cdot 3HF$ and $Et_4NF\cdot 2HF$ gave better chemical yields relative to $Et_4NF\cdot 3HF$, while the latter gave the better diastereoselectivity. Chemical fluorination using *N*-fluoro-2,4,6-trimethylpyridinium triflate gave a diastereoselectivity which was superior to that attained by electrochemical fluorination. This result suggest that the most stable calculated conformation **4e** is not present for sufficient time to react with a fluoride ion during the course of the electrochemical fluorination because of some interaction between the cationic intermediate and the surface of the anode. More detailed study is necessary for clarification of this interesting feature.

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