Pergamon

Tetrahedron 58 (2002) 9273–9278

TETRAHEDRON

Electrolytic partial fluorination of organic compounds. Part 65: Regioselective anodic difluorination of oxazolyl sulfides☆

Sayed M. Riyadh, Hideki Ishii and Toshio Fuchigami*

Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

Received 22 July 2002; accepted 12 September 2002

Abstract—Electrochemical fluorination of 2-alkylthio-4-methyloxazoles has been successfully carried out using $Et_4NF{\cdot}nHF$ (n=4, 5) as the supporting electrolyte and fluoride source to provide the corresponding 2-alkylthio-4,5-difluoro-4-methyl-2-oxazolines, and fluorination did not take place at α to the sulfur atom. In the case of electrochemical fluorination of 2-methylthio-4-cabomethoxyoxazole afforded a 2,5-difluoro-3-oxazoline derivative in addition to a 4,5-difluoro-2-oxazoline one. In contrast, anodic fluorination of 2,4,5-trimethyloxazole devoid of a thio group resulted in no formation of fluorinated products.

1. Introduction

The substituent effect caused by fluorine atom(s) with minimal steric disturbance contributes to the importance of fluorinated molecules in biochemistry.[2] The high electronegativity and the lipophilicity of the carbon–fluorine bond enable organofluorine compounds to be generally biologically stable. These characteristic features of fluorine have prompted the synthesis of many fluorinated bioactive compounds.[3] Consequently, there is a growing interest in the synthesis of fluorine-containing heterocycles. On the other hand, oxazoles are found in many naturally occurring and biologically active materials. In particular, important applications of oxazoles functionalized at both the 2- and 4-positions have been found in the synthesis of more complex natural products.[4–7] Oxazoles are also useful as antiepileptic drugs,[8] sedative and muscle-relaxant[9] which is effective against a wide range of enteric infection. Furthermore, 2-oxazolines have recently been found to be versatile synthetic intermediates[10–12] as therapeutic agent[13] and potent growth regulators on species of a Cari and Lepidoptera[14] as well as in a wide variety of application.[13]

Recently, electrochemical fluorination methodology has been established as a unique and useful tool for selective direct fluorination of organic molecules.[15,16] As a result of our research project in electrochemical fluorination of heterocyclic compounds,[17,18] we herein report the anodic fluorination of 2-alkylthiooxazoles as a new efficient entry to fluorinated 2-alkylthio-2-oxazolines. The influence of the electrolytic conditions and substituent groups at the oxazole ring on the anodic fluorination was investigated.

2. Results and discussion

2.1. Synthesis of oxazolyl sulfides

4-Methyl-2-methylthiooxazole (**1**),[19] 2-acetonylthio-4-methyloxazole (**3**),[19] 4,5-dimethyl-2-methylthiooxazole (**5**),[19] and 4-carbomethoxy-2-methylthiooxazole (**7**)[20] were prepared according to the procedures reported in the literatures. 4-Methyl-2-propargylthiooxazole (**2**) was prepared by the reaction of the corresponding 2-mercaptooxazole with propargyl bromide in boiling EtOH. On the other hand, 2-cyanomethylthio-4-methyloxazole (**4**) was prepared by the reaction of 2-mercaptooxazole with chloroacetonitrile in boiling THF in the presence of K_2CO_3 as shown in Scheme 1.

2.2. Oxidation potentials of 2-alkylthiooxazoles 1–7

Prior to the anodic fluorination of 2-alkylthiooxazoles **1**–**7**, we measured the oxidation peak potentials by cyclic voltammetry using a divided cell at a platinum anode in an anhydrous acetonitrile solutions containing Bu_4NBF_4 (0.1 M) using SCE as a reference electrode. These sulfides showed irreversible oxidation peaks, and the first peak potentials (E_p^{ox}) are listed in Table 1.

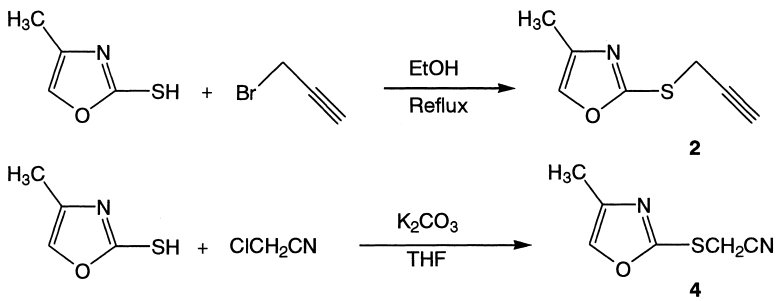
4,5-Dimethyl-2-methylthiooxazole (**5**) was found to be oxidized at a less positive potential than 2,4,5-trimethyloxazole (**6**) devoid of a sulfur atom since the thio group is an effective electroauxiliary.[21] Introduction of

☆ For Part 64, see Ref. 1.

Keywords: electrochemical fluorination; 2-alkylthio-4,5-difluoro-4,5-dihydrooxazole; 2-alkylthio-2,5-difluoro-2,5-dihydrooxazole.

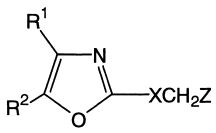
* Corresponding author. Tel.: +81-45-924-5406; fax: +81-45-924-5489; e-mail: fuchi@echem.titech.ac.jp

0040–4020/02/$ - see front matter
PII: S0040-4020(02)01194-8



Scheme 1.

Table 1. Oxidation potentials (peak potentials, E_p^{ox}) of 2-alkylthiooxazoles **1**–**7**



1~7

No.	R^1	R^2	X	Z	E_p^{ox} (*V* vs SCE)[a]
1	CH_3	H	S	H	1.59
2	CH_3	H	S	C≡CH	1.78
3	CH_3	H	S	$COCH_3$	1.67
4	CH_3	H	S	CN	1.84
5	CH_3	CH_3	S	H	1.38
6	CH_3	CH_3	–	H	1.71
7	$COOCH_3$	H	S	H	1.43

[a] Substrate (0.01 M) in 0.1 M $Bu_4N{\cdot}BF_4$/MeCN; sweep rate 100 mV/s.

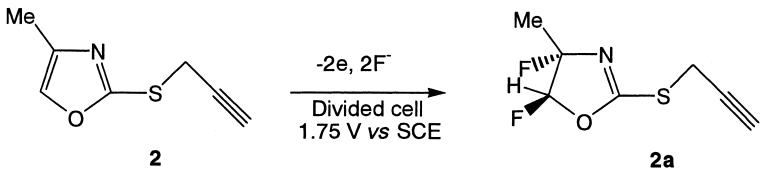
electron-withdrawing groups (*Z*) at the position α to the sulfur atom increases the oxidation potentials of **2**–**4** as compared to 4-methyl-2-methylthiooxazole (**1**).

2.3. Electrochemical fluorination of 4-methyl-2-propargylthiooxazole (2)

Oxazoles are a well-known function as azadienes in hetero-Diels–Alder reactions with olefinic and acetylenic dienophiles.[22] The participation of the oxazole ring as 2π-electron partner using the C_4–C_5 bond in (4+2)-cycloaddition reaction was reported.[23] An electron-releasing group at C_2 of the oxazole ring exerts a relevant effect on the dienophilic activity of oxazole with higher electron density at the C_4–C_5 bond of the oxazole ring.[24] Previously, we reported the electrochemical fluorination of 2-alkylthiothiazoles affording 2-alkylthio-5,5-difluoro-3-thiazolines accompanied by 2-alkylthio-5-fluorothiazoles.[1] Replacement of a thiazole ring by an oxazole ring may change the reaction pathway during the electrochemical fluorination. From these facts in mind, anodic fluorination of 4-methyl-2-propargylthiooxazole (**2**) as a model compound was carried out. The anodic fluorination did not take place at the side-chain but occurred regioselectively at the C_4–C_5 bond of the oxazole ring to form a *vicinal* difluoro-2-oxazoline derivative **2a**. This is in sharp contrast to the anodic fluorination of aryl propargyl sulfides which provided the corresponding α-fluorinated products.[25,26] The electrolysis results are listed in Table 2.

When the electrolysis was carried out with constant current in an undivided cell, *vic*-difluorinated product **2a** was obtained in a low yield (run 1). On the other hand, potentiostatic electrolysis using a divided cell improved the yield significantly (runs 2–7). Under the potentiostatic conditions, the electrolysis using $Et_4NF{\cdot}4HF$/DME at 6 F/mol resulted in the highest product yield (run 2). Longer electrolysis under the same conditions resulted in lower yield of **2a** (run 3). The use of other fluoride salts under similar conditions gave lower fluorinated yields (runs 4–6). In contrast, the use of acetonitrile as an electrolytic solvent led to decrease the yield of **2a** drastically and the starting material **2** was considerably recovered (50%) (run 7).

Table 2. Anodic fluorination of 4-methyl-2-propargylthiooxazole **2**

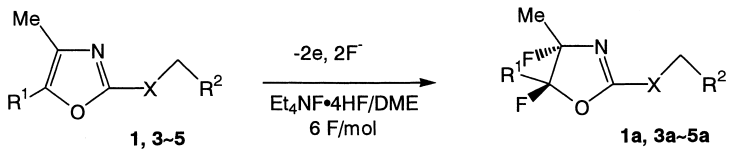


2 **2a**

Run	Supporting electrolyte	Solvent	Charge passed (F/mol)	Yield (%)[a] **2a**
1[b]	$Et_4NF{\cdot}4HF$	DME	6	25
2	$Et_4NF{\cdot}4HF$	DME	6	70 (62)
3	$Et_4NF{\cdot}4HF$	DME	8	60
4	$Et_4NF{\cdot}5HF$	DME	6	60
5	$Et_3N{\cdot}5HF$	DME	6	55
6	$Et_3N{\cdot}3HF$	DME	6	52
7	$Et_4NF{\cdot}4HF$	MeCN	6	13

[a] Determined by ^{19}F NMR; isolated yield was shown in paranthesis.
[b] Under constant current electrolysis using an undivided cell.

Table 3. Anodic fluorination of 2-alkythio-4-methyloxazoles **1**, **3**–**6**



Run	Compound no.	R^1	R^2	X	Applied potential	Yield (%)[a]
1	**1**	H	H	S	1.65	55 (50)
2	**3**	H	$COCH_3$	S	1.70	65 (61)
3	**4**	H	CN	S	1.95	70 (63)
4	**5**	CH_3	H	S	1.40	60 (52)
5	**6**	CH_3	H	–	1.75	–[b]

[a] Determined by ^{19}F NMR; isolated yields are shown in parantheses.
[b] The starting material **6** was mainly recovered.

Regardless of the electrolytic conditions, the difluorinated product **2a** was obtained as a single stereoisomer. In order to determine its stereochemistry, NOE was measured. However, no enhancement of the methyl protons at the 4-position of **2a** was observed in the ^1H NMR spectrum after irradiation of the proton at the 5-position. From this result, the stereochemistry of **2a** would be *trans*.

The electrochemical fluorination was extended to various 2-substituted oxazoles **1**, and **3**–**6**. Under the best conditions obtained above, the electrolysis was carried out until a starting material was mostly consumed. The results are shown in Table 3.

As shown in Table 3, difluorination took place selectivity at the C_4–C_5 bond in the oxazole ring to give *vic*-difluorinated products **1a**, and **3a**–**5a** regardless of substituents at α to the sulfur atom of the side-chain. 4,5-Dimethyl-2-methylthiooxazole (**5**) was also fluorinated and the *vic*-difluorinated product **5a** was obtained in good yield (run 4). In all cases, difluorinated products **1a**, and **3a**–**5a** were isolated as single stereoisomers, whose stereochemistry may be *trans* according to NOE measurement. In these fluorinations, the presence of a thio group is important: 2,4,5-trimethyloxazole (**6**) devoid of a thio group was not fluorinated and the starting material was mostly recovered (90%) (run 5).

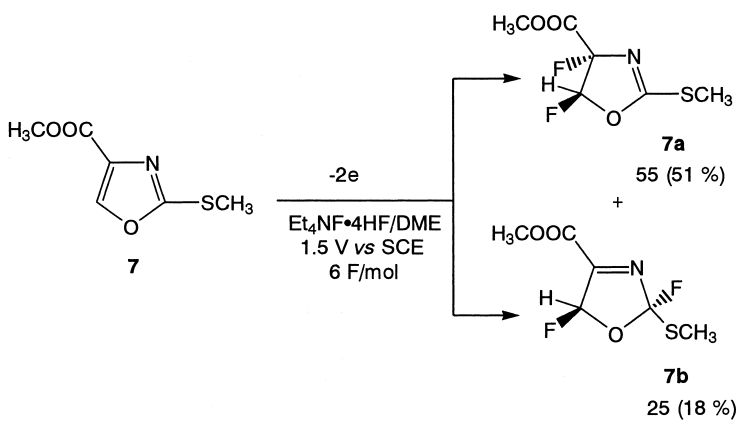
2.4. Anodic fluorination of 4-carbomethoxy-2-methylthiooxazole (7)

Furthermore, the anodic behavior of 4-carbomethoxy-2-methylthiooxazole (**7**), which contains an electron-withdrawing ester group on the C_4–C_5 bond, toward Et_4NF·4HF/DME in a divided cell was investigated as shown in Scheme 2.

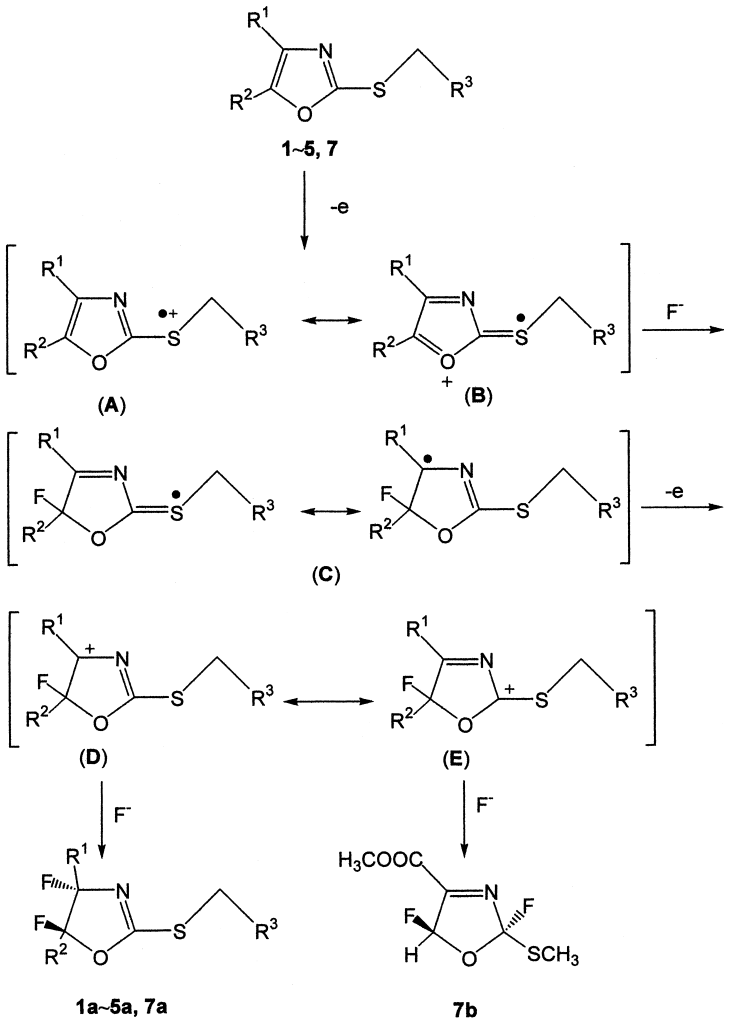
Electrolysis of **7** was carried out by passing 6 F/mol of electricity until the starting material was mostly consumed to give a mixture of two kinds of difluoro products, 2,5-difluoro-2-methylthio-3-oxazoline derivative **7b** in addition to a 4,5-difluoro-2-methylthio-2-oxazoline one **7a** in the ratio of 1:2. In this case, fluorination took place not only at the 4- and 5-positions in the oxazole ring but also at the 2- and 5-positions to give **7a** and **7b**, respectively. The stereochemistry of **7b** seems to be *trans* since long range coupling between the fluorine atom at the 2-position and the proton at the 5-position was observed.

The anodic fluorination seems to proceed with a typical electrochemical-chemical–electrochemical-chemical (ECEC) mechanism as shown in Scheme 3.

Since a thio group activates organic compounds towards electron transfer,[27] one-electron oxidation of a sulfur atom



Scheme 2.



Scheme 3.

of a substrate generates the radical cation **A**, which can have another resonance form **B** because of low aromatic character of the oxazole ring. On the contrary, in the case of anodic fluorination of aryl propargyl sulfides, the resonance form **B** could not be formed due to high aromatic nature of aryl rings.[25,26] The intermediate **B** reacts with a fluoride ion to afford radical intermediate **C**. The subsequent oxidation of **C** yields the carbocation **D**. Finally, a fluoride ion attacks **D** from the less hindered side to form the *trans vic*-difluorinated products **1a**–**5a**, and **7a**. In the case of **7**, the carbomethoxy group at the 4-position destabilizes the cationic intermediate **D**, therefore, a fluoride ion attacks the more stable cationic intermediate **E** to produce the corresponding 2,5-difluoro-3-oxazoline derivative **7b**. Thus, the formation of **7b** is reasonably explained.

In summary, efficient regioselective electrochemical fluorination of 2-alkylthiooxazoles was achieved for the first time. The product selectivity was found to be highly dependent on the substituent group on the oxazole ring. Anodic fluorination of an oxazole derivative devoid of a thio group resulted in no formation of any desired fluorinated products. Therefore, the thio group at the 2-position of oxazole seems to be effective for the anodic fluorination.

3. Experimental

3.1. General

Caution. $Et_4NF{\cdot}4HF$ is toxic and may cause serious burns if it comes in contact with unprotected skin, so proper safety precautions should be taken at all times. Therefore, the use of rubber gloves is recommended to protect the hand.[28]

^1H NMR and ^{19}F NMR spectra were recorded at 270 and 254 MHz, respectively, in $CDCl_3$. The chemical shifts for ^1H NMR are given in δ ppm downfield from internal TMS, and the chemical shifts for ^{19}F NMR are given in δ ppm downfield from external CF_3COOH.

Materials. 2-Alkylthiooxazoles **1**, **3**, **5**,[19] and **7**[20] were prepared according to the literature. $Et_4NF{\cdot}4HF$ and $Et_3N{\cdot}5HF$ were obtained from Morita Chemical Industries Co. Ltd (Japan).

3.1.1. Preparation of 4-methyl-2-propargylthiooxazole (2). To a 100 mL round bottom flask, 4-methyl-2-mercapto-oxazole (1.2 g, 10 mmol), propargyl bromide (1.2 g, 10 mmol) and absolute EtOH (50 mL) was added, the reaction mixture was refluxed for 8 h. EtOH was then

evaporated and the residue was washed with water, extracted with $CHCl_3$, dried over anhydrous $MgSO_4$. After removal of $MgSO_4$, the solvent was evaporated and the residue was purified by silica gel column chromatography using hexane/ethyl acetate (5:1) as an eluent. 50% yield; yellow oil; ^{1}H NMR δ 2.15 (d, 3H, J=1.5 Hz), 2.29 (t, 1H, J=2.6 Hz), 3.91 (d, 2H, J=2.6 Hz), 7.41 (q, 1H, J=1.5 Hz); MS *m/e* 153 (M^+). Anal. calcd for C_7H_7NOS; C, 54.88; H, 4.61; N, 9.14; S, 20.93. Found C, 54.72; H, 4.52; N, 8.95; S, 20.85.

3.1.2. Preparation of 2-cyanomethylthio-4-methyloxazole (4). To a stirred solution of 4-methyl-2-mercaptooxazole (1.2 g, 10 mmol) in THF (40 mL) in the presence of K_2CO_3 (2.0 g, 15 mmol), chloroacetonitrile (0.73 g, 10 mmol) was added. The reaction mixture was refluxed for 2 h, then left to cool and washed with water. The product was extracted with $CHCl_3$ and the extracts were dried over anhydrous $MgSO_4$. After removal of $MgSO_4$, the solvent was evaporated and the residue was purified by silica gel column chromatography using hexane/ethyl acetate (5:1) as an eluent. 75% yield; yellow oil; ^{1}H NMR δ 2.12 (d, 3H, J=1.5 Hz), 3.74 (s, 2H), 7.41 (q, 1H, J=1.5 Hz); MS *m/e* 154 (M^+). Anal. calcd for $C_6H_6N_2OS$; C, 46.74; H, 3.92; N, 18.17; S, 20.80. Found C, 46.68; H, 3.77; N, 17.97; S, 20.72.

3.2. Anodic fluorination of 2-alkylthiooxazoles

An appropriate 2-alkylthiooxazole (1 mmol) was dissolved in a solution of dry DME (30 mL) containing $Et_4NF{\cdot}4HF$ (0.3 M) in a divided cell with a platinum anode and cathode (3×3 cm^2). The electrolysis was carried out under constant potential in a nitrogen atmosphere at room temperature until the starting material was mostly consumed (monitored with TLC). After the electrolysis, the electrolytic solution was passed through a short column of silica gel using ethyl acetate as an eluent. The collected solution was evaporated under vacuum and the product yields were estimated by ^{19}F NMR by using a known amount of monofluorobenzene as an internal standard. The yields were calculated on the basis of the integral ratios between the monofluorobenzene and the fluorinated products. The oily residue was purified by passing through column chromatography on silica gel using hexane/ethylacetate (5:1) as an eluent.

3.2.1. 4,5-Difluoro-4-methyl-2-methylthio-4,5-dihydrooxazole (1a). Pale yellow oil; ^{1}H NMR δ 1.69 (dd, 3H, J=4.4, 20 Hz), 2.61 (s, 3H), 6.09 (dd, 1H, J=9.0, 62 Hz); ^{19}F NMR δ −37.16 (m), −59.11 (ddq, J=4.4, 15, 62 Hz); MS *m/e* 167 (M^+). Anal. calcd for $C_5H_7F_2NOS$; C, 35.92; H, 4.22; N, 8.38; S, 19.18. Found C, 35.71; H, 4.03; N, 8.09; S, 18.92.

3.2.2. 4,5-Difluoro-4-methyl-2-propargylthio-4,5-dihydrooxazole (2a). Pale yellow oil; ^{1}H NMR δ 1.69 (dd, 3H, J=4.5, 20 Hz), 2.31 (t, 1H, J=2.6 Hz), 3.87 (d, 2H, J=2.6 Hz), 6.12 (dd, 1H, J=9.0, 62 Hz); ^{19}F NMR δ −37.47 (m), −59.21 (ddq, J=4.5, 15, 62 Hz); MS *m/e* 191 (M^+). Anal. calcd for $C_7H_7F_2NOS$; C, 43.97; H, 3.69; N, 7.33; S, 16.77. Found C, 44.17; H, 3.82; N, 7.11; S, 16.71.

3.2.3. 2-Acetonylthio-4,5-difluoro-4-methyl-4,5-dihydrooxazole (3a). Pale yellow oil; ^{1}H NMR δ 1.69 (dd, 3H, J=4.3, 20 Hz), 2.33 (s, 3H), 4.03 (s, 2H), 6.12 (dd, 1H, J=9.0, 62 Hz); ^{19}F NMR δ −37.39 (m), −59.12 (ddq, J=4.3, 15, 62 Hz); MS *m/e* 209 (M^+). Anal. calcd for $C_7H_9F_2NO_2S$; C, 40.19; H, 4.34; N, 6.69; S, 15.33. Found C, 40.17; H, 4.35; N, 6.58; S, 15.28.

3.2.4. 2-Cyanomethylthio-4,5-difluoro-4-methyl-4,5-dihydrooxazole (4a). Yellow oil; ^{1}H NMR δ 1.69 (dd, 3H, J=4.1, 20 Hz), 2.89 (s, 2H), 6.19 (dd, 1H, J=9.0, 61 Hz); ^{19}F NMR δ −38.35 (m), −59.18 (ddq, J=4.1, 15, 61 Hz); MS *m/e* 192 (M^+). Anal. calcd for $C_6H_6F_2N_2OS$; C, 37.50; H, 3.15; N, 14.58; S, 16.68. Found C, 37.37; H, 3.16; N, 14.42; S, 16.48.

3.2.5. 4,5-Difluoro-4,5-dimethyl-2-methylthio-4,5-dihydrooxazole (5a). Yellow oil; ^{1}H NMR δ 1.46 (m, 6H), 2.55 (s, 3H); ^{19}F NMR δ −29.13 (m), −36.51 (m); MS *m/e* 181 (M^+). Anal. calcd for $C_6H_9F_2NOS$; C, 39.77; H, 5.01; N, 7.73; S, 17.70. Found C, 39.97; H, 5.16; N, 7.94; S, 17.83.

3.2.6. 4-Carbomethoxy-4,5-difluoro-2-methylthio-4,5-dihydrooxazole (7a). Yellow oil; ^{1}H NMR δ 2.65 (s, 3H), 2.81 (s, 3H), 6.23 (dd, 1H, J=10, 61 Hz); ^{19}F NMR δ −48.51 (dd, J=10, 15 Hz), −59.92 (dd, J=15, 61 Hz); MS *m/e* 211 (M^+). Anal. calcd for $C_6H_7F_2NO_3S$; C, 34.12; H, 3.34; N, 6.63; S, 15.18. Found C, 34.33; H, 3.44; N, 6.43; S, 15.06.

3.2.7. 4-Carbomethoxy-2,5-difluoro-2-methylthio-2,5-dihydrooxazole (7b). Pale yellow; mp 40°C; ^{1}H NMR δ 2.56 (s, 3H), 3.89 (s, 3H), 6.46 (dd, 1H, J=14, 62 Hz); ^{19}F NMR δ −64.83 (dd, J=14, 62 Hz), −69.73 (dd, J=14, 14 Hz); MS *m/e* 211 (M^+). Anal. calcd for $C_6H_7F_2NO_3S$; C, 34.12; H, 3.34; N, 6.63; S, 15.18. Found C, 34.44; H, 3.29; N, 6.43; S, 15.13.

Acknowledgements

This work was financially supported by a Grant-in-Aid for Scientific Research on Priority Aides (A) 'Exploitation of Multi-Element Cyclic Molecule' from the Ministry of Education, Science, Sports and Culture of Japan. We are also grateful to Morita Chemical Industries Co., Ltd, for generous gifts of fluoride salts.

References

1. Riyadh, S. M.; Fuchigami, T. in press.
2. Filler, R.; Kobayashi, Y. *Biomedicinal Aspects of Fluorine Chemistry*; Kodansha Ltd/Elsevier: Tokyo, 1982.
3. (a) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123. (b) Bannai, K.; Kurozumi, S. *Yuki Gosei Kagaku Shi* **1984**, *42*, 794.
4. (a) Williams, D. R.; Clark, M. P.; Berliner, M. A. *Tetrahedron Lett.* **1999**, *40*, 2287. (b) Williams, D. R.; Clark, M. P. *Tetrahedron Lett.* **1999**, *40*, 2291.
5. Lui, P.; Panek, J. S. *Tetrahedron Lett.* **1998**, *39*, 6134.
6. Meyers, A. I.; Lawson, J. P.; Walker, D. G.; Linderman, R. J. *J. Org. Chem.* **1986**, *51*, 5111.
7. Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1998**, *39*, 3149.

8. Withrow, C. D. *Adv. Neurol.* **1980**, *27*, 577.
9. Tubaro, E. *Boll. Chim. Farm.* **1965**, *104*, 602.
10. Reuman, M.; Meyers, A. I. *Tetrahedron* **1985**, *41*, 837.
11. Maryanoff, B. E. *Chemistry of Heterocyclic Compounds*; Turchi, I., Ed.;, 1986; Vol. 45, p 963.
12. Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297.
13. Frump, J. A. *Chem. Rev.* **1971**, *71*, 483.
14. Suzuki, J.; Kikuchi, Y.; Ishida, T.; Ikeda, T.T. EP 645085.
15. (a) Fuchigami, T. In *Organic Electrochemistry*, 4th ed.; Lund, H., Hammerich, O., Eds.; Dekker: New York, 2001; pp 1035–1050. (b) Fuchigami, T. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI: Stamford, CT, 1999; pp 41–130. (c) Fuchigami, T.; Higashiya, S.; Hou, Y.; Dawood, K. M. *Rev. Heteroatom Chem.* **1999**, *19*, 67.
16. Noel, M.; Suryanarayanan, V.; Chellammal, S. *J. Fluorine Chem.* **1997**, *83*, 31.
17. Konno, A.; Shimojo, M.; Fuchigami, T. *J. Fluorine Chem.* **1998**, *87*, 137.
18. Tajima, T.; Ishii, H.; Fuchigami, T. *Tetrahedron Lett.* **2001**, *42*, 4857.
19. Nuhn, P.; Wagner, G. *Arch. Pharm.* **1968**, *301*, 186.
20. Compper, R.; Heinemann, U. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 296.
21. Sugawara, M.; Mori, K.; Yoshida, J. *Electrochim. Acta* **1997**, *42*, 1995.
22. (a) Turchi, I. J.; Dewar, M. J. S. *Chem. Rev.* **1975**, *75*, 389. (b) Turchi, I. J. *Ind. Engng Chem. Prod. Res. Dev.* **1981**, *20*, 32. (c) Lakhan, R.; Ternai, B. *Adv. Heterocycl. Chem.* **1974**, *17*, 99. (d) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869. (e) Reddy, G. S.; Blatt, M. V. *Tetrahedron Lett.* **1980**, *21*, 3627. (f) Liotta, D.; Saindan, M.; Ott, W. *Tetrahedron Lett.* **1983**, *24*, 2473. (g) Levin, J. I.; Weinreb, S. M. *J. Org. Chem.* **1984**, *49*, 4325. (h) Jacobi, P. A.; Walker, D. G.; Odeh, I. M. A. *J. Org. Chem.* **1981**, *46*, 2065. (i) Kozikowski, A. P.; Hassan, N. M. *J. Org. Chem.* **1977**, *42*, 2039.
23. Dondoni, A.; Fogagnolo, M.; Mastellari, A.; Pedrini, P. *Tetrahedron Lett.* **1986**, *27*, 3915.
24. Dondoni, A.; Fanti, G.; Fogagnolo, M.; Mastellari, A.; Medici, A.; Pedrini, P. *J. Org. Chem.* **1984**, *49*, 3478.
25. Riyadh, S. M.; Ishii, H.; Fuchigami, T. *Tetrahedron* **2001**, *57*, 8817.
26. Riyadh, S. M.; Ishii, H.; Fuchigami, T. *Tetrahedron* **2002**, *58*, 5877.
27. Yoshida, Y. *J. Synth. Org. Chem. Jpn* **1995**, *53*, 53.
28. Peters, D.; Metchen, R. *J. Fluorine Chem.* **1996**, *79*, 161.