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Electrochemical fluorination of organic compounds 92. Anodic fluorination of sulfides having oxazolidinone and its application to the synthesis of fluoroallylamine☆

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ABSTRACT

Anodic fluorination of sulfides having oxazolidinone at the α-position was successfully carried out by controlled potential electrolysis at platinum plate electrodes in DME containing $Et_3N{\cdot}3HF$ using an undivided cell to provide the corresponding α-monofluorinated products. The fluorinated product was readily converted into the corresponding fluoroallylamine in good yield by treatment with an alkaline solution.

1. Introduction

Fluorinated organic compounds are receiving much attention because of their unique physical, chemical, and biological properties [1–6]. Electrochemical reactions have recently been shown to be a powerful and useful tool in organic synthesis and they are expected as a part of the next generation organic synthetic technique toward Green Sustainable Chemistry (GSC). For these reasons, electrochemical partial fluorinations have been studied by several groups since the end of the 1970s [7–13]. In electrochemical partial fluorination, constant potential electrolysis is effective for selective oxidation to generate reactive cationic species, which react with fluoride ions to provide the desired fluoroorganic compounds [10,14–17]. Anodic fluorination of organic substrates has been usually accomplished in acetonitrile (MeCN) containing fluoride ions. However, MeCN electrolytic solutions very often cause severe passivation of the anode. Moreover, desired fluorinated products were not always obtained in good yields due to a side acetoamidation reaction [9,18]. In our recent study, we found that dimethoxyethane (DME) was much more suitable than MeCN for the anodic fluorination [19–21]. α-Fluorosulfides are highly useful for pharmaceutical and synthetic applications [22,23]. Therefore, we have systematically studied regioselective anodic fluorination of various heterocyclic sulfides [24–27]. On the other hand, fluoroallylamines are very important building blocks for new functional materials, however, their synthesis is limited. Therefore, the development of its efficient synthetic method is highly desired. Recently, we have reported successful synthesis of fluoroallylalchol using anodic fluorination of a sulfide having dioxolanone [28,29]. With these facts in mind, the synthesis of fluoroallylamines is also attempted utilizing anodic fluorination as a key-step.

In this paper, we report the effective anodic fluorination of sulfides having oxazolidinones at their α-position and its application to the synthesis of fluoroallylamine.

2. Experimental

2.1. General

^1H, ^{13}C and ^{19}F NMR spectra were obtained on a JEOL JNM EX-270 in a deuteriochloroform ($CDCl_3$) solution using tetramethylsilane as an internal standard, unless otherwise stated. ^{19}F NMR spectra were given in δ ppm with $CFCl_3$ as an external standard (actual internal standard was monofluorobenzene). Cyclic voltammetry was performed using ALS CH instruments Electrochemical Analyzer Model 600A. Mass spectra were obtained by EI method with Shimadzu GCMS-QP5050A. High-resolution mass spectra were obtained on JEOL MStation JMS-700 mass spectrometer operating at the ion-

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ization energy of 70 eV. Preparative electrolysis experiments were carried out using a Hokutodenko Potentiostat/Galvanostat HA-501.

2.2. Material

The starting sulfide, 3-methyl-5-(phenylthio)methyl oxazolidinone (**1a**) was prepared as follows. To a solution of 5-chloromethyl-2-oxazolidine (0.68 g, 5 mmol) and benzenethiol (0.66 g, 6 mmol) in DMF (30 ml) was added potassium carbonate (1.38 g, 10 mmol) at room temperature and the solution was stirred for 12 h. After the reaction, water was added to the solution. The resulting solution was extracted repeatedly with ethyl acetate and the extracts were dried over $MgSO_4$. The extraction solvent was concentrated in vacuo and the residue was dissolved in DMF (30 ml), and then sodium hydride (0.24 g, 10 mmol) was added to the DMF solution at −20 °C. After the solution was stirred for 30 min, methyl iodide (1.41 g, 10 mmol) was added and stirred at room temperature for 1 h. After the reaction, water was added. The resulting solution was extracted repeatedly with ethyl acetate and the extracts were dried over $MgSO_4$. The extraction solvent was removed by evaporation, and the remaining material was subjected to column chromatography on silica gel (hexane:EtOAc = 4:1) to give 0.85 g (76.1% yield) of pure 3-methyl-5-(phenylthio)methyloxazolidinone (**1a**).

2.2.1. 3-Methyl-5-(phenylthio)methyloxazolidinone (*1a*)

^{1}H NMR ($CDCl_3$): δ 7.41–7.28 (m, 5H), 4.56 (m, 1H), 3.67–3.60 (m, 2H), 3.04–2.96 (m, 1H), 2.86 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 133.9, 130.4, 129.2, 127.2, 71.2, 51.3, 37.8, 31.1. HRMS calc. for $C_{11}H_{13}NO_2S$: *m*/*z* 223.0663; found: *m*/*z* 223.0638.

2.2.2. 3-Phenoxycarbonyl-5-(phenylthio)methyloxazolidinone (*1b*)

^{1}H NMR ($CDCl_3$): δ 7.46–7.16 (m, 10H), 4.73–4.63 (m, 1H), 4.26–4.20 (m, 2H), 3.98–3.92 (m, 1H), 3.46–3.06 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 130.9, 129.4, 129.3, 127.6, 126.3, 121.1, 71.6, 47.9, 37.9. HRMS calc. for $C_{17}H_{15}NO_4S$: *m*/*z* 329.0717; found: *m*/*z* 329.0726.

2.3. ^{19}F NMR measurement

^{19}F NMR spectra of $Et_3N{\cdot}3HF$ (0.25 mmol) were measured in $CDCl_3$ solely and in mixed solvents of $CDCl_3$ (3 cm^3) with DME (1 cm^3) at 20 °C and 40 °C.

2.4. General procedure of anodic fluorination

Constant potential electrolysis (1.45 V vs. SCE) of **1a** (1 mmol) was carried out at a platinum plate anode and cathode (one side area: 4 cm^2) at 20 °C in MeCN, DME or CH_2Cl_2 (10 cm^3) containing $Et_3N{\cdot}3HF$ (40 equiv. of F^- to the **1a**) using an undivided cell under a nitrogen atmosphere. After electrolysis, the supporting electrolyte was removed by silica gel short column chromatography. The product **2a** was isolated by silica gel column chromatography (hexane:EtOAc = 4:1).

2.4.1. 5-Fluoro(phenylthio)methyl-3-methyloxazolidinone (*2a*) (more polar isomer)

^{1}H NMR ($CDCl_3$): δ 7.56–7.37 (m, 5H), 5.85 (dd, *J* = 53.7, 3.8 Hz, 1H), 4.71–4.70 (m, 1H), 3.65–3.54 (m, 2H), 2.90 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 133.6, 130.3, 130.1, 129.1, 125.6, 100.3 (d, *J* = 226.5 Hz), 73.2 (d, *J* = 14.7 Hz), 44.8 (d, *J* = 2.6 Hz); ^{19}F NMR ($CDCl_3$): δ −88.48 (dd, *J* = 54.6, 14.7 Hz) (less polar isomer): ^{1}H NMR ($CDCl_3$): δ 7.56–7.37 (m, 5H), 5.72 (dd, *J* = 49.8, 6.0 Hz, 1H), 4.71–4.70 (m, 1H), 3.65–3.54 (m, 2H), 2.90 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 133.6, 130.3, 130.1, 129.0, 125.7, 99.6 (d, *J* = 226.5 Hz), 72.3 (d, *J* = 14.1 Hz), 44.4 (d, *J* = 3.2 Hz); ^{19}F NMR ($CDCl_3$): δ −81.27 (dd, *J* = 51.7, 9.4 Hz). HRMS calc. for $C_{11}H_{12}FNO_2S$: *m*/*z* 241.0569; found: *m*/*z* 241.0556.

2.4.2. 5-Fluoro(phenylthio)methyl-3-phenoxycarbonyloxazolidinone (*2b*) (more polar isomer)

^{1}H NMR ($CDCl_3$): δ 7.67–7.18 (m, 10H), 5.94 (dd, *J* = 54.0, 3.2 Hz, 1H), 4.27–4.23 (m, 1H), 4.19–4.08 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 149.8, 133.3, 129.4, 129.2, 126.4, 121.1, 100.2 (d, *J* = 226.5 Hz), 72.6 (d, *J* = 15.6 Hz), 45.2 (d, *J* = 2.2 Hz); ^{19}F NMR ($CDCl_3$): δ −89.55 (dd, *J* = 54.5, 16.8 Hz) (less polar isomer): ^{1}H NMR ($CDCl_3$): δ 7.67–7.18 (m, 10H), 5.78 (dd, *J* = 51.3, 11.2 Hz, 1H), 4.27–4.23 (m, 1H), 4.19–4.08 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 149.8, 133.3, 129.4, 129.2, 126.4, 121.1, 99.9 (d, *J* = 226.5 Hz), 72.2 (d, *J* = 15.1 Hz), 44.1 (d, *J* = 3.4 Hz); ^{19}F NMR ($CDCl_3$): δ −82.62 (dd, *J* = 51.8, 11.2 Hz).; HRMS (diastreomeric mixture) calc. for $C_{17}H_{14}FNO_4S$: *m*/*z* 347.0628; found: *m*/*z* 347.0638.

2.5. Oxidation of *2b* with mCPBA

To a solution of **2b** (0.19 g, 0.5 mmol) in dry CH_2Cl_2 (2 ml) was added *m*CPBA ($C_7H_5ClO_3$: *m*-chloroperoxybenzoic acid) (0.22 g, 1.3 mmol) at 0 °C and stirred for 6 h at room temperature under a nitrogen atmosphere. After filtration, the filtrate was washed with saturated aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and brine. The organic layer was separated and dried over $MgSO_4$ and then filtered. The extraction solvent was removed by evaporation, and the remaining material was subjected to column chromatography on silica gel (hexane:EtOAc = 1:1) to give 0.15 g (81% yield) of pure **3b**.

2.5.1. 5-Fluoro(phenylsulfonyl)methyl-3-phenoxycarbonyloxazolidinone (*3b*)

^{1}H NMR ($CDCl_3$): δ 8.09–7.16 (m, 10H), 5.41 (ddd, *J* = 24.8, 9.2, 6.8 Hz, 1H), 4.54–4.48 (m, 1H), 4.40–4.33 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 149.8, 135.7, 133.7, 130.1, 129.8, 129.7, 129.5, 129.4, 128.2, 126.5, 98.8 (d, *J* = 226.9 Hz), 68.9 (d, *J* = 19.5 Hz), 43.0 (d, *J* = 6.7 Hz); ^{19}F NMR ($CDCl_3$): δ −118.30 (dd, *J* = 49.9, 25.7 Hz); HRMS calc. for $C_{17}H_{14}FNO_6S$: *m*/*z* 379.0526; found: *m*/*z* 379.0528.

2.6. Alkaline hydrolysis of *3b*

To a solution of **3b** (0.10 g, 0.3 mmol) in EtOH (1 ml) was added sodium carbonate (0.05 g, 0.5 mmol) and the solution was stirred for 1 h at room temperature under a nitrogen atmosphere. After the reaction, the solution was evaporated under reduced pressure, and water was added. The resulting solution was extracted repeatedly with ethyl acetate and the extracts were dried over $MgSO_4$. The extraction solvent was removed by evaporation, and the remaining material was subjected to column chromatography on silica gel (hexane:EtOAc = 1:1) to give of **4b** (0.10 g, quant.).

2.6.1. N-(3-fluoro-3-phenylsulfonyl-2-propenyl)phenyl carbamate (*4b*)

^{1}H NMR ($CDCl_3$): δ 8.00–7.57 (m, 10H), 6.31 (dt, *J* = 31.9, 6.8 Hz, 1H), 4.92 (m, 1H), 4.36 (m, 1H); ^{19}F NMR ($CDCl_3$): δ −49.11 (d, $J_{F-Htrans}$ = 33.3 Hz); HRMS calc. for $C_{16}H_{14}FNO_4S$: *m*/*z* 335.0628; found: *m*/*z* 335.0626.

3. Results and discussion

The starting 3-methyl- and 3-phenoxycarbonyl-5-(phenylthio)methyl oxazolidinones (**1a,b**) were synthesized in good yields as shown in Scheme 1.