

Highly selective anodic monofluorination of 4-arylthio-1,3-dioxolan-2-ones: a marked solvent effect on product selectivity

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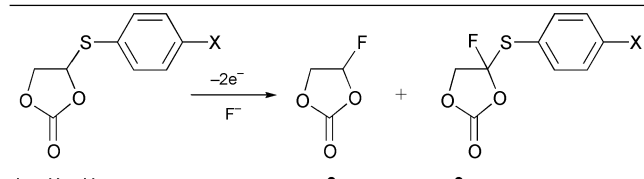
This is the first example of a solvent effect on fluorinated product selectivity; anodic fluorination of 4-arylthio-1,3-dioxolan-2-ones in CH_2Cl_2 containing a fluoride supporting electrolyte using an undivided cell provided the fluoro-desulfurization product, 4-fluoro-1,3-dioxolan-2-one preferentially while anodic fluorination in DME resulted in α -fluorination, without desulfurization, selectively.

Fluorinated ethylene carbonates seem to be promising organic electrolytic solvents or additives for rechargeable Li batteries since introduction of fluorine atom(s) into ethylene carbonate is expected to increase its electrochemical stability and decrease its melting point. We have studied selective anodic fluorination of various organic compounds.^{1,2} The selective anodic fluorination has many advantages since the fluorination can be carried out in one step under safe conditions and the use of hazardous reagents is not required. So far, limited examples of selective anodic fluorination of oxygen-containing heterocycles have been reported.³ With these facts in mind, we have attempted anodic fluorination of ethylene carbonates having an arylthio group **1** using various supporting fluoride salts and solvents.

At first, we investigated anodic fluorination of 4-phenylthio derivative **1a** under various conditions. Constant current electrolysis was carried out at platinum plate electrodes in an undivided cell at rt until **1a** was completely consumed. The results are summarized in Table 1.

As shown in Table 1, anodic fluorodesulfurization of **1a** proceeded selectively in $\text{Et}_4\text{NF}\cdot 4\text{HF}-\text{CH}_2\text{Cl}_2$ and $\text{Et}_3\text{N}\cdot 5\text{HF}-\text{CH}_2\text{Cl}_2$ to provide monofluorinated product **2**⁴ in moderate to good yields (runs 3 and 5). In sharp contrast, α -fluorination of **1a** took place preferentially in $\text{Et}_4\text{NF}\cdot 4\text{HF}-\text{DME}$ to give **3a**⁵ (run 4). In this case, difluorinated products such as **4** (Scheme 2) were not formed. This can be explained in terms of the oxidation potential of **3a** (E_p^{ox} : 2.2 V vs. SCE) being 0.3 V higher than that of **1a** (E_p^{ox} : 1.9 V vs. SCE).

Table 1 Anodic fluorination of 4-arylthio-1,3-dioxolan-2-ones



1a: X = H
1b: X = Cl

Run	Substrate		Supporting electrolyte	Solvent	Electricity/ F mol ⁻¹	Yield (%) ^a	
	1	2				2	3
1	1a	Et ₄ NF·3HF	CH ₂ Cl ₂	3.1	29	16	
2	1a	Et ₄ NF·3HF	DME	7.2	5	40	
3	1a	Et ₄ NF·4HF	CH ₂ Cl ₂	5.2	53	Trace	
4	1a	Et ₄ NF·4HF	DME	3.4	28	54	
5	1a	Et ₄ NF·5HF	CH ₂ Cl ₂	5.5	67	Trace	
6	1b	Et ₄ NF·4HF	DME	3.1	20	80	
7	1b	Et ₄ NF·5HF	CH ₂ Cl ₂	4.2	96	0	

^a Determined by ¹⁹F-NMR spectroscopy.

Next, we extended this anodic fluorination to the 4-(4-chlorophenylthio) derivative **1b**. Similarly, the use of $\text{Et}_3\text{N}\cdot 5\text{HF}-\text{CH}_2\text{Cl}_2$ provided **2** exclusively in almost quantitative yield (run 7) while the use of $\text{Et}_4\text{NF}\cdot 4\text{HF}-\text{DME}$ afforded **3b**⁶ selectively in good yield (run 6). Thus, it was found that electrolytic conditions, particularly electrolytic solvents, greatly affected the fluorinated product selectivity. Such marked product selectivity depending on electrolytic solvents has not been previously reported for anodic fluorination.

In order to clarify the solvent effects, we investigated anodic fluorination of **1b** in a mixed solvent of DME and CH_2Cl_2 containing $\text{Et}_4\text{NF}\cdot 4\text{HF}$. As shown in Fig. 1, the product ratio of **2** to **3b** increased with an increase in the ratio of CH_2Cl_2 to DME. Notably, addition of only 25% CH_2Cl_2 to DME caused a dramatic change in the product ratio and **2** was mainly formed in ca. 60% yield.

This interesting phenomenon can be explained as follows. The fluorination can be rationalised by postulating a radical cation intermediate **A** as shown in Scheme 1.

CH_2Cl_2 has a poor ability to solvate carbocations, therefore, **A** seems to be unstable in CH_2Cl_2 . Consequently it is reasonable to assume that desulfurization followed by fluorination mainly takes place prior to α -fluorination of **A**.⁷ On the other hand, DME is known to strongly coordinate cations.⁸ Therefore, DME should stabilize the intermediate **A** and DME also enhances the fluoride ion nucleophilicity.⁹ Then, the deprotonation of **A** with fluoride ions takes place prior to desulfurization followed by further oxidation to generate cation **B** and this cation reacts with a fluoride ion to provide the α -fluorinated product.

Furthermore, we examined anodic fluorodesulfurization of **3a**. As shown in Scheme 2, anodic fluorodesulfurization of **3a** in $\text{Et}_4\text{NF}\cdot 4\text{HF}-\text{CH}_2\text{Cl}_2$ and $\text{Et}_3\text{N}\cdot 5\text{HF}-\text{CH}_2\text{Cl}_2$ proceeded to give desired difluorinated product **4**¹⁰ in reasonable yield. However, anodic fluorodesulfurization of **3a** did not take place at all in $\text{Et}_4\text{NF}\cdot 4\text{HF}-\text{DME}$ and **3a** was almost recovered.

Finally, we also examined chemical fluorination of **1a**. However, treatment of **1a** with various *N*-fluoropyridinium

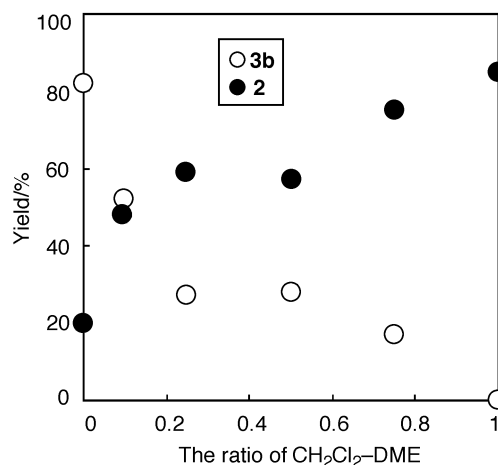
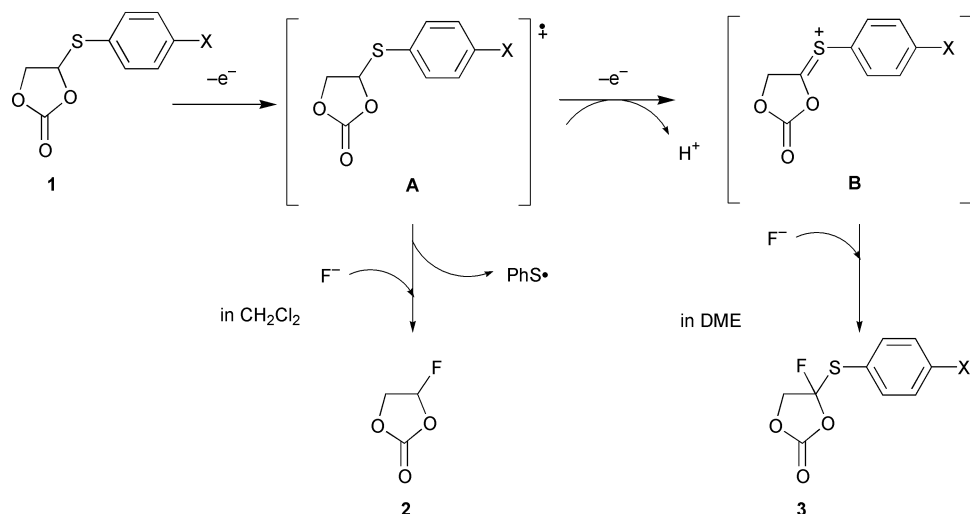
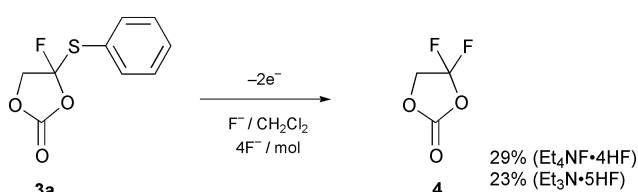


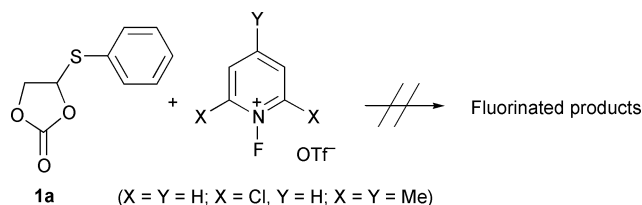
Fig. 1 Dependence of yield of **2** and **3b** on the ratio of CH_2Cl_2 to DME.



Scheme 1



Scheme 2



Scheme 3

triflates in CH_2Cl_2 resulted in the formation of none of the desired fluorinated products, as shown in Scheme 3. Therefore, electrochemical fluorination is more advantageous than conventional chemical methods for such heterocyclic sulfides.

In summary, we have developed a novel synthesis of fluorinated ethylene carbonates using anodic fluorination and we also found a unique marked solvent effect on fluorinated product selectivity.

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Notes and references

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- 4-Fluoro-1,3-dioxolan-2-one (2)**: colorless cubes: mp 19.0–20.0 °C; $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 6.31 (ddd, $J = 64, 1.3, 4.0$ Hz, 1H), 4.70–4.49 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 67.8 MHz) δ 152.65, 104.98 (d, $J = 237$ Hz), 70.67 (d, $J = 28$ Hz); $^{19}\text{F-NMR}$ (CDCl_3 , 254 MHz) δ -44.42 (ddd, $J = 64, 34, 21$ Hz); MS (m/z) 106 (M^+), 62 ($\text{M} - \text{CO}_2$); Anal. calc. for $\text{C}_3\text{H}_2\text{FO}_3$: C, 33.98; H, 2.85; F, 17.91; O, 45.26. Found C, 33.73; H, 2.91; F, 17.72%.
- 4-Fluoro-4-phenylthio-1,3-dioxolan-2-one (3a)**: colorless oil; $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 7.66–7.62 (m, 2H), 7.50–7.39 (m, 3H), 4.63 (dd, $J = 16.8, 10.9$ Hz, 1H), 4.47 (dd, $J = 26.4, 10.9$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 67.8 MHz) δ 150.64, 136.21, 130.89, 129.70, 125.03, 119.54 (d, $J = 270$ Hz), 73.88 (d, $J = 31$ Hz); $^{19}\text{F-NMR}$ (CDCl_3 , 254 MHz) δ 0.54 (dd, $J = 27, 17$ Hz); MS (m/z) 214 (M^+); HRMS calc. for $\text{C}_9\text{H}_7\text{FO}_3\text{S}$: 214.0100. Found: 214.0133.
- 4-Fluoro-4-(p-chlorophenylthio)-1,3-dioxolan-2-one (3b)**: colorless needles; mp 60.0–61.0 °C; $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 7.60–7.57 (m, 2H), 7.43–7.40 (m, 2H), 4.66 (dd, $J = 16.8, 10.9$ Hz, 1H), 4.47 (dd, $J = 26.4, 10.9$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 67.8 MHz) δ 150.40, 137.72, 137.43, 129.96, 123.34, 119.21 (d, $J = 271$ Hz), 73.83 (d, $J = 31$ Hz); $^{19}\text{F-NMR}$ (CDCl_3 , 254 MHz) δ 0.93 (dd, $J = 27, 17$ Hz); MS (m/z) 250 (M^+); HRMS calc. for $\text{C}_9\text{H}_6\text{ClFO}_3\text{S}$: 247.9710. Found: 247.9720.
- In this reaction, the formation of diphenyl disulfide was detected by MS and $^1\text{H-NMR}$.
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- 4,4-Difluoro-1,3-dioxolan-2-one (4)**: $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 4.72 (t, $J = 11$ Hz, 2H); $^{19}\text{F-NMR}$ (CDCl_3 , 254 MHz) δ 3.90 (t, $J = 12$ Hz); MS (m/z) 124 (M^+); HRMS calc. for $\text{C}_3\text{H}_2\text{F}_2\text{O}_3$: 123.9972. Found: 123.9939.