Selective Electrochemical Fluorination of Organooxygen Compounds in Ionic Liquids

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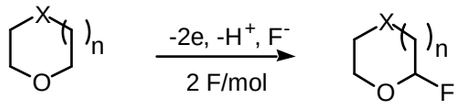
Ionic liquids (ILs) are becoming widely recognized as solvents for green organic synthesis. However, there have been only few papers dealing with electroorganic synthesis in ILs.[1,2)]

In this work, we studied the electochemical partial fluorination of organooxygen compounds in ILs. Anodic fluorination of cyclic ethers (1,3,5) were successfully carried out under solvent-free conditions using ionic liquids such as Et_4NF nHF(n=4,5) as shown in Table 1.[3)]

Table 1. Anodic Fluorination of Cyclic Ethers



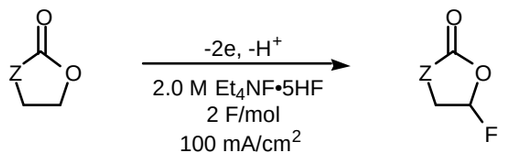
(X = O, C; n = 0 ,1)

1,**3**,**5** **2**,**4**,**6**

Run	Ether No.	n	X	Product	Yield/%[a]
1	**1**	0	C	**2**	80
2	**3**	1	O	**4**	77
3	**5**	0	O	**6**	56

[a] Determined by ^{19}F-NMR.

Anodic fluorination of lactone **7** and cyclic carbonate **9** was achieved similarly as shown in Scheme 1. This fluorination did not proceed in organic solvents.



7: Z = CH_2
9: Z = O

8: Z = CH_2 (75%)
10: Z = O (87%)

Scheme 1

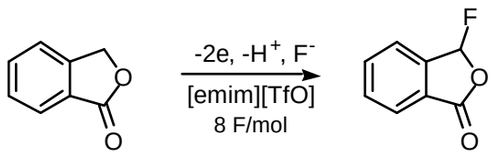
We also attempted anodic fluorination of phthalide (**11**) in ordinary organic solvents and ILs such as 1-ethyl-3-methylimidazolium triflate [emim][TfO] (Fig.1). The fluorination did not proceed well in organic solvents, while the fluorination in IL provided fluorinated product **12** in good yield as shown in Table 2.

$CF_3SO_3^-$

[emim][TfO]

Fig.1

Table 2. Anodic Fluorination of Phthalide (11)



11 **12**

Run	Solvent	Supporting Electrolyte	Yield/%[a]
1	MeCN	Et_3N•5HF	16
2	DME	Et_4NF•4HF	16
3	[emim][TfO]	Et_3N•5HF	63
4	[emim][TfO]	Et_4NF•5HF	65(41)[b]

[a] Determined by ^{19}F-NMR.
[b] Isolated Yield

Thus, we have demonstrated successful solvent-free electrochemical synthesis using ionic liquids.

References:

1) Ishii, H.; Fuchigami, T. *Electrochemistry* **2002**, *70*, 46.
2) Sekiguchi,K.; Atobe, M.; Fuchigami, T. Fuchigami, *Electrochem. Commun*., in press.
3) Hasegawa, M.; Ishii, H.; Fuchigami, T. *Tetrahedron Lett*. **2002**, *43* ,1503.