

# Electroorganic Reactions in Ionic Liquids. Anodic Fluorodesulfurization of Phthalide, Ethylene Carbonate, and Glucopyranosides Having Arylthio Groups

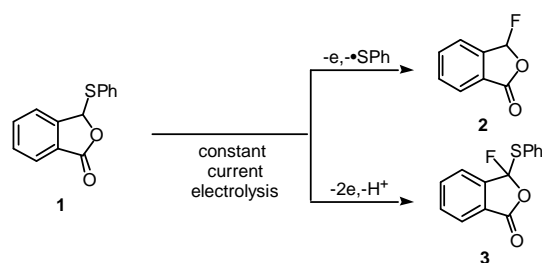
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Electrochemical partial fluorination of various compounds has been studied mainly in organic solvents containing supporting fluoride salts such as  $\text{Et}_3\text{N}\cdot n\text{HF}$  ( $n = 2\sim 5$ ) and  $\text{Et}_4\text{NF}\cdot n\text{HF}$  ( $n = 3\sim 5$ ) [1]. The fluorinated product selectivity and fluorination efficiency are very often greatly affected by the kinds of solvents and supporting fluoride salts [2,3]. Therefore, a choice of combination of a solvent and supporting fluoride salt is of much importance. The use of organic solvents like acetonitrile sometimes causes anodic passivation which results in low efficiency for anodic fluorination. However, interesting recent development in electrochemical fluorination is the use of liquid salts like  $\text{Et}_3\text{N}\cdot 3\text{HF}$  and  $\text{Et}_4\text{NF}\cdot 4\text{HF}$  without any solvents as the electrolytic media. Although a number of papers dealing with anodic fluorination have been published, there have been still limited examples of anodic fluorination in such ionic liquid fluoride salts [4,5]. With these facts in mind, anodic fluorodesulfurization of oxygen-containing heterocyclic compounds was attempted using fluoride salts as reaction media as follows [6].

Anodic fluorodesulfurization of 3-phenylthiophthalide, 4-phenylthio-1,3-dioxolan-2-one, and 1-arylthio-2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranoside in ionic liquids like  $\text{Et}_3\text{N}\cdot n\text{HF}$  ( $n = 4\sim 5$ ) and  $\text{Et}_4\text{NF}\cdot n\text{HF}$  ( $n = 4, 5$ ) without any solvents provided the corresponding monofluorinated products exclusively in moderate to good yields. In sharp contrast, the anodic fluorination in  $\text{Et}_3\text{N}\cdot 3\text{HF}$  with and without co-solvents resulted in  $\alpha$ -fluorination without desulfurization exclusively or preferentially.

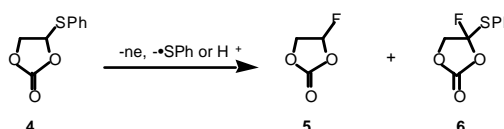
Table 1  
Media effect on anodic fluorination of 3-phenylthiophthalide (1)



| Run | Reaction Media                         | Charge Passed F/mol | Yield/% <sup>a</sup> |    |
|-----|--|---------------------|----------------------|----|
|     |  |                     | 2                    | 3  |
| 1   | $\text{Et}_3\text{N}\cdot 3\text{HF}$  | 4.2                 | 4                    | 21 |
| 2   | $\text{Et}_3\text{N}\cdot 4\text{HF}$  | 4.2                 | 77                   | -  |
| 3   | $\text{Et}_3\text{N}\cdot 5\text{HF}$  | 3.2                 | 96                   | -  |
| 4   | $\text{Et}_4\text{NF}\cdot 4\text{HF}$ | 3.3                 | 99                   | -  |
| 5   | $\text{Et}_4\text{NF}\cdot 5\text{HF}$ | 4                   | 93                   | -  |

a) Determined by  $^{19}\text{F}$ -NMR.

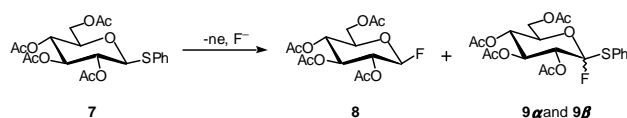
Table 3  
Media effect on anodic fluorination of 4-phenylthio-1,3-dioxolan-2-one (4)



| Run | Reaction Media                        | Charge Passed F/mol | Yield % <sup>a</sup> |    |
|-----|---------------------------------------|---------------------|----------------------|----|
|     |                                       |                     | 5                    | 6  |
| 1   | $\text{Et}_3\text{N}\cdot 3\text{HF}$ | 3.2                 | -                    | 12 |
| 2   | $\text{Et}_3\text{N}\cdot 4\text{HF}$ | 3.6                 | 51                   | -  |

a) Determined by  $^{19}\text{F}$ -NMR.

Table 3  
Anodic fluorination of 7 under various conditions



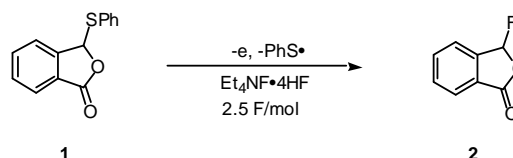
| Run            | Solvent                  | Supporting Electrolyte                | Charge Passed F/mol | Yield/% <sup>a</sup> |            |           |
|----------------|--------------------------|---------------------------------------|---------------------|----------------------|------------|-----------|
|                |                          |                                       |                     | 8                    | 9 $\alpha$ | 9 $\beta$ |
| 1 <sup>b</sup> | DME                      | $\text{Et}_3\text{N}\cdot 3\text{HF}$ | 4                   | -                    | 10         | 22        |
| 2              | THF                      | $\text{Et}_3\text{N}\cdot 3\text{HF}$ | 4                   | -                    | 12         | 55        |
| 3              | MeCN                     | $\text{Et}_3\text{N}\cdot 3\text{HF}$ | 4                   | -                    | 11         | 46        |
| 4              | $\text{CH}_2\text{Cl}_2$ | $\text{Et}_3\text{N}\cdot 3\text{HF}$ | 4                   | -                    | 17         | 41        |
| 5 <sup>c</sup> | -                        | $\text{Et}_3\text{N}\cdot 3\text{HF}$ | 4                   | 12                   | 5.7        | 20        |
| 6              | -                        | $\text{Et}_3\text{N}\cdot 4\text{HF}$ | 4.2                 | 62                   | -          | -         |
| 7 <sup>d</sup> | -                        | $\text{Et}_3\text{N}\cdot 4\text{HF}$ | 4                   | 66                   | -          | -         |

a) Determined by  $^{19}\text{F}$ -NMR. b) 7 (46%) was recovered.

c) Multi products were formed. d) 0.1 eq.  $\text{Et}_4\text{NBr}$  was added.

It was also demonstrated that the electrochemical fluorodesulfurization of 3-phenylthiophthalide under solvent-free conditions was achieved repeatedly four times by the reuse of a fluoride salt,  $\text{Et}_4\text{NF}\cdot 4\text{HF}$ . This is the first example of fluorodesulfurization by the reuse of an ionic fluoride salt.

Table 4  
Recyclable anodic fluorodesulfurization of 3-phenylthiophthalide (1) in  $\text{Et}_4\text{NF}\cdot 4\text{HF}$



| Cycle           | Yield of 2/% <sup>a</sup> |
|-----------------|---------------------------|
| 1 <sup>st</sup> | 99                        |
| 2 <sup>nd</sup> | 96                        |
| 3 <sup>rd</sup> | 93                        |
| 4 <sup>th</sup> | 94                        |

a) Determined by  $^{19}\text{F}$ -NMR.

## References:

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