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Electrolytic Partial Fluorination of Organic Compounds. X. Selective Anodic Fluorination of Organic Tellurium Compounds[1]

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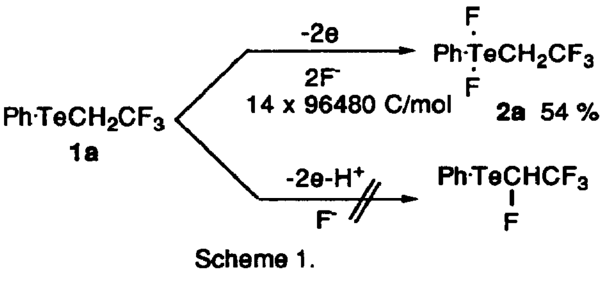
Abstract: Anodic oxidation of various types of organic tellurium compounds was carried out in the presence of fluoride ions and difluorination occurred at the tellurium atom selectively in excellent yields and with high current efficiencies regardless of their structures. This is the first example of anodic fluorination of tellurides and also that of electrosynthesis of hypervalent tellurides.

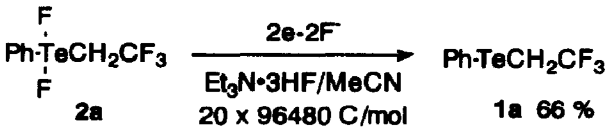
In the course of our studies on the selective anodic fluorination of organic sulfur and selenium compounds,[2] it was found that electron-withdrawing groups markedly promoted the fluorination at the position α to the sulfur[3] and selenium atoms.[4] This finding promoted us to attempt anodic fluorination of other chalcogeno compounds, tellurides. In contrast to the cathodic reduction of organic tellurium compounds,[5] there has been no study on their anodic behavior so far. In this paper, we wish to report the first example of selective anodic fluorination of tellurides bearing electron-withdrawing groups together with simple alkyl phenyl telluride and diphenyl telluride.

Anodic fluorination of phenyl 2,2,2-trifluoroethyl telluride (**1a**)[6] was first attempted in MeCN containing Et3N•3HF using an undivided cell under galvanostatic conditions.[7] Fluorination proceeded, however fluorine was not introduced at the position α to the tellurium atom and it was found that difluorination took place at the tellurium atom selectively (Scheme 1). Since a large amount of electricity was necessary and the yield of **2a**[8]



Scheme 1.

was not so high, it was assumed that the difluorinated product **2a** should be subjected to cathodic reduction during the electrolysis. In fact, we confirmed that **2a** could be reduced to regenerate **1a** in reasonable yield by cathodic reduction in the same electrolytic solution in a divided cell (Scheme 2). Then, anodic fluorination of **1a** was carried out at a controlled potential using a divided cell.[9] Expectedly, the electrolysis was completed after passing 2 x 96480 C/mol and the difluorinated product **2a** was obtained in excellent yield. Anodic fluorination of telluride bearing an electron-withdrawing difluoromethyl group (**1b**) provided difluorinated product **2b**[10] similarly in high yield and α-fluorinated product was not formed (Table 1, Run 4). Even simple methyl phenyl telluride (**1c**) and diphenyl telluride (**1d**) underwent efficient difluorination (Table 1, Runs 6 and 8).

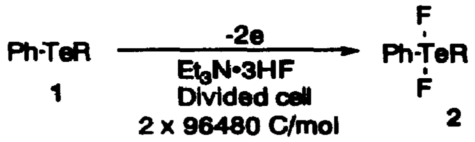


Scheme 2.

Recently, we found that fluoride ion promoted anodic α-methoxylation of sulfides[11] and selenides.[12] Then, we have attempted anodic α-methoxylation of **1a** and **1b** in methanol containing $Et_3N{\bullet}3HF$. However, in both cases, α-methoxylation did not occur at all and difluorination at the tellurium atom took place selectively (Table 1, Runs 2 and 5). Previously, we showed that the strong electron-withdrawing CF_3 group markedly promoted anodic α-acetoxylation of 2,2,2-trifluoroethyl sulfides[13] and selenides[14] and that fluoride ions facilitated anodic α-acetoxylation of sulfides.[15] However, anodic oxidation of **1a** in acetic acid containing $Et_3N{\bullet}3HF$ provided **2a** solely in good yield and α-acetoxylated product was not formed (Table 1, Runs 3). Thus, the telluride **1a** did not undergo anodic α-substitution, which is totally different to the cases of the corresponding sulfide and selenide. In this electrolytic solution, tellurides **1c** and **1d** also gave difluorinated products **2c** and **2d**, but did not form any acetoxylated tellurides.

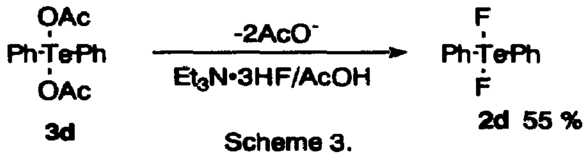
It is well known that the nucleophilicity of fluoride ions is extremely low compared to methanol and acetic acid. However, efficient difluorination always proceeded even in methanol and acetic acid. The products, difluorinated tellurides are so called hypervalent compounds. It is well known that hypervalent compounds easily undergo ligand exchange reaction.[16] Therefore, it is reasonable to assume that in methanol and acetic acid in the presence of fluoride ions, anodic methoxylation and acetoxylation take place first at the tellurium atom,[17] and then exchange of these oxygen-ligands with fluoride ligands occurs in the course of the electrolysis since more electronegative ligands (fluorine) stabilize hypervalent compounds more strongly in general. In order to confirm such ligand exchange, diphenyl tellurium diacetate (**3d**)[18] was treated with acetic acid containing $Et_3N{\bullet}3HF$, which was used for anodic fluorination (Table 1, Runs 3, 7, and 9). Expectedly, the fluorinated product **2d** was formed in reasonable yield (Scheme 3). Therefore, it was clarified that this anodic fluorination proceeded *via* acetoxylated tellurides as a key intermediate.

Table 1. Anodic Difluorination of Tellurides 1



Run	Telluride (1) R	Solvent	Anodic potential V vs SSCE	Yield %
1	CF_3CH_2 (1a)	MeCN	1.5	86
2	CF_3CH_2 (1a)	MeOH	1.1	75
3	CF_3CH_2 (1a)	AcOH	a)	70
4	CHF2 (1b)	MeCN	1.6	86
5	CHF2 (1b)	MeOH	1.2	86
6	Me (1c)	MeCN	1.0	81
7	Me (1c)	AcOH	a)	78
8	Ph (1d)	MeCN	1.0	77
9	Ph (1d)	AcOH	a)	75

a) Constant current (3.3 mA/cm^2) electrolysis of 1 (1.5 mmol) was carried out in 0.26 mol/dm^3 $Et_3N•3HF/AcOH$ (20 cm^3).



Scheme 3.

Hypervalent difluorinated tellurium compounds such as 2c[19] and 2d[19] have been prepared by using dangerous F_2 gas[19] and COF_2[20] or costly XeF_2[21] in Teflon equipment so far. In contrast, this electrochemical fluorination does not require any dangerous or costly reagents and can be carried out in normal laboratory glassware without precautions. Thus, we have demonstrated that the electrochemical technique is a versatile method for the preparation of fluorinated hypervalent tellurium compounds.

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6. Telluride **1a** was prepared by the reaction of PhTeLi with 2,2,2-trifluoroethyl *p*-toluenesulfonate in DMF. The yield was 18 %. ^{19}F NMR ($CDCl_3$, ext CF_3COOH), $\delta = 17.51$ (t, CF_3, $J = 12$ Hz).
7. Constant current (12.5 mA/cm^2) electrolysis of **1a** (1.5 mmol) was carried out in 0.26 mol/dm^3 $Et_3N{\bullet}3HF$ / MeCN (20 cm^3) using platinum electrodes (2 x 2 cm^2) at ambient temperature. After the electrolysis, usual work-up was done.
8. **2a**: ^{19}F NMR ($CDCl_3$, ext CF_3COOH), d = 22.57 (broad s, 3F, CF_3) and -41.47 (s, 2F, TeF_2).
9. Electrolysis of **1a** (1.5 mmol) was performed at platinum electrodes (3 x 4 cm^2) in a divided cell with an anion-exchange membrane (ACH-45T, Tokuyama Soda). Solutions (20 cm^3) of 0.26 mol/dm^3 and 0.52 mol/dm^3 $Et_3N{\bullet}3HF$ / MeCN were used as an anolyte and a catholyte, respectively.
10. **2b**: ^{19}F NMR (MeCN, ext CF_3COOH), $\delta = -34.17$ (d, 2F, CF_2H, $J = 49.6$ Hz) and -60.16 (s, 2F, TeF_2).
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17. In fact, it was confirmed that acetoxylation occurred at the tellurium atom in the anodic oxidation of these tellurides in the presence of only acetate anions.
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