Electrochemistry of Hypervalent Compounds III¹⁾. Electrosynthesis of Hypervalent Tellurium Compounds Having Te-O Bonds

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1 INTRODUCTION

Hypervalent compounds have unique molecular structures and they exhibit quite interesting reactivities²⁻⁴⁾. Although the chemistry of hypervalent compounds has been intensively studied, only few examples of electrosynthesis of hypervalent compounds have been reported to date⁵⁾. In particular, there has been no report on the electrosynthesis of hypervalent tellurium compounds⁶⁾. From these view points, we have recently studied anodic oxidation of various types of organotellurium compounds in the presence of fluoride ions and we have found that hypervalent difluorotellurium compounds are formed in excellent yields and with high current efficiencies regardless of their structures and electrolytic solvents⁷⁾.

In this paper, we wish to report the electrosynthesis of hypervalent tellurium compounds bearing Te-O bonds in one step under mild conditions. Diphenyl telluride **1a** and methylphenyl telluride **1b** were selected as model compounds in this study. Electrosynthesis was attempted in MeOH containing various supporting electrolytes such as NaClO₄, Et₄NOTs, and PhCOOLi.

2 EXPERIMENTAL

Using an H-shaped cell divided with an anion-exchange membrane (IE-DF34-5 TOSOH), controlled-potential electrolysis was carried out at Pt electrodes (3 x 4 cm²) as anode and cathode in 20 cm³ of 0.15 mol dm⁻³ NaClO₄ / MeOH (0.15 mol dm⁻³ PhCOOLi / MeOH, 0.075 mol dm⁻³ Et₄NOTs / MeOH) containing 1.5 mmol of telluride **1**. Electricity was passed until the starting material **1** had been completely consumed.

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2a: ¹H NMR (CDCl₃) δ = 7.1 ~ 7.8 (m, Ar-H). MS (30 eV) m/e 284 (PhTePh⁺), 207 (PhTe⁺), 77 (Ph⁺). Anal. Calcd for C₂₄H₁₉O₄ClTe • 0.5NaClO₄: C, 39.85; H, 2.64%. Found: C, 39.77; H, 2.95%.

3a: Anal. Calcd for C₂₀H₂₀O₄STe: C, 49.63; H, 4.16; S, 6.62%. Found: C, 49.19; H, 3.56; S, 6.69%.

3b: ¹H NMR (CDCl₃) δ = 2.10 (s, 3H, OCH₃), 2.30 (s, 3H, C₆H₄CH₃), 2.70 (s, 3H, TeCH₃), 6.80 ~ 8.00 (m, 9H, Ar-H). Anal. calcd for C₁₅H₁₈O₄STe: C, 42.60; H, 4.30%. Found: C, 42.11; H, 4.18%.

4a: ¹H NMR (CDCl₃) δ = 7.29 ~ 7.53 (m, 18H, Ar-H), 7.84 ~ 8.03 (m, 12H, Ar-H). MS (30 eV) m/e 449 [PhTe(OCOPh)₂⁺], 405 (Ph₂TeOCOPh⁺), 328 (PhTeOCOPh⁺), 284 (PhTePh⁺), 207 (PhTe⁺). IR (KBr) 1620, 1575 cm⁻¹ (ν co). Anal. Calcd for C₃₈H₃₀O₅Te • H₂O: C, 54.34; H, 3.60%. Found: C, 54.13; H, 3.56%.

4b: ¹H NMR (CDCl₃) δ = 2.70 (s, 6H, CH₃), 7.25 ~ 7.48 (m, 12H, Ar-H), 7.91 ~ 7.98 (m, 8H, Ar-H). MS (30 eV) m/e 449 [PhTe(OCOPh)₂⁺], 343 [Ph(Me)TeOCOPh⁺], 284 [MeTe(O)OCOPh⁺], 222 (PhTeCH₃⁺), 207 (PhTe⁺). IR (KBr) 1600, 1570 cm⁻¹ (ν co).

3 RESULTS AND DISCUSSION

First, anodic oxidation of diphenyl telluride **1a** was attempted in MeOH containing NaClO₄ using a cell divided with an anion-exchange membrane under potentiostatic conditions. It was found that **1a** gave a dimeric product **2a** in a moderate yield (scheme 1). Previously, Torii *et al.* obtained a similar dimeric sulfonium salt by anodic oxidation of diphenyl sulfide in LiClO₄ / MeCN⁸⁾. The product **2a** seems to be formed via cation radical intermediate generated by one-electron oxidation of **1a** in a manner similar to the case of diphenyl sulfide⁸⁾.

Next, anodic oxidation of tellurides **1** was carried out in MeOH containing Et₄NOTs instead of NaClO₄. Interestingly, both tosylation and methoxylation occurred at the tellurium atom of **1** to provide hypervalent products **3** although the yields were low

due to the formation of a large amount of complicated mixtures. In these cases, the dimeric products such as **2a** was not formed. It should be noted that tosylation and methoxylation took place simultaneously to the same extent, although the tosylate ion is a very weak nucleophile as compared to a methoxide ion. This is reasonable, however, because electronegative ligands such as tosylate stabilize hypervalent compounds more strongly in general²⁾.

Finally, anodic oxidation of tellurides **1** was further investigated by changing the supporting electrolyte from Et₄NOTs to PhCOOLi. Quite interestingly, the products were dramatically changed in the electrolytic system and anhydrous dimeric products **4** were formed in good yields. Although methanol was used as a solvent in this reaction, methoxylation did not take place at all. This is also reasonable in consideration to that electronegative ligands stabilize well hypervalent compounds²⁾. Thus, it is interesting that the anodic behavior of organotellurium compounds greatly depend on the supporting electrolytes.

Hypervalent tellurium compounds bearing two same oxygen functional groups as a ligand are well known. But, the products **3** have two different kinds of oxygen ligands such as methoxy and sulfonyloxy groups. Such tellurium compounds are entirely new. From the similar reason, the products **4** are also new type of hypervalent tellurium compounds. Since

the formation mechanisms of **3** and **4** are unclear at the present time, a further study is necessary.

In summary, we have demonstrated that the electrochemical technique is a promising method for the development of new types of hypervalent compounds since they can be easily prepared in one step under quite mild conditions.

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