

Migration of Acetoxy Group from Tetracoordinated Tellurium Compound, 12,12-Diacetoxy-5*H*,7*H*-dibenzo[*b,g*][1,5]tellurathiocin, Induced by Transannular Te-S Interaction

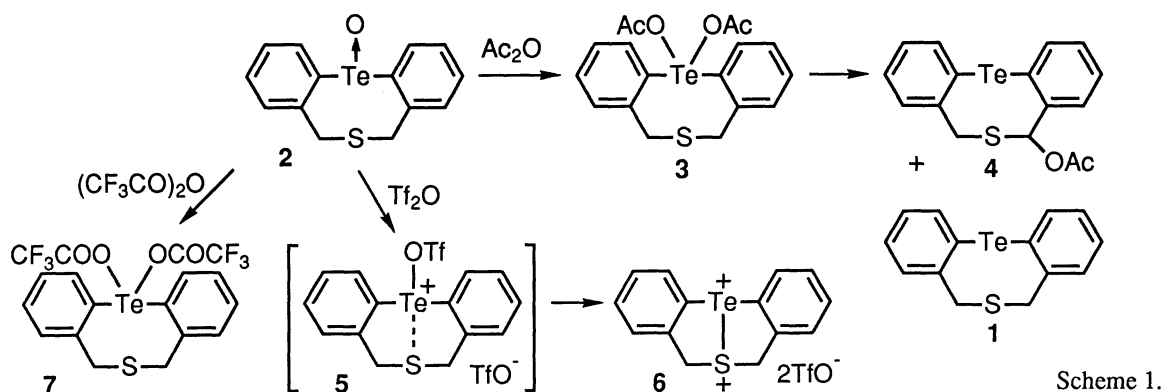
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The reaction of 12-oxo-5*H*,7*H*-dibenzo[*b,g*][1,5]tellurathiocin with acetic anhydride afforded a 12,12-diacetoxy-substituted tellurane (3). Heating of the benzene solution of 3 gave a remote α -acetoxyated sulfide and the parent 5*H*,7*H*-dibenzo[*b,g*][1,5]tellurathiocin.

The preparation and structure of hypervalent organochalcogen compounds are of considerable current interest.^{1,2)} However, the reactivity of tetracoordinated tellurium compounds, telluranes, has received less attention.²⁾ We have now found that the reaction of the telluroxide 2 with acetic anhydride gave the title compound 3 which led to the corresponding remote α -acetoxyated sulfide 4 and the tellurathiocin 1 on heating. This paper reports a new reaction mode for the group transfer from tellurane induced by transannular interaction.

Typically, the treatment of telluroxide 2 (100 mg, 0.28 mmol) with Ac₂O (30 mg, 0.29 mmol) in anhydrous CH₂Cl₂ (10 mL) at room temperature for 3 h gave the tellurane 3 in 87% yield.^{3,5,6)} Bis-trifluoroacetoxy-substituted tellurane (7) was formed in the analogous reaction of 2 with (CF₃CO)₂O.⁵⁾

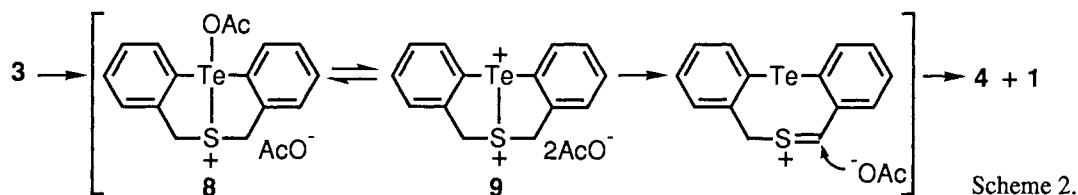


Surprisingly, a solution of 3 in benzene was refluxed to afford the products 4 (23%) and 1 (60%), after purification by silica-gel column chromatography (Scheme 1).⁷⁾ Similarly, 2 was allowed to react with a large excess of acetic anhydride at 100 °C for 36 h under an Ar atmosphere; the compounds 4 and 1 were obtained in 25% and 60% isolated yields, respectively. However, a distinct difference in reactivity between 3 and 7 was found, *i.e.*, the benzene solution of 7 was definitely stable even under reflux.

In contrast, the telluroxide 2 led to a tellurathia dication salt (6) (81%) upon treatment with trifluoromethanesulfonic anhydride, Tf₂O, at -20 °C (Scheme 1).⁸⁾ This reaction may proceed *via* the initial formation of a (trifluoromethylsulfonyloxy)telluronium salt (5) which is subsequently converted into the dication 6 by

nucleophilic displacement of the CF_3SO_3^- ion by the remote sulfur atom, *i.e.*, by a transannular reaction. Interestingly, when the dication salt **6** was allowed to react with $\text{CH}_3\text{CO}_2\text{Na}$ in CH_3CN at 80°C , the reduction product **1** was formed in 66% yield.⁹⁾

In order to explain the formation of **4** and **1** from **3**, we propose the following pathway: **3** is initially converted into a sulfoniotellurane (**8**) or a dication (**9**) by a transannular Te-S interaction (Scheme 2). Subsequently, proton abstraction from **8** or **9** and acetoxylation take place to give **4**. The neutral **1** is generated from the reduction of **9** with AcO^- , which is the case for the reaction of dication salt **6** with $\text{CH}_3\text{CO}_2\text{Na}$.



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References

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- 2) "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1986), Vol. 1, Chap. 3 and 14.
- 3) The telluroxide **2** was obtained by hydrolysis of 12,12-dibromo derivative of **1**.⁴⁾
- 4) H. Fujihara, Y. Takaguchi, J.-J. Chiu, T. Erata, and N. Furukawa, *Chem. Lett.*, **1992**, 151.
- 5) **3**: Mp 161°C (decomp); ^1H NMR (CDCl_3) δ 1.85 (s, 6H, CH_3), 3.49, 4.03 (br ABq, 4H, CH_2), 7.36-7.54 (m, 6H, ArH), 7.90-7.93 (m, 2H, ArH); ^{13}C NMR (CDCl_3) δ 22.3, 31.1, 127.7, 132.7, 132.8, 133.2, 137.0, 141.3, 177.5. Anal. Found: C, 46.86; H, 3.91%. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{STe}$: C, 47.20; H, 3.96%.
7: Mp $193\text{--}193.5^\circ\text{C}$ (decomp); ^1H NMR (CD_2Cl_2) δ 4.09, 4.48 (ABq, $J=15.7$ Hz, 4H, CH_2), 7.34-7.57 (m, 6H, ArH), 8.23-8.26 (m, 2H, ArH); ^{13}C NMR (CD_2Cl_2) δ 38.9, 130.3, 130.4, 131.1, 131.8, 132.4, 139.9, 160.9; ^{19}F NMR (CD_2Cl_2) δ 87.8 (relative to C_6F_6).
- 6) Although it was reported that the reaction of diphenyl telluroxide with Ac_2O gave the diacetoxo derivative, its reactivity has been virtually unknown.²⁾
- 7) **4**: Mp 124°C ; IR (KBr) 1749 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.15 (s, 3H, CH_3), 4.05, 4.62 (ABq, $J=14.9$ Hz, 2H, CH_2), 7.00-7.53 (m, 6H, ArH), 7.68 (brs, 1H, CH), 8.00-8.10 (m, 2H, ArH); MS, m/z 400 (M^+). Anal. Found: C, 47.97; H, 3.46%. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{STe}$: C, 48.12; H, 3.51%.
- 8) **6**: Mp 142°C (decomp); ^1H NMR (CD_3CN) δ 4.52, 4.89 (ABq, $J=16.5$ Hz, 4H, CH_2), 7.57-7.66 (m, 6H, ArH), 8.09-8.12 (m, 2H, ArH); ^{13}C NMR (CD_3CN) δ 42.8, 130.5, 131.3, 131.7, 132.3, 133.3, 142.3; ^{19}F NMR (CD_3CN) δ 87.8 (relative to C_6F_6); ^{125}Te NMR (CH_3CN) δ 1111 (relative to Me_2Te).
- 9) The disulfide dication salt of 1,5-dithiacyclooctane could be reduced with $\text{CH}_3\text{CO}_2\text{Na}$ by electron transfer: unpublished results.

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