

LETTERS TO THE EDITOR

Regioselective Reaction of Tellurium Tetrabromide with Allyl Phenyl Ether

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Earlier, we have studied the reaction of selenium dichloride with allyl phenyl ether in chloroform at the equimolar ratio of the reagents leading to a fusion product, 3-chloromethyl-2,3-dihydro-1,4-benzoxaselenine, in 90% yield [1, 2]. With two-fold excess of allyl phenyl ether, the reactions of selenium dihalides in chloroform or carbon tetrachloride result in bis(3-phenoxy-2-halopropyl)selenides in 90–98% yield [1].

Tellurium tetrachloride readily reacts with alkenes to give the addition products [3]. The reactivity of tellurium tetrabromide is lower than that of TeCl_4 , and there are very few data on the addition of TeBr_4 to alkenes [3, 4]. The reactions of tellurium tetrahalides with allyl phenyl ether were not described in the literature.

In continuation of our studies of the addition reactions of selenium and tellurium halides to alkenes [5–9], we have investigated the reaction of tellurium tetrabromide with allyl phenyl ether. With chloroform or carbon tetrachloride as a solvent the conversion of the reagents was very low. The use of methanol substantially accelerates the addition reaction and leads to full conversion of allyl phenyl ether. The reaction proceeds regioselectively with the insertion of the methoxy group and the formation of the Markovnikov adduct, the earlier unknown 2-methoxy-3-phenoxypropyltellurium tribromide **I** (Scheme 1).

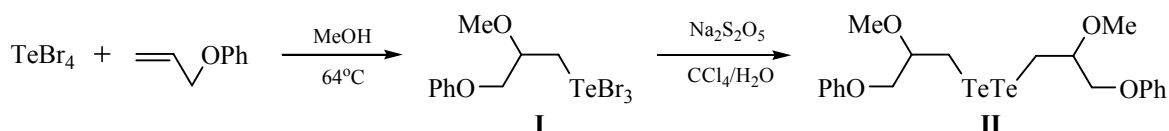
Product **I** was obtained quantitatively by 10 h reflux of equimolar amounts of the reagents. Neither the formation of bis-adduct $[\text{PhOCH}_2\text{CH}(\text{OMe})\text{CH}_2]_2\text{TeBr}_2$ nor possible methanolysis of the $\text{Te}-\text{Br}$ bond was observed.

The reduction of product **I** with sodium pyrosulfite in two-phase system $\text{CCl}_4/\text{H}_2\text{O}$ affords the earlier unknown bis(2-methoxy-3-phenoxypropyl)ditelluride (**II**) in 92% yield.

The structure of compounds **I** and **II** was proved by the ^1H , ^{13}C NMR spectroscopy and was confirmed by elemental analysis. The splitting of the CH_2 signal in the ^{13}C NMR spectrum of compound **I** by the coupling with the tellurium atom with $^1J_{\text{Te}-\text{C}} = 192 \text{ Hz}$ [9] is indicative of addition of the tellurium atom to the terminal carbon atom of the allyl phenyl ether.

Therefore, based on the chemo- and regioselective reaction of tellurium tetrabromide with allyl phenyl ether, compounds **I** and **II** were obtained, which are new functional products and synthons for organic synthesis. Note that tellurium tetrabromide, unlike TeCl_4 , is readily available and can be obtained by the reaction of tellurium with bromine at room temperature. Its availability as well as the chemo- and regioselectivity of its reactions open new possibilities in the chemistry of organotellurium compounds.

Scheme 1.



2-Methoxy-3-phenoxypropyltellurium tribromide (I), waxy yellowish substance. ^1H NMR spectrum, δ , ppm: 3.33 s (3H, OCH_3), 3.85–3.98 m (3H, OCH , CH_2Te), 4.29 m (1H, CH_2O), 4.54 m (1H, CH_2O), 6.84 m (3H, Ph), 7.22 m (2H, Ph). ^{13}C NMR spectrum, δ , ppm: 56.78 (CH_3O), 57.17 (TeCH_2 , $^1J_{\text{CTe}}$ 192 Hz), 70.00 (CH_2O), 77.36 (CHO), 114.85 (Ph), 121.04 (Ph), 129.77 (Ph), 158.73 (Ph). Found, %: C 22.26; H 2.28; Br 44.73; Te 24.35. $\text{C}_{10}\text{H}_{13}\text{O}_2\text{Br}_3\text{Te}$. Calculated, %: C 22.55; H 2.46; Br 45.01; Te 23.96.

Bis(2-methoxy-3-phenoxypropyl)ditelluride (II), dark-red oil. ^1H NMR spectrum, δ , ppm: 3.50 s (3H, OCH_3), 3.52–3.70 m (3H, OCH , CH_2Te), 3.99 m (1H, CH_2O), 4.06 m (1H, CH_2O), 6.86 m (3H, Ph), 7.02 m (2H, Ph). ^{13}C NMR spectrum, δ , ppm: 8.78 (TeCH_2), 57.50 (CH_3O), 69.54 (CH_2O), 80.23 (CHO), 114.44 (Ph), 120.83 (Ph), 129.19 (Ph), 158.42 (Ph). Found, %: C 40.75; H 4.32; Te 43.27. $\text{C}_{20}\text{H}_{26}\text{O}_4\text{Te}_2$. Calculated, %: C 41.02; H 4.48; Te 43.58.

NMR spectra were registered on a Bruker DPX-400 spectrometer with working frequencies of 400.13 (^1H) and 100.61 (^{13}C) in $\text{DMSO}-d_6$ (compound **I**) or CDCl_3 (compound **II**), internal reference HMDS.

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