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An unexpected tetrahydrofuran ring opening: synthesis and structural characterization of $Ph_3PO(CH_2)_4TeBr_4$

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Received 27th September 2001, Accepted 18th October 2001
First published as an Advance Article on the web 31st October 2001

$Ph_3PO(CH_2)_4TeBr_4$ was obtained when treating $TeBr_4$ with triphenylphosphine in tetrahydrofuran as a result of a novel mode of THF ring opening.

The reaction of tellurium tetrachloride with triphenylphosphine has been reported to afford Ph_3PCl_2 and Te(0),[1] as well as $TeCl_2$, Te(0), and Ph_3PO that is assumed to be formed upon hydrolysis of Ph_3PCl_2.[2] In this work we report the study of a related reaction involving the treatment of triphenylphosphine with tellurium tetrabromide in tetrahydrofuran, as a part of a systematic study of the preparation and structural characterization of new tellurium halides. The reaction unexpectedly leads to the opening of the tetrahydrofuran ring and the formation of $Ph_3PO(CH_2)_4TeBr_4$ (**1**). While the ring opening of THF and other cyclic ethers with main-group[3] and transition metal[4] Lewis acids is well-known, information involving the interaction between tetrahydrofuran and tellurium halides is very sparse.

$Ph_3PO(CH_2)_4TeBr_4$ (**1**) was isolated by treating $TeBr_4$ with an equimolar amount of triphenylphosphine in tetrahydrofuran.† The ${}^{31}P\{{}^1H\}$, ${}^{13}C\{{}^1H\}$ and ${}^{125}Te$ NMR spectra of **1** were recorded in acetonitrile,‡ and its crystal and molecular structure were elucidated by X-ray crystallography.§ The molecule is formally a zwitterion with the negative charge on a tellurium atom and the positive charge on a phosphorus atom. Such zwitterionic compounds containing tellurium are very rare, and the X-ray structures have been reported only for tetrachloro[(3-allyl-2-methyl-oxazolin-5-yl)methyl]tellurium[5] and $[Fe_3(CO)_9Te_4(\mu_3\text{-}CTeBr_4)]$.[6]¶

The molecular structure of $Ph_3PO(CH_2)_4TeBr_4$ is shown in Fig. 1. The tellurium atom exhibits square-pyramidal coordination with an apical Te–C bond and four basal Te–Br bonds. The Te(1)–C(4) length is 2.177(6) Å which is slightly longer than a Te–C single bond (the sum of the covalent radii of tellurium and carbon is 2.14 Å),[7] but it is comparable to the Te–C bond [2.179(10) Å] in $[Fe_3(CO)_9Te_4(\mu_3\text{-}CTeBr_4)]$.[6] The Te–Br distances range from 2.6776(8)–2.6952(9) Å. These values can also be compared to those of the corresponding bonds in $[Fe_3(CO)_9Te_4(\mu_3\text{-}CTeBr_4)]$ that show a range of 2.660(2)–2.669(2) Å.[6] The terminal Te–Br bonds in $C_6H_{10}Te_2Br_6$ [2.536(6)–2.548(9) Å[8]] and those in $[(4\text{-}EtOPh)TeBr_3]_2$ [2.509(3) to 2.548(2) Å][9] also exhibit lengths that are consistent with the bond lengths observed in **1**. The Te–Br bonds involving bridging Br ligands in the latter two compounds are expectedly longer.[8,9] The P–O length in **1** [1.581(4) Å] is significantly longer than the double bond observed in Ph_3PO [1.46(1) Å],[10] but shorter than a typical P–O single bond (the sum of the covalent radii of phosphorus and oxygen is 1.76 Å).[7]

It is interesting to note that the tellurium atom in **1** exhibits virtually no secondary bonding[11] like that observed for a TeX_5^- anion (X = Cl, Br) in $(C_8H_8S_2N)[TeCl_5]\cdot 1.5C_4H_8O_2$,[12] $(H_3O)[TeBr_5]\cdot C_4H_8O_2$,[13] and $(AsPh_4)[TeCl_5]\cdot H_2O$.[14] There is only a weak interaction between the tellurium atom and a chlorine atom of the solvent molecule.

The formation of **1** during the reaction of $TeBr_4$ and PPh_3 is a consequence of a tetrahydrofuran ring opening. Such a ring opening is initiated by various d- and f-block compounds and is thought to be a consequence of the coordination of the THF oxygen to the electropositive transition metal center, because it polarizes the C–O bond and renders the α-carbon susceptible to nucleophilic attack.[4] Upon ring opening the oxygen atom therefore remains coordinated to the metal atom and the nucleophile is bonded to the carbon atom.

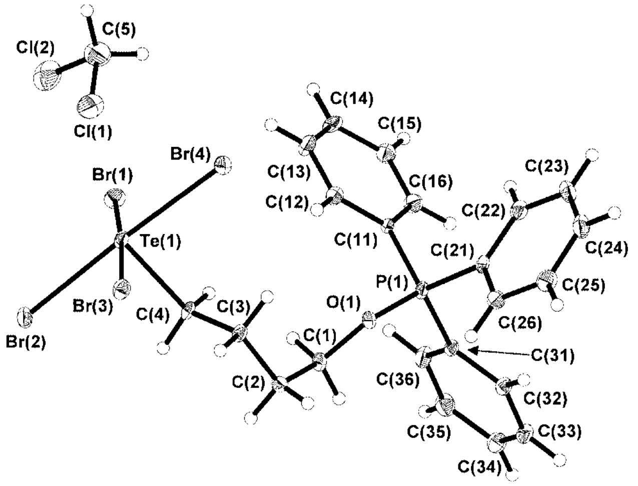
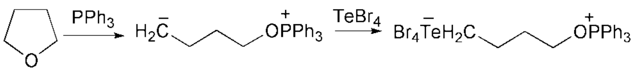


Fig. 1 The molecular structure of $Ph_3PO(CH_2)_4TeBr_4$ indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level. Selected bond lengths (Å): Te(1)–Br(1) 2.6952(9), Te(1)–Br(2) 2.6823(9), Te(1)–Br(3) 2.6776(8), Te(1)–Br(4) 2.6933(9), Te(1)–C(4) 2.177(6), P(1)–O(1) 1.581(4). Selected bond angles (°): Br(1)–Te(1)–Br(2) 86.70(3), Br(1)–Te(1)–Br(3) 174.79(3), Br(1)–Te(1)–Br(4) 91.95(3), Br(2)–Te(1)–Br(3) 88.27(3), Br(2)–Te(1)–Br(4) 176.67(3), Br(3)–Te(1)–Br(4) 93.00(3), C(4)–Te(1)–Br(1) 86.1(2), C(4)–Te(1)–Br(2) 89.4(2), C(4)–Te(1)–Br(3) 92.5(2), C(4)–Te(1)–Br(4) 87.5(2), O(1)–P(1)–C(11) 108.7(3), O(1)–P(1)–C(21) 104.0(3), O(1)–P(1)–C(31) 110.8(3), C(11)–P(1)–C(21) 111.7(3), C(11)–P(1)–C(31) 109.8(3), C(21)–P(1)–C(31) 111.7(3).



Scheme 1

This ring opening pathway, however, does not explain the formation of $Ph_3PO(CH_2)_4TeBr_4$ (**1**), since tellurium is found to be bonded to carbon and triphenylphosphine is bonded to oxygen.‖ In a similar fashion to the reaction of elemental sulfur with triphenylphosphine,[15] the ring opening in THF may be effected by an attack of triphenylphosphine at the THF oxygen resulting in the formation of an open-chain intermediate that consequently interacts with $TeBr_4$ (Scheme 1).

It has also been reported that phenyltellurotrimethylsilane $PhTeSiMe_3$ reacts with esters and ethers in the presence of a catalytic amount of Lewis acid (ZnI_2) resulting in the cleavage of the C–O bond with tellurium bonding to carbon and silicon to oxygen.[16]

DOI: 10.1039/b108790h

A systematic study of the reactions of tellurium tetrahalides with triphenylphosphine in tetrahydrofuran and the factors affecting the THF ring opening as well as product distribution are currently in progress.

Financial support from the Academy of Finland is gratefully acknowledged.

Notes and references

† $Ph_3PO(CH_2)_4TeBr_4$ (**1**). Solid PPh_3 (0.297 g, 1.13 mmol) was added to a stirred solution of 0.501 g (1.12 mmol) $TeBr_4$ in tetrahydrofuran (10 ml). The reaction mixture was stirred for 1 h. During this time a grey solid precipitated. The precipitate was filtered off. $Ph_3PO(CH_2)_4TeBr_4$ was obtained as yellow crystals from the filtrate. Yield 0.117 g (13.4%). Upon prolonged stirring for several days, the yield grew to *ca.* 50%. $C_{22}H_{23}Br_4OPTe$: Found: C 34.45; H 2.98. Calc.: C 33.85; H 2.84%. NMR (MeCN, 25 °C): δ_{Te} 1225; δ_P 63.3; δ_C 136.6 (s, 3C), 134.1 (d, 6C, $J_{PC} = 11$ Hz), 130.7 (d, 6C, $J_{PC} = 13$ Hz), 72.1 (s, 1C), 59.6 (s, 1C), 31.1 (s, 1 C), 24.1 (s, 1C). The resonance due to three quaternary phenyl carbon atoms bound to phosphorus was not observed in the spectrum.

‡ The $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^{125}Te spectra were recorded on a Bruker DPX 400 spectrometer operating at 161.98, 100.61 and 126.24 MHz, respectively. The spectra were measured unlocked in acetonitrile. The ^{31}P and ^{13}C chemical shifts are reported relative to H_3PO_4 (85%) and TMS, respectively. The ^{125}Te shift is reported relative to neat Me_2Te [$\delta(Me_2Te) = \delta(H_6TeO_6) + 712$].

§ Crystal data for $C_{22}H_{23}Br_4OPTe \cdot CH_2Cl_2$: Crystals were obtained by recrystallization from CH_2Cl_2. FW = 866.54, monoclinic, space group $P2_1/n$, $a = 9.4844(3)$, $b = 13.9433(4)$, $c = 21.7799(7)$ Å, $\beta = 94.217(1)°$; $U = 2872.46(15)$ Å^3; $Z = 4$; $D_c = 2.004$ g cm^{-3}, $F(000) = 1648$; μ(Mo-Kα) = 6.857 mm^{-1}, $T = 120$ K, crystal dimensions 0.15 × 0.10 × 0.07 mm^3. Reflections (36143 total, 5439 unique, θ range 2.38–26.00°, $R_{int} = 0.1015$) were collected on a Nonius-Kappa CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods[17a] and refined on F^2.[17b] The calculated hydrogen atoms were included in the final refinement (the phenyl rings: C–H = 0.95 Å; the methylene groups: C–H = 0.99 Å). The final $R_1 = 0.0589$ and $wR_2 = 0.0939$ [4509 reflections with $F_o > 4\sigma(F_o)$] ($R_1 = 0.0785$ and $wR_2 = 0.0983$ all data). Maximum and minimum values in the final difference Fourier synthesis are 1.141 and −0.908 e Å^{-3}. CCDC reference number 171629. See http://www.rsc.org/suppdata/dt/b1/b108790h/ for crystallographic data in CIF or other electronic format.

¶ The positive charge in $[Fe_3(CO)_9Te_4(\mu_3\text{-}CTeBr_4)]$ is delocalized among the three Fe(III) centers, each carrying a formal charge of $+\frac{1}{3}$.

|| This bonding arrangement was verified by interchanging O(1) and C(4) and re-refining the crystal structure. The new refinement was significantly poorer [R_1 (obs) = 0.0634; wR_2 (all data) = 0.1084; *cf.* footnote §]. Furthermore, the principal anisotropic thermal parameters of O(1) showed high values [$U_{eq} = 0.074(2)$], whereas those of C(4) were not all positive [$U_{eq} = -0.0001(11)$]. The corresponding U_{eq} values of O(1) and C(4), when they were assigned as in **1** (see Fig. 1), were 0.023(1) and 0.025(1), respectively. While no ^{125}Te satellites where observed in the ^{13}C NMR resonance of C(4) due to low solubility of **1**, the appearance of four virtual singlets in the alkyl carbon region [72.1–24.1 ppm] indicates no P–C bond. If carbon were directly bonded to phosphorus, one resonance would appear as a doublet with a large coupling constant.

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