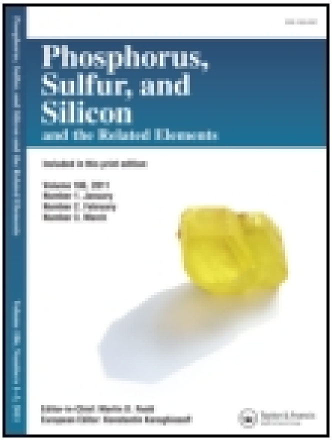

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Functionalized Organotellurium Halides: Synthesis, Characterization, and Observation of Intra- and Intermolecular Secondary Bonding

Ashok K. S. Chauhan [a], Arun Kumar [a] & R. C. Srivastava [a]
[a] Chemistry Department, Lucknow University, Lucknow, India

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Functionalized Organotellurium Halides: Synthesis, Characterization, and Observation of Intra- and Intermolecular Secondary Bonding

Ashok K. S. Chauhan
Arun Kumar
R. C. Srivastava
Chemistry Department, Lucknow University, Lucknow, India

Activated tellurium, but not selenium, reacts with para-*substituted benzoylmethyl bromides as well as with iodoacetamide at their melting points in absence of a solvent to give bis(*p-*substituted benzoylmethyl)tellurium dibromides, (*p-$YC_6H_4COCH_2)_2TeBr_2$*, (Y = H, Me, and MeO) and bis(acetamido)tellurium diiodide, $(H_2NCOCH_2)_2TeI_2$, respectively. Quick reduction of (*p-$YC_6H_4COCH_2)_2TeBr_2$*, with sodium metabisulphite in a two-phase system yields crystalline (*p-$YC_6H_4COCH_2)_2Te$*. These tellurides undergo smooth oxidative addition of halogens, interhalogen ICl or a pseudohalogen $(SCN)_2$. Intramolecular coordination of the carbonyl group in these functionalized diorganotellurium dihalides is evident from IR spectra and shorter Te···O (carbonyl) distances in comparison to the sum of van der Waals radii and completes six coordination around Te atom. Not unexpectedly, therefore, intermolecular secondary bonding effects of the type Te···O, Te···X and X···X are missing in $(PhCOCH_2)_2TeBr_2$, (*p-$MeOC_6H_4COCH_2)TeBr_2$ *and $(PhCOCH_2)_2TeI_2$. Instead, these compounds provide rare examples, among organotellurium compounds, of supramolecular architecture, where C—H···Br and C—H···O hydrogen bonds and π-π (phenyl ring) interactions appear to be the noncovalent intermolecular associative forces that dominate the crystal packing.*

Keywords Functionalized organotelluriums; organotellurium(IV) halides; secondary bonding; supramolecular association

INTRODUCTION

Nonfunctionalized organotellurium halides almost invariably exhibit a great propensity of tellurium to form intermolecular Te···X and/or X···X secondary bonds. In the solid state, such noncovalent secondary

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Address correspondence to Ashok K. S. Chauhan, University of Lucknow, Chemistry Department, Lucknow 226007, India. E-mail: akschuhan@hotmail.com

bonds (even clustered about the region thought to be occupied by the lone pair) are responsible for the specific color of crystalline organotellurium iodides[1,2] and are believed to provide a new bonding motif for supramolecular self-assembly and crystal engineering.[3] The electronic structure of secondary-bonded organotellurium halides has been explained either as a manifestation of hypervalence of tellurium in terms of electron rich three-center bonding[4–6] or as directional donor-acceptor bonding,[7–9] though the two approaches are, in fact, equivalent.[10] When the organic ligand attached to the tellurium is functionalized and possesses a nucleophillic atom A (viz. N, O, S or X) in close proximity, intramolecular Te···A secondary interactions are expected. The effect of intramolecular secondary bonding on supramolecular association involving intermolecular Te···X secondary bonds has not been looked into.

The available routes to prepare functionalized organotellurium halides involve moisture sensitive $TeCl_4$ or n-BuLi together with rigorous anhydrous oxygen-free atmosphere. We report here our successful attempts of inserting elemental tellurium across C_{sp3}- X bond activated by an aroyl or amide group and the role of Te···A secondary bonding in the supramolecular motifs of some representative functionalized organotellurium halides.

RESULTS AND DISCUSSION

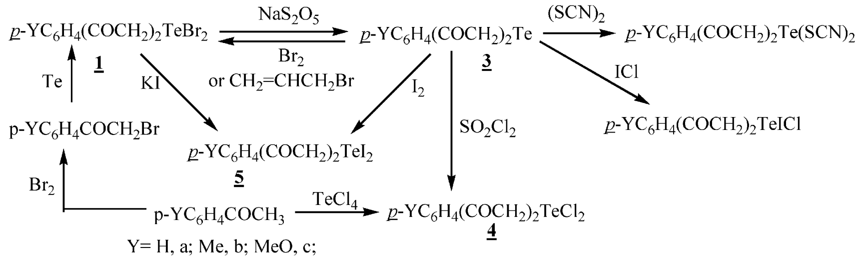
As the Grignard reagents or organolithiums of organic substrates with carbonyl functionality are not readily accessible, the direct reaction of elemental tellurium with β-halocarbonyl compounds was attempted. Thus tellurium (but not selenium) inserted across $C_{(sp^3)}$-Br bond is activated by the presence of a benzoyl group to give crystalline $(p\text{-}YC_6H_4COCH_2)_2TeBr_2$ (Y = H, **1a**; Me, **1b**; OMe, **1c**) (Eq. (1)). This reaction is of particular relevance as it provides a route to functionalized organotellurium halides directly from elemental tellurium and an organic halide and involves the use of neither air/moisture sensitive reagents like $TeCl_4$ or n-BuLi nor deoxygenated N_2/Ar atmosphere. This also represents the only example of tellurium insertion across a carbon-bromine bond though Me_2TeI_2 and cyclo-$(CH_2)_nTeI_2$, (n = 4 or 5) have been prepared earlier by a similar insertion reaction with MeI[14] or $I(CH_2)_nI$.[15,16] However, failure of *para*-halobenzoylmethyl bromides (Y = Cl, Br) to add oxidatively to Te(0) apparently demonstrates the importance of having an activating substituent in *para* position of the benzoyl group.

$$p\text{-}YC_6H_4COCH_2Br + Te \rightarrow (p\text{-}YC_6H_4COCH_2)_2TeBr_2 \qquad (1)$$

$$Y = H, Me, OMe$$

Iodoacetamide also reacted in the sense of Eq. (1) to give the crystalline bis(acetamido)tellurium(IV) diiodide, $(NH_2COCH_2)_2TeI_2$, **2**, while iodoacetic acid failed to react in an analogous manner. The ethylene ketal of benzoylmethyl bromide (the protected carbonyl compound), 2-bromoethanol, 2-bromoethoxy trimethylsilane, N-bromoethylphthalimide, as well as 2-bromothiophene did not react with elemental tellurium even on heating up to 100°C for several hours. It appears, therefore, that the insertion of elemental Te across the $C_{(sp^3)}$-Br bonds is facilitated by presence of an activating functionality like the carbonyl group at the α-carbon atom.

Reduction of the newly synthesized bromides **1**, could be achieved with $Na_2S_2O_5$ in a two phase system (CH_2Cl_2-H_2O). Separation of the yellow organic layer within 5 to 10 minutes afforded the corresponding dialkyltellurides **3**, which can be stored at low temperature for a couple of weeks. Scheme 1 depicts oxidative additions of halogens, an interhalogen and a pseudohalogen to **3**, that have been affected in quantitative yields. The addition product of ICl with **3** affords satisfactory elemental analyses and IR and NMR data while that of thiocyanogen having insufficient solubility appears to be mixed with a small quantity of thiocyanogen polymer. Interestingly, reaction of **3** with allyl bromide resulted in the formation of the dibromides instead of the expected telluronium salt $[(p\text{-}YC_6H_4COCH_2)_2Te(C_3H_5)]^+Br^-$ but with HCl (from $CH_3COCl + CH_3OH$) elemental tellurium separated.



SCHEME 1

Characterization of the bis(p-substituted benzoylmethyl)tellurium-(IV and II) derivatives is based upon elemental analyses, IR and NMR, (^{1}H, ^{13}C and ^{125}Te) spectral data and has been substantiated by the single-crystal X-ray diffraction data for the compounds **1a**, **1c**, and **4a**.[17,18] Significant lowering of the carbonyl stretching frequency ($\Delta\upsilon$CO $\sim$ 40 cm^{-1}) in the IR spectra of the dihalides indicates intramolecular coordination of the carbonyl oxygen to the central Te(IV), which is also evident from the Te$\cdots$O distances (2.818–2.938 Å) that are shorter than the sum of van der Waals radii (3.58 Å) though longer than the sum of covalent radii (2.03 Å) of the two atoms. Surprisingly, no significant change in the υ(CO) is observed between the tellurium(IV) and tellurium(II) though a comparison of δCH_2 values clearly indicates that the methylene protons in the Te(IV) species **1**, **4**, and **5** are more shielded than the corresponding Te(II) compounds **3**. The proton-decoupled ^{125}Te NMR spectra in $CDCl_3$ show only a single resonance for **1** (~677) and **3** (~487 ppm relative to Me_2Te) which is in accordance with enhanced shielding of Te environment in the tellurides, **3** with respect to that in the corresponding telluranes, **1**. The ^{125}Te MAS NMR chemical shift of **1a** (635 ppm), **1b** (667 ppm), and **1c** (661 ppm) compare reasonably well with the values observed in $CDCl_3$ solution.

Molecular association via intermolecular Te···X secondary bonding is a characteristic feature of nonfunctionalized organotellurium(IV) halides due to which the primary Te—X bond lengths are affected.[19,20] The longer and unequal apical Te—X bond distances observed in case of **1a**, **1c**, and **4a** are typical of the reported bond lengths when intermolecular Te···X secondary bonding is absent.[20,21] Crystal packing in these compounds also is devoid of any intermolecular Te···O secondary bonds and it is interesting to note that Te(IV) atom prefers intramolecular donor-acceptor Te···O interaction to complete its six coordination even though it leads to the formation of strained four-membered heterocyclic rings. The remarkable feature of solid state structures of functionalized organotellurium(IV) halides is the presence of C—H···A hydrogen bonds (A is an electronegative atom, O or Br). The chemically-meaningful (methylene)CH···Br distance of 2.951 Å in **1a** and (methylene/methoxy)CH···O distances in the range between 2.45–2.68 Å qualify the criterion for a bonafide C—H···A hydrogen bond.[22] The dominant noncovalent interaction in assembling the molecular units leading to a supramolecular structure, therefore, appears to be the stronger and energetically favorable C—H···A hydrogen bonds as compared to Te···X secondary bonds. Such C—H···A hydrogen bonds are rare in organotellurium(IV) halides but common in case of organic[23,24] and nonorganic crystals.[25] The crystal packing analysis of **5a** show no such hydrogen bonding due to low electronegativity of iodine and probably π-π tacking[26] appears to be the only noncovalent intermolecular force that dominates secondary bonding involving electron rich heavier atoms (Te and I).

EXPERIMENTAL

The commercial Te powder was washed with conc. HCl and water, dried at ~120°C and grinded before use.

(a) Synthesis of (p-$MeC_6H_4COCH_2)_2TeBr_2$, **1b**: A mixture of Te powder (10 mmol) and p-$MeC_6H_4COCH_2Br$ (22 mmol) was heated gently with stirring until the mixture solidified. The solid was washed with cold dichloromethane and then extracted with hot chloroform. Evaporation of the solvent followed by recrystallization with $CHCl_3$/pet.ether afforded **1b** in about 65% yield.**1a** and **1c** were prepared similarly.

Because of the poor yield in absence of solvent, $(NH_2COCH_2)_2TeI_2$, **2** was prepared in refluxing toluene (yield $\sim$ 70%).

(b) Oxidative addition reactions of **3**: to a cold solution of freshly-prepared **3** (1.2 mmol) was slowly added Br_2 (1.2 mmol) in CCl_4 (10 mL). After stirring at ambient temperature for 2 h, the solvent was removed and the residue crystallized from $CHCl_3$/pet ether to give the corresponding dibromides **1**, which had same m.p. and IR spectra as the ones prepared in (a). (p-$YC_6H_4COCH_2)_2TeCl_2$, **4** and (p-$YC_6H_4COCH_2)_2TeI_2$, **5** were prepared similarly from the corresponding **3** and SO_2Cl_2 and I_2, respectively. Analogous oxidative addition of ICl and $(SCN)_2$ afforded (p-$YC_6H_4COCH_2)_2TeICl$ and (p-$YC_6H_4COCH_2)_2Te(SCN)_2$.

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