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SYNTHESIS AND CHARACTERIZATION OF (*m*-BROMOBENZYL-*p* -ANISYL)-TELLUROETHER

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ABSTRACT

In this article, we have reported the synthesis and characterization of (*m*-bromobenzyl-*p*-anisyl)-telluroether. This molecule is soluble in common organic solvents. We characterized this molecule with the help of elemental analysis, ^{1}H, and ^{13}C NMR spectroscopy techniques. We have prepared this molecule through the synthesis of dianisyl-di-telluride via the Grignard route. Thereafter dianisyl-di-telluride was reduced to get anisyl-tellurate. The in situ-generated anisyl-tellurate was further treated with *m-bromobenzene* bromide.

Keywords: Telluroether, S_n Reaction, Synthesis, ^{1}H-NMR, ^{13}C-NMR

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INTRODUCTION

In 1783 tellurium element was revealed by F. J. M. von Reichenstein. The term tellurium was derived from the Latin word tellus which means “Earth”. The term Tellurium was coined by Martin Heinrich Klaproth who isolated it in 1798. The electronic configuration of Tellurium is [Kr] $4d^{10}$ $5s^2$ $5p^4$. Several isotopes of Tellurium occur in nature in the following proportion (Table-1).[1]

Table-1: Natural Abundance of Tellurium Isotopes in Percent

Isotopes of Tellurium	Natural Abundance (%)
^{120}Te	0.09
^{122}Te	2.55
^{123}Te	0.89
^{124}Te	4.74
^{125}Te	7.07
^{126}Te	18.84
^{128}Te	31.74
^{130}Te	34.08

In the periodic table, it is represented by the symbol Te which belongs to the 16th group and 5th period under the chalcogen family of the periodic table, having an atomic mass of 127.6 g/mol and atomic number 52.[2] Tellurium is a brittle silver-white metalloid and its chemical property are almost similar to sulfur and selenium. Tellurium elements during the flame test in the air give greenish-blue flame and form dioxide. The tellurium was first time observed in ores mined in the gold districts of Transylvania. The melting point, boiling point, and density of Tellurium are 449.51 ℃, 988 ℃, and 6.24 g/cm^3 respectively. Tellurium is toxic in nature and a non-essential element. Tellurium occurs in various oxidation states ranging from −2 to +6. From electronic configuration, it can be predicted that Tellurium is two electrons short of completely filled valence shell. In 1840 Wöhler developed the first organotellurium compound dialkyl tellurides.[3] In 2004 numerous review articles were published on organoselenium and organotellurium compounds discussing their pharmacological and toxicological effects.[4] One more review has been published which significantly discusses the organoselenium and organotellurium compounds' effect on mitochondrial activity.[5] A

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magnificent review published on telluroxanes: Synthesis, structure, and applications explains the structures, synthesis, and applications of organotelluroxanes.[6] Recently we have published a series of organotellurium compounds through the insertion route.[7] Some relevant details about the element are summarized below in Fig.-1:

$_{52}Te^{127.6}$	
M.P. (°C)	449.5
B.P. (°C)	988.0
d (g/cm^3)	6.24
Atomic radius (Å)	1.43
Covalent radius (Å)	1.36
van der Waal's radius (Å)	2.06

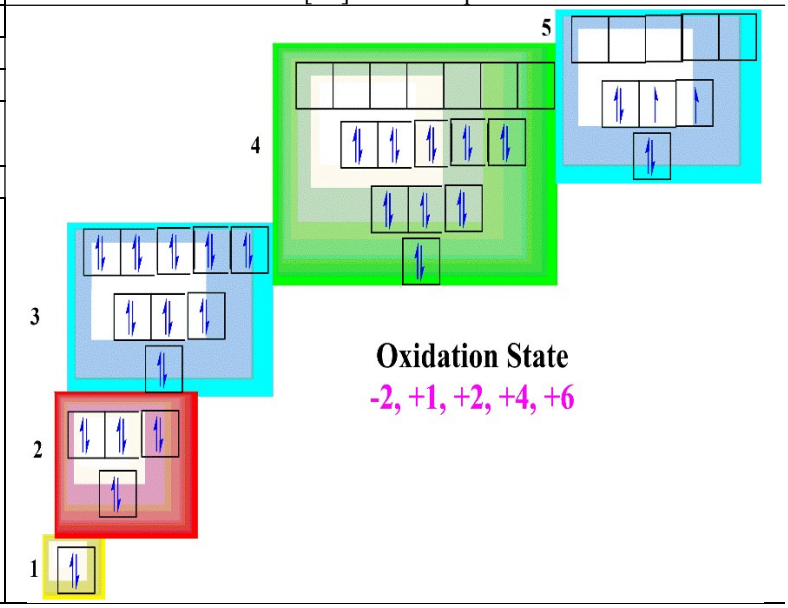


Fig.-1: Some Relevant Details about the Element Tellurium

In 21st century, organotellurium compounds have attracted attention due to their distinctive properties in the areas of organic and inorganic chemistry. The organotellurium compounds also play a prominent role in material science and possess potential applications in the electronic industry. Tellurium oxides are employed in memory chips, in re-writable compact discs, Blu-ray discs, and digital discs.[8-10] Similarly, semi-conducting metal telluride has a broad diversity of potential applications, such as thermo-electric materials in cooling instruments, solar panels & most importantly, in the form of quantum dots.[11-13] Recently organotellurides have been demonstrated that they are better Glutathione Peroxidase mimics than their selenium counterparts.[14]

Types of Organotellurium Compounds

The organotellurium compounds can be divided into three categories on the basis of oxidation state; subcategories are based upon the number of organic groups attached to the tellurium atom (Fig.-2).

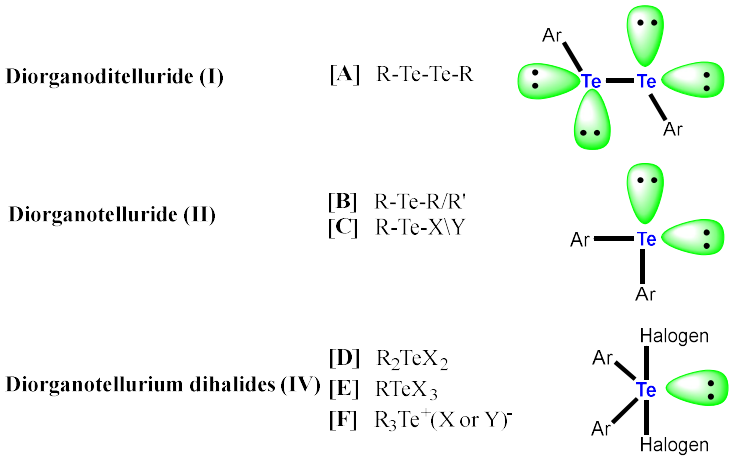


Fig.-2: Types of Organotellurium Compounds

Diorgano-di-tellurides (I)
This class of compounds has been used as ideal synthons in the synthesis of many recent clusters or organotellurium-metal complexes.[15] These derivatives exhibit a characteristic orange to pale or dark red color. The aliphatic organo-di-tellurides are liquids with a pungent odor whereas the aromatic derivatives are crystalline solids. Pure liquids or solids are stable enough that can be handled in air but the solutions of di-tellurides can oxidize when it is exposed to air for a long period of time.

Diorganotellurides (II)
The thermal stability and sensitivity to the atmosphere of these compounds are dependent on the organic moiety. Dialkyltellurides with higher molecular weight and most diaryltellurides (except phenyl) are solid with low melting points whereas lower members are colorless or yellow liquids with unpleasant and penetrating smells.

Diorganotellurium dihalides(IV)
It is the most extensively studied class of organotellurium, easily prepared & structurally well characterized through single crystal X-ray diffraction technique. These are stable and odorless crystalline compounds except the aliphatic organotellurium trihalides which decompose slowly in contact with light to elemental tellurium. The chlorides, bromides, and iodide derivatives exhibit a characteristic physical property of colorless to yellow, yellow to orange, and red to brown color respectively. Above mentioned organotellurium compounds including those of the hypervalent Te(IV), all have Te atom bearing lone pair of electrons. In case the organic ligands also possess some nucleophilic atoms *viz*. N, O, S, or P, the resulting compounds are likely to bear interesting features with respect to their coordination chemistry and supramolecular association.

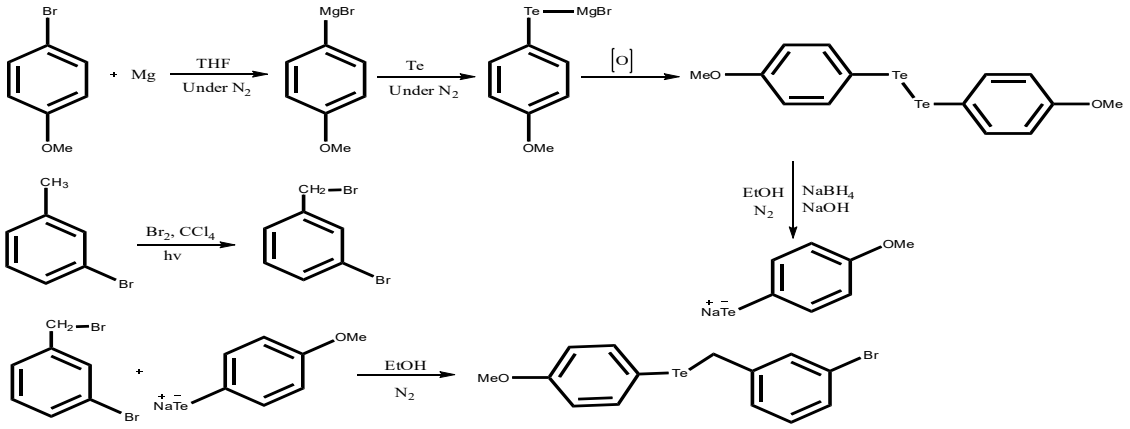
EXPERIMENTAL

Synthesis of *m*-bromobenzyl Bromide[16]
We took 12.1 ml (100 mmol) of *m*-bromotoluene, dissolved it in 50 ml of dry carbon tetrachloride solvent, and charged it into a two-necked round bottom with a reflux condenser and dropping funnel. The round bottom is heated to a boil and the hydrogen atom to be replaced there is added a drop to drop 5.13 ml (100 mmol) of bromine. During this reaction, the mixture was irradiated with a 500-watt bulb. The bromination reaction was completed in 3 hours. The hydrogen bromide gas evolved during the reaction was carried to water by passing it through a glass tube and PVC tubing which were connected to the reflux condenser and finally hydrogen bromide gas dissolved into water. At the end of the reaction, the irradiation is stopped. The solution was washed with cold water, then a cold aqueous solution of sodium bicarbonate, and again washed with cold water, and then dried with sodium sulfate overnight, after this solution was concentrated. The yield of the *m*-bromobenzyl bromide, 6 g (24%), m.p. 41°C. Again *m*-bromobenzyl bromide was purified by recrystallization from ethanol. Found: C, 33.6; H, 2.4. $C_7H_6Br_2$ requires C, 33.6; H, 2.4; δ_H (300.1 MHz; $CDCl_3$; Me_4Si) 4.43 (2 H, s, CH_2), 7.22 (1 H, m, aryl proton), 7.33 (1 H, m, aryl proton), 7.43 (1 H, m, aryl proton), 7.55 (1 H, m, aryl proton).

Synthesis of (3-bromobenzyl)(4-methoxyphenyl)Telluride(II)
We took a solution of *p*-dianisyl di-telluride 5 mmol, (2.486 g) in freshly distilled 30 ml of ethanol solvent. The reaction mixture was cooled at 0 °C with the ice bath, through septa nitrogen gas pass to di-telluride solution to flush out dissolved oxygen from the solution for 5 to 8 minutes. Then 1.13 g ground $NaBH_4$ (30 mmol) was under nitrogen gas at 0 °C. The reaction mixture was stirred for 50 to 60 minutes at room temperature. *m*-bromobenzyl bromide 2.49 g (10 mmol) has been added to the prepared solution of *p*-$MeOC_6H_5TeNa$ at 0 °C. This reaction mixture has been stirred at room temperature for up to 4 hours. The solvent ethanol was distilled from the reaction mixture, and the residue was dissolved in DCM solvent and washed with water lower organic layer was separated again organic layer was washed with water and put on the Na_2SO_4 overnight. The reaction was monitored with the help of TLC. The solvent is distilled off and the obtained compound is purified by column-chromatography. Afforded yellow color dense liquid. Yield: 2.030 g (57 %). Found: C, 41.6; H, 3.5, Te, 31.6. $C_{14}H_{13}BrOTe$ requires C, 41.54; H, 3.44; Te, 31.52 δ_H (300.1 MHz; $CDCl_3$; Me_4Si) 3.88 (2 H, s, CH_2), 6.76-7.46 (4 H, m, aryl).

RESULTS AND DISCUSSION

In 2019 we developed a novel methodology for regioselective palladation reaction of CNN pincer ligand with $Pd(OAc)_2$.[17] Thereafter we also reported synthesis and single crystal x-ray studies of unsymmetrical selenoethers. Along with this we also explored cleavage of the Selenium-Carbon bond.[18] The selenoethers ligand was prepared by the treatment of *in situ* produced aryl selenide with 2-(bromomethyl)naphthalene afforded a series of selenoethers as yellow color needle-shaped crystals. Similarly, in this article, we have installed *in situ* generated aryltellurate (p-$MeOC_6H_4Te^-$) on *m*-bromobenzyle bromide (Scheme-1. All compounds have been confirmed with the help of proton-NMR and elemental analysis.



Scheme-1: Synthesis of (3-bromobenzyl)(4-methoxyphenyl)Telluride(II)

CONCLUSION

In this article we have the first time reported (*m*-bromobenzyl-*p*-anisyl)-telluroether through the treatment of *m*-bromobenzyl bromide with in situ generated *p*-anisyltellurate. The *p*-anisyltellurate was prepared by the reduction of dianisyl ditelluride with $NaBH_4$ in ethanol solvent under nitrogen. The reported compound was confirmed with the help of proton-NMR and elemental analysis.

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CONFLICT OF INTERESTS

The authors announce that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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