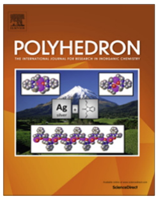
Polyhedron 73 (2014) 45–50

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Electrophilic cyclization of homopropargyl tellurides: Synthesis and supramolecular structures of 2-aryl-3-iodo-1-phenyl-tellurophenium iodides and polyiodides

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ARTICLE INFO

Article history:
Received 29 November 2013
Accepted 11 February 2014
Available online 19 February 2014

Keywords:
Electrophilic cyclization
Tellurophenium iodides and polyiodides
Supramolecular assemblies

ABSTRACT

The synthesis of five new 2-aryl-3-iodo-1-phenyl-tellurophenium iodides and polyiodides via electrophilic cyclization of homopropargyl tellurides using I_2 as an electrophile is described. The homopropargyl tellurides **1a** and **1b** react with different amounts of molecular iodine to give $[C_{16}H_{14}TeI]I$ (**2**), $[C_{16}H_{14}TeI]I_3$ (**3**), $\{[C_{16}H_{14}ITe]_4[I_3^-]_3[I^-]\cdot 2I_2\}$ (**4**), $[C_{17}H_{16}OTeI]I$ (**5**), and $[C_{17}H_{16}OTeI]I_3$ (**6**). All of these compounds display inter and/or intramolecular secondary interactions between Te···I and/or I···I in the solid state, and these interactions are responsible for the formation of various supramolecular assemblies.

1. Introduction

Tellurium is a versatile metalloid that is commonly used as a base for several important materials, including catalysts and semiconductors, and it is used to prepare synthetic intermediates in organic synthesis that enable the introduction of various functional groups [1–8]. Among these compounds, organotellurium(II) derivatives and vinylic tellurides in particular provide powerful intermediates for the synthesis of more elaborate alkenes, such as natural products [6]. Many organotellurium(IV) compounds with different ligands have been prepared and studied to date [9–12]. Tellurium(IV) iodides are of great interest because they can promote structural diversity due to the tellurium geometry. In the solid state, Te and I atoms interact strongly to form inter- and intramolecular secondary interactions through the stereochemically active lone pair at the Te center. These interactions enable the formation of supramolecular networks. In the context of supramolecular chemistry, all possible combinations of secondary interactions are important for creating dimers and polymeric chains that form 1D, 2D, and 3D networks of the tellurium iodides [13–18].

On the other hand, the electrophilic cyclization of alkynes containing a nucleophile near to the triple bond, which is activated by the presence of an electrophilic source, such as iodine, copper halides, and ArSeBr, represents an important protocol for the preparation of highly substituted heterocycles [19]. The mechanism underlying this reaction involves the coordination of an electrophile to the π C–C bond of the alkyne, followed by the nucleophilic anti-attack of the non-ligand heteroatom electron pair to the activated unsaturated C–C bond to give the heterocycle [19]. Inspired by this reaction, our recent success in this area [20], and continuing interest in the synthesis and applications of chalcogenophenes [21–24], we envisioned the preparation of dihydrotellurophenium iodides **2**–**6** using 1-arylltelluro-3-alkynes **1** and molecular iodine as an electrophilic source (Scheme 1).

We report here the synthesis of five new 2-aryl-3-iodo-1-phenyl-tellurophenium iodides and polyiodides via the electrophilic cyclization of homopropargyl tellurides using I_2 as an electrophile. The products (**2**–**6**) were obtained in the presence of 1, 2, or 3 equiv. I_2 in CH_2Cl_2/THF at room temperature and under inert conditions. In all compounds, $[C_{16}H_{14}TeI]I$ (**2**), $[C_{16}H_{14}TeI]I_3$ (**3**), $\{[C_{16}H_{14}ITe]_4[I_3^-]_3[I^-]\cdot 2I_2\}$ (**4**), $[C_{17}H_{16}OTeI]I$ (**5**) and $[C_{17}H_{16}OTeI]I_3$ (**6**), the tellurium atom is present in the oxidation state +4.

Initially, we focused our study on the synthesis of the homopropargyl tellurides **1** using homopropargyl tosylates and diaryl ditellurides. The arylltellurolate anion, generated *in situ* by the reaction of diaryl ditelluride with $NaBH_4$ in THF/EtOH, reacted with a solution of the homopropargyl tosylate in THF at room temperature and under an inert atmosphere for 6 h via a S_N2 reaction [25,26]. The homopropargyl tellurides **1a** and **1b** are shown in Scheme 2 and were obtained in good yields.

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http://dx.doi.org/10.1016/j.poly.2014.02.013
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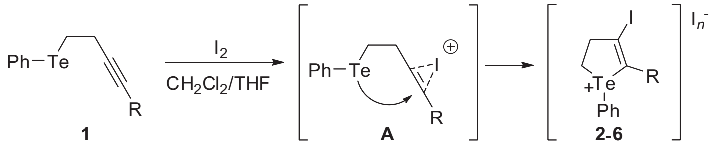
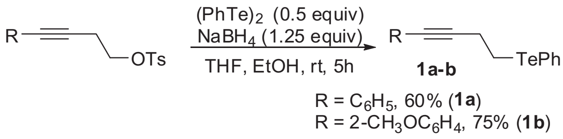


Scheme 1. General synthesis of dihydrotellurophenium iodides **2**–**6**.



Scheme 2. Synthesis of homopropargyl aryltellurides **1a** and **1b**.

With the starting materials **1** in hand, we turned out our attention to the preparation of the dihydrotellurophenium iodides **2**–**6** via an electrophilic cyclization mechanism involving iodine as an electrophilic source. The products are presented in Scheme 3. The compounds **2**–**4** were prepared by reacting the homopropargyl phenyltelluride **1a** with 1, 2, or 3 equivalents of molecular iodine. The compounds **5** and **6** were synthesized by the reactions of the homopropargyl 2-methoxyphenyl telluride **1b** with 1 or 2 equivalents of I_2 using THF/CH_2Cl_2 as solvent. All products obtained were isolated by crystallizing the mother solution via slow evaporation of the solvents.

It is important to note that the dihydrotellurophenium iodides **2**–**6** isolated in this work can be considered as intermediates of an electrophilic cyclization reaction. The crucial step in many electrophilic cyclization reactions [19] involves the removal of the carbonic group bonded to the heteroatom via a S_N2 displacement (step **B**). S_N2 displacement proceeds in the presence of a nucleophile to generate the expected heterocycle **7** and the co-product **8** (Scheme 4).

To avoid the formation of **7**, we selected homopropargyl tellurides having an aryl group directly bonded to the tellurium atom, once that these compounds are unable to undergo a S_N2 reaction (Schemes 1 and 4).

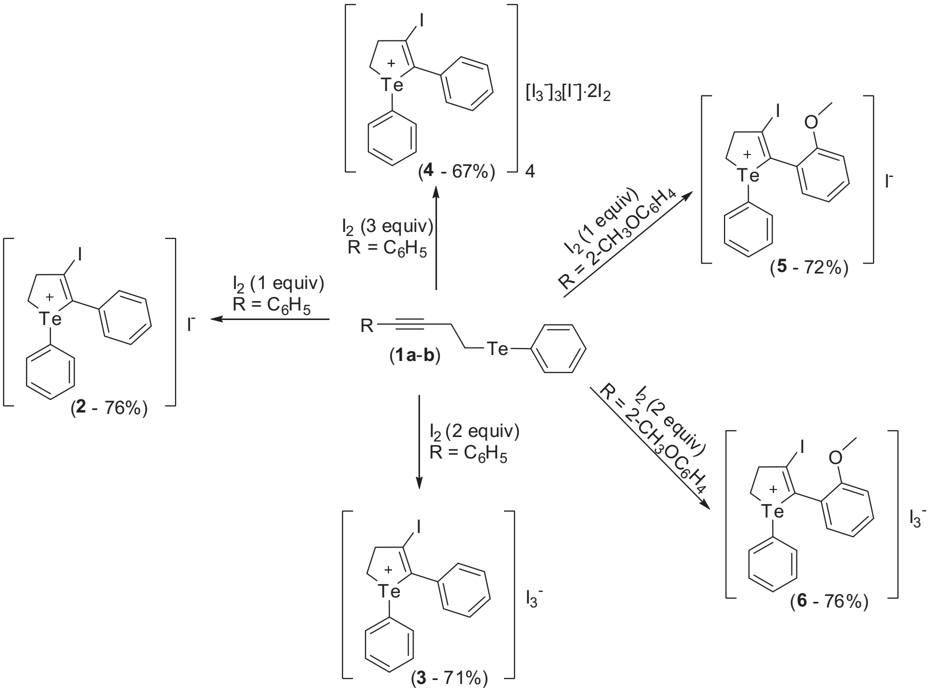
2. Experimental

2.1. General

All manipulations were conducted under an Ar (argon) atmosphere using standard Schlenk techniques and dry solvents. These solvents were purified and dried according to literature procedures [27]. Elemental analyses (CHN) were carried out using a VARIO EL (Elementar Analysen systeme GmbH) analyzer. Infrared spectra were measured using a Bruker Tensor 27 mid-IR spectrometer. Melting points were determined on a Microquímica MQAPF-301 melting point apparatus and are uncorrected.

2.2. Preparation of $[C_{16}H_{14}ITe]I$ (**2**)

To a solution of 0.083 g (0.25 mmol) **1a** in 10 mL CH_2Cl_2 was added 0.063 g (0.25 mmol) I_2 dissolved in 10 mL THF. The mixture was stirred for 3 h. The slow evaporation of the orange solution gave yellow crystals of **2**. Yield: 76% based on **1a**. Properties: yellow crystalline substance. Melting point: 144 °C–145 °C. Elemental *Anal.* Calc. for $C_{16}H_{14}I_2Te$ (587.69) C, 32.70; H, 2.40. Found: C, 32.73; H, 2.29%. IR (KBr, cm^{-1}): 3046 (w), 3011 (w), 2948 (w), 1601 (m), 1486 (m), 1475 (m), 1434 (m), 881 (m), 766 (m), 729 (s), 700 (s), 682 (m), 558 (w), 445 (w). High resolution ESI + MS (*m*/*z*) of $[C_{16}H_{14}ITe]^+$: calc.: 462.9197, Found: 462.9207.



Scheme 3. The synthesis of compounds **2**–**6** were conducted using the starting material **1** (0.25 mmol) and different equivalents of molecular iodine in a CH_2Cl_2/THF solvent at room temperature over 3 h.