

## Synthesis of 1,2-ditellurane

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### Abstract

Freshly prepared solutions of disodium ditelluride react with diiodobutane to give small yields of 1,2-ditellurane. In contrast, reactions of  $\alpha,\alpha$ -bis(chloromethyl)-*o*-xylene and phthaloyl chloride give 3,4-benzo-1-telluracyclopentane and tellurophthalic anhydride respectively.

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### Introduction

Organotellurium compounds have attracted considerable interest in various fields such as molecular conductors [1], organic synthesis [2], and ligand chemistry [3]. Open-chain organyl ditellurides are versatile intermediates in the synthesis of several classes of organotellurium derivatives. Incorporation of the ditelluride group into a cyclic system may be expected to enhance the reactivity at the Te–Te bond as a result of strain involving both entropic and enthalpic effects [4]. Examples of cyclic ditellurides include naphthalene-1,8-ditelluride (IV) [5] and 5,6:11,12-bis(ditelluro)tetracene (V) [6], in which the five-membered heterocycles are fused to aromatic rings. The ditelluride group is also present in the novel heterocycle *cis*-3,5-dibenzylidene-1,2,4-tritellurole (VI) [7].

Whereas cyclic alkyl disulphides [4] and diselenides [8] have been known for some time, to the best of our knowledge no cyclic alkyl ditellurides have been previously described. In combination of our programme on the synthesis and reactions of ditelluroate anions, we report here the synthesis of I, the first six-membered ring species containing a Te–Te bond.

### Experimental

#### *Synthesis*

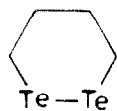
All preparations of disodium ditelluride were performed under argon in argon-saturated solvents in a three-necked flask fitted with a septum, a glass stopper and a condenser connected to a argon cylinder. Two methods of preparation were used. These are illustrated for the reaction of 1,4-diiodobutane with  $\text{Na}_2\text{Te}_2$  [6].

*1,2-Ditellurane (I):*

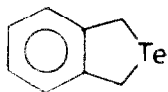
*Method A.* 1,4-Diiodobutane (19 mmol) in DMF (20 ml) was added dropwise to a magnetically stirred solution of  $\text{Na}_2\text{Te}_2$  (30 mmol, 100 ml DMF) at room temperature. The mixture was heated at 45–55°C for 5 h, and then added to distilled water (200 ml). Extraction with diethyl ether, followed by drying ( $\text{CaCl}_2$ ) and evaporation of the extract left a red semi-solid. Chromatography ( $\text{SiO}_2$ , petroleum ether 60–80°C containing 40% dichloromethane) followed by recrystallisation from n-hexane yielded I as a reddish-brown crystalline solid: m.p. 92–95°C, yield 0.6 g (11%). Anal. Found: C, 15.37; H, 2.46.  $\text{C}_4\text{H}_8\text{Te}_2$  calcd.: C, 15.42; H, 2.5%.

*Method B.* A solution of  $\text{Na}_2\text{Te}_2$  (17.6 mol) in water (100 ml) was prepared by the published method [9] and to the cooled solution a solution of 1,4-diiodobutane (10.7 mmol) and tetrabutylammonium hydrogen sulphate (0.1 g) in benzene (100 ml) was added dropwise. The mixture was stirred for 36 h at room temperature, then organic layer was separated, washed with water, and dried over anhydrous sodium sulphate. The solvent was removed in vacuo. Chromatographic purification of the residue followed by recrystallisation from n-hexane gave the same compound as obtained by method A in 15% yield.

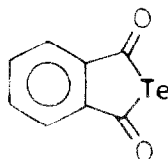
Filtration of the aqueous layer yielded a black solid which was washed several times with water, DMF, and tetrahydrofuran then dried in vacuo. Prolonged Soxhlet extraction of the highly insoluble solid with carbon disulphide gave a deep-red, viscous, foul-smelling residue, which was assumed to be  $[(\text{CH}_2)_4\text{Te}_2]_n$ .



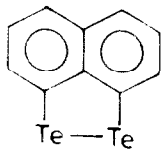
(I)



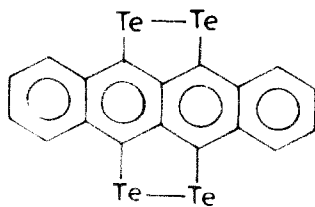
(II)



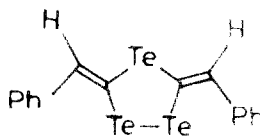
(III)



(IV)



(V)



(VI)

*Bis(tribromotelluro)butane (Br<sub>3</sub>Te(CH<sub>2</sub>)<sub>4</sub>TeBr<sub>3</sub>)*

The deep-red viscous oil obtained from the aqueous layer in a repetition of method B was dissolved in chloroform (100 ml). Addition of an excess of bromine at room temperature with stirring led to separation of the yellow bis(tribromotelluro)butane, which was recrystallised from chloroform and dried in vacuo: m.p. 139–140 °C. Anal. Found: C, 6.34; H, 0.99. C<sub>4</sub>H<sub>8</sub>Br<sub>6</sub>Te<sub>2</sub> calcd.: C, 6.06; H, 1.01%. NMR (DMSO-*d*<sub>6</sub>) δ (ppm): 2.67 (s, CH<sub>2</sub>Te), 2.24 (s, C–CH<sub>2</sub>).

*3,4-Benzo-1-telluracyclopentane (II): Method A*

Reaction of α,α-dichloro-*o*-xylene with Na<sub>2</sub>Te<sub>2</sub> afforded pale yellow flakes in 15% yield, m.p. 44 °C (Lit. 44–46 °C [10]), NMR (CDCl<sub>3</sub>) δ 6–7.2 (4H, m) and 4.5 ppm (4H, s) with satellites (*J*(<sup>125</sup>Te–<sup>1</sup>H) 23 Hz). Anal. Found: C, 41.05; H, 3.43. C<sub>8</sub>H<sub>8</sub>Te calcd.: C, 41.46; H, 3.86%.

*Tellurophthalic anhydride (III): Method B*

Reaction of phthaloyl chloride with Na<sub>2</sub>Te<sub>2</sub> under phase transfer catalysis gave a yellow crystalline solid, m.p. 127 °C (Lit. 127 °C [11]), yield 11%, IR (KBr): ν(CO) 1790, 1730, 1690 cm<sup>-1</sup>.

*Dimethyl ditelluride: Method A*

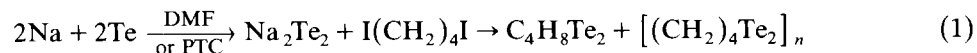
Reaction of Na<sub>2</sub>Te<sub>2</sub> with methyl iodide at 0 °C for 1 h gave a dark red viscous liquid in 35% yield. This was distilled under vacuum at 70 °C (3 mmHg). NMR (CDCl<sub>3</sub>) δ 2.65 ppm (s) [12]. UV-visible (hexane) λ<sub>max</sub> 398 nm. Anal. Found: Te, 86.4. C<sub>2</sub>H<sub>6</sub>Te<sub>2</sub> calcd.: Te, 89.41%.

*Physical measurements*

Spectral data were recorded with the following instruments: NMR, Hitachi R-600; IR, Perkin–Elmer 681; UV-visible, Shimadzu UV-260, Raman, Jobin-Yuon Ramanor HG-25 using He–Ne excitation (6238 Å); MS, Varian MAT 1125. Elemental analyses for carbon and hydrogen were carried out by the Regional Sophisticated Instrumentation Centre, Lucknow. Tellurium was analysed volumetrically [13].

**Results and discussion**

The novel heterocycle I has been obtained by reaction between Te<sub>2</sub><sup>2-</sup> and the appropriate organic dihalide. In an earlier study of the reaction between Te<sub>2</sub><sup>2-</sup> and a series of α,ω-dihaloalkanes, Nogami et al. [14] observed only the formation of polymeric ditellurides. We have found that this is not the case for all dihaloalkanes, and 1,4-diiodobutane reacts under mild conditions with Na<sub>2</sub>Te<sub>2</sub> in DMF or under phase transfer catalysis (PTC) conditions to give the novel heterocycle I along with the polymeric ditelluride (eq. 1).



Freshly-prepared I is a brownish-red crystalline solid soluble in common organic solvents. It was characterised by elemental analysis and mass spectrometry. The mass spectrum showed a molecular ion cluster (peak maximum at 316); the mass

spectral pattern is easily understood in terms of loss of one tellurium to give  $[\text{C}_4\text{H}_8\text{Te}]^+$  then loss of  $[\text{C}_4\text{H}_8]$  to give  $\text{Te}_2^{+}$ ; no peaks with  $m/e$  values higher than  $M^+$  were observed. The absorption spectrum of I in hexane consists of a broad band centered at  $\lambda$  400 nm with a long tail into the visible region. The Raman spectrum in hexane showed the  $\nu(\text{Te}-\text{Te})$  band at  $180\text{ cm}^{-1}$ , a value consistent with reported values of  $167\text{--}180\text{ cm}^{-1}$  for  $\nu(\text{Te}-\text{Te})$  [15]. The proton NMR spectrum of I in  $\text{CDCl}_3$  consists of only two somewhat broadened peaks at  $\delta$  3.2 ppm ( $\text{CH}_2\text{Te}$ ) and  $\delta$  1.9 ppm ( $\text{CH}_2\text{C}$ ), in 1/1 integration ratio.

The insoluble black residue obtained in the reaction was subjected to Soxhlet extraction to give a viscous red oil, assumed to be low molecular weight polymeric ditelluride,  $[(\text{CH}_2)_4\text{Te}_2]_n$ . This was characterised by reaction with bromine to give the yellow solid bis(tribromotelluro)butane (a multidentate Lewis acid) produced by cleavage of the  $\text{Te}-\text{Te}$  bond by bromine.

We expected that the reaction of  $\alpha,\alpha$ -dichloro-*o*-xylene and phthaloyl chloride with  $\text{Na}_2\text{Te}_2$  would lead to the corresponding substituted 1,2-ditellurane, but instead we obtained the known cyclic tellurides II and III, respectively. Conventional phase-transfer catalysis in the reaction of  $\text{Na}_2\text{Te}_2$  with phthaloyl chloride yielded III, and no detectable ditelluride product. This was not totally surprising in view of the fact  $\text{Na}_2\text{S}_2$  is known to react with phthaloyl chloride to form only the five-membered ring species thiophthalic anhydride [16].

Dimethyl ditelluride, which we required for the study of its ligand chemistry, was conveniently prepared in DMF in moderate yields, thus avoiding the use of liquid ammonia.

## Acknowledgements

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