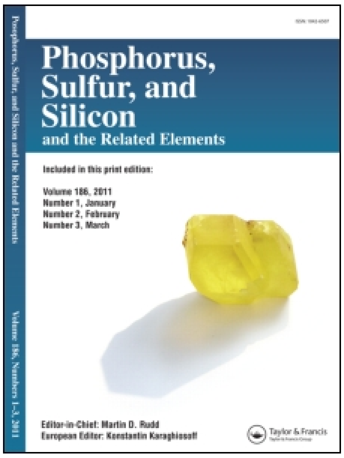

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Synthesis of Bis(Alkyltelluro)Methanes and their Complexation with Cadmium(II)

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A novel and convenient route for the synthesis of a series of bis(alkyltelluro)methanes (alkyl=ethyl, isopropyl, n-butyl and n-hexyl) is described by one pot methylene insertion reaction using dialkyl ditellurides, sodium borohydride and chloroform. The cadmium(II) complexes of bis(isopropyltelluro)methane were also synthesized. The bis(alkyltelluro)methanes were characterized by elemental analysis, ^{1}H and ^{125}Te NMR. The product of the complexation of bis(isopropyl telluro)methane with Cd(II) have been characterized by elemental analysis, ^{1}H, TGA and FAB mass spectrometry. The dialkyltelluroether ligands may be useful in organic synthesis and their complexes with cadmium(II) can be considered a potential single source of metal-organic chemical vapor deposition (MOCVD) precursors for advanced electronic materials.

Keywords: Ditellurides; bis(alkyltelluro)methanes; complexation; MOCVD precursor

INTRODUCTION

There has been a considerable recent interest in the chemistry of organotellurium compounds mainly due to their potential applications in synthesis[1], nuclear medicine[2], photography[3] and new conducting materials[4]. The technology to use tellurium containing compounds as single source precursors in MOCVD process for the formation of technologically advanced semiconducting materials[5,6] is now fairly well developed.

Our recent work on alkyls of tellurium and cadmium prompted us to attempt the synthesis of single source precursors with Cd - Te bond. For this purpose we synthesized a variety of bis(alkyltelluro)methanes to be used as ligands for complexation with Cd (II). Bis(alkyl/aryltelluro)methanes are important reagents in organic synthesis[7,8] and are useful starting materials for the preparation of other kinds of organotellurium compounds[9]. These compounds have been previously synthesized by various workers following different methods[10-18]. In this communication we report a novel and convenient route for the synthesis of a series of bis(alkyltelluro)methanes in yields ranging from 60 to 75%, using a one pot reaction of dialkyl ditellurides, sodium borohydride and chloroform. The Cd (II) complex of bis(isopropyltelluro)methane has been synthesized and characterized.

RESULTS AND DISCUSSION

Dialkyl ditellurides (**1a** - **4a**) were synthesized from Na_2Te_2, formed by the reaction of sodium borohydride with tellurium powder, followed by subsequent reaction with alkyl bromides (**1**-**4**) (eq. 1). The dialkyl ditellurides were purified by vacuum distillation and flash column chromatography and characterized by ^1H and ^{125}Te NMR (Table 1).

$$\mathrm{Te}\ \xrightarrow[\text{(ii) RBr}\ (\mathbf{1-4})]{\text{(i) NaBH}_4/\text{H}_2\text{O}}\ \underset{(\mathbf{1a-4a})}{\mathrm{R_2Te_2}} \tag{1}$$

R = Et (**1**, **1a**), i-Pr (**2**, **2a**), n - Bu (**3**, **3a**), n - hexyl (**4**, **4a**).

Bis(alkyltelluro)methanes (**5** - **8**) have been synthesized in yields ranging from 60 to 75% using a one pot reaction of compounds **1a** - **4a** with sodium borohydride in ethanol containing some chloroform. The addition of aqueous alkaline sodium borohydride to the dark purple ditellurides (**1a** - **4a**) yielded a colorless solution, indicating the formation of sodium tellurolate, NaTeR (eq. 2).

$$\mathrm{R_2Te_2}\ \xrightarrow{\text{NaBH}_4\ /\text{NaOH/H}_2\text{O}}\ \mathrm{2RTeNa} \tag{2}$$

TABLE 1. Physical and analytical data of dialkyl ditellurides

Compounds[a]	B.p. (°C / mmHg)[b]	Yield (%)	^1H NMR, δ ppm ($CdCl_3$, TMS)	^{125}Te NMR, δ ppm ($CdCl_3$, Me_2Te)
$(CH_3CH_2)_2Te_2$ **(1a)**	80-82/ 7	78	1.5(t,6H); 3.1(q,4H)	187
$[(CH_3)_2CH]_2Te_2$ **(2a)**	60-62/ 12	81	1.57(d,12H); 3.45 (m,2H)	311
$(CH_3CH_2CH_2CH_2)_2Te_2$ **(3a)**	111-112/ 1.5	79	0.9(t,6H); 1.2 - 2, (m,8H); 3.15(t,4H)	135
$(CH_3CH_2CH_2CH_2CH_2CH_2)_2Te_2$ **(4a)**	-	58	0.7(t,6H); 1.1-1.8, (m,16H); 3.2(t,4H)	138

[a] Satisfactory analysis obtained; [b] Uncorrected

The bis(alkyltelluro)methanes (**5** - **8**) were formed by the reaction of sodium alkyltellurolate with chloroform (eq. 3).

$$2\ RTeNa \xrightarrow{CHCl_3} R{-}Te{-}CH_2{-}Te{-}R \qquad (3)$$

(5 - 8)

R = Et (**5**), i-Pr (**6**), n-Bu (**7**), n-hexyl (**8**)

The fact that the reaction occurs in the presence of a base, chloroform and sodium borohydride, suggests that the reacting entity in this reaction is dichlorocarbene, which on reaction with the sodium alkyltellurolate (NaTeR) produces the bis(alkyltelluro)methanes. The following mechanism can be proposed for their formation[18].

$$\mathrm{CHCl3} \xrightarrow{\mathrm{OH}^-} \mathrm{CCl3}^- \xrightarrow{-\mathrm{Cl}^-} :\mathrm{CCl2} \xrightarrow{\mathrm{RTe}^-} (\mathrm{RTe})\mathrm{CCl2}^-$$

$$\xrightarrow{-\mathrm{Cl}^-} (\mathrm{RTe})\ddot{\mathrm{C}}\mathrm{Cl} \xrightarrow{\mathrm{RTe}^-} (\mathrm{RTe})2\mathrm{CCl}^- \xrightarrow{-\mathrm{Cl}^-} (\mathrm{RTe})2\mathrm{C}:$$

$$\xrightarrow[\text{from borohydride}]{\mathrm{H}^-} (\mathrm{RTe})2\mathrm{CH}^- \xrightarrow[\text{from solvent}]{\mathrm{H}^+} (\mathrm{RTe})2\mathrm{CH2}$$

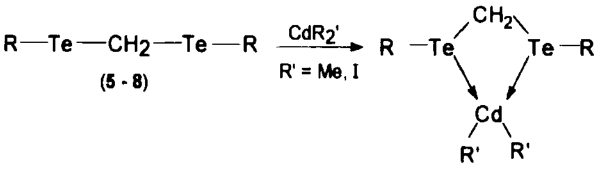
The elemental (C, H) analysis data of compounds **5** - **8** are in agreement with the calculated values. The ^{125}Te NMR of these compounds are also in excellent agreement with the data reported for bis(alkyltelluro)methanes synthesized by other routes[11], except compound **8** which is a new compound. The results of the ^{1}H and ^{125}Te NMR of these compounds are summarized in table 2.

TABLE 2. Physical and analytical data of bis(alkyltelluro)methanes

Compounds[a]	Yield (%)	^{1}H NMR, δ ppm (CdCl$_3$, TMS)	^{125}Te NMR, δ ppm (CdCl$_3$, Me$_2$Te)
$(CH_3CH_2Te)_2CH_2$ (**5**)	70	3.4 (s,Te-C$\underline{H}_2$-Te)	401
$[(CH_3)_3CHTe]_2CH_2$ (**6**)	74	3.33 (s,Te-C$\underline{H}_2$-Te)	557
$(CH_3CH_2\,CH_2CH_2Te)_2CH_2$ (**7**)	60	3.6 (s,Te-C$\underline{H}_2$-Te)	343
$(CH_3CH_2\,CH_2\,CH_2\,CH_2\,CH_2Te)_2CH_2$ (**8**)	68	3.9 (s,Te-C$\underline{H}_2$-Te)	306

[a] satisfactory elemental analysis

Bis(isopropyltelluro)methane (**6**) formed a complex with Cd(II) compounds (eq. 4).



(4)

(9, 10)

R = i-Pr, R' = Me (9)
R = i-Pr, R' = I (10)

Compound **9** is sparingly soluble in DMSO and compound **10** is sparingly soluble in THF, DMF and DMSO. In the ^{1}H NMR spectrum, the CH and the CH_2 (methylene) protons of compound **10** merges between 3.28 to 3.35 ppm and the CH_3 protons of the isopropyl group appeared at 1.48 ppm. We were able to record ^{1}H NMR spectrum only for compound **10**. It was not possible to record ^{1}H, ^{13}C and ^{125}Te NMR for compound **9**, due to solubility problems. The complexes of metal halides with these ligands have generally been found to be poorly crystalline and sparingly soluble in common organic solvents, making their satisfactory characterization difficult[19].

The TGA analysis of compound **10** reveals the final residue as CdTe+Te, and compound **9** did not yield the stoichiometric CdTe+Te as the final residue which might be due to its polymeric nature. The TGA results are summarized in table 3.

TABLE 3. TGA analysis data of the cadmium (II) complexes

Compound	IDT (°C)[a]	FDT (°C)[b]	D_{max} (°C)[c]
9	150	240	192
	622	725	661
10	120	270	160.3
	310	440	404.5
	500	625	567.9

[a]IDT - initial decomposition temperature; [b]FDT - final decomposition temperature; [c]D_{max} - maximum decomposition temperature

The major fragments observed in the FAB mass spectra for compounds **9** and **10** are as follows:

Compound 9:

$[H_2Te_2]\,CH_2Cd\rceil^{\dot{+}}$
(m/e) = 391

$HTeCd\rceil^{\dot{+}}$
(m/e) = 245

$HTeCH_2Cd\rceil^{\dot{+}}$
(m/e) = 257

$[(CH_3)_2CH]_2Cd\rceil^{+}$
(m/e) = 200

$Te_2H_2\rceil^{\dot{+}}$
(m/e) = 262

$[(CH_3)_2CH]_2Cd(CH_3)_2\rceil^{\dot{+}}$
(m/e) = 230

Compound 10:

$[(CH_3)_2CHTe]_2CH_2.CdI_2\rceil^{\dot{+}}$
(m/e) = 728 (m+)

$[(CH_3)_2CH]_2TeCdI_2\rceil^{+}$
(m/e) = 580

$H_2Te_2CH_2I\rceil^{\dot{+}}$
(m/e) = 403

$Te_2H_2\rceil^{\dot{+}}$
(m/e) = 262

$TeH_2\rceil^{+}$
(m/e) = 132

$(CH_3)_2CHTeCH_2TeH.CdI_2\rceil^{\dot{+}}$
(m/e) = 686

$[(CH_3)_2CH]_2Te.CdI\rceil^{\dot{+}}$
(m/e) = 454

$H_2TeCdI\rceil^{\dot{+}}$
(m/e) = 369

$HCdI\rceil^{\dot{+}}$
(m/e) = 238

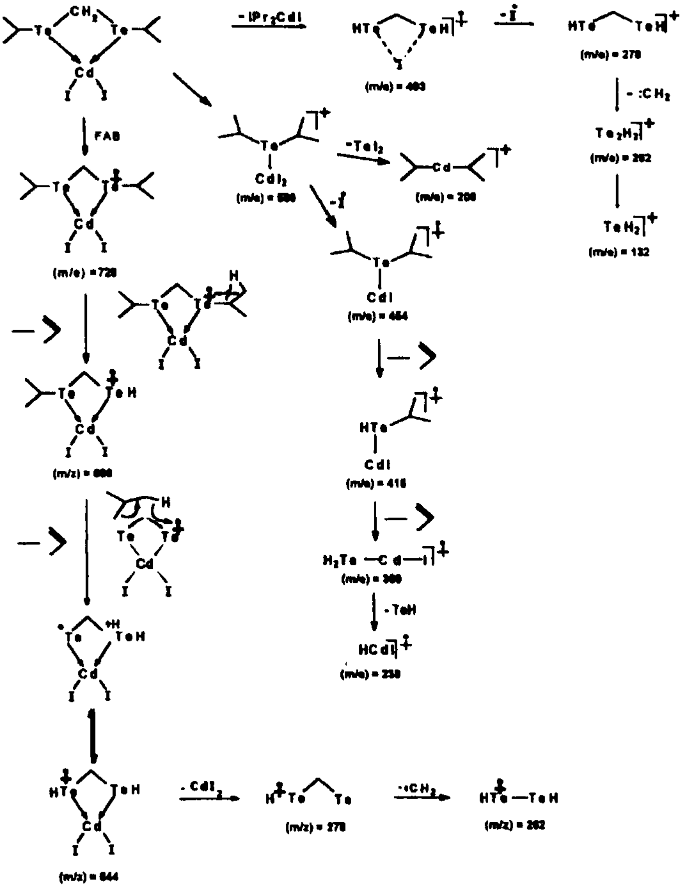
$H_2Te_2CH_2.CdI_2\rceil^{\dot{+}}$
(m/e) = 644

$(CH_3)_2CHTeH.CdI\rceil^{\dot{+}}$
(m/e) = 415

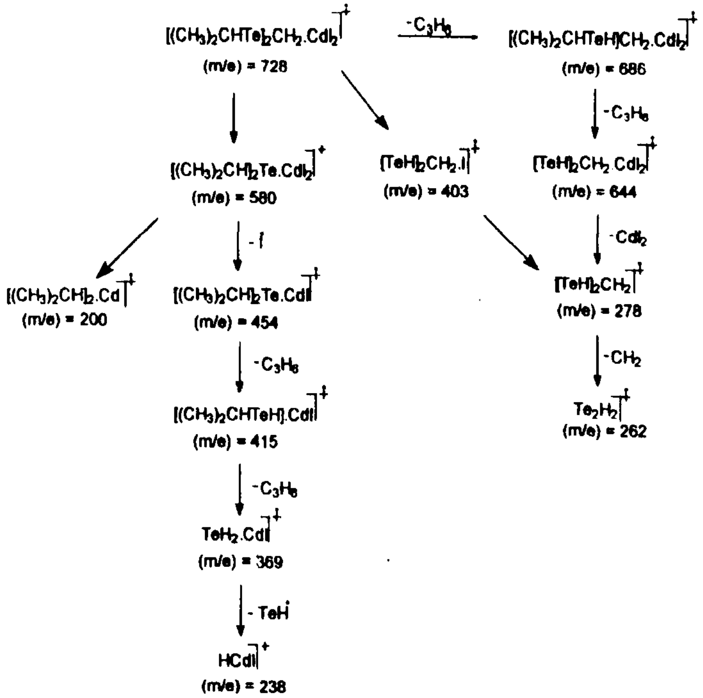
$H_2Te_2CH_2\rceil^{\dot{+}}$
(m/e) = 278

$[(CH_3)_2CH]_2Cd\rceil^{+}$
(m/e) = 200

The mechanism of the fragmentation pattern of compound **10** is given in scheme 1.



SCHEME 1. FAB mass spectrum of compound **10** (mechanism of the fragmentation pattern)



FAB Mass Fragmentation

In this preliminary study on the complexation of Cd (II) with bis(alkyltelluro)methanes, we concentrated mainly on bis(isopropyl telluro)methanes, as diisopropyltelluride is widely used as MOCVD precursor for the preparation of mercury cadmium telluride (MCT) and CdTe due to its availability in a very pure form as well as its low temperature growth of thin film[20].

EXPERIMENTAL SECTION

All the reactions were carried out under Nitrogen or Argon using standard vacuum line techniques. Solvents were carefully purified by standard procedures[21] and were freshly distilled and degassed prior to use. Boiling points and melting points are uncorrected. Ethyl bromide (Aldrich), isopropyl bromide (E-merck, Germany), n-butyl bromide, n-hexyl bromide and cadmium iodide (Aldrich) were used as received. Dimethylcadmium was synthesized and purified in our laboratory following published procedure[22]. Tellurium metal (5N) was obtained from NFC, Hyderabad, India. Merck silica gel 60 (70 - 230 and 230 - 400 mesh) was used for flash column chromatography. ^1H and ^{125}Te NMR spectra were obtained at 300 and 94.75 MHz, respectively, on a Varian VXR 300S Spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal standard for ^1H and Me_2Te as external standard for ^{125}Te NMR. FAB mass spectra were recorded on a JEOL SX/DA - 6000 mass spectrometer/Data system using Argon (6kv, 10mA) as the FAB gas. Thermogravimetric analysis of the samples were carried out under argon atmosphere using TGA VS. 1A Du Pont 2100 analyser at a heating rate of 20K min^{-1}.

Synthesis of ditellurides (1a - 4a)

Typical procedure: An alkaline solution of $NaBH_4$ (0.375 mol) in 10 mL of degassed distilled water was slowly added to a magnetically stirred slurry of tellurium powder (100 mesh, 3.19g, 0.025 mol) at room temperature during 30 min. The reaction mixture was refluxed till the tellurium metal dissolved. The solution turned dark purple indicating the formation of Na_2Te_2. To this solution was added the alkyl bromide (0.0375 mol) dropwise with constant stirring at 0°C. The reaction mixture was stirred further for three hours. The organic layer was extracted with ether and washed with degassed water. The ether extract was dried over sodium sulphate under argon. On removal of the excess of solvent followed by vacuum distillation, dark brown liquids of dialkyl ditellurides were obtained. Compounds **1a**-**3a** were purified by vacuum distillation and compound **4a** was purified by flash column chromatography using silica gel 60 with hexane as eluent.

Diethyl ditelluride (**1a**) - Yield: 3.05 g (78%), b. p. = 80-82^{0}C /7mm Hg (lit. 86^{0}C/ 9mm Hg)[23], diisopropyl ditelluride (**2a**) - Yield : 3.4g (81%), b. p. = 60 - 62^{0}C /12 mm Hg, di-n-butyl ditelluride (**3a**) - Yield : 3.65g (79%), b. p. = 111-112^{0}C/1.5mm Hg (lit 93^{0}C/0.5mm)[23], Di-n-hexylditelluride (**4a**) - Yield : 3.08g (58%).

Synthesis of bis(alkyltelluro)methanes (5 - 8)

Typical procedure: A solution of sodium borohydride (0.0375 mol in 20 mL of 10% NaOH) was added dropwise to an ethanolic solution of dialkyl ditellurides (0.0125 mol in 50 mL ethanol) with constant stirring at room temperature in oxygen free argon atmosphere, until it became colourless. Chloroform (25 mL) was added all at once and the mixture was further refluxed for 30 min. The yellow chloroform layer was separated and washed with degassed water. The organic layer was dried over sodium sulphate under argon. The product was obtained by removal of chloroform and the purity was checked by TLC.

Bis(ethyltelluro)methanes (**5**): Yield- 2.86g (70%),

Bis(isopropyltelluro)methane (**6**): Yield- 3.29g (74%),

Bis(n-butyltelluro)methane (**7**): Yield- 2.88g (60%),

Bis(n-hexyltelluro)methane (**8**): Yield- 3.73g (68%).

Complexation of dimethylcadmium with bis(isopropyltelluro) methane (9)

Dimethylcadmium (2.137g, 15 mmol) was added dropwise to the ethanolic solution of compound **6** (5.38g, 0.015 mol) in dry ethanol (20mL) with constant stirring at room temperature. The yellow precipitate formed was separated, washed with petroleum ether (40^0 - 60^0C) and acetonitrile. It was then vacuum dried. M.p. 124-126^{0}C (decomp.). Yield - 6.2g (83%).

Complexation of Cadmium Iodide with bis(isopropyltelluro) methane (10)

Cadmium (II) iodide (5.49g, 0.015 mmol) in ethanol (20mL) was added dropwise to the ligand **6** (5.38g, 0.015 mol) in diethylether (20mL) at room temperature with constant stirring. The yellow precipitate formed was filtered, washed with ethanol and petroleum ether (40^0 - 60^0C) and vacuum dried. M.p. 126-127^{0}C (decomp.) Yield : 9.414g (87%).

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