1,1,2,3,4,5 - Hexahydro Tellurophene [$C_4H_8Te(II)$] and 1,3-Dihydro-2λ^4-Benzotellurole [$C_8H_8Te(II)$] Derivatives

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ABSTRACT

Convenient route of synthesis of the type $R_2TeX'Y$ and $R_2Te(CH_3)X''$ were dove loved by the reactions of $R_2Te(II)$ [$R_2 = C_4H_8$, C_8H_8] with IX'(X'= Cl, Br), RI (R = CH_3, C_2H_5) and CH_3X'' (X''= Cl, Br, NO_3, C_6H_5OCO).These complexes have been characterised through elemental analysis (Table 1) and ^1H NMR spectral data (Table 2). The ^1H NMR spectra of C_4H_8TeICl, C_4H_8TeIBr, $C_4H_8TeCH_3I$, $C_4H_8TeCH_3Cl$, $C_4H_8TeCH_3Br$, $C_4H_8TeCH_3NO_3$, $C_4H_8TeCH_3OCOC_6H_5$, $C_8H_8TeCH_3I$, and C_8H_8Te -C_2H_5I have been recorded in $CDCl_3$ at 300 MHz. The study indicates that the heterocycles of $C_4H_8Te(II)$ and $C_8H_8Te(II)$ undergo oxidative addition reactions readily resulting in the increase in the oxidation number of central tellurium atom.

1. INTRODUCTION

A perusal of the literature reveals that a number of diorganotellurium(II) compounds have been prepared by the reduction of diorganotellurium(IV) dihalides with a variety of reducing agents(1-7). Compounds of the formula $R_2Te(II)$ readily undergo oxidation addition reactions and which can be classified as (a) oxidative addition reactions with halogen, interhalogens and pseudohalogens (b) oxidative addition reactions with organic halides (c) oxidative addition reactions with N- haloamides or-imides. Reports on several complexes of diorganotellurides with mercuric halide and Cu(I) halides are available(8-21).

Among oxidative addition reactions of diorganotellurides (II) with halogen, interhalogens and pseudohalogens, synthesis of diorganotellurium dihalides have been reported earlier by Irgolic (1-7) (Eq.1).

$$R_2Te + X_2 \rightarrow R_2TeX_2 \text{ (X= halogens)} \quad (1)$$

In 1976, Sadekov et.al (22) reported the synthesis of $(p\text{-}RC_6H_4)_2TeF_2$ (R= H, MeO) by oxidative addition reaction of tellurides with SF_4. Various compounds formed through the reaction of interhalogen & pseudohalogens with diorganotellurides have been reported(23-27). Srivastava et.al(28) reported the oxidative addition reactions of organotellurium (II) with interhalogens (XY = ICl, IBr, ICN, BrCN) leading to the formation of organotellurium (IV) compounds of the formula RR′TeXY (R= R′= C_6H_5, p-$CH_3OC_6H_4$; R= C_6H_5, R′= p-$CH_3OC_6H_4$). Later on Srivastava et.al(29) prepared several triorganotelluronium compounds by treating R_2Te (R=Ph, p- $MeOC_6H_4$) with C_6H_5X(X= Cl, Br), cyclohexyl iodide, CH_3I and CH_2=$CHCH_2Br$. Oxidative addition reaction of $R_2Te(II)$ with N-haloamides or – imides have been reported for the first time from our laboratory(30). Among heterocyclic diorganotellurides, several compounds of the type C_8H_8TeXY (XY = halogen, interhalogen, organic halide, benzamide) formed through oxidative

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addition reactions of 1, 3-dihydro-2 λ^4- benzotellurole [$C_8H_8Te(II)$] and their molecular adducts with $HgCl_2$ and Cu_2Cl_2 have been reported by Srivastava et.al(31). Further the synthesis, spectroscopic studies and the solution behaviour of a series of cyclic telluronium salts of 1-organo-3,4-benzo-1-telluracyclopentane have been reported by Ali. Z. AL-Rubai et.al(32). In solvents of low polarity these compounds are associated to dimers via a weak ionic interaction. These associations were confirmed by X-ray and other structural studies(33). The above compounds were stable towards reductive elimination(34-37).

With a view to extend this work and check the reactivity of organotellurium(II), we have synthesised and characterised some new heterocyclic diorganotelluride derivatives of the type $R_2TeX'Y$ and $R_2Te(CH_3)X''$ by the reactions of $R_2Te(II)$ [$R_2 = C_4H_8$, C_8H_8] with IX' (X'= Cl, Br), RI (R = CH_3, C_2H_5) and CH_3X'' (X'' = Cl, Br, NO_3, C_6H_5OCO). These complexes have been characterised through elemental analysis and ^1H NMR spectral data.

2. EXPERIMENTAL

$C_4H_8TeI_2$(38), $C_8H_8TeI_2$(31), $C_4H_8Te(II)$(37), $C_8H_8Te(II)$(32), $C_4H_8TeCH_3^+I^-$ (37) and $C_8H_8TeCH_3^+I^-$ were prepared by the literature methods or by the methods developed by us. Synthesis of $C_4H_8Te(II)$ and $C_8H_8Te(II)$ and their oxidative addition product are described as follows:

2.1 Preparation of C_4H_8Te (II) and $C_8H_8Te(II)$

To the boiling methanolic solution of $C_4H_8TeI_2$ (5g, 11.42mmol), $NaBH_4$ was added in a flask flushed with dry nitrogen until the orange colour of methanolic solution disappeared. The solution was filtered and poured in 150ml of distilled water in a beaker. Pale yellow milky solution obtained. It was then extracted with diethyl ether several times. The combined ether extracts were dried over $CaCl_2$ and kept overnight. It was filtered and reduced and $C_4H_8Te(II)$ was used *in situ* for further reactions. $C_8H_8Te(II)$ (*in situ*) was similarly prepared by the reaction of (5g, 10.30mmol) of $C_8H_8TeI_2$ and $NaBH_4$.

2.2 Preparation of C_4H_8TeXY (XY= ICl, IBr)

$C_4H_8Te(II)$ (*in situ*) (.4195g.2.28mmol) was taken in a flask flushed with nitrogen. To this was added ICl dropwise until the yellow colour of the original reaction mixture turned orange with orange solid. It was further stirred in ice for 1/2 h more. Orange crystalline solid (C_4H_8TeICl) was obtained which was filtered and recrystallised with dry ether. (Yield = 0.140g, 17.71%, m.p.105 °C). Reaction of $C_4H_8Te(II)$ in situ (.4195, 2.28mmol) with IBr (.472g, 2.28mmol), in similar, way yielded C_4H_8TeIBr (Yield= 0.240g (26.89%), m.p.°C).

2.3 Preparation of $C_4H_8TeCH_3I$

In a typical experiment, to the ethereal solution of $C_4H_8Te(II)$ (0.4195g, 2.28mmol) was added CH_3I (.3244g, 2.28mmol) in a flask flushed with dry nitrogen. Yellow crystalline solid was obtained. It was filtered and dried under vacuum (Yield 0.208g (27.96%), m.p.200°C).

2.4 Preparation of $C_4H_8TeCH_3^+X^-$ (X =Cl, Br, NO_3, C_6H_5OCO)

In a typical experiment, $C_4H_8TeCH_3^+I^-$ (0.458g, 1.41mmol), $AgOOCC_6H_5$(0.3052g, 1.41mmol) and dry acetone (~15ml) were taken in a flask flushed with nitrogen. The reaction mixture was stirred for 2h under nitrogen and then filtered to remove AgI and excess of silver benzoate. The filtrate was reduced. White crystalline solid of $C_4H_8TeCH_3OCOC_6H_5$ was obtained. It was filtered and dried under vacuo (Yield: 0.183g (40.71%), m.p.40°C). $C_4H_8TeCH_3^+Cl^-$, $C_4H_8TeCH_3^+Br^-$ and $C_4H_8TeCH_3^+NO_3^-$, were prepared similarly using $C_4H_8TeCH_3^+I^-$ (0.458g, 1.41mmol) and corresponding AgCl (0.203g, 1.41mmol), AgBr (0.266g,1.41mmol) and $AgNO_3$ (0.240g,1.41mmol) respectively.

2.5 *Preparation of C_8H_8TeXY ($XY= CH_3I, C_2H_5I$)*

In a typical experiment, an ethereal solution of $C_8H_8Te(II)$ (0.92g, 3.97mmol) was mixed with CH_3I (.564g, 3.97mmol) in a flask flushed with nitrogen and allowed to stir. for 48 h. The mixture deposited a yellow crystalline solid which was separated and stirred in fresh ether for ~12 h. $C_8H_8TeCH_3I$ was then filtered, washed with solvent ether and dried in vacuo (Yield 1.33g (89.62%), m.p.210°C). $C_8H_8TeC_2H_5^+I^-$ (Yield 1.25g (81.19%), m.p. 200C) was prepared similarly using $C_8H_8Te(II)$ (0.92g,3.8mmol) and ethyl iodide (.6196g, 3.97mmol).

3. RESULTS AND DISCUSSION

The 1,1,2,3,4,5-hexahydro tellurophene and 1,3-dihydro-2λ^4-benzotellurole derivatives obtained from $C_4H_8Te(II)$ and $C_8H_8Te(II)$ are listed in Table 8.1. They are solids, stable at room temperature and they are not effected by the atmospheric moisture. They are soluble in common organic solvents such as chloroform, acetone and benzene.

Proton Nuclear Magnetic Tesonance (^{1}H NMR) Spectra: The ^{1}HNMR spectra of C_4H_8TeICl, C_4H_8TeIBr, $C_4H_8TeCH_3I$, $C_4H_8TeCH_3Cl$, $C_4H_8Te CH_3Br$, $C_4H_8TeCH_3NO_3$, $C_4H_8TeCH_3$ OCO C_6H_5, $C_8H_8TeCH_3I$, and C_8H_8Te -C_2H_5I have been recorded in $CDCl_3$ at 300 MHz. The ^{1}HNMR data of these complexes are listed in table 8.2 and discussed as follows;

3.1 *^{1}H NMR spectrum of C_4H_8TeICl*

The ^{1}HNMR spectra of the title complex shows two sets of resonances due to methylene ring protons attached to tellurium ($TeCH_2$) and methylene ring protons attached to carbon ($TeCH_2CH_2$). Two singlets centered at 3.02 ppm and 2.02 ppm are observed due to $TeCH_2$ & $TeCH_2CH_2$ protons respectively.

3.2 *^{1}H NMR spectrum of C_4H_8TeIBr*

The ^{1}HNMR spectra of C4H8TeIBr also shows two sets of resonances as discussed in the spectrum of the C_4H_8TeICl. Two singlets centered at 3.04 ppm and 2.66 ppm are due to $TeCH_2$ & $TeCH_2CH_2$ protons respectively.

3.3 *^{1}H NMR spectrum of $C_4H_8TeCH_3I$*

In the ^{1}H NMR spectrum of the title complex, three types of protons viz. (i) $TeCH_2$ (ii) $TeCH_2CH_2$ and (iii) CH_3 protons are present. A singlet at 2.51 ppm is due to the methyl protons whereas two singlets centered at 3.40 ppm and 2.80 ppm are attributed to $TeCH_2$ and $TeCH_2CH_2$ protons respectively. The integration of the peak areas corresponds to the proposed stoichiometry of the complex.

3.4 *^{1}H NMR spectrum of $C_4H_8TeCH_3Cl$*

The ^{1}HNMR spectrum of the $C_4H_8TeCH_3Cl$ shows three types of protons viz. (i) $TeCH_2$ (ii) $TeCH_2CH_2$ and (iii) CH_3 protons. Three singlets centered at 2.48 ppm, 3.20 ppm and 2.82 ppm are attributed to CH_3, $TeCH_2$ and $TeCH_2CH_2$ protons respectively. The integration of the peak areas corresponds to the proposed stoichiometry of the complex.

3.5 *^{1}H NMR spectrum of $C_4H_8TeCH_3Br$*

In the ^{1}H NMR spectrum of the above complex, three singlets centered at 2.48 ppm, 3.68 ppm and 2.90ppm are attributed to CH_3, $TeCH_2$ and $TeCH_2CH_2$ protons respectively. The integration of the peak areas corresponds to the proposed stoichiometry of the complex.

3.6 *^{1}H NMR spectrum of $C_4H_8TeCH_3NO_3$*

The ^{1}H NMR spectra of $C_4H_8TeCH_3NO_3$ shows two singlets for $TeCH_2$ and $TeCH_2CH_2$ protons at 3.54 ppm and 2.71 ppm respectively. The CH_3 protons appear as a singlet at 2.41 ppm. The integration of the peak areas corresponds to the proposed stoichiometry of the complex.

3.7 ^{1}H NMR spectrum of $C_4H_8TeCH_3OCOC_6H_5$

In the ^{1}H NMR spectrum of the above complex, four types of protons viz. (i) $TeCH_2$ (ii) $TeCH_2CH_2$ (iii) CH_3 protons and (iv) C_6H_5 protons are present. Three singlets centered at 3.00 ppm, 2.58 ppm and 2.38ppm are attributed to $TeCH_2$ protons, $TeCH_2CH_2$ protons and CH_3 protons respectively. A multiplet centered at 7.20 ppm is due to C_6H_5 protons. The integration of the peak areas of $TeCH_2$, $TeCH_2CH_2$, CH_3 and C_6H_5 protons corresponds to the proposed stoichiometry of the complex.

Table -1 : Characterisation data of C4H8TeIX (X =Cl, Br), C4H8TeCH3X (X =Cl, Br, I, NO3, OCOC6H5) and C8H8TeRX (R= CH3, C2H5; X =I)

S. No.	Complex	M.P. (°C)	Colour	Yield (%)	Elemental Analysis (%) obsd. (calcd.)		
					C	H	Te
1.	C_4H_8TeICl	105	Orange	17.71	13.83 (13.87)	2.30 (2.31)	36.86 (36.87)
2.	C_4H_8TeIBr	105	Yellow	26.89	12.27 (12.29)	2.03 (2.05)	32.66 (32.67)
3.	$C_4H_8TeCH_3I$	200	Yellow	27.96	18.41 (18.43)	3.32 (3.38)	39.16 (39.19)
4.	$C_4H_8TeCH_3Cl$	80	Dull White	25.52	25.60 (25.63)	4.65 (4.70)	54.48 (54.51)
5.	$C_4H_8TeCH_3Br$	90	Pale Yellow	31.14	21.52 (21.54)	3.92 (3.95)	45.74 (45.80)
6.	$C_4H_8TeCH_3NO_3$	110	Dull White	30.56	23.01 (23.02)	4.19 (4.22)	48.92 (48.96)
7.	$C_4H_8TeCH_3OCOC_6H_5$	40	White	40.71	44.98 (45.06)	4.99 (5.01)	39.89 (39.92)
8.	$C_8H_8TeCH_3I$	210	Yellow	89.62	28.88 (28.91)	2.93 (2.94)	34.15 (34.15)
9.	$C_8H_8TeC_2H_5I$	200	Yellow	81.19	30.92 (30.96)	3.33 (3.35)	32.90 (32.92)

Table -2 : 1H NMR data of C4H8TeIX (X =Cl, Br), C4H8TeCH3X (X =Cl, Br, I, NO3, OCOC6H5) and C8H8TeRX (R= CH3, C2H5; X =I)

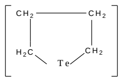
S. No.	Complex	Chemical shift (δ) ppm				
		$TeCH_2$ Protons	$TeCH_2CH_2$ Protons	CH_3 Protons	CH_2 Protons	$C_6H_5^+/C_6H_4^{++}$ Protons
1.	C_4H_8TeICl	3.02 (s)	2.02 (s)	-	-	-
2.	C_4H_8TeIBr	3.04 (s)	2.66(s)	-	-	-
3.	$C_4H_8TeCH_3I$	3.40(s)	2.80(s)	2.51(s)	-	-
4.	$C_4H_8TeCH_3Cl$	3.20(s)	2.82(s)	2.48(s)	-	-
5.	$C_4H_8TeCH_3Br$	3.68(s)	2.90(s)	2.48(s)	-	-
6.	$C_4H_8TeCH_3NO_3$	3.54(s)	2.71(s)	2.41(s)	-	-
7.	$C_4H_8TeCH_3OCOC_6H_5$	3.00(s)	2.58(s)	2.38(s)	-	7.20(m)$^+$
8.	$C_8H_8TeCH_3I$	5.01(t)	-	2.53(s)	-	7.19^{++}
9.	$C_8H_8TeC_2H_5I$	4.28(d)	-	3.20(q)	1.47(m)	7.19^{++}

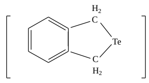
3.8 ^{1}H NMR spectrum of $C_8H_8TeCH_3I$

In the ^{1}H NMR spectrum of the title complex, three types of protons viz. (i) $TeCH_2$ protons (ii) C_6H_4 protons and (iii) CH_3 protons are present. The spectra of the above complex shows three signals, one as a sharp singlet at 2.53 ppm due to CH_3 protons, a triplet centered at 5.01 ppm due to $TeCH_2$ protons and the phenyl protons appear as a multiplet at 7.19 ppm. The integration of the peak areas corresponds to the proposed stoichiometry of the complex.

3.9 ^{1}H NMR spectrum of $C_8H_8TeC_2H_5I$

The ^{1}H NMR spectrum of the above complex shows four signals. A doublet is centered at 4.28 ppm and is due to $TeCH_2$ protons. A multiplet centered at 7.19 ppm is due to C_6H_4 protons. A multiplet centered at 1.47 ppm and a quartet centered at 3.20 ppm is attributed to CH_2 protons and CH_3 protons respectively. The integration of the peak areas corresponds to the proposed stoichiometry of the complex.

The study indicates that the heterocycles of C4H8Te(II) 

and C8H8Te(II) 

undergo oxidative addition reactions readily resulting in the increase in the oxidation number of central tellurium atom.

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