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SYNTHESIS AND CHARACTERIZATION OF SOME NEW UNSYMMETRICAL DIORGANOTELLURIUM COMPOUNDS CONTAINING AMINO AND HYDROXYMETHYL GROUPS

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Keywords: Unsymmetrical diaryl tellurides, amino groups, hydroxymethyl groups,
tellurium tetrabromide, benzyl alcohol.

ABSTRACT

A new series of unsymmetrical diaryl telluride dibromides (*i.e.* 4-HOCH₂C₆H₄(Ar)TeBr₂ where Ar = 2-NH₂-5-BrC₆H₃ (1); 2-NH₂-5-CH₃OC₆H₃ (2); 2-NH₂-5-NO₂C₆H₃ (3) were prepared from the reaction of 4-hydroxymethylphenylmercury chloride with the corresponding 2-aminoaryl tellurium tribromides in glacial acetic acid. Reduction of compounds 2 and 3 by hydrazine hydrate in boiling ethanol gave the unsymmetrical diaryl tellurides (4 and 5, respectively). Reaction of compound 5 with SOCl₂ and I₂ gave 4-hydroxymethylphenyl 2-amino-5-nitrophenyl tellurium dichloride (6) and 4-hydroxymethylphenyl 2-amino-5-nitrophenyl tellurium diiodide (7), respectively in good yields. All new compounds were characterized by elemental analysis, IR, ¹H NMR, ¹³C NMR and mass spectroscopic data.

INTRODUCTION

Organotellurium compounds containing a hydroxy group within the same organic radical are well documented in literature [1-3]. Phenols reacted with tellurium tetrachloride under relatively mild conditions in chloroform or carbon tetrachloride solution gave insoluble

aryltellurium trichlorides even when a twofold quantity of phenols presents [4-6].

There are few examples in the literature dealing with aromatic tellurides bearing amino groups. Such compounds were prepared either by direct [7-9] or indirect methods [10-12].

The syntheses of organic polymers containing tellurium are very rare in the literature. Our previous works [13,14] described the synthesis of new polymers from amine-substituted organic tellurium [13] and from organotellurium compounds containing hydroxymethyl groups *ortho* or *para* to tellurium atoms in the aryl residue [14].

To the best of our knowledge, there is no method to prepare organotellurium compounds containing amino and hydroxymethyl groups within the same organic tellurium molecule. Thus, the aim of the present work was to synthesize some new unsymmetrical diaryltellurium compounds containing both amino and hydroxymethyl groups within the same compound, in the hope to use them as precursors for the synthesis of new polymers containing tellurium.

EXPERIMENTAL

Synthesis

4-Hydroxymethylphenylmercury chloride was prepared from benzyl alcohol and mercuric acetate according to a literature method [15]. 2-amino-5-bromophenyltellurium tribromide, 2-amino-5-methoxyphenyltellurium tribromide and 2-amino-5-nitrophenyltellurium tribromide were prepared as described previously [13].

4-Hydroxymethylphenyl 2-amino-5-bromophenyl tellurium dibromide (1).

A solution of 4-hydroxymethylphenylmercury chloride (0.34g; 1mmol) and 2-amino-5-bromophenyltellurium tribromide (0.54 g; 1 mmol) in glacial acetic acid (50 ml) was refluxed for 4h. The hot solution was filtered hot. The filtrate was cooled to room temperature. A yellowish-brown precipitate was formed upon cooling to room temperature. The product was recrystallized from glacial acetic acid to afford yellow-brown precipitate in 78% yield, m.p. 192-194°C.

4-Hydroxymethylphenyl 2-amino-5-methoxyphenyl tellurium dibromide (2).

2-Amino-5-methoxyphenyltellurium tribromide (0.49g; 1mmol) and 4-hydroxyphenyl-mercury chloride (0.34 g; 1mmol) were refluxed in glacial acetic acid for 4h by the same

procedure described for compound 1. Yellowish brown precipitate was obtained, m.p. 168-170°C, with yield 75%.

4-Hydroxymethylphenyl 2-amino-5-nitrophenyl tellurium dibromide (3).

This compound was prepared by the same method above using 2-amino-5-nitrophenyltellurium tribromide (0.50g; 1 mmol) and 4-hydroxymethylphenylmercury chloride (0.34g; 1 mmol) as reactants to obtain yellow solid in 70% yield, m.p. 124-126°C.

4-Hydroxymethylphenyl 2-amino-5-methoxyphenyl telluride (4).

A suspension of 4-hydroxymethylphenyl 2-amino-5-methoxyphenyl tellurium dibromide (0.30g; 0.56 mmol) in 30 cm³ of ethanol was heated under reflux. Hydrazine hydrate (1.5g) in 20 cm³ of ethanol was added dropwise until evolution of nitrogen ceased. The solution was then filtered hot. The filtrate was evaporated to dryness to afford a yellow precipitate. Recrystallization from ethanol/hexane (4/1) gave a pale yellow solid in 63% yield, m.p. 127-129°C.

4-Hydroxymethylphenyl 2-amino-5-nitrophenyl telluride (5).

4-Hydroxymethylphenyl 2-amino-5-nitrophenyl tellurium dibromide (0.30g; 0.56 mmol) was treated with hydrazine hydrate (1.5g in 20 cm³ of ethanol) in a similar way described for the preparation of 4. Yellow solid was obtained in 72% yield, m.p. 133-135°C.

4-Hydroxymethylphenyl 2-amino-5-nitrophenyl tellurium dichloride (6).

Into a solution of 4-hydroxymethylphenyl 2-amino-5-nitrophenyl telluride (5) (0.20g; 0.54 mmol) in 20 cm³ of dry ether was added dropwise thionyl chloride (0.12g; 1.08 mmol) with stirring at room temperature. Removing of the solvent gave a yellow solid of compound 6. Recrystallization from ethanol gave pale yellow crystals in 76% yield, m.p. 167-170°C.

4-Hydroxymethylphenyl 2-amino-5-nitrophenyl tellurium diiodide (7).

A solution of iodine (0.035g; 0.27 mmol) in ether (10 cm³) was added with stirring to a solution of compound **5** (0.1g; 0.27 mmol) in ether (25 cm³). A brown precipitate was formed. Recrystallization from ethanol/hexane (4/1) gave red-brown crystals in 60% yield, mp. 171-173°C.

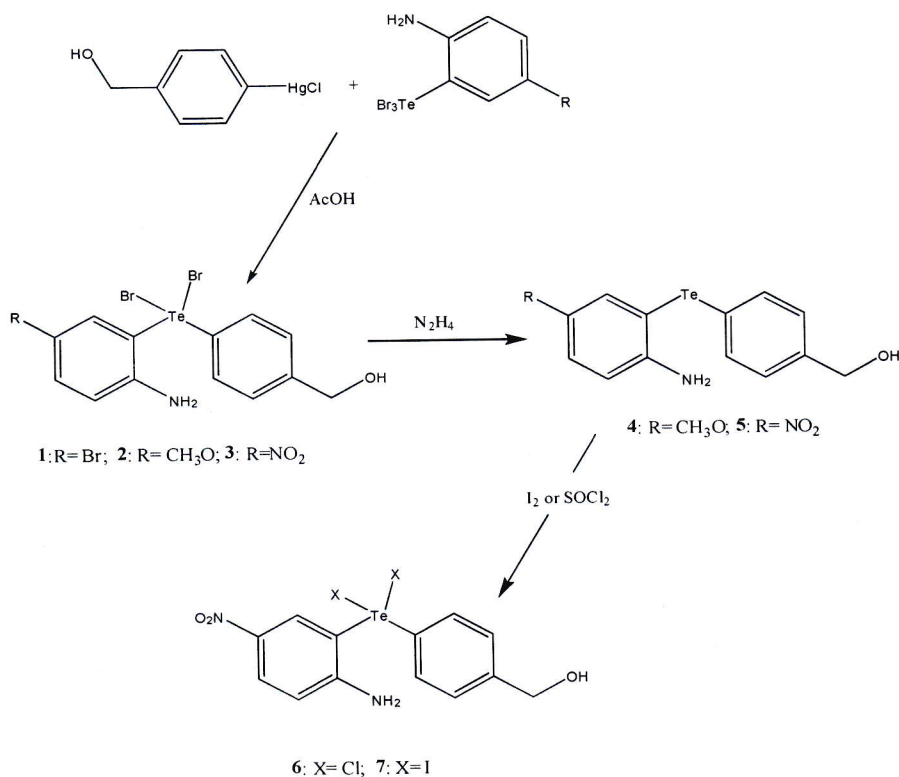
PHYSICAL MEASUREMENTS

¹H and ¹³C NMR spectra were obtained on a Bruker LA-250 MHz (250MHz) spectrometer with TMS as an internal reference. IR spectra were recorded as KBr discs in the of 4000-200 cm⁻¹ on a Pye-Unicam SP3-300 Infrared spectrophotometer. Microanalysis for carbon, hydrogen and nitrogen were obtained on a Perkin-Elmer 240B Elemental Analyzer and at Advanced Laboratory, Tripoly, Libya. All melting points were determined by a Philips Harris melting point apparatus and are

uncorrected. Mass spectra (EI) were obtained using Finnigan MAT-1125 mass spectrometer and measurements were carried out on ¹³⁰Te isotope.

RESULTS AND DISCUSSION

In the present work a series of new unsymmetrical diaryl telluride dibromides were prepared by a new and a convenient method. The preparation of compounds **1-3** based on *trans*-telluration of the corresponding 4-hydroxymethylphenylmercury chloride by 2-aminoaryl tellurium tribromide using glacial acetic acid as a solvent (Scheme 1). Attempts to use dioxane or chloroform as a solvent for the *trans* telluration of 4-hydroxymethylphenylmercury chloride yielded the corresponding compound in low yield (<15 %). Thus, it seems likely that glacial acetic acid is a good solvent for such reactions compare with dioxane and chloroform used in this study.



Scheme 1. Methods of preparation of compounds 1-7.

The new compounds **1**, **2**, and **3** were obtained as yellow to brown solids in 70- 80% yield, Table 1. Reduction of compounds **2** and **3** by hydrazine hydrate in boiling ethanol gave 4-hydroxyphenyl 2-amino-5-methoxyphenyl telluride (**4**) and 4-hydroxyphenyl 2-amino-5-

nitrophenyl telluride (**5**), respectively, Scheme 1. Reaction of compound **5** with SOCl_2 and I_2 afforded its dichloro- (**6**) and diiodo- (**7**) derivatives, respectively in good yields, Table 1.

Table (1). Yields, Mp, Analytical and NMR Data for Compounds **1–7**.

Compounds	M.p(°C)	Yield (%)	Analysis ^a			¹ H NMR; DMSO-d ₆ (ppm vs. TMS)
			C	H	N	
1	192-194	78	27.23 (27.59)	1.86 (2.12)	2.13 (2.47)	5.62-6.74(s*, 3H, CH ₂ +OH); 6.66(d, 1H, Ar-H); 7.027.26(m, 6H, Ar-H); 7.98(s, 1H, NH); 8.32(s, 1H, NH).
2^b	158-160	75	31.16 (31.45)	3.11 (3.20)	2.37 (2.62)	3.22(s, 3H, OCH ₃); 5.13(s, 1H, OH), 5.21(s, 2H, CH ₂); 6.75(d, 2H, Ar-H); 6.78(s, 1H, Ar-H); 6.91(d, 2H, Ar-H); 7.08(d, 2H, Ar-H); 7.48(d, 2H, NH ₂).
3	124-126	70	28.88 (29.35)	2.12 (2.25)	4.78 (5.26)	6.55(s, 2H, CH ₂); 6.60(s, 1H, OH); 6.72(s, 1H, Ar-H); 7.79(d, 2H, Ar-H); 7.83(d, 2H, Ar-H), 8.18-8.22(m, 2H, Ar-H), 10.56(s, 2H, NH ₂).
4	127-129	63	46.74 (47.11)	3.96 (4.20)	3.56 (3.92)	
5	133-135	72	40.62 (41.98)	2.98 (3.22)	7.31 (7.53)	5.69(s, 2H, CH ₂); 5.72(s, 1H, OH); 6.76(s, 1H, Ar-H); 7.79-8.19(m, 4H, Ar-H); 8.218-8.34(m, 2H, Ar-H), 10.43(d, 2H, NH ₂).
6^c	167-170	76	34.29 (35.25)	2.48 (2.71)	5.28 (6.32)	6.55(s, 2H, CH ₂); 6.59(s, 1H, OH); 6.72(s, 1H, Ar-H), 7.75(d, 2H, Ar-H); 7.80(d, 2H, Ar-H); 8.04(d, 2H, Ar-H); 10.55(s, 1H, NH); 11.43(s, 1H, NH).
7	171-173	60	24.66 (24.94)	1.72 (1.91)	4.28 (4.47)	5.66-5.82(s*, 3H, CH ₂ + OH); 6.64(d, 2H, Ar-H); 7.76-8.15(m, 6H, Ar-H); 9.30(s, 1H, NH); 9.65(s, 1H, NH).

^a broad singlet.

^aCalculated values in parentheses.

^b¹³C NMR in DMSO-d₆: 53.4, 68.1, 115.0, 115.1, 116.0, 119.3, 128.0(2C), 137.9(2C), 140.4(2C), 150.0.

^c¹³C NMR in DMSO-d₆: 68.0, 115.8, 117.0, 121.6, 123.8, 127.0(2C), 133.4(2C), 134.0, 140.7, 155.5.

The principal IR-active bands of compounds 1-7 fall in the region 3500-3100 and 1700-1620 cm^{-1} , the first being characteristic of ν (O-H) and ν (N-H), the second of the internal deformation mode of N-H. The weak but sharp band between 280-297 cm^{-1} can be assigned to the Te-C_{Ar} [16,17].

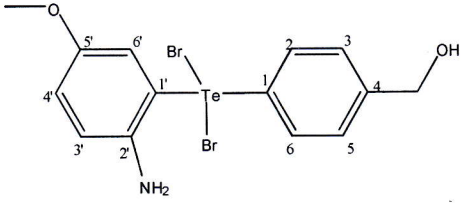
The ^1H NMR spectra for compounds 1-7 are presented in Table 1. At room temperature, there is a clear evidence in the ^1H NMR spectra for significant N $\rightarrow$ Te intramolecular interaction in solution since the proton resonance of the NH₂ appears as a doublet in all studied compounds. Thus, it seems likely that 1,4-Te...N interaction occurred in these compounds. Such interactions were observed in tellurated Schiff bases studied by X-ray [18] and by a computational study [19]. In all cases the resonances for the proton of the OH group appear as a singlet in the region 5.20-6.60 ppm (Table 1). In general, the OH signals were shifted to lower field compared with organic tellurium compounds containing hydroxymethyl groups [14]. This is probably due to the intermolecular interaction between

OH and NH₂ groups. This means that both hydroxymethyl and amino groups may be involved in intra- or/and inter-molecular interactions. It is worth noting that Singh and coworkers gave many examples for such interactions [20].

The CH₂ protons for all studied compounds appeared as a singlet between 5.20-6.55 ppm (Table 1). The aryl protons show the expected resonance for substituted benzene, as shown in Table 1. The ^{13}C NMR spectra of compounds 2 and 6 show the expected resonance signals and are consistent with their structure (Table 1). The large variation for carbon atoms bearing tellurium can be explained by the polarity of the Te-C bond [21,22].

The HSQC NMR spectrum of compound 2 shows that the ^{13}C peak at 68.1 ppm is bonded to the ^1H with peak at 5.21 ppm. Thus, the correlation of protons and carbon in aromatic rings such as in positions (4' and 6'), (3 and 5), (2 and 3) and in position 3' are shown in Table 2.

Table (2). HSQC data for compound 2.

Compound	^1H	^{13}C	Assignment
	5.21	68.1	C, H (CH ₂ OH)
	6.75	115, 115.1	C, H (4', 6')
	6.78	119.3	C, H (3')
	6.91	128.0	C, H (3, 5)
	7.08	137.9	C, H (2, 6)

The mass spectrum (EI) of compound 2 was recorded at 70 eV, and gave further support for its structure. The molecular ion peak is absent and the highest ion peak being observed at m/z 408 which corresponds to the loss of OMe and Br from the molecular ion. The base peak was observed at m/z 363. Other fragments such as $\text{C}_{12}\text{H}_9\text{Te}^+$, $\text{C}_{12}\text{H}_9^+$, $\text{C}_{12}\text{H}_{10}^+$, Te^+ , Br^+ were also observed.

The structures of the dihalo compounds (1, 2, 3, 6 and 7) are unlikely to be as simple as shown and are likely to be pseudo-trigonal-

bipyramidal with two halides in apical positions, and the lone pair of electrons and aryls in the equatorial plane [23].

In conclusion a new series of unsymmetrical diaryltellurium compounds containing both amino and hydroxymethyl groups within the same molecule were prepared. These new compounds can be used as precursors for the synthesis of new polymers containing tellurium.

ACKNOWLEDGEMENT

The authors thank Professor N. Al-Masoudi, Konstanz University, Germany, for providing some CHN analysis, NMR and mass spectra. We are grateful to Dr. Mohamad Al-Lafi, Advanced Laboratory, Tripoly, Libya, for providing some CHN analysis and I.R Spectra. We are grateful to the Department of Chemistry, College of Arts and Science in Tarhona, University of Almergab, Tarhona, Libya for providing the facilities.

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