Journal of Organometallic Chemistry, 443 (1993) 67–70

JOM 22974

Synthesis and characterization of new organotellurium compounds containing an *ortho*-amino group

Ali Z. Al-Rubaie, Najih I. Al-Salim and Shaker A.N. Al-Jadaan

Department of Chemistry, College of Science, University of Basrah, Basrah (Iraq)

(Received February 11, 1992)

Abstract

A range of novel organotellurium compounds with an amino group *ortho* to the tellurium atom (*i.e.* $ArTeBr_3$ and Ar_2Te, where $Ar = 2\text{-}NH_2\text{-}5\text{-}R\text{-}C_6H_3$; $R = CH_3$, Br, NO_2) have been prepared by a convenient new route involving reaction of the corresponding 2-aminoarylmercury chloride with tellurium tetrabromide. Reduction of $ArTeBr_3$ gave the compounds Ar_2Te_2 in good yield; these were treated with chlorine to give $ArTeCl_3$ in quantitive yield.

1. Introduction

In recent years, there has been considerable interest in the preparation and characterization of organotellurium compounds bearing an azo [1–3] or azomethine [4–6] group *ortho* to a tellurium atom. In general aromatic compounds containing tellurium and an amino group *ortho* to each other are rather difficult to prepare [8,9] and only a few examples of this class of organotellurium compounds had been reported.

McWhinnie and co-workers [1,2] reported the synthesis of bis(*o*-aminophenyl)ditelluride by reduction of (2-phenylazophenyl-C,Ń)tellurium trichloride with $NaBH_4$. 2-Aminophenyl ethyl telluride was prepared by reduction of 2-nitrophenylethyltelluride and used in the preparation of benzo[*b*]-3-azatellurophene [10].

The preparation of organotellurium compounds with an acetamido group *ortho* to the tellurium atom and their use as precursors in the preparation of 2-methylareno-3-azatellurophene [11] and as ligands for Cu^I, Cu^{II}, Ag^I, Hg^{II} and Cd^{II} [12,13] has been recently described.

Recent work [14,15] on the preparation and ligand properties of $1\text{-}(NMe_2)\text{-}2\text{-}(TeAr)\text{-}4\text{-}MeC_6H_3$ has prompted us to report our results in this area. We describe below the synthesis of new compounds with the NH_2–group *ortho* to the tellurium atom by a new direct and convenient procedure.

2. Experimental details

2.1. *Physical measurements*

Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded for KBr discs with a Pye-Unicam SP3-300s instrument. Elemental analyses (C, H, N) were obtained for all the compounds on a Perkin–Elmer 240B Elemental Analyzer or on a CHN Corder-MI-Uanaca. ^1H NMR spectra were obtained with a JEOL EX-90 instrument. They were recorded in DMSO-d_6 solution containing Me_4Si as internal reference and are reported in δ units.

2.2. *Synthesis*

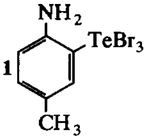
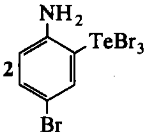
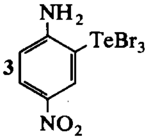
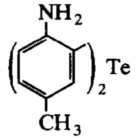
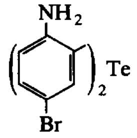
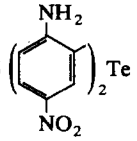
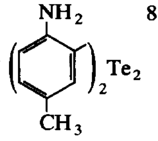
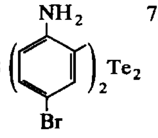
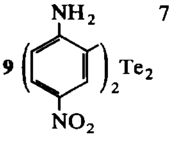
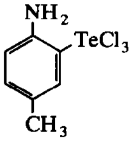
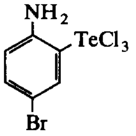
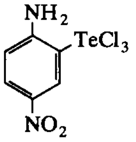
2-Amino-5-bromophenylmercury chloride (m.p. 204°C, 87% yield) and 2-amino-5-nitrophenylmercury chloride (m.p. 238°C, 85%) were prepared by the method used for the preparation of 2-amino-5-methylphenyl mercury chloride (m.p. 158–160°C, 86% yield) [11]. The C, H, N analyses for these compounds agreed well with calculated values.

Correspondence to: Prof. Dr. A.Z. Al-Rubaie.

0022-328X/93/$6.00

2-Amino-5-methylphenyltellurium tribromide (**1**), 2-amino-5-bromophenyltellurium tribromide (**2**) and 2-amino-5-nitrophenyltellurium tribromide (**3**) were prepared by reaction of tellurium tetrabromide with the corresponding 2-aminoarylmercury chloride. The general preparation route is illustrated by the following example.

TABLE 1. Isolated yield and some analytical data for compounds 1–12

Compound	Yield (%)	Melting point (°C)	Colour	Found (calc.) (%)		
				C	H	N
1 	79	256	Yellow	18.08 (17.75)	1.85 (1.75)	2.59 (2.95)
2 	71	220	Yellowish-brown	13.24 (13.38)	1.01 (0.99)	2.60 (2.60)
3 	36	84	Brown	14.15 (14.28)	0.95 (0.99)	5.29 (5.55)
4 	58	102	Brown	46.68 (46.46)	4.78 (4.72)	8.51 (8.24)
5 	43	118–120	Yellowish-brown	30.41 (30.69)	2.18 (2.14)	5.56 (5.96)
6 	55	228	Yellow	35.54 (35.86)	2.22 (2.50)	13.74 (13.94)
7 	87	190–192	Orange	36.20 (36.96)	3.36 (3.44)	5.76 (5.99)
8 	75	116	Orange-yellow	24.11 (24.13)	1.53 (1.69)	4.42 (4.69)
9 	77	97	Orange-red	27.42 (27.22)	2.21 (1.90)	10.19 (10.58)
10 	86	220–222	Yellow	24.38 (24.72)	2.24 (2.37)	3.92 (4.12)
11 	72	240–241	Pale-yellow	17.26 (17.79)	1.17 (1.24)	3.06 (3.45)
12 	57	234–236	Yellowish-orange	19.23 (19.42)	1.61 (1.35)	7.29 (7.55)

2.2.1. 2-Amino-5-methylphenyltellurium tribromide (1)

A mixture of 2-amino-5-methylphenylmercury chloride (8.6 g, 25 mmol) and tellurium tetrabromide (10.5 g, 23.4 mmol) in glacial acetic acid (150 cm^3) was refluxed for 14 h., under dry nitrogen. The solution was filtered hot and then cooled to afford a yellow precipitate, which was recrystallized from glacial acetic acid to give yellow crystals of m.p. 256°C.

2.2.2. Bis(2-amino-5-methylphenyl) telluride (4)

A solution of 2-amino-5-methylphenylmercury chloride (8.6 g, 25 mmol) and tellurium tetrabromide (5.6 g, 12.5 mmol) in dry dioxane (100 cm^3) was refluxed for 2 h. The mixture was filtered hot and on cooling deposited the 2:1 complex of dioxane and mercuric chloride as white plates, which were filtered off. The filtrate was added in small portions to ice-water with stirring during which a dark brown precipitate was formed. The residue was dissolved in hot methanol (200 cm^3), the solution was heated under reflux, and a solution of hydrazine hydrate (3.6 g) in methanol (100 cm^3) was added slowly to the refluxing solution. The solution was then filtered and cooled to room temperature to afford brown crystals of the product, which was recrystallized from benzene; m.p. 120°C.

Bis(2-amino-5-bromophenyl) telluride (**5**) and bis(2-amino-5-nitrophenyl) telluride (**6**) were prepared similarly. Bis(2-amino-5-methylphenyl) ditelluride (**7**), bis(2-amino-5-bromophenyl) ditelluride (**8**) and bis(2-amino-5-nitrophenyl) ditelluride (**9**) were all prepared by the following route.

2.2.3. Bis(2-amino-5-methylphenyl) ditelluride (7)

To a suspension of 2-amino-5-methylphenyltellurium tribromide (7.1 g, 15 mmol) in 200 cm^3 of ethanol and 30 cm^3 of water was added dropwise to a solution of hydrazine hydrate (1.8 g, 55 mmol) in ethanol (40 cm^3). The resulting solution was warmed gently until the crystals of tribromide had disappeared. Recrystallization from chloroform/ethanol gave orange crystals, m.p. 190–192°C.

2.2.4. 2-Amino-5-methylphenyltellurium trichloride (10)

Bis(2-amino-5-methylphenyl) ditelluride (2.34 g, 5 mmol) was dissolved in dry chloroform, and dry chlorine was bubbled through the solution until the red colour had disappeared; a pale yellow precipitate was formed immediately. The solution was evaporated to dryness and the residue recrystallized from methylene chloride to give yellow crystals, m.p. 220–222°C.

2-Amino-5-bromophenyltellurium trichloride (**11**) and 2-amino-5-nitrophenyltellurium trichloride (**12**) were prepared similarly.

3. Results and discussion

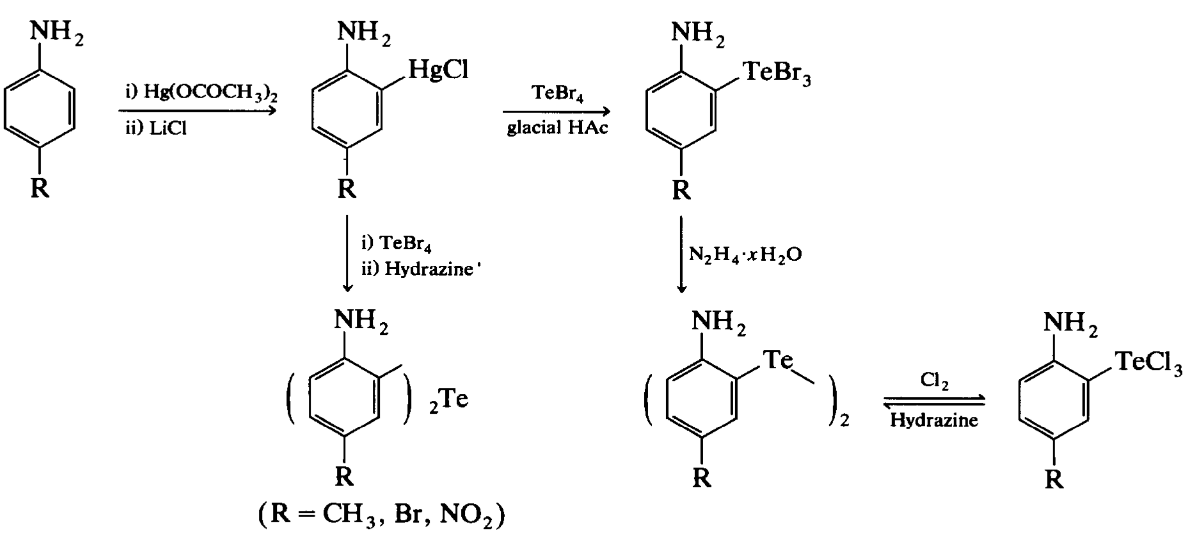
We have shown that 2-aminoaryltellurium tribromides (**1**, **2** and **3**) can be readily prepared in yields ranging from 36 to 79% by treating tellurium tetrabromide with the corresponding 2-aminoarylmercury chloride in glacial acetic acid. It is noteworthy that when dioxane or chloroform was used as solvent the yield of 2-aminoaryl tellurium tribromides was very low (< 5%).

The tellurides (*i.e.* compounds **4**, **5** and **6**) were prepared by reduction of the corresponding bis(2-aminoaryl)tellurium dibromides (not isolated) which were obtained by treating tellurium tetrabromide (1 mol) with the appropriate 2-aminoarylmercury chloride (2 mol) in dry dioxane (see Table 1).

The tribromides (compounds **1**, **2** and **3**) were reduced with an ethanolic solution of hydrazine hydrate to give the ditellurides (compounds **7**, **8** and **9**) in almost quantitative yields. The crystalline, orange ditellurides were dissolved in dry chloroform, and Cl_2 gas was passed through to afford the 2-aminoaryltellurium trichlorides (compounds **10**, **11** and **12**) in good yields. Attempts to prepare compounds **10**, **11** and **12** from reaction between tellurium tetrachloride and 2-aminoarylmercury chlorides were unsuccessful, and gave unidentified products. It is noteworthy that the reaction of $TeCl_4$ with some mercurated Schiff bases gave some oxygenated products [3]. These trichlorides (**10**, **11** and **12**) regenerated the corresponding ditellurides in about 80% yields on treatment with hydrazine hydrate in ethanol.

The methods used for the preparation of all these new compounds are shown in Scheme 1. Yields, melting points, colours, and C, H, N analytical data for all the compounds are shown in Table 1.

The IR spectra of these compounds (**1**–**12**) give characteristic bands that are quite similar to those of the mercury chlorides confirming that telluration has occurred at the position initially occupied by HgCl. All the compounds showed medium bands due to N–H asymmetric and symmetric stretching (ν_{as} and ν_s) in the



Scheme 1.

range 3455–3400 and 3345–3290 cm^{-1}, respectively. The spectra showed strong bands at 1600 cm^{-1} due to the internal deformation mode of N–H. This band appears in aniline and amine compounds at 1600 cm^{-1} [16,17].

The trichlorides (**10**, **11** and **12**) show strong bands at 325, 320 and 310 cm^{-1}, respectively which are attributed to ν(Te–Cl) [18]. The bands assigned to ν(Te–Cl) were absent from the spectra of the corresponding tribromides (**1**, **2** and **3**).

The ν(Te–C$_{\text{phenyl}}$) vibrations in the IR spectra for all compounds are consistent with those reported previously for aryltellurium compounds [19].

A comparison of the ν(N–H) bands in the IR spectra of compounds **1**–**12** with those of *p*-toluidine, *p*-bromoaniline and *p*-nitroaniline indicates that the NH$_2$ frequencies in the new compounds are shifted to a lower position. This may indicate that the NH$_2$ group coordinates to the tellurium atom by donation of the lone pair of nitrogen, as was observed for bis(*o*-aminophenyl)ditelluride [1].

^{1}H NMR spectra were measured for compounds **1**, **4**, **6**, **7**, **8**, **10** and **12** in DMSO-d_6 to look for a possible interaction between the tellurium atom and the NH$_2$ group. These compounds give the aryl proton signals at *ca.* 6.96–8.48 ppm and signals due to NH$_2$ protons at *ca.* 3.32–4.70 ppm. The values are within the typical ranges for aromatic amines [20]. One additional signal in the spectra of these compounds at around δ 2.00 ppm is due to methyl protons in **1**, **4**, **7** and **10**.

Studies of coordination of this type of organotellurium compound with transition metals are in progress.

References

1 R. E. Cobbledick, F. W. B. Einstein, W. R. McWhinnie and F. H. Musa, *J. Chem. Res. (S)*, (1979) 145.

2 M. A. K. Ahmed, W. R. McWhinnie and T. A. Hamor, *J. Organomet. Chem.*, *281* (1985) 205.

3 M. A. K. Ahmed, A. E. McCarthy and W. R. McWhinnie, *J. Chem. Soc. Dalton Trans.*, (1986) 771.

4 N. I. Al-Salim, T. A. Hamor and W. R. McWhinnie, *J. Chem. Soc., Chem. Commun.*, (1986) 453.

5 K. Y. Abid, N. I. Al-Salim, M. Greaes, W. R. McWhinnie, A. A. West and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, (1989) 1697.

6 H. B. Singh and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, (1985) 821.

7 V. I. Minkin, A. A. Maksimenko, G. K. Mehrotra, A. G. Maslakov, O. E. Kompan, I. D. Sadekov, Yu. T. Struchkov and D. S. Yufit, *J. Organomet. Chem.*, *348* (1988) 63.

8 K. J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974.

9 H. B. Singh, N. Sudha, A. A. West and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, (1990) 907.

10 M. Mbuyi, M. Evers, G. Tihange, A. Luxen and L. Christiane, *Tetrahedron Lett.*, *24* (1983) 5873.

11 T. Junk and K. J. Irgolic, *Phosph. and Sulfur*, *38* (1988) 121.

12 A. M. Fingan, *M.Sc. thesis*, University of Basrah, 1989.

13 S. A. N. Al-Jadaan, *M.Sc. thesis*, University of Basrah, 1990.

14 A. K. Singh, V. Srivastava and B. L. Khandelwal, *Polyhedron*, *9* (1990) 495.

15 B. L. Khandelwal, *The 6th International Conference on the Chemistry of Selenium and Tellurium, Osaka, Japan, 1991*, Abstract p. 18.

16 N. Fuson, M. L. Josien, R. L. Powell and E. Vtterbacks, *J. Chem. Phys.*, *20* (1952) 145.

17 S. F. Mason, *J. Chem. Soc.*, (1958) 3619.

18 W. R. McWhinnie and P. Thavornyutikarn, *J. Chem. Soc., Dalton Trans.*, (1972) 551.

19 W. R. McWhinnie and M. G. Patel, *J. Chem. Soc., Dalton Trans.*, (1972) 199.

20 R. M. Silverstein, G. C. Bassel and T.C. Moril, *Spectroscopic Identification of Organic Compounds*, 4th edition, Wiley, New York, 1981.