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SYNTHESIS AND CHARACTERIZATION OF SOME NEW ORGANOTELLURIUM COMPOUNDS CONTAINING AN ORTHO-ACETAMIDO GROUP

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Abstract—A wide range of organotellurium compounds containing an acetamido group in the position *ortho* to the tellurium atom have been prepared and characterized according to their elemental analyses, IR, ^{1}H NMR and mass spectral data.

There is increasing interest in the chemistry of organotellurium compounds containing nitrogen donors in the position *ortho* to the tellurium atom.[1–10] It has been shown that azo,[1–4] Schiff bases,[5] substituted pyridine,[6] *N*,*N*-dimethylbenzyl amine,[7] 1-(NMe$_2$)-2-TeAr-4-MeC$_6$H$_3$[8,9] and *para*-substituted anilines[10] can be orthotellurated by different methods.

Junk and Irgolic[11] described the preparation of organotellurium compounds containing an acetamido group in the position *ortho* to tellurium, namely 2-acetamido-5-methyl-, -5-tert-butyl- and -5-chlorophenyltellurium trichlorides, by reacting the corresponding 2-acetamidoarylmercury chloride with TeCl$_4$ in glacial acetic acid. Their ditellurides have been used as precursors in the preparation of 2-methylareno-3-azatellurophenes.[11]

Our previous work,[12] on the thermal behaviour of some organotellurium compounds containing an *ortho*-acetamido group, showed that these compounds extruded tellurium in addition to one or two acetamido groups in one or two steps.[12]

In this paper we describe the preparation and characterization of a number of new organotellurium compounds (**1**–**20**). Figure 1 gives the new organotellurium compound structures and numbers used in this study.

EXPERIMENTAL

Physical measurements

IR spectra were recorded as KBr pellets in the range 4000–200 cm^{-1} using a Pye-Unicam SP3-300s IR spectrophotometer. ^{1}H NMR spectra were obtained using Varian-200 (200 MHz) spectrometer solutions in CDCl$_3$ or DMSO-d_6 using TMS as internal standard. Microanalyses for carbon, hydrogen and nitrogen were carried out using a Perkin–Elmer 240B Elemental Analyser or a CHN Corder-MT3 Uanac instrument. Tellurium analysis was carried out by use of a Shimadzu-AA630-3Z atomic absorption spectrophotometer as described previously.[13] Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Mass spectral data were measured on a Finnigan MAT 1125 mass spectrometer (Universität Konstänz, Germany) at 70 eV for all compounds relative to ^{130}Te.

Synthesis

The compounds *p*-EtOC$_6$H$_4$TeCl$_3$,[14] *p*-MeOC$_6$H$_4$TeCl$_3$,[14] *p*-HOC$_6$H$_4$TeCl$_3$,[15] 2-acetamido-5-methylphenyltellurium trichloride,[11] bis(2-acetamido-5-methylphenyl)ditelluride[11] and tellurium tetrabromide were prepared according to published procedures. Solvents were dried and distilled before use.

2-Acetamido-5-bromophenylmercury chloride (m.p. 250°C, 96% yield) and 2-acetamido-5-nitro-

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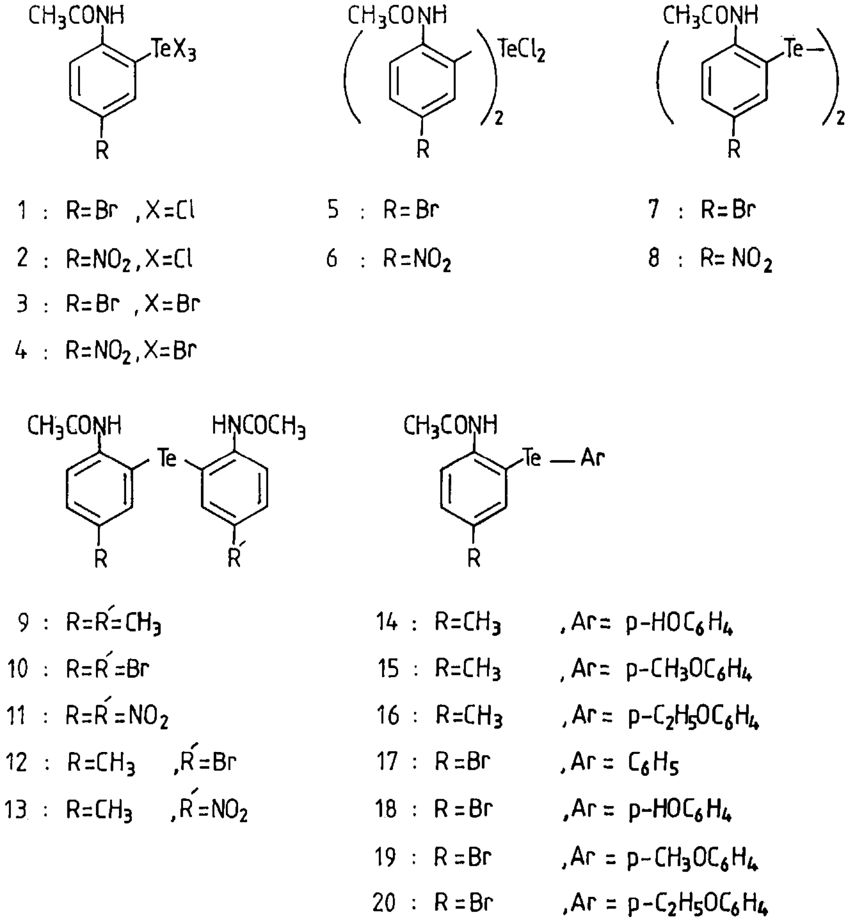

Fig. 1. New organotellurium structures and numbers used.

phenylmercury chloride (m.p. 214°C, 81% yield) were prepared by the same method as for the preparation of 2-acetamido-5-methylphenyl mercury chloride.[11] The carbon, hydrogen and nitrogen analyses for these compounds agreed well with the calculated values and are not reported.

2-Acetamido-5-bromophenyltellurium trichloride (**1**) and 2-acetamido-5-nitro-phenyltellurium trichloride (**2**) were prepared by a similar method as described for the preparation of 2-acetamido-5-methylphenyltellurium trichloride.[11]

2-Acetamido-5-bromophenyltellurium tribromide (**3**). A solution of 2-acetamido-5-bromophenyl mercury chloride (23.4 g; 52 mmol) and tellurium tetrabromide (23.4 g; 52 mmol) in glacial acetic acid (300 cm^3) was refluxed for 24 h. The solution was filtered hot. After cooling the yellow precipitate which formed was filtered off. Treatment of the solid with charcoal in hot glacial acetic acid gave a brown product of m.p. 152–154°C.

Compound **4** was prepared by the same method as for compound **3**.

Bis(2 - acetamido - 5 - bromophenyl)tellurium dichloride (**5**) and bis(2-acetamido-5-nitrophenyl) tellurium dichloride (**6**) were prepared by the same method, which is given as follows. Compound **1** (3.32 g; 4.89 mmol) and 2-acetamido-5-bromophenyl mercury chloride (2.19 g; 4.89 mmol) were mixed in 1,4-dioxane (40 cm^3). The mixture was stirred under reflux for 3 h. Cooling the mixture gave crystals of a mercury(II) halide–dioxane complex, which were removed by filtration. Concentration of the filtrate, followed by addition of petroleum ether (60–80°C), gave the crude product. The product was recrystallized from ethanol to give yellow crystals of m.p. 160°C.

The ditellurides **7** and **8** were prepared by the reduction of compound **1** and **2**, respectively, by hydrazine hydrate in boiling ethanol.[10]

Bis(2-acetamido-5-methylphenyl)telluride (**9**). 2-Acetamido-5-methylphenyl mercury chloride (2.69 g; 7 mmol) and 2-acetamido-5-methylphenyltellurium trichloride (2.67 g; 7 mmol) in 30 cm^3 of 1,4-dioxane were refluxed for 4 h. The hot mixture was filtered. On cooling, $HgCl_2 \cdot 2diox$ complex was separated as white crystals and removed by filtration. The filtrate was added in small portions to ice-distilled water with continuous stirring, during which a yellow precipitate was formed which was dissolved in hot methanol. Hydrazine hydrate in hot methanol was added dropwise until the evolution of nitrogen ceased. The resulting solution was poured into 1 dm^3 of water and a yellow solid formed. The product was recrystallized from chloroform to give a yellow precipitate, m.p. 138°C.

Compounds **10** and **11** were prepared by the same above method used for **9**.

2-Acetamido-5-methylphenyl-2′-acetamido-5′-bromophenyltelluride (**12**). 2-Acetamido-5-bromophenyl mercury chloride (3.13 g; 7 mmol), 2-acetamido-5-methylphenyltellurium trichloride (2.67 g; 7 mmol) and dry dioxane (30 cm^3) were refluxed for 3 h. The hot mixture was filtered and the filtrate cooled to room temperature. The filtrate was added in small portions to ice-water with continuous stirring. The yellow precipitate was reduced by potassium metabisulphite in aqueous medium at 0°C.

Compound **13** was prepared by the same method as above.

Compounds **14–16** and **18–20** were all prepared by the reaction of aryltellurium trichloride with the corresponding 2-acetamidoaryl mercury chloride. The general synthesis is illustrated by the following example.

2-Acetamido-5-bromophenyl-4′-ethoxyphenyltelluride (**20**). *p*-Ethoxyphenyltellurium trichloride (5.0 g; 14 mmol) and 2-acetamido-5-bromophenylmercury chloride (6.32 g; 14 mmol) were refluxed in 40 cm^3 of dioxane for 3 h. The hot mixture was filtered and cooled to room temperature. The $HgCl_2 \cdot 2diox$ complex was removed by filtration. A yellow precipitate of 2-acetamido-5-bromophenyl-4′-ethoxyphenyltellurium dichloride was filtered and dried. The yellow solid was reduced by potassium metabisulphite in distilled water at 0°C.

2-Acetamido-5-bromophenyl-phenyltelluride (**17**). A mixture of 2-acetamido-5-bromophenyltellurium trichloride (2.23 g; 5 mmol) and triphenyltin chloride (1.93 g; 5 mmol) in 25 cm^3 of toluene was refluxed for 3 h. The hot mixture was filtered. The filtrate was reduced to 10 cm^3 and followed by addition of petroleum ether (b.p. 60–80°C) to give a pale yellow precipitate of the corresponding dichloride. The product was reduced without further purification by sodium sulphide nonahydrate in aqueous medium at 100°C.

RESULTS AND DISCUSSION

Isolated yields, melting points, colour, and carbon, hydrogen and nitrogen analytical data for all new organotellurium compounds are shown in Table 1.

The present work describes the synthesis of new organotellurium compounds by reacting arylmercury chloride with $TeCl_4$, $TeBr_4$ or aryltellurium trichloride to produce the required tellurium-containing materials. Thus, TeX_4 (X = Cl, Br) and 2-acetamidoarylmercury chloride are capable of producing 2-acetamidoaryltellurium trihalides (i.e. compounds **1–4**) when brought together in a 1 : 1 ratio. Reduction of **1** and **2** by ethanolic solution of hydrazine hydrate yielded the corresponding ditellurides (**7** and **8**), respectively.

The reaction of 2-acetamidoaryltellurium trichlorides with 2-acetamidoarylmercury chlorides is a convenient method for the preparation of symmetrical (**9–11**) and unsymmetrical (**12** and **13**) tellurides. The primary product in these reactions is the diaryltellurium dichloride (not isolated, except **5** and **6**), which is subsequently reduced by hydrazine hydrate.

Compounds **14–16** and **18–20** were prepared similarly by reacting *p*-ethoxy-, *p*-methoxy- or *p*-hydroxyphenyltellurium trichlorides with appropriate 2-acetamidoarylmercury chlorides in dry dioxane, followed by reduction of the dichlorides by potassium metabisulphite in aqueous medium at 0°C. Compound **17** was prepared by reacting compound **1** with triphenyltin chloride in dry toluene as shown in eq. (1):

$$\begin{array}{l} \text{2-HNCOCH}_3\text{-5-BrC}_6\text{H}_3\text{TeCl}_3 + \text{Ph}_3\text{SnCl} \longrightarrow \\ \qquad\qquad (\text{2-HNCOCH}_3\text{-5-BrC}_6\text{H}_3)\text{PhTeCl}_2 \\ \qquad\qquad\qquad\qquad \big\downarrow \text{red} \\ \qquad\qquad \text{2-HNCOCH}_3\text{-5-BrC}_6\text{H}_3\text{-Te-Ph} \end{array} \tag{1}$$

IR spectra (KBr discs) of all compounds showed medium bands due to N—H stretching vibration in the region 3230–3280 cm^{-1} and very strong bands in range 1600–1665 cm^{-1} due to ν(C═O). The trichlorides (i.e. **1** and **2**) and the dichlorides (**5** and **6**) showed strong bands at 315, 320, 320 and 330 cm^{-1}, respectively, which are attributed to ν(Te—Cl).[10,16,17] The bands assigned to ν(Te—Cl) were absent in the spectra of the corresponding bromide derivatives (i.e. compounds **3** and **4**). The ν(Te—C$_{\text{phenyl}}$) vibrations in the IR spectra of all compounds are consistent with earlier reports on aryltellurium compounds.[18,19] Table 2 lists the important vibration frequencies for some selected compounds.

In the ^{1}H NMR spectra, the expected ratio of aliphatic to aromatic protons was observed. The methyl protons (CH_3CO) appeared as a singlet at

Table 1. Physical and analytical data for the new compounds (**1**–**20**)

Compound	Colour	Melting point (°C)	Yield (%)	Analysis (%)[a] C	H	N
1	White	230–232	64	21.4 (21.5)	1.5 (1.6)	3.4 (3.1)
2	Yellow	154	38	23.1 (23.3)	1.8 (1.7)	6.5 (6.8)
3	Brown	152–153	48	19.0 (19.3)	1.3 (1.4)	2.2 (2.8)
4	Pale yellow	95–96	41	17.9 (17.6)	1.7 (1.3)	4.9 (5.1)
5	White	160	45	30.6 (30.7)	2.3 (2.2)	4.1 (4.5)
6	Yellow	198–200	39	*b*	*b*	*b*
7	Orange–red	225	46	28.4 (28.2)	2.1 (2.1)	4.4 (4.1)
8	Orange–red	240–242	52	31.8 (31.3)	2.4 (2.3)	8.8 (9.1)
9	Pale yellow	138	62	51.3 (50.99)	4.5 (4.7)	6.4 (6.6)
10	Yellow	128	75	34.9 (34.7)	2.7 (2.5)	5.2 (5.1)
11	Yellow	120	58	39.7 (39.5)	2.7 (2.9)	11.2 (11.5)
12	Yellow	162	57	41.4 (41.8)	3.8 (3.5)	5.5 (5.7)
13	Yellow	92	72	45.9 (45.8)	3.6 (3.8)	9.5 (9.2)
14	Pale yellow	216	68	48.9 (48.8)	3.9 (4.1)	9.5 (9.2)
15	Pale yellow	106	59	49.8 (50.2)	4.7 (4.5)	3.5 (3.7)
16	White	182	64	51.3 (51.4)	4.9 (4.8)	3.6 (3.5)
17	Yellow	125	53	40.0 (40.2)	2.9 (2.9)	3.4 (3.3)
18	Pale yellow	168	65	38.7 (38.8)	2.6 (2.8)	6.0 (6.0)
19	Pale yellow	139	66	40.4 (40.2)	3.3 (3.1)	3.5 (3.1)
20	White	158	79	41.6 (41.6)	3.7 (3.5)	3.2 (3.0)

[a] Calculated values are given in parentheses.
[b] Te, Found: 22.7. Calc. 22.9%.

Table 2. Some IR and ^{1}H NMR data for selected compounds

Compound	IR (cm^{-1}) ν(NH)	ν(C=O)	ν(C—N)	ν(Te—C)	^{1}H NMR (ppm) in CDCl$_3$[a]
1	3260s	1640s	1290s	280w	2.12 (CH$_3$, s, 3H); 6.97 (NH, sb, 1H); 7.28 (Ar-H3, d, 1H); 8.02 (Ar-H4, d, d, 1H); 8.34 (Ar-H6, d, 1H)
2	3280s	1655s	1295s	280w	2.09 (CH$_3$, s, 3H); 6.97 (NH, sb, 1H); 7.79 (Ar-H3, d, 1H); 8.18 (Ar-H4, d, d, 1H); 8.57 (Ar-H6, d, 1H)
7	3280s	1660s	1295s	280w	2.15 (CH$_3$, s, 3H); 6.47 (NH, sb, 1H); 7.22 (Ar-H3, d, 1H); 8.16 (Ar-H4, d, d, 1H); 8.38 (Ar-H6, d, 1H)
8	3260s	1660s	1280s	285w	2.11 (CH$_3$, s, 3H); 6.24 (NH, sb, 1H); 7.08 (Ar-H3, d, 1H); 7.59 (Ar-H4, dd, 1H); 7.85 (Ar-H6, d, 1H)
9	3240s	1635s	1290s	285w	1.88 (CH$_3$, s, 3H); 2.21 (CH$_3$, s, 3H); 6.25 (NH, sb, 1H); 7.25–8.34 (Ar-H, m, 3H)
10	3240s	1640s	1290s	290w	2.25 (CH$_3$, s, 3H); 7.25 (NH, sb, 1H); 7.15–8.35 (Ar-H, m, 3H)
19	3240s	1640s	1290s	280w	2.13 (CH$_3$, s, 3H); 6.25 (NH, sb, 1H); 7.05–8.26 (Ar-H, m, 8H)
20	3250m	1635s	1290s	280w	1.39 (CH$_3$, t, 3H); 2.04 (CH$_3$, s, 3H); 3.96 (CH$_2$, q, 2H); 7.75 (NH, sb, 1H); 6.70–8.16 (Ar-H, m)

[a] Compounds **1** and **2** in DMSO-d_6.

around 2.00 ppm, while the NH proton appeared as a broad singlet in the range *ca* 6.20–7.25 ppm. Some representative ^1H NMR data for the new compounds are gathered in Table 2.

The electron-impact mass spectrum of one of the derivatives (**1**) was recorded. As with organotellurium compounds,[19] a molecular ion is absent. This can be attributed either to pyrolytic decomposition, in the direct inlet, under the high temperature which was used, or to electron impact. Some ions visible in the spectrum are $[M-HCl]^{+\cdot}$, $[M-HCl-Cl_2]^{+\cdot}$, $[M-CH_3CO-Te]^{+\cdot}$, $[TeH]^{+\cdot}$ and $[C_5H_3]^{+\cdot}$.

Evidence is available to suggest that the new organotellurium compounds may form complexes with a range of metal salts.

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REFERENCES

1. R. E. Cobbledick, F. W. B. Einstein, W. R. McWhinnie and F. H. Musa, *J. Chem. Res.* (*S*) 1979, 145; (*M*) 1979, 1901.
2. M. A. K. Ahmed, W. R. McWhinnie and T. A. Hamor, *J. Organomet. Chem.* 1985, **281**, 205.
3. M. A. K. Ahmed, A. E. McCarthy, W. R. McWhinnie and F. J. Berry, *J. Chem. Soc., Dalton Trans.* 1986, 771.
4. A. Z. Al-Rubaie, A. I. Auoob and T. A. K. Al-Allaf, *Iraqi J. Chem.*, in press, 1994.
5. (a) H. B. Singh and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.* 1985, 821; (b) 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.* 1988, **348**, 63.
6. H. J. Gysling, H. R. Luss and A. Gardner, *J. Organomet. Chem.* 1980, **184**, 417.
7. H. B. Singh, N. Sudha, A. A. West and T. A. Hamor, *J. Chem. Soc., Dalton Trans.* 1990, 907.
8. B. L. Khandelwal, *6th International Conference on the Chemistry of Selenium and Tellurium*, Osaka, Japan, Abstract, p. 18 (1991).
9. A. K. Singh, V. Srivastava and B. L. Khandelwal, *Polyhedron* 1990, **9**, 495.
10. A. Z. Al-Rubaie, N. I. Al-Salim and S. A. N. Al-Jadaan, *J. Organomet. Chem.* 1993, **443**, 67.
11. T. Junk and K. J. Irgolic, *Phosphorus and Sulfur* 1988, **38**, 121.
12. A. Z. Al-Rubaie, N. I. Al-Salim and S. A. N. Al-Jadaan, *Thermochim. Acta* 1993, **215**, 235.
13. P. Thavornyutikarn, *J. Organomet. Chem.* 1973, **51**, 237.
14. (a) N. Petragnani and J. V. Comasseto, *Synthesis* 1986, 1; (b) N. Petragnani, *Tetrahedron* 1960, **11**, 15.
15. B. L. Khandelwal, K. Kumar and F. J. Berry, *Inorg. Chim. Acta* 1981, **47**, 135.
16. W. R. McWhinnie and P. Thavornyutikarn, *J. Chem. Soc., Dalton Trans.* 1972, 551.
17. W. E. Rudizski, T. M. Aminabhavi, N. S. Biradar and C. S. Patil, *Inorg. Chim. Acta* 1982, **67**, 177.
18. W. R. McWhinnie and M. G. Patel, *J. Chem. Soc., Dalton Trans.* 1977, 199.
19. A. Z. Al-Rubaie, *J. Organomet. Chem.* 1990, **382**, 383.