Asian Journal of Chemistry Vol. 7, No. 4 (1995), 685–690

New Organotellurium Compounds Cyclized from Phthalic Anhydride Derivatives

ALA'A I. AYOOB† and TALAL A.K. AL-ALLAF*
Chemistry Department, College of Science, University of Mosul, Mosul, Iraq

New heterocyclic tellurium(IV) compounds of the general formula $C_{10}H_8O_3Te(R)(X)$, where R = X = Cl^-, Br^-, I^-, or R = methyl, ethyl, allyl; X = Br^-, I^-, have been prepared starting from 2,3-dimethyl-1,3-butadiene and maleic anhydride *via* conversion into several intermediates to give the cyclic tellurium(IV) compounds as final products. These compounds have been characterized on the basis of their physical properties. The IR spectral data for these compounds showed a characteristic absorption band, attributable to Te—C bonds. The ^1H NMR spectra recorded in DMSO-d_6 showed considerable stability towards reductive-elimination reactions and do not interact with solvent used. The molar conductivities measured in DMSO or DMF indicate that these compounds are weak electrolytes and there is some ion pairing.

INTRODUCTION

An extensive work was done on the synthesis of organotellurium compounds and their stability in both inert and donor solvents. The compounds $C_4H_8Te(R)(X)$[1] and $C_8H_8Te(R)(X)$[2] showed a noticeable stability when present in both inert or donor solvents, also stable towards reductive-elimination reactions. In contrast, diaryl telluride[3, 4] and phenoxy tellurine[5] compounds showed some instability towards reductive-elimination reactions by interacting with the donor solvent used. Furthermore, the five-membered ring quinoxaline tellurium compound, *i.e.*, $C_8H_8N_2TeI_2$[6] was also prepared and found to form complex species on using an excess of the reactants in 2-ethoxyethanol as solvent.

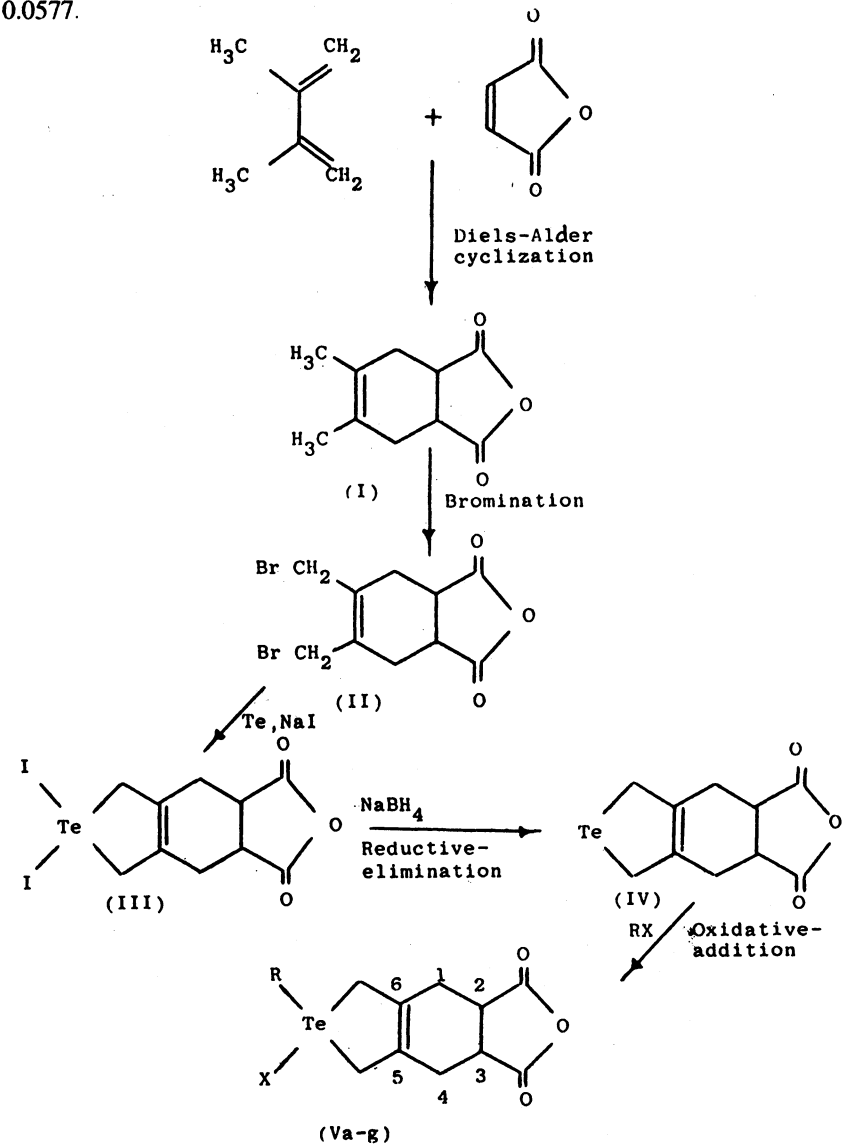
As a continuation of our previous work on the preparation of the tellurium(IV) compounds $(2\text{–}CH_3)C_5H_9\text{–}1\text{–}Te(R)(X)$[7] and their behaviours in donor solvents (DMSO and DMF), we are presenting here, the synthesis and properties of new type of tellurium(IV) compounds, *i.e.*, $C_{10}H_8O_3Te(R)(X)$ *via* long processes starting from 2,3-dimethy-1,3-butadiene and maleic anhydride (Scheme-1).

EXPERIMENTAL

^1H NMR spectra were recorded on a Hitachi Perkin-Elmer R-248 HR-60 MHz spectrometer using the deuterium signal of the solvent (DMSO-d_6) as a field lock signal. IR spectra were recorded on a Beckman TM spectrometer with KBr discs in the range 4000–400 cm^{-1}. Solution conductivities were measured with a WTW

†Chemistry Department, College of Science, University of Basrah, Basrah, Iraq.

conductivity meter LBR, using a standard conductivity cell with cell constant of 0.0577.



Scheme 1. Preparation of $C_{10}H_8Te(R)(X)$ compounds. (For R and X see text.)

Preparation of the Compounds

1,2,3,4-tetrahydro-5,6-dimethyl phthalic anhydride (I)

The freshly distilled 2,3-dimethyl-1,3-butadiene (0.05 mL) was added to the finely crushed maleic anhydride at room temperature. An exothermic reaction was observed for few minutes, then it was left aside at room temperature for completion. The unreacted maleic anhydride was removed from the solid by

extraction with cold water several times until the extract did not give acidic test with the congo red. The white solid was dried in air, then crystallized from petroleum ether (60–80°C) to give pure white product (m.p. 79–81°C).

1,2,3,4-tetrahydro-5,6-dibromomethyl phthalic anhydride (II)

Compound (I) (0.1 mol) was mixed with N-bromosuccinimide (0.2 mol) and benzoyl peroxide (0.5 g) in carbon tetrachloride (100 mL). The mixture was refluxed for *ca.* 30 min., then left aside to cool down to room temperature. The reaction mixture was filtered to remove any solid that might form. The filtrate was evaporated to dryness and the solid residue was crystallized from ethanol to give white product, m.p. (130–132°C).

1,2,3,4-tetrahydro-5,6-[2H] diiodo telluropheno phthalic anhydride (III)

Compound (II) (0.1 mol) was mixed with powdered tellurium metal (0.1 mol) and sodium iodide (0.4 mol), and 2-ethoxyethanol was added. The mixture was heated slowly with continuous strirring for ca. 2 h until the colour of the solution became deep red. The reaction mixture was filtered immediately, then allowed to cool to room temperature, followed by the addition of distilled water (ca. 300 mL). The brown solid thus formed, was filtered off, washed with water and dried in air. The crude product was crystallized from ethanol to give brown crystals.

1,2,3,4-tetrahydro-5,6-[2H] telluropheno phthalic anhydride (IV)

The compound (III) (0.01 mol) was dissolved in ethanol (30 mL) and the solution was heated slowly under continuous stirring. Small portions of sodium borohydride were added carefully and the solution was filtered, and distilled water (30 mL) was added. The organic product was extracted with ether (3 × 30 mL) and the ethereal layer was collected and dried over magnesium sulphate. Slow evaporation of the ether gave the off-white solid product.

1,2,3,4-tetrahydro-5,6-[2H] dibromo telluropheno phthalic anhydride (Va)

Bromine solution in ether was added under continuous stirring to a stoichiometric amount of compound (IV) in ether. The off-white solid thus formed was filtered off, washed with ether and crystallized from ethanol to give white crystals.

1,2,3,4-tetrahydro-5,6-[2H] dichloro telluropheno phthalic anhydride (Vb)

This was prepared by a method similar to that reported[7], by treating the compound (IV) with sulphonyl chloride. White crystals were formed on crystallization of the product from ethanol.

1,2,3,4-tetrahydro-5,6-[2H] halo (X) alkyl (R) telluropheno phthalic anhydride

$$X = I^-,\ R = CH_3\ (Vc),\ C_2H_5\ (Vd),\ C_3H_5\ (Ve);$$

$$X = Br^-,\ R = C_2H_5\ (Vf),\ C_3H_5\ (Vg).$$

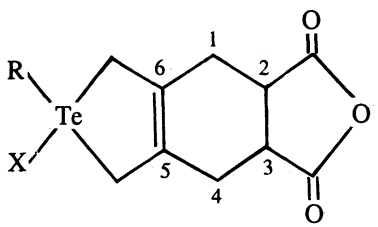
These were prepared by the reaction of compound (IV) with alkyl halide (RX).

RESULTS AND DISCUSSION

The new tellurium compounds $C_{10}H_8O_3\ Te(R)(X)$, $R = X = Cl^-$, Br^-, I^- or

R = CH_3, C_2H_5, C_3H_5; X = Br^-, I^-, were prepared as presented in Scheme 1. The physical properties of these compounds are listed in Table-1, and their ^1H NMR spectral data recorded in DMSO-d_6 are briefed in Table-2.

TABLE-1
PHYSICAL PROPERTIES OF TELLURIUM COMPOUNDS.



Comp.*	X	R	Colour	m.p. (°C)	IR data (cm^{-1})				Conductivity† (Λ_M) ($ohm^{-1}cm^2mol^{-1}$)	
					ν(C—H)	ν(Te—C)	ν(C=C)	ν(C=O)	DMSO	DMF
III	I	I	brown	185–187	2870	460	1610	1680, 1725	15.3	16.4
IV	—	—	off-white	135–136	2870	480	1615	1685, 1730	—	–
Va	Br	Br	white	176–177	2875	485	1610	1680, 1725	12.7	13.5
Vb	Cl	Cl	white	161–163	2870	480	1610	1680, 1725	7.6	9.9
Vc	I	CH_3	white	207–209	2870	525	1610	1690, 1730	18.9	26.6
Vd	I	C_2H_5	off-white	215–217	2870	530	1610	1690, 1730	17.2	25.2
Ve	I	C_3H_5	off-white	203–204	2870	535	1615	1690, 1730	25.3	46.3
Vf	Br	C_2H_5	white	211–213	2870	515	1610	1690, 1730	21.3	35.7
Vg	Br	C_3H_5	white	195–197	2870	535	1615	1690, 1730	30.1	50.1

* Elemental analyses for the compounds were satisfactory.
† Molar conductivities were measured for 10^{-3} M solutions of the compounds. $[(C_2H_5)_4N]Cl$: Λ_M 30(DMSO), 80(DMF) ohm^{-1} cm^2 mol^{-1}.

The IR spectral data for these compounds showed no unusual features. The IR absorption band appeared at *ca.* 725 cm^{-1} for ν(C—Br) of compound (II) (Scheme 1) completely disappeared in the tellurium compounds (III, IV, Va–g) and a characteristic band at *ca.* 525 cm^{-1} appeared, which is attributed to ν(Te—C). Other bands attributed to ν(C—H) ν(C=C) and ν(C=O) were also observed (Table-1).

TABLE-2
PROTON CHEMICAL SHIFT (δppm)[X] FOR THE TELLURIUM COMPOUNDS

Comp.	Formula	Chemical shift (ppm) and assignment[Y]	
I	$C_{10}H_{10}O_3$	1.65 (s)	—CH_3
		2.25 (s)	H(Cl, 4)
II	$C_{10}H_8O_3Br_2$	2.40 (s)	H(Cl, 4)
		3.30 (s)	—CH_2Br
III	$C_{10}H_8O_3TeI_2$	2.40 (s)	H(Cl, 4)
		3.25 (s)	Te—CH_2
IV	$C_{10}H_8O_3Te$	2.25 (s)	H(Cl, 4)
		3.10 (s)	Te—CH_2
Va	$C_{10}H_8O_3TeBr_2$	2.35 (s)	H(Cl, 4)
		3.20 (s)	Te—CH_2
Vb	$C_{10}H_8O_3TeCl_2$	2.30 (s)	H(Cl, 4)
		3.18 (s)	Te—CH_2
Vc	$C_{10}H_8O_3Te(CH_3)I$	1.80 (s)	—CH_3
		2.35–2.55 (m)	H(Cl, 4)
		3.10–3.50 (m)	Te—CH_2
Vd	$C_{10}H_8O_3Te(C_2H_5)I$	1.35 (t)	—CH_3
		2.59 (q)	—$CH_2(C_2H_5)$
		2.35–2.45 (m)	H(Cl, 4)
		3.20–3.40 (m)	Te—CH_2
Ve	$C_{10}H_8O_3Te(C_3H_5)^ZI$	3.65 (d)	Te—$CH_2(\alpha)$
		4.90–5.50 (m)	CH(β)
		5.75–5.85 (m)	$CH_2(\gamma)$
		2.35–3.45 (m)	H(Cl, 4)
		3.35–3.40 (m)	Te—CH_2
Vf	$C_{10}H_8O_3Te(C_2H_5)Br$	1.40 (t)	—CH_3
		2.59 (q)	—$CH_2(C_2H_5)$
		2.35–2.45 (m)	H(Cl, 4)
		3.30–3.40 (m)	Te—CH_2
Vg	$C_{10}H_8O_3Te(C_3H_5)^ZBr$	3.55 (d)	Te—$CH_2(\alpha)$
		4.70–5.20 (m)	CH(β)
		5.50–5.65 (m)	$CH_2(\gamma)$
		2.30–2.45 (m)	H(Cl, 4)
		3.35–3.45 (m)	Te—CH_2

[X]Downfield from internal TMS, using DMSO-d_6 as a solvent
[Y]Abbreviations, s, d, t, q, m are for singlet, doublet, triplet, quartet and multiplet respectively.
[Z]Greek letters, α, β and γ are for numbering the allyl carbons —CH_2—CH=CH_2 respectively.

The molar conductivities (Λ_M) for the compounds were measured in DMSO and DMF solutions (Table-1) for 10^{-3} M concentration (C). The data obtained from the plots between Λ_M versus $\sqrt{C}$ showed that these compounds are weak electrolytes in both solvents. The results obtained with the present tellurium

compounds are almost certainly similar to those obtained from our previous compounds[7], which indicate that an appreciable ion pairing between the cation (tellurium site) and the anion exists, but in DMSO at least, the values of Λ_M (Table-1) nearly approach those expected for 1 : 1 electrolytes. Similar to our previous observations with the compounds (2–CH_3) C_5H_9–1–Te(R)(X), R = X = Cl^-, Br^-, I^-; the values of Λ_M for the present dihalide compounds (III, Va and Vb) are less than those for the rest of tellurium compounds (Table-1). Again this may be attributed to the possible association of these compounds *via* weak ionic bonds in both solvents or due to inductive effects caused by the halogen attached covalently to tellurium.

The ^1H NMR data for the compounds $C_{10}H_8O_3Te(R)(X)$ (R = X = I^-, III; Br^-, Va; Cl^-, Vb) (Table-2) showed two singlets, *e.g.*, at 2.4 and 3.2 ppm which are attributed to H(Cl, 4) and H_2C—Te protons respectively (Scheme 1). On substituting one halogen by alkyl group, *i.e.*, CH_3, C_2H_5 or C_3H_5, the ^1H NMR pattern became more complicated, which showed multiplet signals for H(Cl, 4) and H_2C-Te protons, due to splitting of these protons by the protons of the alkyl group, as well as due to the disappearance of the symmetry of these compounds. Furthermore, the ^1H NMR spectrum of the compound (Vc), *i.e.* $C_{10}H_8O_3Te(CH_3)I$ was recorded in DMSO-d_6 at each 30 min interval, and showed that there is no change in the spectrum even after 24 h. This confirmed the fact that these compounds are rather stable towards reductive elimination reactions, which are common with the diaryl telluride compounds[3, 4]. Moreover, no signal appeared at *ca.* 2 ppm; characteristic to the methyl protons of d_6-DMSO, indicating that there is no interaction between these compounds and the solvent, which was observed with the telluronium salts derived from phenoxy tellurine[5].

ACKNOWLEDGEMENT

The authors are grateful to Dr. Mikdad T. Ayoub, Chemistry Department, College of Science, University of Mosul, Iraq, for assistance in naming the tellurium compounds of the present work.

REFERENCES

1. A.Z. Al-Rubaie, W.R. McWhinnie, P. Granger and S. Chapelle, *J. Organometal. Chem.*, **234**, 287 (1982).
2. A.Z. Al-Rubaie, H.A. Al-Shirayda, P. Granger, and S. Chapelle, *J. Organometal. Chem.*, **287**, 321 (1985).
3. F.H. Musa and W.R. McWhinnie, *J. Organometal. Chem.*, **159**, 37 (1978).
4. N.S. Dance, W.R. McWhinnie, J. Mallaki, and Z.M. Mirzai, *J. Organometal. Chem.*, **198**, 131 (1980).
5. D.P. Rainville and R.A. Zingaro, *Inorg. Chim. Acta*, **86**, L33 (1984).
6. H.B. Singh, W.R. McWhinnie, T.M. Hamor, and R.H. Jones, *J. Chem. Soc. Dalton Trans.*, 23 (1984).
7. A.I. Ayoob, T.A.K. Al-Allaf, and S.A. Mohammed, *Asian J. Chem.* (in press).

(*Received*: 5 April 1994; *Accepted*: 20 January 1995) AJC-938