Synthesis of the New Bidentate Tellurium Ligands, $(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{CH}_2)_n\text{Te}(\text{C}_6\text{H}_4\text{OEt-}p)$ (n = 1, 5, 6, 7, 9, or 10)

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The reaction between NaTeR ($\mathrm{R = C_6H_4OEt}$-p) and $\mathrm{Br(CH_2)_nBr}$ (n = 1, 5, 6, 7, 9, or 10) gives the bis(tellurides) $\mathrm{(RTe)_2(CH_2)_n}$. For the single case of n = 5, a telluronium salt $[\mathrm{R\overline{Te(C}H_2)_5}]\mathrm{Br}$ may be isolated under some experimental conditions. The new materials are characterised spectroscopically and, in particular, the $^{13}\mathrm{C}$-{^{1}H} n.m.r. spectra are discussed. Attempts to brominate some of the higher members of the series led to rupture of the Te–aryl bond and the isolation of $\mathrm{(Br_3Te)_2(CH_2)_n}$, where n = 6 or 10.

We recently reported the synthesis of $[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2\text{CH}_2$ in charge-transfer complexes with dihalogenomethanes,[1] but it was observed that the reaction of NaTeR (R = aryl) with dibromoalkanes $\mathrm{Br(CH_2)_nBr}$ (n = 2, 3, or 4) failed to give the bis(tellurides), since for n = 2, rapid elimination of ditelluride occurred to give ethene; and for n = 3 or 4 nucleophilic attack by $\mathrm{RTe^-}$ was followed by a rapid internal quaternisation on tellurium. In this report we describe the successful syntheses of the bis(tellurides) $[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2(\text{CH}_2)_n$, where n = 5, 6, 7, 9, or 10, which we required for study of their ligand chemistry.

Experimental

(a) *Syntheses.*—The method is conveniently demonstrated with reference to 1,5-dibromopentane.

1,5-*Bis*(p-*ethoxyphenyltelluro*)*pentane*. Bis(p-ethoxyphenyl) ditelluride (4.97 g, 10 mmol) in benzene (10 cm^3) and ethanol (20 cm^3) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6 g) in a 1 mol dm^{-3} solution of sodium hydroxide (12 cm^3) was added dropwise, the reaction mixture becoming colourless on completion of the addition. 1,5-Dibromopentane (2.3 g, 10 mmol) was added immediately and the mixture was stirred without heating for 1.75—2 h, after which it was poured into distilled water. The organic layer was separated and again washed with water, after which acetonitrile was added to induce precipitation. The precipitate was separated and dried *in vacuo* over $\mathrm{P_4O_{10}}$. Recrystallisation (twice) from acetonitrile gave an orange-yellow *product*, m.p. 63—65 °C, in 52% yield.

Exactly similar methods were used to prepare $[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2(\text{CH}_2)_n$ (n = 6, 7, 9, and 10). (There is no significance in the omission of n = 8.)

1-*Bromo*-1-p-*ethoxyphenyl*-1λ^4-*telluracyclohexane*. In the case of 1,5-dibromopentane only it was possible, by variation of experimental conditions, to observe intramolecular quaternisation on tellurium. Thus, bis(p-ethoxyphenyl) ditelluride (4.97 g, 10 mmol) in benzene (10 cm^3) and ethanol (20 cm^3) was heated to reflux under dinitrogen and treated with a solution of sodium tetrahydroborate (0.6 g) in 1 mol dm^3 sodium hydroxide (12 cm^3). 1,5-Dibromopentane (9.2 g, 40 mmol) was added and the still warm mixture was stirred for 30 min during which time a white precipitate deposited. Separation of the precipitate, drying over $\mathrm{P_4O_{10}}$, and recrystallisation from acetonitrile gave a white *compound*, m.p. 203—204 °C, in 50% yield.

Bis(p-*ethoxyphenyltelluro*)*methane*. This compound can be prepared by reaction of the stoicheiometric quantities of $\mathrm{NaTe(C_6H_4OEt}$-$p)$ and $\mathrm{CH_2I_2}$. On separation of the organic layer and treatment with acetonitrile at 0 °C over 1.5—1.75 h, the material was obtained as a yellowish green solid of m.p. 42—43 °C in 52% yield.

Reaction of $[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2(\text{CH}_2)_n$ (n = 6 *or* 10) *with bromine*. Excess of bromine in $\mathrm{CCl_4}$ was mixed with a benzene solution of $[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2(\text{CH}_2)_n$ and the resulting solution was shaken at room temperature for 3 d.

Table 1. Elemental analyses and molar conductivities of new organotellurium compounds (R = p-$\mathrm{EtOC_6H_4}$)

		Analysis				
		Found (%)		Calc. (%)		
Compound	Yield (%)	C	H	C	H	Λ_M/ohm^{-1} cm^2 mol^{-1}
$\mathrm{(RTe)_2(CH_2)_n}$						
n = 5	52	44.2	4.30	44.4	4.90	4.1 (dmf)
n = 6	60	45.5	5.30	45.4	5.20	1.7 (dmf)
n = 7	47	46.6	5.50	46.4	5.40	3.9 (dmf)
n = 9	50	47.8	5.90	48.1	5.80	3.2 (dmf)
n = 10	55	49.4	6.10	49.0	6.00	2.5 (dmf)
$[\mathrm{R\overline{Te(C}H_2)_5}]\mathrm{Br}$	50	40.0	4.70	39.1	4.80	99.3 (water) 61.2 (dmf)
$\mathrm{(Br_3Te)_2(CH_2)_6}$	40	9.10	1.30	8.80	1.50	
$\mathrm{(Br_3Te)_2(CH_2)_{10}}$	40	13.3	1.50	13.7	2.30	

The yellow precipitate of $(\text{Br}_3\text{Te})_2(\text{CH}_2)_n$ was filtered off, washed with CCl_4 and benzene, and dried *in vacuo* to m.p. 151—153 °C ($n = 6$; yield 42%) or 157—159 °C ($n = 10$; yield 40%).

Analytical data are gathered into Table 1, together with some other physical data.

(b) *Physical Measurements.*—Infrared spectra (4 000—200 cm^{-1}) were measured with a Perkin-Elmer 599B spectrophotometer and mass spectra with an AEI MS9 instrument (70 eV, 1 eV = 1.60×10^{-19} J). Elemental analyses were by the Analytical Services Section, Department of Molecular Sciences, Aston University. Conductivities, measured over a concentration range where necessary, were determined with a Mullard bridge.

Proton and ^{13}C n.m.r. spectra were determined with Perkin-Elmer R 12B and JEOL FX 90Q instruments respectively. In both cases SiMe_4 was the internal standard. ^1H N.m.r. data are in Table 2 and the ^{13}C data constitute Table 3.

Discussion

Our previous attempts to synthesize $(\text{RTe})_2(\text{CH}_2)_n$ ($n = 3$ or 4; R = aryl) were frustrated by the fact that under all conditions tried, internal quaternisation was always faster than nucleophilic attack by RTe^- on the second C–Br bond of the precursor $\text{Br}(\text{CH}_2)_n\text{Br}$.[1] In the one case of 1,5-dibromopentane it is possible, by manipulating the experimental conditions, to obtain either a telluronium salt or the bis(telluride). Thus, the white material obtained by use of excess of 1,5-dibromopentane has a high conductivity in both dimethylformamide (dmf) and water (Table 1) although the concentration dependence of this conductivity in dmf indicates significant ion pairing. The mass spectrum of the compound shows a parent ion at $m/e = 402$ (based on ^{130}Te), which indicates association in the gas phase; the fragmentation pattern is very similar to those observed for related compounds. The ^{13}C n.m.r. data (Table 3) are also quite conclusive for the cyclic compound $[(p\text{-EtOC}_6\text{H}_4)\overline{\text{Te}(\text{C}}\text{H}_2)_5]\text{Br}$.

Table 2. ^1H N.m.r. data of new organotellurium compounds (R = p-EtOC_6H_4)

Compound	Chemical shift*	
	Aromatic region	Aliphatic region
$(\text{RTe})_2(\text{CH}_2)_n$		
$n = 5$	6.72, 7.62 [J(AB) 8.66]	4.0 (q), 2.8 (t), 1.5 (m)
$n = 6$	6.72, 7.62 [J(AB) 8.66]	4.08 (q), 2.8 (t), 1.5 (m)
$n = 7$	6.72, 7.62 [J(AB) 8.66]	4.0 (q), 2.75 (t), 1.5 (m)
$n = 9$	6.72, 7.62 [J(AB) 8.66]	4.0 (q), 2.85 (t), 1.5 (m)
$n = 10$	6.74, 7.64 [J(AB) 8.66]	4.0 (q), 2.85 (t), 1.5 (m)
$[\text{R}\overline{\text{Te}(\text{C}}\text{H}_2)_5]\text{Br}$	6.75, 7.65 [J(AB) 8.66]	4.0 (q), 2.8 (t), 1.5 (m)
$(\text{Br}_3\text{Te})(\text{CH}_2)_6$		2.5 (s), 2.1 (s), 1.4 (m)

* *versus* SiMe_4; J values in Hz.

The bis(aryltelluro)alkanes prepared have been characterised by elemental analysis. The ^1H n.m.r. spectra integrate for the correct ratio of aromatic to aliphatic protons and the compounds are non-electrolytes in dmf. I.r. spectra show bands characteristic of the alkane chain and of the aryl groups; no bands may be assigned to ν(C–Br), and ν[C–Te(aliphatic)] is tentatively assigned to bands around 520 cm^{-1}. The mass spectra did not show parent ions and it appears that in each case the alkane backbone is eliminated to give ditelluride. However, the probe temperature was approximately 200 °C and separate experiments revealed that if heating of the bis(tellurides) was continued beyond the melting point, release of ditelluride was observed below 200 °C. Thus, as is commonly the case for organyltellurium compounds, the mass spectrum is that of pyrolysis products.

The reaction of the bis(aryltelluro)alkanes with bromine led to rupture of the Te–aryl linkage, a conclusion supported by analysis and the absence of aromatic resonances from the ^1H and ^{13}C n.m.r. spectra (Table 2), and from the absence of characteristic aromatic vibrations in the i.r. spectrum. The good solubility of these new bis(tribromotelluro)alkanes suggests that they may be monomeric, the co-ordination requirements of the tellurium atoms being satisfied by their mutual interaction *via* bromo-bridges in a manner similar to that observed by Hazell[2] for di-μ-bromo-μ-cyclohexane-1,2-diyl-bis(dibromotellurium).

The most interesting of the data obtained for these new compounds, and certainly the most useful for subsequent investigations of their ligand chemistry, are the ^{13}C n.m.r. spectra (Table 3). The aromatic region is assigned following the literature[1,3] and need not be discussed further. In the aliphatic region the resonances arising from the p-$\text{CH}_3\text{CH}_2\text{O}$- group are readily assigned around δ 63 and 15 p.p.m. relative to SiMe_4. The remaining aliphatic resonances were found to parallel those of the n-alkanes[4–6] rather than those of $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ and $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{AsPh}_2$.[7] For the n-alkanes the C(1) resonance is seen between δ 13.5 and 13.9 p.p.m. relative to SiMe_4, and for the tellurium compounds it may be assigned between δ 8.7 and 9.1 p.p.m. Not surprisingly, when electron density is removed from the tellurium atom, as in the tribromide (Table 3), this resonance undergoes a significant down-field shift (this also

Table 3. ^{13}C N.m.r. data of new organotellurium compounds (R = p-EtOC_6H_4)

Compound	δ*/p.p.m.										
	Aliphatic region							Aromatic region			
	C(1)	C(2)	C(3)	C(4)	C(5)	OCH_2	CH_3	*Ipso*	*Ortho*	*Meta*	*Para*
$(\text{RTe})_2(\text{CH}_2)_n$											
$n = 5$	8.7	31.0	34.0			63.4	14.9	96.1	141.0	115.6	159.9
$n = 6$	8.8	31.0	31.4			63.3	14.8	100.2	140.9	115.5	159.0
$n = 7$	9.1	29.1	31.9	29.7		63.6	14.9	100.6	141.1	115.8	159.3
$n = 9$	9.1	28.8	31.8	29.0	?	63.4	14.8	100.5	140.9	115.6	?
$n = 10$	9.0	28.8	31.8	29.4	29.6	63.3	14.7	100.3	140.8	115.5	159.0
$(\text{Br}_3\text{Te})_2(\text{CH}_2)_6$	59.7	29.8	27.0								
$[\text{R}\overline{\text{Te}(\text{C}}\text{H}_2)_5]\text{Br}$	27.5	26.3	21.3			63.3	14.9	?	137.1	115.4	159.9

* *versus* SiMe_4.

occurs if the tellurium acts as a Lewis base). For the pentane and hexane derivatives, the C(2) and C(3) resonances are assigned at succesively lower fields, however the remaining compounds, as with the n-alkanes, show the C(3) resonance in an anomalous position. This does not appear to be well understood, but it has been suggested that for n-decane, for example, the formation of a pseudo-six-membered ring may be responsible.[4,7] If this is the case, it appears to occur in the tellurium derivatives yet not in the $Ph_2P(CH_2)_nPPh_2$ or $Ph_2As(CH_2)_nAsPh_2$ series;[7] since the P and As atoms carry two bulky substituents and the Te atom only one, steric factors could be invoked to account for the difference.

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