78 Organometallics 1988, 7, 78-83

Synthesis, Properties, and Multinuclear NMR ($^{125}Te\{^1H\}$, $^{13}C\{^1H\}$, ^1H) Studies of Di- and Polytelluroether Ligands

Eric G. Hope, Tim Kemmitt, and William Levason*

Department of Chemistry, The University, Southampton S09 5NH, U.K.

Received April 27, 1987

Convenient syntheses for RTeLi (R = Me or Ph) from RLi and tellurium in tetrahydrofuran at low temperatures are described. The RTeLi react readily with organic dihalides $X(CH_2)_nX$ (X = Cl or Br), the products depending upon the temperature and the carbon chain length (n). Thus at low temperatures CH_2Cl_2 and $Cl(CH_2)_3Cl$ produce high yields of $RTe(CH_2)_nTeR$ (n = 1 or 3), but at room temperature $Cl(CH_2)_nCl$ (n = 2 or 3) affords R_2Te_2 and olefin. 1,4-Dihalobutanes give R_2Te and $\overline{Te(CH_2)_3CH_2}$, while $Cl(CH_2)_5Cl$ produced mixtures of R_2Te, $RTe(CH_2)_5TeR$, and $\overline{Te(CH_2)_4CH_2}$. Preparations for $RTe(CH_2)_6TeR$, $MeTe(CH_2)_{10}TeMe$, and $MeC(CH_2TeMe)_3$ are described. PhTeLi and $C(CH_2Br)_4$ gave $C(CH_2TePh)_4$, but MeTeLi unexpectedly gave $\overline{CH_2CH_2C}(CH_2TeMe)_2$. The products have been characterized by ^1H, $^{13}C\{^1H\}$, and $^{125}Te\{^1H\}$ NMR and mass spectrometry and by the preparation of derivatives. Trends in the ^{125}Te chemical shifts and $^1J_{Te-C}$, $^2J_{Te-C}$, and $^2J_{Te-H}$ coupling constants are discussed and compared with the corresponding ^{77}Se data of selenium analogues.

Introduction

Although the first diorgano telluride Et_2Te was made as long ago as 1840,[1] organotellurium chemistry has developed slowly. Studies were hindered by the low stability of many compounds that were often light and air sensitive and frequently extremely malodorous. Currently organotellurium chemistry is a field of rapidly growing interest[2,3] with applications in such diverse areas as synthesis,[3] new conducting materials,[4] and nuclear medicine,[5] while developments in FT NMR instrumentation have made direct observation of ^{125}Te nuclei relatively straightforward,[6] providing a specific and sensitive probe for the tellurium environment. The studies of the ligand properties of organotellurium species still lag well behind those of sulfur and selenium analogues[7,8] and are mainly restricted to R_2Te or RTe^- species. We were interested in extending our recent studies[9] of the coordination chemistry of diselenoethers and ^{77}Se NMR to tellurium analogues, and here we describe attempts to prepare di- and polytelluroether ligands with Me or Ph terminal groups and a variety of carbon backbones. Few compounds of this type have been described,[10-16] and the data on these is very limited. A preliminary account of this work has appeared.[17]

Results

RTeLi (R = Me, Ph). Solutions of RTeLi in tetrahydrofuran (THF) are very conveniently obtained by an analogous route to MeSeLi,[18] essentially adding RLi to a frozen mixture of THF and powdered tellurium and allowing the mixture to warm to room temperature. The reaction with MeLi occurs rapidly but that with PhLi is slower and the mixture is stirred at room temperature to complete the reaction. In both cases all the Te dissolves to give a clear yellow solution that is stable under nitrogen. Yields are high in contrast to the PhLi/Se reaction that gives indifferent yields.[18] Various other routes to RTe^- are known[19] including cleavage of R_2Te_2 with alkali metal/liquid NH_3, with Rongalite (NaO_2SCH_2OH) in water, or with $NaBH_4$/EtOH, but the syntheses described above avoids the prior synthesis of R_2Te_2 and provides RTeLi in a solvent in which the organic halides are soluble, facilitating further reaction. These RTeLi solutions were treated with the appropriate haloorganic either at ambient temperature or refrozen (−196 °C), the halide was added, and the mixture allowed to thaw (for brevity the latter conditions are referred to as "frozen RTeLi" subsequently). After hydrolysis, the organic phase was dried and the solvent removed in vacuo. In view of the instability of many organotellurium compounds, ^{125}Te NMR spectra were routinely recorded upon the crude products and upon the pure components after subsequent separations, which provided to be the best way of identifying minor products.

RTeLi + $X(CH_2)_nX$ Reactions (X = Cl, Br, or I; n = 1–6, 10). It is convenient to deal with each dihalide in turn.

The reaction of PhTeLi with CH_2X_2 at room temperature or above was reported to give a poor yield of $PhTeCH_2TePh$,[11] but reaction of CH_2Cl_2 or CH_2I_2 with frozen RTeLi gave good yields of $RTeCH_2TeR$ (R = Me, 76%; R = Ph, 66%). The ^{125}Te NMR spectra of these ditelluromethanes (Table I) are in excellent agreement with the data reported[15] for the products of the R_2Te_2 + CH_2N_2 reactions. Attempted quaternization with MeI failed to give pure telluronium salts, but white crystalline tetrachlorides $RCl_2TeCH_2TeRCl_2$[15] were readily isolated

---

[1] Wohler, F. *Ann. Chem.* **1840**, *35*, 111.

[2] Irgolic, K. J *The Organic Chemistry of Tellurium*; Gordon and Breach: New York, 1974.

[3] Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, 1986; Vol. 1.

[4] Miller, J. S., Ed. *Extended Linear Chain Compounds*; Plenum: New York, 1982; Vol. 2.

[5] Knapp, F. F., Jr.; Ambrose, K. R.; Callaghan, A. P. *J. Nucl. Med.* **1980**, *21*, 251; **1980**, *21*, 258.

[6] Luthra, N. P.; Odom, J. D. In ref 3, pp 189–241.

[7] Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 265.

[8] Gysling, H. J. In ref 3, pp 679–855.

[9] Gulliver, D. J.; Hope, E. G.; Levason, W.; Murray, S. G.; Marshall, G. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1265. Gulliver, D. J.; Hope, E. G.; Levason, W.; Murray, S. G.; Marshall, G. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2185. Hope, E. G.; Levason, W.; Webster, M.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1986**, 1003. Hope, E. G.; Jewiss, H. C.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1479.

[10] Petragnani, N.; Toscano, V. G. *Chem. Ber.* **1970**, *103*, 1652.

[11] Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314.

[12] Petragnani, N.; Schill, G. *Chem. Ber.* **1970**, *103*, 2271.

[13] De Silva, K. G. K.; Monsef-Mirzai, Z.; McWhinnie, W. R. *J. Chem. Soc., Dalton Trans.* **1983**, 2143.

[14] Pathirana, H. M. K. K.; McWhinnie, W. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2003.

[15] Jones, C. H. W.; Sharma, R. D. *Organometallics* **1986**, *5*, 805.

[16] Pathirana, H. M. K. K.; McWhinnie, W. R.; Berry, F. J. *J. Organomet. Chem.* **1986**, *312*, 323.

[17] Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* **1987**, *6*, 206.

[18] Drake, J. E.; Hemmings, R. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1730.

[19] Reference 2, p 45 and references therein.

0276-7333/88/2307-0078$01.50/0 © 1988 American Chemical Society

Table I. $^{125}Te\{^1H\}$ **and** ^1H **NMR Data**

	$\delta(^{125}Te)$	$\delta(^1H)$		
		MeTe	CH_2Te	others[a]
Me_2Te	0			
MePhTe	329 (lit. 329)[b]	2.1 (s) (21.5)		
Me_2Te_2	55 (lit. 49)	2.6 (s) (23.5)		
$MeTeCH_2TeMe$	212 (lit. 213.5)[15]	1.95 (s) (21.5)	3.4 (s) (26)	
$MeCl_2TeCH_2TeCl_2Me$	836.5 (lit. 834)[15]	3.05 (s) (27)	4.75 (s) (22)	
$MeTe(CH_2)_3TeMe$	104	1.85 (s) (20)	2.6 (t) (26)	2.05 (q)
$Me_2Te(CH_2)_3TeMe_2(I)_2$	494	2.1 (s) (24)	2.75 (t)	2.3 (q)
$MeTe(CH_2)_3OH$	105	1.9 (s) (20)	2.7 (t) (24)	2.0 (q), 3.7 (t), 2.6 (s)
$MeTe(CH_2)_6TeMe$	106	1.9 (s) (20)	2.6 (t) (26)	1.4 (m), 1.6 (m)
$Me_2Te(CH_2)_6TeMe_2(I)_2$	426	2.0 (s) (24)	2.6 (t)	1.1–1.6 (m)
$MeTe(CH_2)_{10}TeMe$	104.5	1.9 (s) (21)	2.6 (t)	1.7 (q), 1.3 (m)
$Me_2Te(CH_2)_{10}TeMe_2(I)_2$	418	2.0 (s) (21)	2.6 (m)	1.3 (m)
$MeC(CH_2TeMe)_3$	21	1.8 (s) (21)	2.9 (s) (22)	1.2 (s)
$\overline{Te(CH_2)_3CH_2}$	234		3.2 (t) (25.5)	2.05 (m)
$\overline{Te(CH_2)_4CH_2}$	210		2.6 (t) (26)	2.0 (m), 1.6 (m)
$\overline{CH_2CH_2C}(CH_2TeMe)_2$	65	1.9 (s) (20)	2.85 (s) (25)	0.65
Ph_2Te	685 (lit. 688)			
Ph_2Te_2	417 (lit. 420)			
$PhTeCH_2TePh$	584 (lit. 588)[15]		3.75 (s) (21)	
$PhCl_2TeCH_2TePhCl_2$	880 (lit. 858)[15]		4.7 (s) (21)	
$PhTe(CH_2)_3TePh$	466		2.8 (t) (28)	2.15 (q)
$PhMeTe(CH_2)_3TePhMe(I)_2$	609.7, 610.3	2.4 (s) (25)	3.0 (t)	2.0 (q)
$PhTe(CH_2)_6TePh$	468		2.8 (t) (26)	1.8 (m), 1.3 (m)
$PhMeTe(CH_2)_6TePhMe(I)_2$	600.7, 600.5	2.3 (s) (25)	2.9 (t)	~2.0 (m)
$C(CH_2TePh)_4$	407		3.2 (s) (23)	

[a] The aryl proton resonances at 7.1–7.7 ppm are not listed. [b] All literature data from ref 6 unless otherwise indicated.

Table II. $^{13}C\{^1H\}$ **NMR Data (ppm)**

	MeTe	C_1	C_2	C_n	aromatics		
					ipso	ortho	meta, para
Me_2Te	-21.5 (158)						
Me_2Te_2	-19.9 (178)						
MePhTe	-16.7 (163)				112.5 (...)	136.7 (55)	127.0, 129.0
$MeTeCH_2TeMe$	-15.3 (164)	-45.7 (206)					
$MeCl_2TeCH_2TeCl_2Me$	+29.5 (192)	+43.3 (285)					
$MeTe(CH_2)_3TeMe$	-23.3 (162)	5.2 (153)	33.6 (32)				
$Me_2Te(CH_2)_3TeMe_2(I)_2$	+5.4 (173)	24.6 (150)	21.5 (52)				
$MeTe(CH_2)_3OH$	-22.7 (160)	-1.6 (151)	33.8 (38)	62.8			
$MeTe(CH_2)_6TeMe$	-22.8 (163)	3.0 (148)	31.0	31.5			
$MeTe(CH_2)_{10}TeMe$	-22.9 (161)	3.4 (146)	31.9	29.4, 29.0, 28.9			
$MeC(CH_2TeMe)_3$	-19.6 (180)	21.4 (168)	38.5	28.1			
$\overline{Te(CH_2)_3CH_2}$	...	5.8 (126)	35.8 (28)				
$\overline{Te(CH_2)_4CH_2}$	...	-3.6 (131)	28.6 (27)	29			
$\overline{CH_2CH_2C}(CH_2TeMe)_2$	-22.0 (161)	16.4 (153)		17.7, 22.3			
Ph_2Te					114.7 (...)	137.8 (54)	127.5, 129.2
$PhTeCH_2TePh_2$	...	-6.2 (210)			116.0 (...)	137.6 (50)	127.8, 128.0
$PhCl_2TeCH_2TePhCl_2$	...	53.9 (266)			137.2 (332)	129.3 (52)	131.4, 133.9
$PhTe(CH_2)_3TePh$	...	10.5 (157)	33.2 (32)		111.7 (280)	138.2 (56)	127.3, 129.0
$PhTe(CH_2)_6TePh$	...	8.4 (152)	31.6 (36)	31.0	111.8 (280)	138.3 (55)	127.4, 128.0
$C(CH_2TePh)_4$		24.9 (178)	42.6		113.0 (280)	139.0 (60)	129.3, 128.0

from reaction with Cl_2/CCl_4. 1,2-Dichloro- or dibromoethane and RTeLi gave only R_2Te_2 and ethene, irrespective of the temperature of reaction, consistent with previous reports,[13,14,20] and no other tellurium species were detected in the ^{125}Te NMR spectra of the crude products. Similarly at room temperature RTeLi and $X(CH_2)_3X$ (X = Cl or Br) gave R_2Te_2 and olefin as major products as reported,[13,14] but in marked contrast addition of the 1,3-dihalopropane to frozen RTeLi gave high yields of $RTe(CH_2)_3TeR$ (R = Ph, 85%; R = Me, 73%).[17] Once isolated the ligands are quite stable under nitrogen and were recovered unchanged after being heated for several hours at 100 °C. Careful reexamination of the products from the room-temperature synthesis by ^1H and $^{125}Te\{^1H\}$ NMR revealed very small amounts of $RTe(CH_2)_3TeR$ were present, but without prior knowledge of the spectral characteristics, it is not surprising that they have not been detected previously.

The reaction of frozen MeTeLi with $Cl(CH_2)_4Cl$ gave Me_2Te and a compound with $\delta(^{125}Te)$ 234 identified by its mass (parent ion *m/z* 186) and $^{13}C\{^1H\}$ and ^1H NMR spectra (Tables I and II) as the tellurocycle 1. The identity of 1 was confirmed by comparison of the NMR spectra with those of a genuine sample of telluracyclopentane prepared from Na_2Te and $Br(CH_2)_4Br$ in water.[21] Similarly frozen PhTeLi and $Br(CH_2)_4Br$ gave 1 and Ph_2Te ($\delta(^{125}Te)$ 685), which were easily separated by fractionation in vacuo. However frozen PhTeLi and $Cl(CH_2)_4Cl$ gave 1, Ph_2Te, and a small amount of a third product with $\delta(^{125}Te)$ 474, which is reasonable for a $PhTeCH_2CH_2CH_2CH_2-$ moiety (cf. PhTe-*n*-Bu, 468

---

(20) Pluscec, J.; Westland, A. D. *J. Chem. Soc.* **1965**, 5371.

(21) Farrar, W. V.; Gulland, J. M. *J. Chem. Soc.* **1945**, 11.

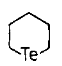
ppm).[22] The possibility that this was the desired $PhTe(CH_2)_4TePh$ was however ruled out by the $^{13}C\{^1H\}$ spectrum which (after elimination of the resonances of 1 and Ph_2Te) showed four aryl C and *four* distinct CH_2 resonances at δ 7.1, 28.8, 34.4, and 43.8 (confirmed as methylene groups by a DEPT experiment). Attempts to separate this product by flash column chromatography on silica failed but from the ^{13}C resonances especially that at 43.8 ppm and a weak triplet at 3.5 ppm in the ^1H spectrum both characteristic of a $-CH_2Cl$ group, it was identified as $PhTe(CH_2)_4Cl$. The data are inconsistent with a cyclic telluronium salt (cf. ref 14 and 23) which would have only two $^{13}C(CH_2)$ resonances and for which $\delta(^{125}Te)$ is expected some ca. 200 ppm to higher frequency. We have been unable to obtain a larger proportion of $PhTe(CH_2)_4Cl$ by varying the reaction conditions, and it is not present at all if the reaction is carried out >−10 °C. The reactions of frozen RTeLi with $Cl(CH_2)_5Cl$ resembled the 1,4-dichlorobutane reactions in that R_2Te and the heterocycle telluracyclohexane **2**, $\overline{Te(CH_2)_4CH_2}$, $\delta(^{125}Te)$ 210, were the major products, and these were the *only* products from the room-temperature reactions. However, at low-temperatures MeTeLi gave two further minor products $\delta(^{125}Te)$ 107 and 105 ppm (intensity ratio ca. 10:1). After removal of most of **2** by distillation, the residue had a $^{13}C\{^1H\}$ spectrum with δ(MeTe) −22.9 and five substantial CH_2 resonances 2.5, 28.3, 30.8, 31.7, and 44.3 ppm, showing it to be mainly $MeTe(CH_2)_5Cl$. This was confirmed by the observation of parent ion with the correct isotope pattern at m/z ~250 in the mass spectrum. It seems likely that the $\delta(^{125}Te)$ 105 is due to $MeTe(CH_2)_5TeMe$, but the yield is too small to allow its isolation. In the $PhTeLi/Cl(CH_2)_5Cl$ reaction minor products with $\delta(^{125}Te)$ 469 and 472 ppm are tentatively identified as $PhTe(CH_2)_5Cl$ and $PhTe(CH_2)_5TePh$ on the basis of similar spectroscopic evidence.

The frozen $PhTeLi/Cl(CH_2)_6Cl$ reaction afforded three tellurium-containing species with $\delta(^{125}Te)$ 685 (Ph_2Te), 468, and 230. Flash column chromatography on a portion of this mixture separated pure Ph_2Te and $PhTe(CH_2)_6TePh$ (δ 468), while vacuum distillation of another portion yielded Ph_2Te as the *only* volatile (<150 °C (0.1 torr)) product. Similarly frozen MeTeLi and $Cl(CH_2)_6Cl$ gave Me_2Te and two species with $\delta(^{125}Te)$ 110 and 230. In this case vacuum distillation gave pure $MeTe(CH_2)_6TeMe$ (120 °C (0.2 torr)), $\delta(^{125}Te)$ 110. The species with $\delta(^{125}Te)$ 230 common to both preparations initially appeared likely to be a heterocycle $\overline{Te(CH_2)_5CH_2}$, despite the unusual seven-membered ring (selenepane $\overline{Se(CH_2)_5CH_2}$ was prepared many years ago,[24] but the tellurium analogue is not known). However it failed to distill (compare $\overline{Te(CH_2)_4CH_2}$, bp 45 °C (2 torr[25])), did not cleanly elute from a column, and is thus probably oligomeric or a mixture of oligomers $-Te(CH_2)_6-)_n$. Both $RTe(CH_2)_6TeR$ ligands were fully characterized (Tables I and II) and readily produced ditelluronium salts with MeI in acetone. 1,10-Dichlorodecane and frozen MeTeLi gave $MeTe(CH_2)_{10}TeMe$, $\delta(^{125}Te)$ 104.5, and a material with $\delta(^{125}Te)$ 232 ppm which was not characterized further but is probably an oligomer.

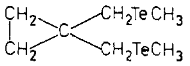
***cis*-MeTeCH═CHTeMe.** Several attempts were made to prepare the cis vinylic ligand MeTeCH═CHTeMe, by reaction of MeTeLi with *cis*-ClCH═CHCl in THF, in ethanol in the presence of an equimolar amount of NaOEt,[26] and from $MeTeSiMe_3$ and *cis*-ClCH═CHCl in MeCN.[27] In all cases the ^1H NMR spectra of the products contained no −HC═CH− resonances, and the only tellurium-containing product was Me_2Te_2. The syntheses of *cis*-RSeCH═CHSeR (R = Me or Ph from RSeNa and *cis*-ClCH═CHCl in ethanol containing NaOEt[26]), are straightforward and stereospecific, and our failure to prepare MeTeCH═CHTeMe analogously again appears to demonstrate the increased tendency to elimination rather than substitution in telluroether chemistry.

Polytelluroethers. 1,1,1-Tris((methyltelluro)methyl)ethane, $MeC(CH_2TeMe)_3$, was obtained as an orange oil by reaction of excess MeTeLi with $MeC(CH_2Br)_3$; the excess $MeTe^-$ is necessary to avoid incomplete replacement of bromine. Similarly tetrakis((phenyltelluro)methyl)methane, $C(CH_2TePh)_4$, was prepared from $C(CH_2Br)_4$ and excess PhTeLi. After several recrystallizations to remove Ph_2Te_2 impurity, it was obtained as a white powder, mp 188 °C. Unexpectedly $C(CH_2Br)_4$ and MeTeLi gave a yellow oil with $\delta(^{125}Te)$ 65. The ^{125}Te resonance seems too high a frequency for $C(CH_2TeMe)_4$, while the ^1H NMR spectrum consists of three singlets at 2.85 (25), 1.9 (20), and 0.65 ppm. The corresponding $^{13}C\{^1H\}$ spectrum has resonances at −22.0 (161) (TeMe), 16.4 (153) (CH_2Te), 17.7 (CH_2C), and 22.3 ppm, which led to the characterization of this material as a cyclopropane derivative $\overline{CH_2CH_2C}(CH_2TeMe)_2$ (**3**). It is notable that $C(CH_2SeMe)_4$ is produced straightforwardly albeit in poor yield from $C(CH_2Br)_4$ and MeSeLi.[26]

(1)



(2)



(3)

NMR Spectra. **^{1}H.** The proton spectra of the telluroethers (Table I) are unexceptional with δ(MeTe) at ca. 2.0 and $\delta(MeTeCH_2)$ at 2.6–2.8, except for $RTeCH_2TeR$ which have $\delta(CH_2)$ at 3.4–3.8. Generally $^2J_{Te-H}$ is 20–30 Hz, approximately 2–3 times greater than $^2J_{Se-H}$ in the corresponding selenoethers.[26] Quaternization of the tellurium or conversion to the dichlorides shifts δ(Me) and $\delta(CH_2)$ to high frequency but does not greatly change the magnitude of $^2J_{Te-H}$.

$^{13}C\{^1H\}$. The literature data of ^{13}C chemical shifts in organotellurium compounds are rather sparse. The chemical shifts of MeTe− groups are to low frequency of TMS (−15 to −24 ppm), an effect observed for ^{13}C atoms bonded to other heavy atoms including I and Pb and explained similarly as due to electron spin-orbit interactions on the heavy atom.[28] The CH_2–Te resonances in $TeR(CH_2)_nTeR$ are found in the range ca. −6 to +6 ppm, except for $MeTeCH_2TeMe$ where it is highly shielded (−45.7 ppm). In the PhTe group, the ipso-carbon resonance was found at ca. 110–116 ppm and the ortho carbon at 136–139 ppm.

The $^1J_{Te-C}$ coupling constants are ca. 150–180 Hz for Me–Te and CH_2–Te groups in $MeTe(CH_2)_nTeMe$, except for $RTeCH_2TeR$ which are again anomalous with $^1J_{Te-C}$ for Te–CH_2 considerably larger (205–210 Hz). Even with ^1H decoupling $^2J_{Te-C}$ proved difficult to measure accurately

---

[22] O'Brien, D. H.; Deren, N.; Huang, C. K.; Irgolic, K. J.; Knapp, F. F., Jr. *Organometallics* **1983**, *2*, 305.

[23] Al-Rubaie, A. Z.; Alshirayda, H. A. Y.; Granger, P.; Chapelle, S. *J. Organomet. Chem.* **1985**, *287*, 321.

[24] Morgan, G. T.; Burstall, F H.; *J. Chem. Soc.* **1931**, 173.

[25] Morgan, G. T. Burgess, H.; *J. Chem. Soc.* **1928**, 321.

[26] Gulliver, D. J.; Hope, E. G.; Levason, W.; Murray, S. G.; Potter, D. M. Marshall, G. L. *J. Chem. Soc., Perkin Trans. 2* **1984**, 429, and refs therein.

[27] Evers, M. J.; Christiaens, L. E.; Renson, M. J. *J. Org. Chem.* **1986**, *51*, 5196.

[28] Cheremisin, A. A.; Schastnev, P. V. *J. Magn. Reson.* **1980**, *40*, 459.

in many cases but appear to be ca. 30–40 Hz. Slightly smaller values of $^1J_{Te-C}$ and $^2J_{Te-C}$ were observed in the heterocycles 1 and 2. In the aromatic groups, the ipso-carbon resonance that does not enjoy any NOE enhancement was often weak and $^1J_{Te-C}$ correspondingly difficult to measure, but where observed was ca. 280 Hz, while $^2J_{Te-C}$ on the ortho carbon was ca. 50–60 Hz. Comparison of these values with the corresponding $^1J_{Se-C}$ and $^2J_{Se-C}$ values in selenoether analogues[26] reveals that $^1J_{Te-C}$ is about 3 times as great as $^1J_{Se-C}$ but $^2J_{Te-C}$ is nearly 5 times larger on average than $^2J_{Se-C}$.

^{125}Te{^{1}H}. The data on organotellurium compounds have recently been reviewed by Luthra and Odom,[6] who discuss in some detail the problems of the concentration, temperature, and solvent dependence of the chemical shifts. In order to reduce these problems in the present study data were referenced to neat Me_2Te and for pure materials spectra were recorded for 30% w/v solutions in $CHCl_3$. It was clearly not possible to control the concentrations of the constituents when the crude reaction products were examined and deviations in the ^{125}Te chemical shifts of ca. ±5–10 ppm for $CHCl_3$ solutions were typically observed. A large concentration effect was noted for 1 from 259 ppm (neat) decreasing gradually on dilution with $CHCl_3$ to ca. 235 ppm. In practice providing one is aware of the problem, these concentration effects cause few difficulties, and in this study we have found the ^{125}Te shifts to be the most valuable probe for identifying constituents of mixtures and following these through purification procedures.

Studies on RR′Te especially by O'Brien et al.[22] have shown that the effects of R and R′ are approximately additive and that stepwise deshielding of the Te occurs with replacement of the hydrogens in Me_2Te with other groups. Substitutions more remote than the γ-carbon (with respect to the Te) have negligible effects. These correlations may be applied to the ditelluroethers in Table I.

Thus one can compare $MeTe(CH_2)_3TeMe$ (104 ppm) with MeTe-*n*-Bu (103 ppm) in effect $MeCH_2CH_2CH_2-$ is taken as equivalent to $-CH_2CH_2CH_2Te$ with respect to the other tellurium. The chemical shift in $MeTe(CH_2)_3OH$ (105 ppm) conforms to this pattern. Longer chains correspond to changes more remote than the γ-carbon and have no further effects, compare $MeTe(CH_2)_6TeMe$ (106 ppm) and $MeTe(CH_2)_{10}TeMe$ (104.5 ppm). Alternatively one can assign a contribution of ca. 104 ppm to a $-(CH_2)_n-$ ($n > 3$) from $MeTe(CH_2)_nTeMe$ and Me, 0 ppm (from Me_2Te), and 329 ppm to Ph (from PhMeTe) leading to a prediction for $PhTe(CH_2)_nTePh$ of ca. 433 ppm. The measured values for the latter are ca. 466 ppm (Table I). Similarly one can assign a value of 212 ppm for $-CH_2Te$ from $MeTeCH_2TeMe$, leading to a prediction of 541 ppm for $PhTeCH_2TePh$ (experimental value 584 ppm). The error in this last example is larger and is expected since the 212 ppm really refers to a $-CH_2TeMe$ rather than $-CH_2TePh$ group bound to PhTe–. Nonetheless the agreement is good enough to allow new products to be identified with a fair degree of certainty.

Quaternization of the tellurium centers to telluronium salts results in substantial high-frequency shifts in $\delta(^{125}Te)$; the values in Table I are much as expected when compared with Me_3TeI, 443 ppm, and Me_2PhTeI, 550 ppm.[6]

Under high resolution the $PhMeTe(CH_2)_nTeMePh(I)_2$ are seen to give two very closely spaced ^{125}Te resonances, which we attribute to the presence of diastereoisomers resulting from the three different R groups about each Te.

Mass Spectra. The major fragments observed are listed in the experimental section and generaly serve to confirm the constitution of the compounds but are otherwise unexceptional. All the telluroethers except $(PhTeCH_2)_4C$, which pyrolyzed on the probe, gave a parent ion, and the fragmentation patterns were much as expected in comparison with those of the thio-[29] and selenoether[26] analogues. As commonly observed with EI ionization,[30] extensive cleavage of the C–Te bonds was produced, and not infrequently the base peaks were tellurium free ions.

Discussion

The reactions of RS^-[31] or RSe^-[26] with α,ω-dihaloalkanes lead to the corresponding dithio or diselenoethers cleanly and in high yields. In marked contrast as described above the corresponding reactions of RTe^- are very dependent upon the reaction conditions and the specific dihaloalkane used. Thus, for CH_2X_2 predominantly substitution to give $(RTe)_2CH_2$ is found, whereas for XCH_2CH_2X, elimination ($R_2Te_2 + C_2H_4$) exclusively occurs. As the chain length increases, the competition becomes more finely balanced, and for $X(CH_2)_3X$ merely raising the temperature from ca. <–100 to ca. –10 °C changes the reaction from high-yield substitution to form $RTe(CH_2)_3TeR$ to almost exclusively elimination. For C_4 and C_5 chains cyclization to give $\overline{Te(CH_2)_{n-1}CH_2}$ and R_2Te is the favored pathway even at low temperatures, while even with longer chains, C_6 or C_{10}, where cyclization is expected to be unfavorable due to ring strain, there is still a competition between formation of $RTe(CH_2)_nTeR$ and the formation of oligomeric $[-Te(CH_2)_n-]_y$. Nucleophilic attack on RTe^- or *cis*-ClCH=CHCl has also given only the elimination product R_2Te_2 in our hands, although since vinyltellurides CH_2=CHTeR are known,[32] it is possible that RTeCH=CHTeR may be obtainable by other routes. The very marked dependence of the products upon the reaction conditions probably accounts for the differences between the reactions reported here and other studies[13,14] where $X(CH_2)_nX$ (n = 3, 4, or 5) and RTe^- (R = *p*-$EtOC_6H_4$ or sometimes Ph) gave telluronium salts, $\overline{CH_2(CH_2)_{n-1}Te}XR$.

Some useful analogies can be drawn with group VB (15[35]) chemistry and the reactions of R_2E^- (E = P, As, or Sb) with $X(CH_2)_nX$. For E = P or As the usual products are the diphosphines or diarsines $R_2E(CH_2)_nER_2$, although elimination is observed with Me_2As^- and $X(CH_2)_2X$.[33] For E = Sb all attempts to prepare $R_2Sb(CH_2)_2SbR_2$ have failed—reaction of R_2Sb^- with $X(CH_2)_2X$ afford only R_4Sb_2 and C_2H_4, and while $R_2Sb(CH_2)_nSbR_2$ (n = 3–6) is readily obtained, under some conditions Me_2Sb^- and $Br(CH_2)_xBr$ (x = 4 or 5) give cyclic 1-methylstibacycloalkanes $\overline{CH_2(CH_2)_{x-1}Sb}Me$.[34] The latter are also produced by pyrolysis

---

[29] McAuliffe, C. A.; McCullough, F. P.; Sedgwick, R. D.; Levason, W. *Inorg. Chim. Acta* **1978**, *27*, 185.

[30] Sturgeon, G. D.; Gross, M. L. In ref 3, pp 243–285.

[31] *Methoden der Organischen Chemie (Houben-Weyl), Schwefel-, Selen-, Tellur-Verbingdungen*; Muller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1955; Chapter 5.

[32] Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V.; Petragnani, N.; *J. Organomet. Chem.* **1986**, *308*, 211.

[33] McAuliffe, C. A.; Levason, W. *Phosphine, Arsine and Stibine Complexes of the Transition Elements*; Elsevier: Amsterdam, 1979; Chapter 1.

[34] Meinema, H. A.; Martens, H. F.; Noltes, J. G. *J. Organomet. Chem.* **1976**, *110*, 183.

[35] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

of $Me_2Sb(CH_2)_xSbMe_2$, while pyrolysis of longer chain distibines produces oligomers. The analogy between these results and the $RTe^-/X(CH_2)_nX$ reactions is strong.

Despite the more complex syntheses and lower stability of the products, sufficient examples of di- and polytelluroether ligands have been obtained to permit investigation of their coordination chemistry and these studies will be described elsewhere in due course.

Experimental Section

Mass spectra were obtained with an AEI MS 30 instrument at 70 eV using the direct insertion probe and EI ionization. The *m/z* values refer to ^{130}Te ions and are uncorrected for the other Te isotopes. ^1H and ^{13}C NMR spectra were recorded for ca. 40% solutions in $CDCl_3$ relative to internal Me_4Si with a Bruker AM 360 spectrometer. $^{125}Te\{^1H\}$ NMR spectra were obtained from ca. 30% solutions in $CHCl_3$ in 10-mm o.d. tubes, fitted with a Co-axial 5-mm o.d. tube containing D_2O to provide the lock. Spectra were recorded at 25 °C on a Bruker AM 360 at 113.6 MHz and were referenced to external neat Me_2Te. A pulse width of 20 μs and a pulse angle of 90°, with a sweep width of 100 kHz, were used for survey spectra; subsequently the sweep width was decreased to 20 kHz for higher resolution work. Typically spectra required 1000–5000 transients. Values are quoted by using the high-frequency positive convention.

Tellurium pieces, PhLi, and MeLi were obtained from Aldrich Chemical Co., the tellurium being freshly ground before use. Most of the organotellurium compounds have very persistent, repulsive odors, and a good hood is essential for all preparations. Aqueous waste and used glassware can be treated with aqueous NaOCl overnight to remove most of the odor. All preparations were conducted under a dry nitrogen atmosphere, and the telluroethers were generally stored under N_2 at 0 °C in sealed containers. The ditelluroalkanes, in particular, air-oxidize readily to insoluble white materials. Tetrahydrofuran was freshly distilled from sodium wire immediately before use.

1. **Synthesis of (Phenyltelluro)lithium (PhTeLi).** A suspension of tellurium powder (12.8 g, 0.1 mol) in tetrahydrofuran (THF) (100 mL) was frozen in a liquid-nitrogen bath when phenyllithium (55.6 mL of a 1.8 M solution in cyclohexane/diethyl ether; 0.1 mol) was injected into the flask. The mixture was allowed to thaw and magnetically stirred for a further 0.5 h at room temperature. The resulting yellow-orange solution was stored under nitrogen and used within 2 h of preparation.

2. **Synthesis of (Methyltelluro)lithium (MeTeLi).** This was prepared in the same way as (phenyltelluro)lithium, except using methyllithium (66.7 mL of a 1.5 M solution in diethyl ether; 0.1 mol).

3. **Bis(phenyltelluro)methane ($PhTeCH_2TePh$).** Diiodomethane (13.4 g, 0.05 mol) was injected onto a frozen (−196 °C) solution of phenyltellurolithium (0.1 mol) prepared as described. The mixture was allowed to thaw and magnetically stirred at room temperature for ca. 1 h. Hydrolysis (NaCl solution, 100 mL) was followed by separation and extraction of the water layer with several aliquots of diethyl ether. The combined extracts were dried ($MgSO_4$) for 16 h.

The solvent was removed in vacuo, leaving a deep red oil. Separation on a flash silica column, eluting with 40–60 °C petroleum ether, gave a yellow oil: lit.[11] yellow solid; mp 35–36 °C, reported very difficult to crystallize; yield 66%; mass spectrum, *m/z* (relative intensity) 428 ($C_{13}H_{12}Te_2^+$, 21), 412 (3), 284 (4), 221 (7), 207 (6), 154 (12), 91 (100).

The tetrachloride $PhTeCl_2CH_2TeCl_2Ph$ was obtained by stirring bis(phenyltelluro)methane (0.43 g, 1 mmol) in a solution of chlorine (excess) in dichloromethane for ca. 1 h. The solution was concentrated to ca. 10 mL in vacuo and cooled and the white crystalline precipitate filtered off, rinsed with diethyl ether, and dried: yield 0.54 g (95%); mp 164 °C dec. Anal. Calcd for $C_{13}H_{12}Cl_4Te_2$: C, 27.6; H, 2.1. Found: C, 28.0; H, 2.0.

4. **2,4-Ditellurapentane ($MeTeCH_2TeMe$).** A small excess of dichloromethane (4 mL) was injected onto a frozen (−196 °C) solution of (methyltelluro)lithium (0.1 mol) prepared as described. The procedure was followed as for reaction 3 to gain the crude, impure oil—purification being effected by removal of the volatile byproducts in vacuo: yield 76%; mass spectrum, *m/z* 304 ($C_3H_8Te_2^+$, 68), 302 (100), 289 (17), 274 (16), 159 (75), 145 (21), 130 (27) (base peak = parent; 302 ($C_3H_8{}^{128}Te^{130}Te$).

The tetrachloride was prepared as for reaction 3: yield 95%; mp 137 °C dec. Anal. Calcd for $C_3H_8Cl_4Te_2$: C, 8.2; H, 1.8. Found: C, 8.3; H, 1.9.

5. **Reaction of (Phenyltelluro)lithium with 1,2-Dichloroethane.** 1,2 Dichloroethane (4.95 g, 0.05 mol) was injected onto a frozen (−196 °C) solution of (phenyltelluro)lithium (0.1 mol) in THF, following the procedure described for reaction 4. *Recrystallization of the product from 40–60 °C petroleum ether* gave bright orange crystals of diphenyl ditelluride in high yield: mass spectrum, *m/z* (relative intensity) 414 ($C_{12}H_{10}Te_2^+$, 3), 284 (57), 207 (14), 154 (100), 77 (62).

6. **Reaction of (Methyltelluro)lithium with 1,2-Dichloroethane**. The reaction of 1,2-dichloroethane (4.95 g, 0.05 mol) with a solution of (methyltelluro)lithium (0.1 mol) under *the same conditions yielded the red oil dimethyl ditelluride,* identified by its ^{125}Te NMR resonance.

7. **1,3-Bis(phenyltelluro)propane ($PhTe(CH_2)_3TePh$).** 1,3-Dibromopropane (10.1 g, 0.05 mol) was reacted with (phenyltelluro)lithium (0.1 mol) following the procedure for reaction 3 to give a pale orange oil: yield 85%; mass spectrum, *m/z* (relative intensity) 456 ($C_{15}H_{16}Te_2^+$, 3), 414 (1), 379 (2), 337 (5), 249 (22), 207 (34), 77 (100).

The bis(methiodide) $IPhMeTe(CH_2)_3TeMePhI$ was obtained by stirring 1,3-bis(phenyltelluro)propane (0.46 g, 1 mmol) in a solution of iodomethane (excess) in acetone for ca. 1 h. The solution was reduced to ca. 10 mL in vacuo and cooled and the white crystalline precipitate filtered off, rinsed with diethyl ether, and dried: yield 0.68 g (92%); mp 87 °C dec. Anal. Calcd for $C_{17}H_{22}I_2Te_2$: C, 27.8; H, 3.0. Found: C, 28.3; H, 3.1.

8. **2,6-Ditelluraheptane ($MeTe(CH_2)_3TeMe$).** 1,3-Dichloropropane (5.65 g, 0.05 mol) was reacted with (methyltelluro)lithium (0.1 mol), following the procedure for reaction 4, to give a pale yellow oil: yield 73%; mass spectrum, *m/z* (relative intensity) 317 ($C_5H_{12}Te_2^+$, 29), 275 (26), 145 (66), 41 (100), 39 (98).

The bis(methiodide) $IMe_2Te(CH_2)_3TeMe_2I$ was obtained as for reaction 7: yield 88%; mp 153 °C dec. Anal. Calcd for $C_7H_{18}I_2Te_2$: C, 13.7; H, 2.9. Found: C, 13.5; H, 3.0.

9. **Reaction of (Phenyltelluro)lithium with 1,4-Dibromobutane.** The addition of 1,4-dibromobutane (10.8 g, 0.05 mol) to (phenyltelluro)lithium (0.1 mol) under the conditions described as for reaction 3 gave a mixture of two products. These were separated by distillation in vacuo to give a pale yellow/green oil, $\overline{Te(CH_2)_3CH_2}$ [yield 28%; bp 28 °C (1 torr) mass spectrum, (*m/z*) (relative intensity) 186($C_4H_8Te^+$, 2), 130 (5), 55 (48), 43 (100), 42 (13), 28 (32)] and a pale orange oil, Ph_2Te [yield 47%; bp 105 °C (0.3 torr); mass spectrum, *m/z* (relative intensity) 284 ($C_{12}H_{10}Te_2^+$, 34), 207 (10), 154 (100), 91 (15), 77 (78), 51 (40).

10. **Reaction of (Phenyltelluro)lithium with 1,4-Dichlorobutane. Method 1.** The addition of 1,4-dichlorobutane (6.35 g, 0.05 mol) to (phenyltelluro)lithium (0.1 mol) of THF at −196 °C using the method described for reaction 3 gave a crude mixture of oils, which were not separated: diphenyl telluride, ca. 40%, 1-(phenyltelluro)-4-chlorobutane, ca. 5%, and telluracyclopentane, ca. 20% (from NMR).

Method 2. 1,4-Dichlorobutane (6.35 g, 0.05 mol) was injected into a solution of (phenyltelluro)lithium (0.1 mol) in THF submerged in an ice–salt bath at −10 °C. The mixture was stirred for ca. 1 h and allowed to reach room temperature when it was stirred for a further 2 h. The reaction mixture was then hydrolyzed, separated, extracted, and dried in the usual way. Removal of the solvent in vacuo gave the two products diphenyl telluride and telluracyclopentane as for reaction 9, which were not separated.

11. **Reaction of (Methyltelluro)lithium with 1,4-Dichlorobutane.** 1,4-Dichlorobutane (6.35 g, 0.05 ml) was injected onto a frozen (−196 °C) solution of (methyltelluro)lithium (0.1 m) in THF as described, and the procedure was followed to yield a crude oil containing dimethyl telluride, telluracyclopentane, and 1-chloro-5-tellurahexane in similar yields to reaction 10.

12. **Reaction of (Methyltelluro)lithium with 1,5-Dichloropentane. Method 1.** 1,5-Dichloropentane (7.05 g, 0.05 mol) was injected into a solution of (methyltelluro)lithium (0.1 mol) in THF at room temperature. The mixture was stirred for ca. 2 h when it was worked up in the usual way. The resulting

two products were Me_2Te, which was removed in vacuo, and telluracyclohexane, which was an orange oil: bp 45 °C (2 torr); yield 46%.

Method 2. 1,5-Dichloropentane (7.05 g, 0.05 mol) was injected onto a frozen (−196 °C) solution of (methyltelluro)lithium following the procedure described for reaction 3. The resulting crude oil contained four products: Me_2Te, $\overline{Te(CH_2)_4C}H_2$, $MeTe(CH_2)_5Cl$, and $MeTe(CH_2)_5TeMe$. mass spectra: *m/z* (relative intensity) 250 ($C_6H_{13}ClTe^+$, 14), 145 (6), 130 (6), 105 (9), 69 (100); *m/z* (relative intensity) 200 ($C_5H_{10}Te^+$, 34), 172 (3), 158 (12), 144 (9), 130 (11), 69 (88), 41 (100).

13. Reaction of (Phenyltelluro)lithium with 1,5-Dichloropentane. Addition of 1,5-dichloropentane (7.05 g, 0.05 mol) to a frozen (−196 °C) solution of (phenyltelluro)lithium (0.1 mol), following the procedure described, resulted in an orange oil containing Ph_2Te, $\overline{Te(CH_2)_4C}H_2$, $PhTe(CH_2)_5Cl$, and $PhTe(CH_2)_5TePh$. Spectral data were obtained from the crude mixture, and no further attempt to separate the products was made.

14. Reaction of 1,6-Dibromohexane with (Phenyltelluro)lithium. 1,6-Dibromohexane (6.1 g, 25 mmol) was injected onto a frozen (−196 °C) solution of (phenyltelluro)lithium (50 mmol) and the procedure followed as for reaction 3. Separation of the products was effected on a flash silica column, eluting with 40–60 °C petroleum ether to give an orange oil [Ph_2Te (14%)] and a yellow oil [$PhTe(CH_2)_6TePh$ (51%)]. Continued elution increasing the polarity of the solvent 50/50 v/v CH_2Cl_2/petroleum ether (40–60 °C) gave a third band of probably oligomeric material: mass spectrum, *m/z* (relative intensity) 498($C_{18}H_{22}Te_2^+$, 3), 414 (3), 291 (30), 207 (36), 154 (42), 77 (97), 55 (100).

The bis(methiodide) $IPhMeTe(CH_2)_6TeMePhI$ was obtained as for reaction 7; mp 82 °C. Anal. Calcd for $C_{20}H_{28}I_2Te_2$: C, 30.9; H, 3.6. Found: C, 31.2; H, 3.8.

15. Reaction of 1,6-Dichlorohexane with MeTeLi. 1,6-Dichlorohexane (3.87 g, 25 mmol) was injected onto a frozen (−196 °C) solution of (phenyltelluro)lithium (50 mmol) and the procedure followed as for reaction 3. The products were Me_2Te, an involatile oligomeric material, and $MeTe(CH_2)_6TeMe$. Distillation in vacuo gave the ligand as an orange oil: bp 120 °C (0.2 torr); yield 56%; mass spectrum, *m/z* (relative intensity) 374 ($C_8H_{18}Te_2^+$, 7), 359 (6), 290 (5), 275 (20), 229 (32), 214 (11), 145 (39), 83 (37), 55 (100).

The bis(methiodide) $IMe_2Te(CH_2)_6TeMe_2I$ was obtained as for reaction 7; mp 154 °C. Anal. Calcd for $C_{10}H_{24}I_2Te_2$: C, 18.4; H, 3.7. Found: C, 18.3; H, 3.8.

16. Reaction of 3-Bromo-1-propanol with (Methyltelluro)lithium. The same reaction conditions as for reaction 3 but using 3-bromo-1-propanol (6.95 g, 50 mmol) and (methyltelluro)lithium (50 mmol) gave a pale yellow-orange oil in acceptable purity, 4-tellura-1-pentanol: yield 8.3 g (83%); mass spectrum, *m/z* (relative intensity) 204 ($C_4H_{10}OTe^+$, 100), 171 (43), 157 (10), 145 (65), 144 (63), 130 (54).

17. Reaction of Iodobenzene with (Methyltelluro)lithium. Identical reaction conditions were employed as for reaction 3, adding iodobenzene (10.2 g, 50 mmol) to (methyltelluro)lithium (50 mmol). The product methyl phenyl telluride was distilled from the crude oil in vacuo: bp 62–64 °C (0.3 torr); yield 3.9 g (35%); mass spectrum, *m/z* (relative intensity) 222 ($C_7H_8Te^+$, 70), 207 (59), 145 (5), 130 (6), 91 (11), 77 (100).

18. Reaction of 1,10-Dibromodecane with (Methyltelluro)lithium. This was carried out by using the same method as for reaction 3, using 1,10-dibromodecane (7.50 g, 25 mmol) and MeTeLi (50 mmol). Distillation in vacuo gave the product as an orange oil: bp 148 °C (0.4 torr); mass spectrum, *m/z* 430 ($C_{12}H_{26}Te_2^+$, 1.5), 415 (4), 285 (21), 270 (5.5), 145 (12), 97 (23), 83 (100). The bis(methiodide) $IMe_2Te(CH_2)_{10}TeMe_2I$ was obtained as for reaction 7; mp 146–148 °C. Anal. Calcd for $C_{14}H_{32}I_2Te_2$: C, 23.7; H, 4.5. Found: C, 24.1; H, 4.7.

19. Reaction of (Methyltelluro)lithium with 1,1,1-Tris(bromomethyl)ethane. 1,1,1-Tris(bromomethyl)ethane (5.15 g, 17 mmol) was injected onto a twofold excess, frozen (−196 °C) solution of (methyltelluro)lithium (100 mL) in THF. The mixture was allowed to thaw, stirred at room temperature overnight, and refluxed for 1 h. Hydrolysis was followed by separation, extraction (diethyl ether), and drying ($MgSO_4$), followed by removal of solvent in vacuo, to yield a deep red oil. Dimethyl ditelluride was distilled off in vacuo and the residue dissolved in chloroform and filtered and the solvent removed to yield a pale orange oil: 64%; mass spectrum, *m/z* (relative intensity) 504($C_8H_{18}Te_3^+$, 2), 489 (5), 290 (4), 275 (4), 260 (8), 214 (12), 199 (5), 145 (11), 69 (100).

20. Reaction of (Methyltelluro)lithium with Tetrakis(bromomethyl)methane. Tetrakis(bromomethyl)methane (4.85 g, 12.5 mmol) was dissolved in a minimum of dry THF and the solution injected onto a twofold excess of frozen (−196 °C) (methyltelluro)lithium (100 mmol) solution (THF). Following the procedure of reaction 19 gave a yellow oil which was shown to be 1,1-bis((methyltelluro)methyl]cyclopropane: yield 4.0 g (91%); mass spectrum, *m/z* (relative intensity) 358 ($C_7H_{14}Te_2^+$, 2), 343 (15), 290 (9), 275 (28), 198 (14), 145 (24), 130 (14), 67 (100).

21. Reaction of (Phenyltelluro)lithium with Tetrakis(bromomethyl)methane. Tetrakis(bromomethyl)methane (4.85 g, 12.5 mmol) was reacted with (phenyltelluro)lithium by using the same experimental procedure as for reaction 19. The removal of solvent left a solid residue that was recrystallized twice from 40–60 °C petroleum ether to yield the product as a white powder: yield 58%; mp 188 °C. Anal. Calcd for $C_{29}H_{28}Te_4$: C, 39.3; H, 3.2. Found: C, 39.9; H, 3.0.

Acknowledgment. We thank the SERC for support and Mrs. J. M. Street for the ^1H and ^{13}C NMR data.

Registry No. PhTeLi, 52251-60-2; MeTeLi, 60919-62-2; Te, 13494-80-9; PhLi, 591-51-5; MeLi, 917-54-4; CH_2I_2, 75-11-6; $PhTeCH_2TePh$, 55136-88-4; CH_2cl_2, 75-09-2; $PhTeCl_2CH_2TeCl_2Ph$, 100207-50-9; $MeTeCH_2TeMe$, 100207-53-2; $MeTeCl_2CH_2TeCl_2Me$, 100207-47-4; $ClCH_2CH_2Cl$, 107-06-2; PhTeTePh, 32294-60-3; $Br(CH_2)_3Br$, 109-64-8; $PhTe(CH_2)_3TePh$, 105598-31-0; $IPhMeTe(CH_2)_3TeMePhI$, 110850-97-0; CH_3I, 74-88-4; $Cl(CH_2)_3Cl$, 142-28-9; $MeTe(CH_2)_3TeMe$, 105598-32-1; $IMe_2Te(CH_2)_3TeMe_2I$, 110850-98-1; $Br(CH_2)_4Br$, 110-52-1; $\overline{Te(CH_2)_3C}H_2$, 3465-99-4; Ph_2Te, 1202-36-4; $Cl(CH_2)_4Cl$, 110-56-5; $PhTe(CH_2)_4Cl$, 110850-99-2; $Cl(CH_2)_5Cl$, 628-76-2; $\overline{Te(CH_2)_4C}H_2$, 6049-77-0; $MeTe(CH_2)_5TeMe$, 110851-00-8; $Br(CH_2)_6Br$, 629-03-8; $PhTe(CH_2)_6TePh$, 110851-01-9; $IPhMeTe(CH_2)_6TeMePhI$, 110851-02-0; $Cl(CH_2)_6Cl$, 629-03-8; $MeTe(CH_2)_6TeMe$, 110851-03-1; $IMe_2Te(CH_2)_6TeMe_2I$, 110851-04-2; $Br(CH_2)_3OH$, 627-18-9; $MeTe(CH_2)_3OH$, 110851-05-3; PhI, 591-50-4; PhTeMe, 872-89-9; $Br(CH_2)_{10}Br$, 4101-68-2; $MeTe(CH_2)_{10}TeMe$, 110851-06-4; $IMe_2Te(CH_2)_{10}TeMe_2I$, 110851-07-5; $CH_3C(CH_2Br)_3$, 60111-68-4; $C(CH_2Br)_4$, 3229-00-3; $\overline{CH_2CH_2C}(CH_2TeMe)_2$, 110851-08-6; $C(CH_2TePh)_4$, 110851-09-7.