Reaction of Tellurium Hexafluoride with Ethylene Glycol and Other Polyhydric Alcohols

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Tellurium hexafluoride reacts with ethylene glycol under a range of experimental conditions to yield the compounds $F_5TeO\cdot[CH_2]_2\cdot OTeF_5$, *cis*-$(\cdot O\cdot[CH_2]_2\cdot O\cdot)TeF_4$, *cis*- and *trans*-$(\cdot O\cdot[CH_2]_2\cdot O\cdot)_2TeF_2$, and $(\cdot O\cdot[CH_2]_2\cdot O\cdot)_3Te$. Reactions with other polyhydric alcohols, *e.g.*, $HO\cdot[CH_2]_3\cdot OH$, $HO\cdot CH_2\cdot CH(Me)\cdot OH$, $HO\cdot[CH_2]_4\cdot OH$, $HO\cdot[CH_2]_{10}\cdot OH$, $HO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, $MeC(CH_2OH)_3$, and $C(CH_2OH)_4$ have also been investigated and the properties of the products are discussed.

RECENTLY the reactions of tellurium hexafluoride, TeF_6, with a variety of alcohols have been reported [1,2] to yield the mono-, di-, and tri-alkoxotellurium(VI) fluorides, TeF_5OR, $TeF_4(OR)_2$, and $TeF_3(OR)_3$, respectively. We have extended the reactions of TeF_6 to include a number of polyhydric alcohols and in this paper we discuss the results of these investigations.

RESULTS AND DISCUSSION

Tellurium hexafluoride reacted with ethylene glycol to produce a number of compounds depending on the experimental conditions. At room temperature, in the presence of sodium fluoride, equimolar quantities of tellurium hexafluoride and ethylene glycol formed the cyclic compound (I; $n = 2$), while with excess of TeF_6 a mixture of (I; $n = 2$) containing a small proportion of the linear compound (II; $n = 2$) was obtained. When pyridine was used to remove the hydrogen fluoride formed in the reaction (II; $n = 2$) was not observed, but with excess of ethylene glycol (I; $n = 2$) was converted into the new compounds (III; $n = 2$) and (IV; $n = 2$). More vigorous conditions are

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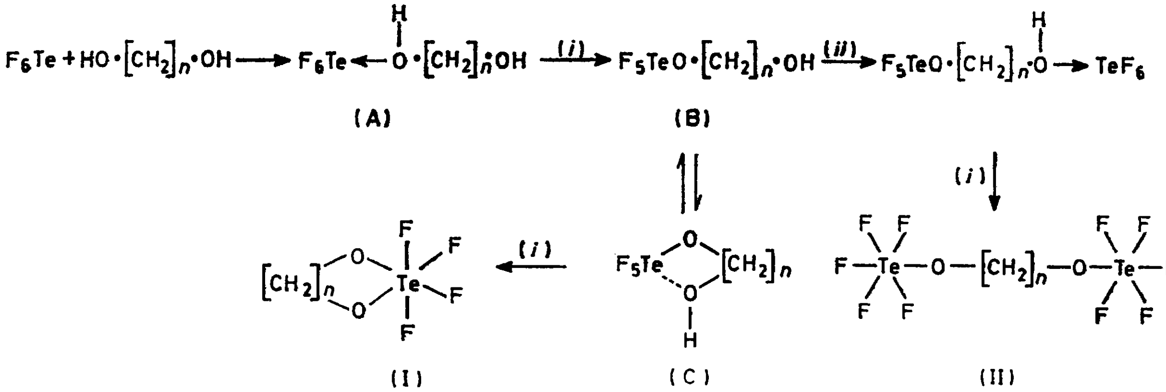
[1] G. W. Fraser and J. B. Millar, *J.C.S. Dalton*, **1974**, 2029.

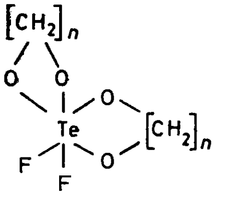
[2] G. W. Fraser and G. D. Meikle, *J.C.S. Perkin II*, **1975**, 312.

necessary to form the fully substituted material (V; $n = 2$), high yields being obtained by reaction of TeF_6 with excess of ethylene glycol in the presence of sodium fluoride in a sealed tube at 80 °C for 7 d.

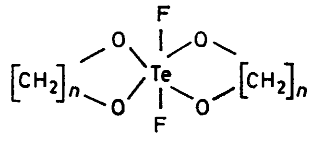
The reactions of TeF_6 with other diols of the type $HO{\cdot}[CH_2]_n{\cdot}OH$ were examined in less detail but two major differences were noted. Under similar experimental conditions to those used above, reaction of $HO{\cdot}[CH_2]_n{\cdot}OH$ ($n = 3$, 4, or 10) with a large excess of TeF_6 produced only the corresponding compound (II) [rather than the mixture of (I) and (II)], while with excess of diol only the corresponding compound (I) [rather than (III) and (IV)] was formed.



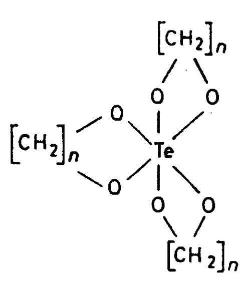
(*i*), −HF; (*ii*), TeF_6



(III)



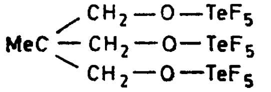
(IV)



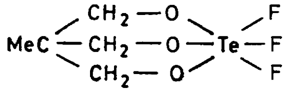
(V)

The ready formation of (II; $n = 3$, 4, or 10) compared with (II; $n = 2$) can be explained if, as is highly probable, the reactions proceed *via* a series of steps. The quantity of (I) and (II) formed in the reactions will depend on the equilibria between (B) and (C); in the case of ethylene glycol, the concentration of (C) is sufficient to produce a large quantity of (I) even in the presence of excess of TeF_6, while with the other diols the concentration of (C) is very small and (II) is formed. In an earlier publication [2] we reported that the products from the reactions of TeF_6 with some substituted alcohols depended on the nature of the substituents and suggested that, in some cases, an interaction between the substituent and the tellurium atom similar to (C) was an important factor. The different reactivities of 2-bromoethanol and 3-bromopropanol suggested that this interaction was more important for a five-membered ring, in agreement with the results shown above. In contrast, the formation of (III)—(V) from the appropriate diol appear to be controlled by steric factors; thus, ethylene glycol forms (III) and (IV) at room temperature and (V) on heating, whereas propane-1,2-diol, propane-1,3-diol, and the other diols discussed above form only (I) at room temperature.

The reactions of TeF_6 with the triols, $MeC(CH_2OH)_3$ and $HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ follow similar patterns to the diols already discussed. In the presence of excess of TeF_6 $MeC(CH_2OH)_3$ formed (VI), whereas with equimolar quantities, or with excess of the triol, (VII) was the only product. The reaction of TeF_6 with glycerol was of interest because the different hydroxyl groups could form products similar to those derived from both ethylene glycol and propane-1,3-diol. However, with excess of TeF_6, only one compound was formed, microanalysis and the ^{19}F n.m.r. spectrum (see below) confirming the structure (VIII). When pentaerythritol reacted with TeF_6 in the molar ratio 1 : 2, the only product was (IX). However, with excess of TeF_6 a mixture was obtained, the products being (X) together with a small quantity of (XI) and a trace of (IX).

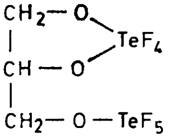


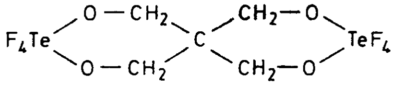
(VI)



(VII)

All the compounds discussed above are colourless liquids or solids, the majority of which can be purified by distillation or sublimation at reduced pressure. Their melting and boiling points are given in the Table. They are soluble in, or miscible with, most non-polar solvents, the solutions for n.m.r. spectroscopy normally being prepared using chloroform as solvent.


(VIII)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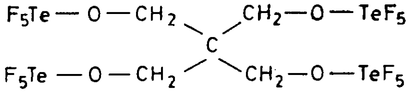
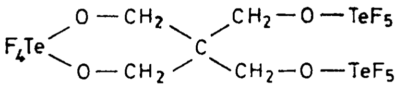

(X)


(XI)

The i.r. spectra of all the compounds [except (V)] showed strong absorptions in the region 720—630 cm^{-1}. These could be assigned to tellurium–fluorine stretching vibrations (Table). As reported previously,[1] the degree of substitution into TeF_6 can normally be deduced from the value of ν(Te–F), since this moves to lower frequency as substitution increases. The compounds all exhibited mass spectra which were consistent with the structures shown but in few cases were the parent ions obtained. The number of fluorine atoms attached to the tellurium atoms could always be determined from the spectra but the loss of a hydrogen atom or of an ' organic ' fragment from the parent ion usually occurred. Similar breakdown patterns have been observed in the mass spectra of other tellurium–fluorine compounds.[3]

			^{19}F N.m.r. spectra (CFCl$_3$)			
Compound	B.p. (θ_c/°C) *	ν(Te–F)/cm^{-1}	Pattern	δ_A/p.p.m.	δ_B/p.p.m.	J(AB)/Hz
(I; $n = 2$)	60 (8)	677	A_2B_2	+44·5	+58·9	161
(I; $n = 3$)	73 (1)	675	A_2B_2	+46·0	+51·5	156
(I; $n = 4$)	72 (4)	670	A_2B_2	+47·7	+56·9	156
(I; $n = 10$)	Decomp.	675	A_2B_2	+47·1	+56·6	157
(II; $n = 3$)	75 (6)	702	AB_4	+44·5	+55·4	182
(II; $n = 4$)	77 (3)	703	AB_4	+44·6	+56·4	182
(II; $n = 10$)	86 (0·03)	706	AB_4	+43·5	+55·9	183
(III; $n = 2$)	60(0·01) [100]	663	A_2	+49·5		
(IV; $n = 2$)	120(0·001) [178]	663	A_2	+40·5		
(V; $n = 2$)	100(0·001) [199]					
(VI)	78(0·02) [55]	710	AB_4	+43·8	+54·5	180
(VII)	60(0·001) [246]	670	A_3	+48·0		
(VIII)	48 (0·02)	713, 688	AB_4	+45·7	+55·7	181
			ABCD		Complex	
(IX)	100(0·02) [140]	680	A_2B_2	+46·4	+59·1	160
(X)	85 (0·001)	715	AB_4	+44·6	+53·9	181
(XI)	85(0·001) [51]	723, 685	AB_4	+44·0	+53·7	180
			A_2B_2	+46·7	+60·1	158

* M.p.s are given in square brackets.

^{19}F N.m.r. spectroscopy was a valuable technique for confirming the structure of the compounds. Those containing TeF_5 and TeF_4 groups [except (VIII)] exhibited characteristic AB_4 and A_2B_2 patterns, respectively, similar to those found in other TeF_6 derivatives.[1] The spectra of (III), (IV), and (VII) consisted of single lines, while no resonance was observed for (V). The chemical shifts and coupling constants are given in the Table. The value of ^{19}F n.m.r. spectroscopy in determining the structures of these compounds could be conclusively shown by examining the spectrum of (VIII). This consisted of a normal AB_4 pattern, together with a more complex series of signals which could not be analysed as a typical A_2B_2 pattern. However, this complex part of the spectrum was superimposable with that observed for compound (I) obtained from propane-1,2-diol, confirming that the TeF_4 group in (VIII) was bonded to adjacent oxygen atoms and not to the two oxygen atoms of the primary-alcohol groups.

While ^{19}F n.m.r. spectroscopy was a valuable tool in this work, it was impossible to distinguish between compounds (III) and (IV) using this technique, since both produced a single-line spectrum. However, the two compounds belong to the point groups C_2 and D_{2h} and therefore, from group theory, the *cis*-isomer, (III), should have coincidences for all the i.r. and Raman absorptions, whereas the *trans*-isomer, (IV), has a centre of symmetry and thus no coincidences should occur. The predictions were confirmed experimentally and the compounds were assigned the appropriate structures on this evidence. Subsequently the isomers were more easily identified by their different chemical shifts in the ^{19}F n.m.r. spectrum.

EXPERIMENTAL

The compounds were prepared at room temperature or in a sealed tube at 80 °C for 7 d, in a similar manner to the

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[3] F. Sladky and H. Kropshofer, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 195.

alkoxotellurium fluorides described previously.[1,2] They could be purified by distillation or sublimation at reduced pressure and their constitutions were confirmed by satisfactory microanalyses for carbon, hydrogen, and fluorine. The isomeric compounds (III) and (IV) were readily separated as the latter was insoluble in water–chloroform and could be filtered off and dried. The *cis*-isomer, (III), was then isolated from the chloroform solution in the normal way.

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