Synthesis of Alkoxotellurium(VI) Fluorides

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The alkoxotellurium(VI) fluorides $TeF_{6-x}(OR)_x$ (x = 1—5) have been synthesised by the reaction of tellurium hexafluoride with the appropriate alcohol or sodium alkoxide, and by the oxidative fluorination of $Te(OR)_4$ with elemental fluorine at low temperature. The ^{19}F n.m.r. spectra of these compounds are described.

THE reactions of tellurium hexafluoride with alcohols have been studied in some detail and the products have been shown to depend on the relative concentrations of the reactants and also on the base used to remove the hydrogen fluoride which is formed according to reaction (1). When sodium fluoride is used as the base and the

$$TeF_6 + xROH \longrightarrow TeF_{6-x}(OR)_x + xHF \qquad (1)$$

reactions are carried out at 20 °C the product is usually the monoalkoxo-derivative $TeF_5(OR)$,[1,2] although ethylene glycol produces *cis*-$TeF_4(\cdot OCH_2CH_2O\cdot)$ under these conditions.[3] If pyridine is used as the base the products depend on the alcohol involved; simple alcohols yield the dialkoxo-compounds $TeF_4(OR)_2$, but under the same experimental conditions certain, more complex, alcohols form the trialkoxo-derivatives $TeF_3(OR)_3$.[4]

We have found that, under more vigorous reaction conditions, further substitution can occur and that all the compounds and isomers in the series $TeF_{6-x}(OR)_x$ (x = 1—5) can be synthesised.

RESULTS AND DISCUSSION

The reactions of TeF_6 with alcohols were carried out in sealed Pyrex reaction tubes (600 cm^3) at 85—90 °C over a period of 9 d using anhydrous sodium fluoride as the hydrogen fluoride scavenger in each reaction. Usually, mixtures of products were formed which could not be separated by fractional distillation due to their similar volatilities. Table 1 lists the alcohols used in the reactions and the relative amounts of each product formed, calculated by analysing the ^{19}F n.m.r. spectrum of the reaction mixture. With the exception of allyl alcohol, little or no decomposition took place at 85—90 °C, but under even more vigorous conditions decomposition usually occurred, *e.g.* when 2-chloroethanol was heated with TeF_6 at 145—150 °C in the presence of NaF total decomposition occurred within 60 h.

Analysis of the ^{19}F n.m.r. spectra of the reaction mixtures gave a value for the average number of alkoxo-groups per molecule, $\bar{N}$ (Table 1). In no instance was the value of $\bar{N}$ commensurate with the amount of alcohol used in the reaction; *i.e.* after 9 d at 85—90 °C none of the reactions had reached completion.

It can readily be seen that the amount of alcohol reacted and the relative concentrations of the products formed vary with the different alcohols used. In an earlier paper[4] the effects of substituted alkoxo-groups, $R'CH_2O$, on the formation at room temperature of trialkoxotellurium(VI) trifluorides were described. The variation of the values of $\bar{N}$ with different substituent groups R′ as shown in Table 1 suggests that similar effects operate at 85—90 °C. The substituent groups R′ causing the greatest degree of substitution can be arranged in the order $MeOCH_2 > ClCH_2 > CF_3 > BrCH_2 > Et$. The relatively low value of $\bar{N}$ for the reaction involving CF_3CH_2OH is probably due to the acidic nature of this alcohol which will not aid the formation of the TeF_6–ROH complex.

In a previous paper[4] we reported that the di- and tri-substituted derivatives, $TeF_4(OR)_2$ and $TeF_3(OR)_3$ respectively, were formed under similar experimental conditions at room temperature. Thus it appears that the formation of tetra- and penta-substituted derivatives, *e.g.* $TeF_2(OCH_2CH_2OMe)_4$ and $TeF(OCH_2CH_2OMe)_5$, only at elevated temperatures is evidence of kinetic control. Whilst excess of n-propanol and TeF_6 react at 85—90 °C to give $TeF_4(OPr^n)_2$, methanol and TeF_6 react at 130—140 °C to form $TeF_3(OMe)_3$.[5] This suggests that the formation of trisubstituted species by

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

[3] G. W. Fraser and G. D. Meikle, *J.C.S. Dalton*, 1975, 1033.

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

[5] J. B. Millar, University of Strathclyde, 1971—1974, unpublished data.

these systems at room temperature would be extremely slow. Anchimeric assistance by substituents incorporated into the alkoxo-groups $R'CH_2O$ therefore appears to be important in determining the rate of reaction and hence the degree of substitution at higher reaction temperatures.

Table 1

Products identified from the reactions of TeF_6 with alcohols carried out at 85—90 °C

Alcohol, ROH (amount/equiv.)	Composition of product	$\bar{N}$	^{19}F N.m.r. spectrum [a] Spin system	δ_A p.p.m.	δ_B p.p.m.	J_{AB} Hz
$MeOCH_2CH_2OH$ (4.5)	9% *fac*-$TeF_3(OR)_3$	4.08	A_3	53.4		
	70% *cis*-$TeF_2(OR)_4$		A_2	56.4		
	4% *trans*-$TeF_2(OR)_4$		A_2	64.0		
	17% $TeF(OR)_5$		A	60.5		
$ClCH_2CH_2OH$ (4.5)	27% *fac*-$TeF_3(OR)_3$	3.50	A_3	49.6		
	26% *mer*-$TeF_3(OR)_3$		AB_2	51.1	55.9	137
	35% *cis*-$TeF_2(OR)_4$		A_2	54.1		
	9% *trans*-$TeF_2(OR)_4$		A_2	59.1		
	3% $TeF(OR)_5$		A	60.5		
$BrCH_2CH_2OH$ (5)	54% *cis*-$TeF_4(OR)_2$	2.56	A_2B_2	45.1	52.5	159
	34% *mer*-$TeF_3(OR)_3$		AB_2	49.9	54.3	136
	4% *fac*-$TeF_3(OR)_3$		A_3	50.9		
	4% *cis*-$TeF_2(OR)_4$		A_2	54.1		
	2% *trans*-$TeF_2(OR)_4$		A_2	58.9		
	2% $TeF(OR)_5$		A	58.4		
CF_3CH_2OH (8)	(*i*) After 9 d					
	77% *mer*- $TeF_3(OR)_3$	3.00	AB_2	56.5	58.9	143
	23% *fac*-$TeF_3(OR)_3$		A_3	54.7		
	(*ii*) After 28 d					
	33% *mer*-$TeF_3(OR)_3$	3.29	AB_2	56.5	58.9	143
	38% *fac*-$TeF_3(OR)_3$		A_3	54.7		
	22% *cis*-$TeF_2(OR)_4$		A_2	58.7		
	7% *trans*-$TeF_2(OR)_4$		A_2	60.6		
Pr^nOH (5)	100% *cis*-$TeF_4(OR)_2$	2.00	A_2B_2	48.0	56.9	158
$CH_2=CHCH_2OH$ [b] (5)						

[a] Chemical shifts relative to $CFCl_3$. [b] Decomposition occurred after 5 d.

We have postulated[4] that the reactions between alcohols and TeF_6 occur *via* the intermediate $F_6Te \leftarrow O(H)R$, *i.e.* the alcohol acts as a Lewis base. Since the corresponding alkoxide ion would be a much stronger Lewis base, the reaction between TeF_6 and the sodium alkoxide should proceed according to equation (2)

$$TeF_6 + xNa[OR] \longrightarrow TeF_{6-x}(OR)_x + xNaF \quad (2)$$

while $TeF_5(OR)$ and $TeF_4(OR)_2$ should be converted also into more highly substituted derivatives by a similar reaction. The results of the reactions of $TeF_5(OMe)$ and *cis*-$TeF_4(OMe)_2$ with sodium methoxide are presented in Table 2, which shows that the tri-, tetra-, and penta-substituted derivatives may be prepared by this method.

Table 2

Products formed by the reaction of sodium methoxide with (*i*) $TeF_5(OMe)$ after 18 h, (*ii*) *cis*-$TeF_4(OMe)_2$ after 72 h

Reaction	Composition of product	^{19}F N.m.r. spectrum [a] Spin system	δ_A p.p.m.	δ_B p.p.m.	J_{AB} Hz
(*i*)	80% *fac*-$TeF_3(OMe)_3$	A_3	58.1		
	20% *mer*-$TeF_3(OMe)_3$	AB_2	59.7	67.9	134
(*ii*)	5% *trans*-$TeF_4(OMe)_2$	A_4	61.6		
	35% *fac*-$TeF_3(OMe)_3$	A_3	57.9		
	30% *mer*-$TeF_3(OMe)_3$	AB_2	59.0	67.1	134
	25% *cis*-$TeF_2(OMe)_4$	A_2	66.8 [b]		
	5% $TeF(OMe)_5$	A	75.8 [c]		

[a] Chemical shifts relative to $CFCl_3$. [b] $J(^{125}Te-F)$ 3 300 Hz. [c] $J(^{125}Te-F)$ 3 240 Hz.

Both the preparative methods so far discussed involve the substitution of alkoxo-groups into tellurium hexafluoride. Selig and his co-workers[6] reported that tellurium(VI) hexamethoxide can be converted into the series $TeF_{6-x}(OMe)_x$ ($x = 1$—5) by treating it with anhydrous hydrogen fluoride. This method is limited by the number of compounds of the type $Te(OR)_6$ which can be prepared. However, tellurium(IV) tetra-alkoxides, $Te(OR)_4$, are more easily accessible and can be synthesised by standard methods.[7,8] Oxidative fluorination of these compounds would be expected to yield the corresponding difluorotellurium(VI) species $TeF_2(OR)_4$. When $Te(OPr^i)_4$ was subjected to elemental fluorine at room temperature, extensive burning and charring took place and no product could be identified. Modifying the reaction conditions by carrying out the reaction at −78 °C, dispersing the $Te(OR)_4$ in $CFCl_3$, and by diluting the fluorine with nitrogen led to good yields of alkoxotellurium(VI) fluorides. The products obtained by the fluorination of $Te(OMe)_4$ and $Te(OPr^i)_4$ are listed in Table 3 together with their ^{19}F n.m.r. spectra which were the principle means of their identification. In addition to the expected *cis*- and *trans*-$TeF_2(OR)_4$

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[6] I. Agranat, M. Rabinovitz, and H. Selig, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 185.

[7] P. Dupuy, *Compt. rend.*, 1955, **240**, 2238.

[8] S. N. Mathur and R. C. Mehrota, *J. Indian Chem. Soc.*, 1965, **42**, 1.

molecules, a number of other derivatives were observed; these were probably formed by disproportionations and/or rearrangements taking place during the fluorination reaction. It was not possible to separate the reaction products by fractional distillation under reduced pressure.

TABLE 3

Products identified from the oxidative fluorination of (*i*) $Te(OMe)_4$, (*ii*) $Te(OPr^i)_4$

Reaction	Composition of product	^{19}F N.m.r. spectrum (δ/p.p.m. from $CFCl_3$)
(*i*)	8% *fac*-$TeF_3(OMe)_3$	58.5
	42% *cis*-$TeF_2(OMe)_4$	67.0
	10% *trans*-$TeF_2(OMe)_4$	72.3
	40% $TeF(OMe)_5$	77.6
(*ii*)	9% *trans*-$TeF_4(OPr^i)_2$	38.3
	27% *fac*-$TeF_3(OPr^i)_3$	46.3
	57% *cis*-$TeF_2(OPr^i)_4$	49.9
	7% *trans*-$TeF_2(OPr^i)_4$ or $TeF(OPr^i)_5$	53.3

Flurine-19 n.m.r. spectroscopy was an extremely valuable technique for the identification of the reaction products previously described. The species *cis*-$TeF_4(OR)_2$ and *mer*-$TeF_3(OR)_3$ gave rise to A_2B_2 and AB_2 spin systems respectively, and their chemical shifts and coupling constants were readily measurable. In contrast, *trans*-$TeF_4(OR)_2$, *fac*-$TeF_3(OR)_3$, *cis*- and *trans*-$TeF_2(OR)_4$, and $TeF(OR)_5$ all exhibit single-line resonances and a more detailed analysis was necessary in order to identify each signal.

Dean and Evans[9] showed that ^{19}F n.m.r. chemical shifts in substituted hexafluorostannates, $[SnF_{6-x}L_x]^{2-}$, relative to $[SnF_6]^{2-}$ may be represented by equation (3)

$$\delta_F = pC + qT \tag{3}$$

where C and T are constants characteristic of a particular substituent, and p and q are the numbers of substituents *cis* and *trans* respectively to the fluorine atoms. This relation is quite acceptable for the series $[SnF_{6-x}L_x]^{2-}$,[9] $WF_{6-x}(OMe)_x$,[10] and $TeF_{6-x}(OH)_x$[11] but Selig found that for $TeF_{6-x}(OMe)_x$ two converging curves are produced by the relation instead of two parallel straight lines.[6] A similar situation was found for all the molecules of the type $TeF_{6-x}(OCH_2R)_x$ described in this paper; the chemical shifts for the species with $x = 0$—3 define the curves on the basis of their known identity or distinctive line patterns of their spectra, and extrapolation of these curves permitted other single-line resonances in the ^{19}F n.m.r. spectra to be identified and assigned. The ^1H n.m.r. spectra of the reaction products were, in all cases, typical of the alkyl groups involved.

EXPERIMENTAL

The preparations of tellurium hexafluoride and mono- and di-alkoxo-derivatives of TeF_6 have been described elsewhere.[1,2] The tellurium(IV) tetra-alkoxides $Te(OMe)_4$ and $Te(OPr^i)_4$ were synthesised according to methods described in the literature.[8]

Reaction of TeF_6 *with Alcohols*.—The ratio of alcohol to TeF_6 used in each reaction is given in Table 1. In a typical reaction, $MeOCH_2CH_2OH$ (12.2 g, 160 mmol) and dry NaF (90 g, 2.1 mol) were placed in a reaction tube (600 cm^3), chilled in liquid nitrogen and evacuated to 0.001 mmHg.* Then TeF_6 (8.6 g, 35.6 mmol) was condensed into the tube which was then sealed. After warming to room temperature the vessel was heated to 85—90 °C for 9 d, cooled, and the products extracted as described previously.[2] The approximate percentage constitution of the product was obtained from its ^{19}F n.m.r. spectrum.

Reaction of $TeF_5(OMe)$ *and* cis-$TeF_4(OMe)_2$ *with Sodium Methoxide*.—Sodium methoxide solution in methanol was placed in a reaction vessel (350 cm^3) which was then cooled to −196 °C and evacuated. The compound $TeF_5(OMe)$ or *cis*-$TeF_4(OMe)_2$ was condensed into the vessel until the $Na[OMe] : TeF_5(OMe)$ and $Na[OMe] : TeF_4(OMe)_2$ molar ratios were *ca.* 8 : 1 and 6 : 1 respectively. The vessel was sealed and set aside at 20 °C for 18 h in the case of the reaction of $TeF_5(OMe)$, and for 72 h in the other instance. The products were extracted with chloroform as described previously,[2] and the approximate percentage compositions of the product mixtures were obtained from their ^{19}F n.m.r. spectra.

Fluorination of $Te(OMe)_4$ *and* $Te(OPr^i)_4$.—The tellurium(IV) tetra-alkoxide (*ca.* 5 g) was added to a conical reaction vessel in a dry-box. The vessel was removed from the dry-box, cooled to −78 °C, and dry $CFCl_3$ (*ca.* 20 cm^3) was condensed on to the $Te(OR)_4$ by means of a vacuum line. This mixture was then vigorously stirred at −78 °C whilst a stream of fluorine diluted with four parts dry nitrogen was passed over it. The reaction was continued for 3 h during which time a four-fold excess of fluorine passed through the reaction vessel. After purging the apparatus with nitrogen, the $CFCl_3$ solvent was allowed to evaporate and the reaction products were extracted with chloroform as previously described.[2] Examination of the ^{19}F n.m.r. spectra of the products allowed the relative quantities of each component present to be determined.

We thank the S.R.C. for the award of a research studentship (to G. D. M.).

[7/425 *Received*, 10*th March*, 1977]

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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