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OXIDATIVE ADDITION AND ISOMERIZATION REACTIONS: THE STEREOSELECTIVE SYNTHESIS OF *CIS*- AND *TRANS*-Ph_2TeX_4

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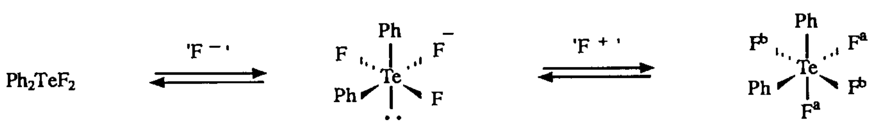
SUMMARY

A study of the stereoselective synthesis of *cis*- and *trans*-Ph_2TeX_4 (X=F,Cl) supports a two pathway mechanism in which oxidative addition leads to the cis isomer while subsequent isomerization leads to the trans isomer.

INTRODUCTION

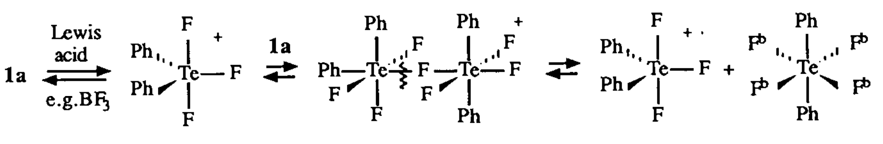
Oxidative addition reactions may produce cis or trans isomers of organotellurium(VI) fluorides [1-5], as illustrated by the formation of either *trans*-Ph_2TeF_4 [1] or *cis*-$(C_6F_5)_2TeF_4$ [2] if XeF_2 or F_2, respectively, is used as the oxidizing agent. We wish to present evidence in support of a two pathway mechanism in which oxidative addition, eq 1, leads to *cis*-Ph_2TeF_4 while a subsequent isomerization, eq 2, leads to *trans*-Ph_2TeF_4.

We postulate that oxidative-fluorination occurs by the stepwise addition of ‘F^-’ and ‘F^+’ [6], where F^- donors include R_4NF, HF, or FHF^-, and F^+ donors include XeF^+ or



(1)

1a (cis)



(2)

1b (trans)

0022-1139/91/$3.50

$FXeFXeF^+$, and that a lone pair of electrons in anion $Ph_2TeF_3^-$ is trans to phenyl, thus ensuring that two phenyl substituents occupy cis positions during oxidation, eq 1. Te(IV) compounds readily form five-coordinate anions [7] and the structures of $MeTeI_4^-$ [8] and $PhTeX_4^-$ [9] confirm that alkyl or phenyl substituents may occupy sites trans to a lone pair.

The isomerization of *cis*- to *trans*-Ph_2TeF_4, eq 2, is assumed to follow a pathway found for other organotellurium(VI) fluorides in which five-coordinate cations are produced by Lewis acids such as PF_5 [10,11], SbF_5 [4], BF_3 or SiF_4, with the latter two species often originating from glass apparatus [10,11].

RESULTS AND DISCUSSION

Eq 1 implies that no reaction can occur unless a source of fluoride ion is present and we have confirmed this by keeping a mixture of Ph_2TeF_2 and XeF_2 in acetonitrile in a Teflon bottle for 48 hr and, occasionally, up to 8 days without reaction. However, addition of Bu_4NF or Et_4NCl results in rapid oxidation within 10 min. Similarly, a mixture of Ph_2TeCl_2 and XeF_2 does not undergo oxidation within 48 hr unless Bu_4NF or Et_4NCl is added, after which oxidation occurs within 10-30 min. Reactions are accompanied by the evolution of xenon gas and a visible colour change from colourless to yellow and back to colourless. Typical conditions for reactions of Ph_2TeX_2, R_4NX and XeF_2 are given in Table 1. We have found that Ph_2TeF_2, Ph_2TeCl_2 or Ph_2TeFCl may be used as Te(IV) starting material, and either R_4NF or R_4NCl may be used as a source of 'X^-', presumably because halide exchange occurs rapidly in $Ph_2TeX_3^-$, as it does in other Te(IV) anions such as $PhTeCl_4^-$ or $PhTeBr_4^-$ [7,12].

Although XeF_2 and Ph_2TeX_2 do not react in carefully dried solvents in Teflon equipment, unless R_4NX is added, this reaction proceeds slowly without R_4NX if carried out in glass apparatus, presumably because glass and solvent eventually produce HF, BF_3 and SiF_4. The formation of BF_3 and SiF_4 from glass implies that H_2O must also be released, and we have identified by ^{19}F NMR small amounts of the known hydrolysis product Ph_2TeF_3OH [13] in solution. At the completion of reactions, HF could be detected by ^{19}F NMR; if reactions were carried out in glassware, small amounts of BF_4^- were observed.

NMR data for diphenyltellurium(VI) halides are given in Table 2. The symmetry of *cis*-$Ph_2TeF_2Cl_2$ $\underline{2}$ is established by its AB ^{19}F NMR spectrum. When reaction conditions were optimized for the formation of $\underline{2}$, as monitored by ^{19}F NMR, it was found that $\underline{2}$ was produced in 82% yield within 30 min, consistent with oxidation according to eq 1, as well as halide exchange via $Ph_2TeX_3^-$.

In another set of experiments, reaction conditions were optimized for the formation of *cis*-Ph_2TeF_3Cl $\underline{3a}$, which was prepared in 84% yield within 30 min, from Ph_2TeCl_2, XeF_2 and Bu_4NF. AB_2 NMR spectra are expected for all three possible isomers of Ph_2TeF_3Cl, but two of these isomers have F^a trans to Cl, which leads to low field ^{19}F chemical shifts, but only stereoisomer *cis*-Ph_2TeF_3Cl $\underline{3a}$ (Table 2) has F^a in a region expected for F^a trans to Ph [5]. The formation of *cis*-Ph_2TeF_3Cl $\underline{3a}$ is consistent with oxidation according to eq 1, as well as halide exchange via $Ph_2TeX_3^-$.

TABLE 1

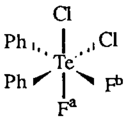
Reaction conditions and % yield of *cis*- and *trans*-Ph_2TeX_4 (X=F,Cl)

Molar ratio of reactants	Reaction conditions	*cis*-Ph_2TeX_4	*trans*-Ph_2TeX_4
Ph_2Te:XeF_2:Et_4NCl; 1:2:0.1	10 min, CD_3CN, NMR tube	1a 14%	1b 40%
Ph_2TeCl_2:XeF_2; 1:2 (no R_4NX)	3 hr, $CDCl_3$, glass tube	1a 0%	1b 49%
Ph_2TeCl_2:XeF_2:Et_4NCl; 1:2:0.1	30 min, CD_3CN, Teflon bottle	1a 1-2%	1b 95%
Ph_2TeCl_2:XeF_2:Et_4NCl; 1:2:2	30 min, CH_2Cl_2, Teflon bottle	2 82%	3b 18%
Ph_2TeCl_2:XeF_2:Bu_4NF; 1:2:1	30 min, CD_3CN, Teflon bottle	3a 84%	1b 16%

The cis isomers described in Table 1 slowly undergo cis-to-trans isomerization in solution, as well as chloride-to-fluoride substitution, presumably via the cation $Ph_2TeX_3^+$. If sufficient fluoride is present in solution, all reactions after several days lead only to *trans*-Ph_2TeF_4. In the case of *cis*-Ph_2TeF_3Cl 3a it was possible to monitor isomerization to *trans*-Ph_2TeF_3Cl 3b, and eventual conversion to *trans*-Ph_2TeF_4. *Trans*-Ph_2TeF_3Cl 3b gives an AB_2 spectrum (Table 2) with F^a at low field (+37 ppm), as expected for F^a trans to Cl, while F^b is in the region expected for F^b trans to F^b [5].

Previously, the synthesis of *trans*-Ph_2TeF_4 [1] was accompanied by small amounts (1-4%) of *cis*-Ph_2TeF_4 [5], and we have now modestly increased the yield of *cis*-Ph_2TeF_4 to 14% within 10 min by adding Et_4NCl (Table 1). After 10 min, *cis*-Ph_2TeF_4 is slowly converted to *trans*-Ph_2TeF_4, eq 2, presumably because Lewis acids such as BF_3 or SiF_4 are produced in glass. That the trans isomer is favoured in the presence of Lewis acids was confirmed by reacting *trans*-Ph_2TeF_4 with PF_5, which led to rapid fluorine exchange and very broad fluorine NMR peaks; on addition of R_4NF, *trans*-Ph_2TeF_4 was recovered, thereby confirming that fluorine exchange rather than decomposition was responsible for the very broad fluorine NMR lines.

Klein and Naumann reported that *cis*-$(C_6F_5)_2TeF_4$ reacts with common organic solvents [2]. Our work leads us to suggest that *cis*-$(C_6F_5)_2TeF_4$ may be undergoing rapid fluorine exchange and isomerization in solution in glass apparatus, rather than decomposition. Such exchange has been stopped in related systems by the addition of F^- or Cl^- because small



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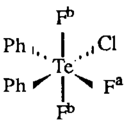
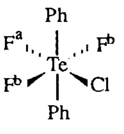


3a



3b

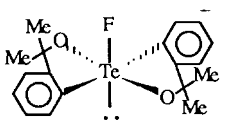


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TABLE 2

NMR data of some diphenyltellurium(VI) halides[1]

Compound and spin system			δF^a	δF^b	$J(F^aF^b)$	$J(TeF^a)$	$J(TeF^b)$	Solvent
cis-Ph_2TeF_4	1a	A_2B_2	-32.7(t)[3]	-75.9(t)[4]	87.3	2884	2675	CD_3CN[2]
trans-Ph_2TeF_4	1b	A_4		-56.7(s)[4]			2997	CD_3CN
cis-$Ph_2TeF_2Cl_2$	2	AB	+63(d)[5]	-43(d)[3]	97.7	2500	2220	CD_3CN
cis-Ph_2TeF_3Cl	3a	AB_2	-19.9(t)[3]	-48.9(d)[4]	88.9	2830	2418	CD_3CN
trans-Ph_2TeF_3Cl	3b	AB_2	+37(t)[5]	-50.2(d)[4]	88.8	2830	2375	CD_2Cl_2

[1] Chemical shifts in ppm and coupling constants in Hz, s=singlet, d=doublet, t=triplet; [2] see ref. [5] for NMR data in $CDCl_3$ solution; [3] F trans to Ph; [4] F trans to F, [5] F trans to Cl.

amounts of Te(VI) cations which are responsible for rapid fluorine exchange are thereby removed [10,11]. These authors also reported the formation of a compound with a coupling constant J(Te-F)=3,540 Hz, which we suggest may be assigned to *trans*-$(C_6F_5)_2TeF_4$; if so, then the isomerization of cis and trans isomers of Ph_2TeF_4 and $(C_6F_5)_2TeF_4$ is similar and consistent with eq 2.

That *trans*-Ph_2TeF_4 was the predominant isomer of our previous synthesis may now be interpreted as follows: since no catalyst was added and since contact with glass was not rigorously excluded, therefore, oxidation was very slow and cis-trans isomerization prevailed.

Martin and co-workers reported that oxidation with BrF_3 gives *trans*-$F_2Te(C_6H_4CMe_2O)_2$ [4]. If the mechanism of eq 1 and 2 is applied to this reaction and BrF_3 is a source of 'F⁻' and 'F⁺', perhaps from ions BrF_4^- and BrF_2^+, then intermediate 4 may have F trans to a lone pair of electrons. Perhaps two bidentate ligands in 4 favour a planar arrangement with F in an apical site, as found for related 5-coordinate P and Si catecholyl derivatives, e.g. $FP(OC_6H_4O)_2$ [14] and $FSi(OC_6H_4O)_2^-$ [15]; in that case addition of 'F⁺' to 4 is predicted to give *trans*-$F_2Te(C_6H_4CMe_2O)_2$, as found experimentally. In the presence of SbF_5, *trans*-$F_2Te(C_6H_4CMe_2O)_2$ isomerizes to *cis*-$F_2Te(C_6H_4CMe_2O)_2$ [4].

In summary, the mechanisms of eq 1 and 2 suggest that the stereochemistry of oxidative addition is determined by the structure of 5-coordinate, 12-electron anions, while the stereochemistry of isomerization is determined by the structure of 5-coordinate, 10-electron cations; both anion and cation may be involved in halide exchange and substitution reactions; various oxidizing agents may serve as sources of 'X⁻' and 'X⁺'; and glassware may serve as a convenient source of Lewis acids.

EXPERIMENTAL

NMR spectra were recorded on a Bruker AM300 spectrometer at 282.4 (^{19}F) and 94.76(^{125}Te) MHz with the use of internal C_6F_6 (-162.9 ppm w.r.t. $CFCl_3$) and external Ph_2Te

(692.3 ppm w.r.t. Me_2Te) as reference. All reactions were routinely monitored by NMR and structural assignments are based on NMR spectra of related phenyltellurium(VI) fluorides [1,5,10,11,13]. Yields are based on ^{19}F NMR integrations.

XeF_2 (PCR/SCM), Ph_2TeCl_2 (K & K), deuterated solvents (Aldrich), and Bu_4NF in THF (Aldrich) were commercial samples and used without further purification. Solutions of Bu_4NF showed traces of BF_4^- and $SiF_6^=$. Et_4NCl (Eastman) was recrystallized from dry CH_3CN and stored in a desiccator over P_2O_5. Ph_2TeF_2 and Ph_2TeFCl were prepared from Ph_2TeCl_2 and COF_2 [10]. All solvents were dried by standard methods and stored over 5 Å molecular sieve, and Teflon equipment was dried at 100°C for several days. XeF_2 reactions were monitored by observing the release of xenon gas bubbles and a change in colour from colourless to yellow and back to colourless, which occurred within the first few minutes if catalysts Bu_4NF or Et_4NCl were used and if the reaction was carried out in Teflon equipment. If the reaction was carried out in glass tubes then a persistent darker yellow colour was observed. Reactions were also carried out in NMR tubes, with and without Teflon liners, and monitored by ^{19}F NMR.

Convenient synthesis of *trans*-Ph_2TeF_4 1b

The original synthesis of 1b, by reaction of Ph_2Te with 2 equiv of XeF_2 or Ph_2TeF_2 and 1 equiv of XeF_2, was repeated. As found previously, oxidation of Ph_2Te to Ph_2TeF_2 occurred within several minutes, but further oxidation to 1b without R_4NX catalyst occurred only after several hours or days.

Commercially available Ph_2TeCl_2 could be used in a more convenient and rapid synthesis of 1b. Solid XeF_2 (13.5 mg, 0.08 mmol) was added to a stirred solution of Ph_2TeCl_2 (14.0 mg, 0.04 mmol in dry CH_2Cl_2 in a Teflon bottle. Et_4NCl (0.6 mg, 0.04 mmol) was added to this mixture with stirring. The colourless solution rapidly turned yellow with vigorous gas evolution. When gas evolution ceased, the solution turned colourless within 10 min. The ^{19}F NMR spectrum of the solution confirmed the formation of 1b in 95% yield. A small amount of HF was also detected. Evaporation of the solvent gave a white solid which was washed with cold acetonitrile. Slow evaporation of dichloromethane solvent gave colourless crystals of *trans*-Ph_2TeF_4 1b, identified by ^{19}F (Table 1), ^{125}Te and ^{13}C NMR, and which were stored in Teflon vials.

Preparation of *cis*-$Ph_2TeF_2Cl_2$ 2 and *trans*-Ph_2TeF_3Cl 3b

Solid XeF_2 (49.1 mg, 0.29 mmol) was added to a solution of Et_4NCl (48.0 mg, 0.29 mmol) in CH_2Cl_2 in a Teflon bottle, but there was no reaction, as judged by ^{19}F NMR, except for the formation of small amounts of HF. Solid Ph_2TeCl_2 (49.4 mg, 0.14 mmol) was added to this mixture and ^{19}F NMR examination (Table 2) after 30 min showed the formation of 2 (82%) and 3b (18%). After a further 45 min, the reaction mixture contained 80% *trans*-Ph_2TeF_4 1b and small amount of 3b. The latter was also converted to *trans*-Ph_2TeF_4 1b after 2 days.

Preparation of *cis*-Ph_2TeF_3Cl 3a

Solid XeF_2 (20 mg, 0.12 mmol) was added to Ph_2TeCl_2 (21 mg, 0.06 mmol) in CH_3CN (2.5 mL) in a Teflon bottle. Ph_2TeCl_2 is insoluble in CH_3CN. No reaction occurred after stirring for several min. Adding Bu_4NF (~0.12 mmol) caused rapid xenon gas evolution and the solution turned yellow. The reaction mixture was stirred for 30 min and the solution became very faintly yellow (almost colourless) and ^{19}F NMR (Table 2) showed the formation of *cis*-Ph_2TeF_3Cl 3a (84%) and *trans*-Ph_2TeF_4 1b (16%). After stirring for 12 hr, the solution contained predominantly *trans*-Ph_2TeF_4 1b.

Products 1a, 2, 3a, 3b were not isolated because of the conversion to *trans*-Ph_2TeF_4 1b, and the latter was recovered from all reactions and washed and re-crystallized as described above.

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