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REACTIONS OF PHENYLTELLURIUM(VI) FLUORIDES WITH ALCOHOLS, AMINES AND SILICON COMPOUNDS*

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SUMMARY

The reactions of phenyltellurium(VI) fluorides, $PhTeF_5$, *trans*-Ph_2TeF_4 and *mer*-Ph_3TeF_3, with alcohols and amines, or their trimethylsilyl derivatives, are described The products $PhTeF_4X$, Ph_2TeF_3X and Ph_3TeF_2X (X=OMe, NMe_2, NEt_2) were characterized by ^{19}F NMR and isomeric structures are assigned on the basis of their NMR spectra Samples of *trans*-Ph_2TeF_4 contain small amounts of *cis*-Ph_2TeF_4

RESULTS AND DISCUSSION

The reactions of phenyltellurium(VI) fluorides [1,2], i e $PhTeF_5$, *trans*-Ph_2TeF_4 and *mer*-Ph_3TeF_3, with alcohols and amines were carried out by using either NaF or R_2NH as the HF acceptor, or by choosing the corresponding trimethylsilyl derivative

$$PhTeF_5 + Me_3SiOR \xrightarrow[-Me_3SiF]{} PhTeF_4OR \xleftarrow[-NaF\ HF]{NaF} PhTeF_5 + ROH$$

$$Ph_2TeF_4 + Me_3SiNR_2 \xrightarrow[-Me_3SiF]{} Ph_2TeF_3NR_2 \xleftarrow[-R_2NH\ HF]{} Ph_2TeF_4 + 2R_2NH$$

The products $PhTeF_4X$, Ph_2TeF_3X and Ph_3TeF_2X (X=OMe, NMe_2, NEt_2) 1-7 were identified on the basis of their ^{19}F NMR spectra (Table 1) which are in agreement with those of related Te(VI) fluorides [1-4] The cis geometry of $PhTeF_4X$ 1-2 is established by the ABC_2 spin system and F^A is assigned to a

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*This paper is dedicated to Professor D C Bradley on the occasion of his retirement

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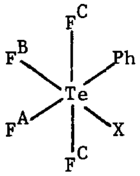
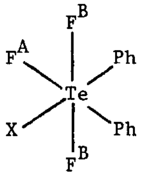
site trans to a phenyl substituent because it has been found that a phenyl group in Ph_3TeF_3 [2], Ph_3TeF_2Cl [1] and Ph_3TeF_2OH [5] produces a large downfield shift in the trans fluorine.



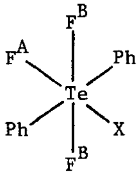
$PhTeF_4X$

1 X=OMe
2 $X=NMe_2$



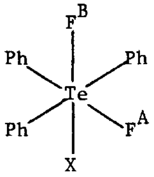
Ph_2TeF_3X

4a $X=NMe_2$
5a $X=NEt_2$



Ph_2TeF_3X

4b $X=NMe_2$
5b $X=NEt_2$



Ph_3TeF_2X

6 X=OMe
7 $X=NMe_2$

Compounds 3-5 have AB_2 spectra and two isomers of Ph_2TeF_3X are shown above. The downfield shift of F^A in 4a and 5a suggests a structure in which F^A is trans to a phenyl substituent, but the structure of Ph_2TeF_3OMe 3 remains uncertain. A third isomer of Ph_2TeF_3X, in which both fluorines are trans to phenyls, would be expected to show a doublet at low field, but this was not observed. For products Ph_3TeF_2X 6-7, we make the assumption that the three bulky phenyl substituents adopt a *mer* arrangement, as confirmed by x-ray crystallography for Ph_3TeF_3 [2] and Ph_3TeF_2OH [5], and in that case the stereochemistry of 6-7 is established by the AB spin system.

Other isomers of 1-7 were also observed by ^{19}F NMR, but they were produced in smaller yields and their characterization is incomplete.

In some reactions, there was evidence of reduction to Te(IV) species, most readily observed by the formation of Ph_2TeF_2 in reactions of diphenyltellurium(VI) compounds. For example, the reaction of Ph_2TeF_4 with MeOH produced some Ph_2TeF_2 which increased when the reaction conditions were changed from 40°C to 50°C.

During the preparation of *trans*-Ph_2TeF_4, a small amount (1-4%) of *cis*-Ph_2TeF_4 was observed and identified by its A_2B_2 NMR spectrum (Table 1). Analogous compounds *cis*-$(C_6F_5)_2TeF_4$ [6] and *cis*-Ph_2SF_4 [7] have been described previously.

TABLE 1

^{19}F nmr data of some phenyltellurium(VI) compounds[a]

Compound		Spin system	δF_A	δF_B	δF_C	$J(F_AF_B)$	$J(F_AF_C)$	$J(F_BF_C)$	$J(F_ATe)$	$J(F_BTe)$	$J(F_CTe)$	Solvent
cis-$PhTeF_4OMe$	1	ABC_2	-45	-49	-60	148	105	130	3330	2940	3288	CD_2Cl_2
cis-$PhTeF_4NMe_2$	2	ABC_2	-34	-47	-73	153	105	123	3150	3400	3115	CD_2Cl_2
Ph_2TeF_3OMe	3	AB_2	-31	-74		29			2920	2768		$CDCl_3$
$Ph_2TeF_3NMe_2$	4a	AB_2	- 8	-88		40			2802	2466		CD_3CN
$Ph_2TeF_3NMe_2$	4b	AB_2	-20	-53		68			2690	2380		CD_3CN
$Ph_2TeF_3NEt_2$	5a	AB_2	-12	-85		43			2784	2450		$CDCl_3$
$Ph_2TeF_3NEt_2$	5b	AB_2	-37	-64		30			2928	2825		$CDCl_3$
Ph_3TeF_2OMe	6	AB	-29	-75		55			2610	2076		CD_2Cl_2
$Ph_3TeF_2NMe_2$	7	AB	- 7	-65		70			2370	2008		CD_3CN
cis-Ph_2TeF_4	8	A_2B_2	-35	-78		88			2880	2685		$CDCl_3$

[a] Chemical shifts are reported in ppm and coupling constants in Hz.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Bruker AM300 spectrometer at 282 4 MHz with the use of C_6F_6 (-162 9 ppm with respect to $CFCl_3$) as internal reference Ph_3TeF [8], $Ph_3Te^+BF_4^-$ [1] and Ph_3TeF_3 [2] were prepared as described in the literature $PhTeCl_3$ was prepared from $TeCl_4$ and Ph_3SnCl [9] and converted to $PhTeF_3$ with the use of AgF [10] The remaining starting compounds were commercial samples and used as supplied

$PhTeF_5$ was prepared by slowly (20 min) adding solid XeF_2 (0 04 g, 0 21 mmol) to a stirred solution of $PhTeF_3$ (0 05 g, 0 19 mmol) in CH_2Cl_2 (2 mL) in a Teflon bottle After further stirring for 3 hr at 25°C, volatile material was removed under vacuum and the remaining viscous oil identified as $PhTeF_5$ by ^{19}F and ^{125}Te NMR and MS [1]

Ph_2TeF_2 was prepared by slowly adding Ph_2Te (0 15 g, 0 53 mmol) in CH_2Cl_2 (2 mL) through a syringe to a stirred solution of XeF_2 (0 1 g, 0 59 mmol) in CH_2Cl_2 (2 mL) at 0°C Stirring was continued at 25°C for about 30 min until the evolution of Xe gas ceased and the yellow colour of the solution disappeared Removal of volatile material under vacuum gave Ph_2TeF_2 which was recrystallized from benzene/n-hexane and identified by ^{19}F NMR [11]

Preparation of *cis*-$PhTeF_4OMe$ 1

(i) MeOH (1 9 mmol), NaF (1 8 mmol) and $PhTeF_5$ (0 31 mmol) in CH_3CN/CH_2Cl_2 (1 1, 2 mL) was stirred in a Teflon bottle for 18 h and then filtered The filtrate was dried under vacuum and a white solid was obtained and identified (Table 1) as *cis*-$PhTeF_4OMe$ 1

(ii) Me_3SiOMe (0 35 mmol) and $PhTeF_5$ (0 2 mmol) in CH_2Cl_2 (1 mL) was kept at 20°C for 12 h, with occasional shaking to give Me_3SiF and *cis*-$PhTeF_4OMe$ 1

Preparation of *cis*-$PhTeF_4NMe_2$ 2

Me_3SiNMe_2 (0 54 mmol) and $PhTeF_5$ (0 24 mmol) in CH_2Cl_2 (1 mL) was kept in an NMR tube at 20°C for 12 hr during which time the solution turned yellow Me_3SiF and other volatile material was removed under vacuum and the remaining solid was identified (Table 1) as *cis*-$PhTeF_4NMe_2$ 2

Preparation of Ph_2TeF_3OMe 3

(i) MeOH (0.61), NaF (0.91 mmol) and *trans*-Ph_2TeF_4 (0.32 mmol) in CH_2Cl_2 (4 mL) was stirred for 2 days, with occasional warming, and then filtered. The filtrate was dried under vacuum and a white solid was obtained and identified (Table 1) as Ph_2TeF_3OMe 3.

(ii) Me_3SiOMe (0.16 mmol) and *trans*-Ph_2TeF_4 (0.10 mmol) in CH_2Cl_2 (1 mL) was kept in an NMR tube at 20°C for 3 days to give Me_3SiF and Ph_2TeF_3OMe 3.

Preparation of $Ph_2TeF_3NR_2$ R=Me (4a-4b) and R=Et (5a-5b)

(i) Me_3SiNMe_2 (0.56 mmol) and *trans*-Ph_2TeF_4 (0.19 mmol) in $CHCl_3$ (1 mL) was kept in a sealed tube at 20°C for 4 days, then heated to 35°C for 1 hour. Two AB_2 NMR spectra were observed (Table 1) and assigned to two isomers of $Ph_2TeF_3NMe_2$, 4a and 4b.

Replacing Me_3SiNMe_2 with Me_3SiNEt_2 in the previous reaction, gave two isomers of $Ph_2TeF_3NEt_2$, 5a and 5b.

(ii) Me_2NH (0.65 mmol), *trans*-Ph_2TeF_4 (0.23 mmol) and $CHCl_3$ (1 mL) was kept in a sealed tube for 5 days at 20°C during which time the solution turned dark yellow and crystals of $Me_2NH\cdot HF$ formed. The latter were removed and the ^{19}F NMR spectra (Table 1) of the solution showed two AB_2 spectra assigned to two isomers of $Ph_2TeF_3NMe_2$, 4a and 4b.

Preparation of Ph_3TeF_2OMe 6

MeOH (0.89 mmol), NaF (2.8 mmol) and *mer*-Ph_3TeF_3 (0.41 mmol) in $CHCl_3$ (3 mL) was kept in a sealed tube at 20°C for 3 days, and then heated to 45°C for 30 min. The solution was filtered and the filtrate dried under vacuum to give a white solid identified as Ph_3TeF_2OMe 6.

Preparation of $Ph_3TeF_2NMe_2$ 7

Me_2NH (0.52 mmol), *mer*-Ph_3TeF_3 (0.28 mmol) and $CHCl_3$ (3 mL) was kept at 20°C for 5 days and then heated to 40°C for 20 min. Solid $Me_2NH\cdot HF$ was removed from the yellow solution which contained $Ph_3TeF_2NMe_2$ 7.

Trans-Ph_2TeF_4 and *cis*-Ph_2TeF_4 8

Solid XeF_2 (0 12 g, 0 70 mmol) was added to a stirred solution of Ph_2TeF_2 (0 16 g, 0 48 mmol) in CH_2Cl_2 (4 mL) at 0°C After stirring for 2 days at 25°C, all volatile material was pumped off to give a white solid which was recrystallized from benzene/n-hexane and identified as *trans*-Ph_2TeF_4 by ^{19}F and ^{125}Te NMR [1]

Trans-Ph_2TeF_4 was also prepared in a one-step reaction by using an excess of XeF_2 (0 12 g, 0 70 mmol) and Ph_2Te (0 08 g, 0 27 mmol) in CH_2Cl_2 It was also recovered from the reaction of XeF_2 and $Ph_3Te^+BF_4^-$ in CH_2Cl_2/CH_3CN

The synthesis of *trans*-Ph_2TeF_4 was occasionally accompanied by the formation of small amounts (1-4%) of *cis*-Ph_2TeF_4 8, identified by its A_2B_2 ^{19}F NMR spectrum (Table 1) Attempts to isolate *cis*-Ph_2TeF_4 were unsuccessful

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