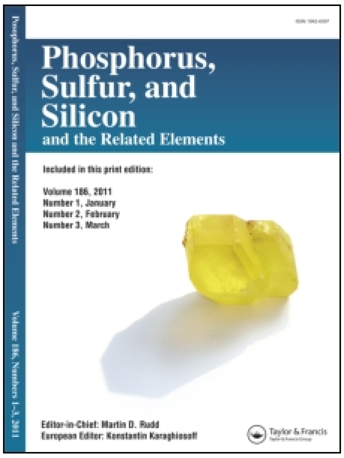

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FLUORINATING PROPERTIES OF $PhTeF_5$ AND $PhSeF_5$ TOWARDS C=C BOND

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Communication

FLUORINATING PROPERTIES OF $PhTeF_5$ AND $PhSeF_5$ TOWARDS C=C BOND

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Phenylselenium pentafluoride and phenyltellurium pentafluoride react with olefins affording appropriate 1,2-difluorides under mild conditions.

Key words: Phenylselenium pentafluoride, phenyltellurium pentafluoride, xenon difluoride, olefins, difluorination, electrophilic addition.

Methods of effective and selective fluorination of organic compounds are of importance in the chemistry of biologically active compounds and drug synthesis.[1a–c] At the same time the reactions leading to the introduction of fluorine or fluorine containing moieties into organic molecules are not numerous. Especially it concerns the methods of electrophilic addition to double and triple carbon-carbon bonds: practically only the fluorination either by hazardous F_2 (or some reactive compounds like CH_3COOF which are prepared *in situ* by means of F_2)[2] or unselective XeF_2[1a,3] is used. Therefore, the implementation of novel electrophilic fluorinating reagents capable of performing mild and selective oxidative fluorination of multiple bonds is of general interest. Recently several papers have appeared concerning the application of new types of electrophilic reagents, namely Se(II) and Se(IV) fluorides, for addition reactions to olefins and acetylenes[4–6] in accordance with following scheme (Equation 1):

$$\text{PhSeF}_2\text{C—CF} \xleftarrow{\text{PhSeF}_3} \text{C=C} \xrightarrow{\text{PhSeF}} \text{PhSeC—CF} \qquad (1)$$

Unfortunately, these reagents have some drawbacks due to the presence of the selenium containing fragment in the product and hence, the necessity to perform further transformations to eliminate it. In the course of our systematic search for novel fluorinating reagents[5,7] we describe in this paper the reactions of olefins with two interesting fluorinating reagents, namely $PhTeF_5$ (**1**) and $PhSeF_5$ (**2**).

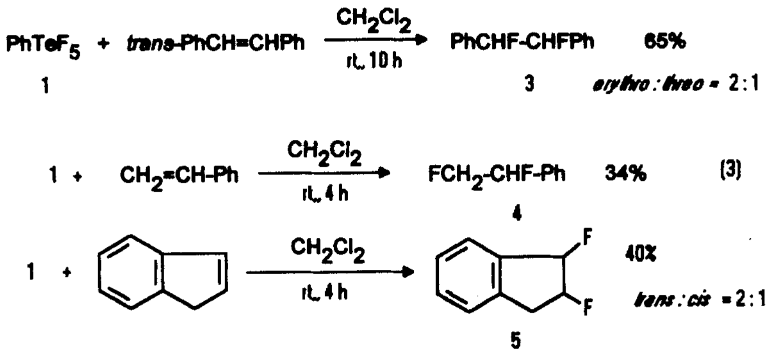
RESULTS AND DISCUSSION

$PhTeF_5$ (**1**) has been described in the literature, though only the nucleophilic displacement of fluoride was investigated[8]; we were unable to find any data concerning $PhSeF_5$ (**2**). Thus, we have prepared them using the reaction of diphenyl diselenide/ditelluride with XeF_2 (Equation 2):

$$Ph_2X_2 + 5\,XeF_2 \xrightarrow[\text{rt}]{CH_2Cl_2,\ -Xe} 2\,PhXF_5 \qquad (2)$$
$$\mathbf{1}\ X = Te$$
$$\mathbf{2}\ X = Se$$

Fluorination of Ph_2Se_2 needs 3–4 h; Ph_2Te_2 reacts faster (some minutes). Both reagents were used without isolation.

We have found, that phenyltellurium pentafluoride, **1**, reacts smoothly with olefins affording the corresponding 1,2-difluorides as the principle products (Equation 3)



(3)

Difluorides **3**–**5** were identified using ^{19}F NMR and mass-spectra. Difluoride **4** was prepared independently from sytrene and XeF_2 according to published procedure.[10]

Generally, phenylselenium pentafluoride, **2**, reacts with olefins in the same manner, also affording 1,2-difluorides, as it is shown in the scheme (Equation 4):

$$\underset{\mathbf{2}}{PhSeF_5} + trans\text{-}PhCH{=}CHPh \xrightarrow[\text{rt, 10 h}]{CH_2Cl_2} \underset{\mathbf{3}}{PhCHF\text{-}CHFPh}\ \ 90\%$$
$$erythro : threo = 4:1 \quad [4]$$

$$\underset{\mathbf{2}}{PhSeF_5} + CH_2{=}CHPh \xrightarrow[\text{rt, 4 h}]{CH_2Cl_2} \underset{\mathbf{4}}{F\text{-}CH_2\text{-}CHF\text{-}Ph} + \underset{\mathbf{6}}{PhSeF_2\text{-}CH_2\text{-}CHF\text{-}Ph} \qquad (4)$$
$$\mathbf{4}+\mathbf{6} = 32\% \quad \mathbf{4}:\mathbf{6} = 1:1$$

Evidently, in both cases the fluorination process is a two step Ad_E-reaction which consists of (i) addition of the $PhTeF_4^+$ ($PhSeF_4^+$) and F^- fragments to the C=C bond and (ii) subsequent nucleophilic substitution of the TeF_4Ph (or SeF_4Ph) fragment by the fluoride to give the C—F bond, followed by the $PhTe(Se)F_2$-anion disproportionation into F^- and $PhTeF_3$ or $PhSeF_3$. The formation of **6** confirms the suggested scheme, because $PhSeF_3$ was shown to be able to react with olefins.[5] In contrast, we have shown that specially prepared $PhTeF_3$ (it was synthesized analogously to $PhSeF_3$)[5] does not react with styrene under these conditions. The weak electrophilic nature of $PhTeF_3$ (which is a by-product in the reaction of **1** with olefins) towards the C=C bond is probably the main reason for the absence of the tellurium analogue of **6** in the reaction mixtures and hence, the absence of undesirable contaminating by-products.

Thus, we may conclude that phenyltellurium pentafluoride, **1**, and, to a lesser extent, phenylselenium pentafluoride, **2**, represent a novel class of mild difluorinating agents for C=C bond and may serve as F_2 equivalent. Different Te(VI) fluorides can be easily prepared, they are rather stable towards hydrolysis,[8] and hence this class of fluorides deserves further investigation as fluorinating agents.

EXPERIMENTAL

^1H and ^{19}F specta ($CDCl_3$) were recorded on a Bruker CXP-200 spectrometer using TMS as internal reference and CF_3COOH as external reference respectively. Mass-spectra were recorded on a Finnigan GC/MS-4021 spectrometer.

General procedure: 5 mmol of XeF_2 were added by portions at rt. to a stirred solution of 1 mmol of Ph_2Se_2 of Ph_2Te_2 in 5 mL of dry CH_2Cl_2 in quartz or teflon vessel. After 3–4 h (3–4 min for Ph_2Te_2) the gas evolution ceased (approximately 5 mmol evolved), 2 mmol of olefin were added in one portion. After appropriate stirring the solvent was removed in *vacuo*, the residue dissolved in $CDCl_3$ + exact quantity of C_6F_6 (internal standard for integration) and analysed by ^{19}F NMR.

^{19}F NMR (188 MHz): **3**: −109 (AA'XX', *erythro*), −105 (AA'XX', *threo*), (see Reference 9); **4**: −147.9 (t.t, $^2J_{H-F}$ = 48 Hz, $^3J_{F-F,H-F}$ = 32 Hz), −111 m (see Reference 10). **5**: −99.3 m, −110.5 m (*trans*); −113.5 m, −123.5 m (*cis*). MS (70 eV): 154 (M^+, 100), 153 (M^+-H, 69), 134 (29) (see Reference 10). **6**: −93.4 m.[11]

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11. We independently prepared **6** from styrene and PhSeF (see Reference 4) with subsequent fluorination of $PhSeCH_2CHFPh$ by XeF_2. ^{19}F NMR spectra of both samples were the same.