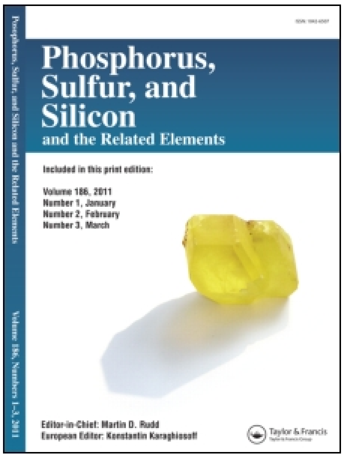

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Breunig, Hans Joachim , Gülec, Sabahittin and Kaller, Rose(1992) 'Reactions of Cyclostibanes or Distibanes with Diselenides or Ditellurides', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 33 — 38

To link to this Article: DOI: 10.1080/10426509208045816

URL: http://dx.doi.org/10.1080/10426509208045816

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 33–38
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REACTIONS OF CYCLOSTIBANES OR DISTIBANES WITH DISELENIDES OR DITELLURIDES

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Abstract Reactions of $(MesSb)_4$ or $(EtSb)_x$ with $(MeSe)_2$, $(PhSe)_2$, $(MeTe)_2$, $(PhTe)_2$ or $(p\text{-}TolTe)_2$ were studied in C_6D_6 in sealed NMR tubes. Products of the type Mes_2SbER (E = Se, Te; R = Me, Ph, p-Tol) and $(p\text{-}TolTe)_2SbMes$ or $Et(SbER)_2$ (E = Se, Te; R = Me, Ph, p-Tol) were obtained. $EtSb(TePh)_2$ was synthesized as red crystals. The telluro stibanes $Me_2SbTePh$ and $Et_2SbTePh$ were prepared from Me_4Sb_2 or Et_4Sb_2 and $(PhTe)_2$.

INTRODUCTION

Compounds with the Sb-Sb bond like organodistibanes or elemental antimony react with diselenides or ditellurides with formation of the Sb-Se or Sb-Te bond and seleno or telluro stibanes of the types R_2SbSeR, R_2SbTeR or $Sb(SeR)_3$ have been synthesized[1-4] by this kind of dismutation. Analogous reactions of organo antimony rings $(RSb)_n$ or polymers $(RSb)_x$ are interesting for the synthesis of dichalcogenostibanes of the type $RSb(ER)_2$ (E = Se[5], Te).

REACTIONS OF $(MesSb)_4$ OR $(EtSb)_x$ WITH DICHALCOGENIDES

A ^{1}H-NMR study of reactions of $(MesSb)_4$ (Mes = 2,4,6-$(CH_3)_3C_6H_2$) or $(EtSb)_x$ with $(MeSe)_2$, $(MeTe)_2$, $(PhTe)_2$ or $(p\text{-}TolTe)_2$ was carried out in sealed NMR tubes in C_6D_6. With a 1 : 4 stoichiometry of the antimony ring with respect to the dichalcogenides the signals of the ring disappeared completely. From the relative intensities of the emerging signals the expected formation of compounds of the type $MesSb(ER)_2$ could not be confirmed with E = Se, R = Me; E = Te; R = Me, Ph. Instead the pattern of signals indicated the formation of the corresponding dimesityl compounds Mes_2SbER and other products of ligand exchange reactions like $Sb(SeMe)_3$. Only in the case of the reaction of $(MesSb)_4$ with $(p\text{-}TolTe)_2$ the expected ditelluro compound $(p\text{-}TolTe)_2SbMes$ was detected by ^{1}H NMR and mass spectra as a major component of the product mixture. Preparative useful results with respect to the desired synthesis of dichalcogeno stibanes were however obtained with $(EtSb)_x$[6]. This polymer reacts with dichalcogenides in C_6D_6 to form ethyldichalcogenostibanes 1 - 5 according to Eq. (1).

$$1/x\ (EtSb)_x + REER \rightarrow \underset{\underline{1}\ -\ \underline{5}}{EtSb(ER)_2} \qquad (1)$$

1: ER = SeMe, 2: ER = SePh, 3: ER = TeMe, 4: ER = TePh, 5: ER = Te-p-Tol

The identification of 1 and 2 by ^{1}H NMR spectra was confirmed by comparison with authentic samples, that had been prepared and isolated before by ligand exchange reactions of Et_2SbER[5]. For the ditellurostibanes 3 and 5 the identification is based

mainly on the ^{1}H-NMR spectral data. In addition to 1 - 5 only very small amounts of side products of the type EtER or Et_2SbER are formed.
The ditelluro compound 4 was also prepared on a larger scale and isolated as red orange crystals in 78 % yield. Solutions of 4 in cyclohexane are orange or yellow. 4 is air sensitive in solution. Diffuse reflection spectra show a red shift of the absorption edge of 80 nm from the saturated orange yellow solution in cyclohexane (maxima at 374 nm and 430 nm) to the solid (maxima at 324 nm, 438 nm, 510 nm). Similar shifts have also been observed in the spectra of thermochromic distibanes[7].

REACTIONS OF DISTIBANES WITH DIPHENYLDITELLURIDE

The distibanes Me_4Sb_2 or Et_4Sb_2 react as neat liquids with Ph_2Te_2 with complete dismutation (Eq. 2) to form the tellurostibanes $Me_2SbTePh$ (6) or $Et_2SbTePh$ (7).

$$R_4Sb_2 + PhTeTePh \rightarrow 2\ R_2TePh \qquad (2)$$

6: R = Me; 7: R = Et.

The tellurostibanes 6 and 7 are yellow air sensitive liquids of good solubility in organic solvents. 7 is a potential rearrangement product of 4 and is indeed formed in minor amounts as a side product of the synthesis of 4.

EXPERIMENTAL

Reactions of $(MesSb)_4$ with dichalcogenides.

To solutions of $(MesSb)_4$ in C_6D_6 solutions in NMR tubes solutions of dichalcogenides were added in a 1:4 molar ratio. The sealed tubes were kept at room temperature for several hours until the spectra were recorded. The reaction of $(MesSb)_4$ with $(MeSe)_2$; $Mes_2SbSeMe$ (^1H NMR, δ, C_6D_6: 1.97 s [3H] $SeCH_3$, 2.07 s [6H] p-CH_3, 2.42 s [12 H] o-CH_3 , 6.68 s [4H] C_6H_2 and $(MeSe)_3Sb$ (2.02 s). The reaction of $(MesSb)_4$ with $(MeTe)_2$ gives $Mes_2SbTeMe$ (^1H NMR, δ, C_6D_6: 1.82 s [3H] $TeCH_3$, 2.08 s [6H] p-CH_3, 2.51 s [12 H] o-CH_3 , 6.69 s [4H] C_6H_2). Reaction of $(MesSb)_4$ with $(PhTe)_2$ gives $Mes_2SbTePh$ (^1H NMR, δ, C_6D_6: 2.08 s [6H] p-CH_3, 2.32 s [12 H] o-CH_3 , 6.69 s [4H] C_6H_2, 6.9 - 7.08 m, 7.78 - 7.85 m [5 H] C_6H_5). Reaction of $(MesSb)_4$ with $(p\text{-}TolTe)_2$ gives $Mes_2SbTe(p\text{-}Tol)$ [^1H NMR, δ, C_6D_6: 2.01 s [3H] p-CH_3 (Tol), 2.08 s [6H] p-CH_3 (Mes), 2.37 s [12 H] o-CH_3 6.69 s [4H] C_6H_2, 6.6 - 6.7 m, 7.7 - 7.8 m [4 H] C_6H_4; MS (120 °C, 70 eV) m/z (rel. int.) 580 (10) M^+] and $MesSb[Te(p\text{-}Tol)]_2$ [^1H NMR, δ, C_6D_6: 1.98 s [6H] p-CH_3 (Tol), 2.05 s [3H] p-CH_3 (Mes), 2.45 s [6H] o-CH_3, 6.7 [2H] s C_6H_2, 6.6 - 6.7 m 7.70 - 7.72 m [8H] C_6H_4; MS (120 °C, 70 eV) m/z (rel. int.) 680 (8) M^+].

Reactions of $(EtSb)_x$ with dichalcogenides.

NMR tubes were charged with solid $(EtSb)_x$ and solutions of the dichalcogenides. The tubes were sealed and stored at 60°C for 6 hrs and cooled to ambient temperature before the spectra were recorded. Reaction of $(EtSb)_x$ with $(MeSe)_2$ gives $EtSb(SeMe)_2$ (1) (^1H NMR, δ, C_6D_6: 1.24 t [3H] CH_3, 1.70 q [2H] CH_2, ^3J = 7.6 Hz, 1.99 s [6H] $SeCH_3$). Reaction of $(EtSb)_x$ with $(PhSe)_2$ gives $EtSb(SePh)_2$ (2) (^1H NMR, δ, C_6D_6: 1.24 t

[3H] CH_3, 1.60 q [2H] CH_2, ^3J = 7.6 Hz, 6.91 - 6.94 m, 7.60 - 7.64 m [10H] C_6H_5). Reaction of $(EtSb)_x$ with $(MeTe)_2$ gives $EtSb(TeMe)_2$ (3) (^1H NMR, δ, C_6H_6: 1.30 t [3H] CH_3, 1.9 q [2H] CH_2, ^3J = 7.6 Hz, 1.8 s [6H] $TeCH_3$). Reaction of $(EtSb)_x$ with $(p\text{-}TolTe)_2$ gives $EtSb[Te(p\text{-}Tol]_2$ (5) (^1H NMR, δ, C_6H_6: 1.29 t [3H] CH_3, 1.88 q [2H] CH_2, ^3J = 7.6 Hz, 1.99 s CH_3 [6H], 6.70 - 6.74 m [4H] 7.74 - 7.80 m [4H] C_6H_4.

Ethylbis(phenyltelluro)stibane (4)

0.5 g (3.4 mmole) $(EtSb)_x$ and 1.4 g (3.4 mmole) Ph_2Te_2 were stirred at 25 °C in 30 ml Et_2O for 2 hrs. until the black solid disappeared. Evaporation of the solvent gave red solid 4. Solving in petroleum ether and cooling the solution to -10 °C gave 1.5 g (78 %) of 4 as red crystals. MS (130 °C, 70 eV) m/z (rel. int.) 562 (10) M^+, 533 (10) M^+ - Et, 410 (20) 77 (100). ^1H-NMR (δ C_6D_6), 1.26 t [3H] CH_3, 1.83 q [2H] CH_2, ^3J = 7.7 Hz, 6.85 - 6.90 m [4H], 6.94 - 6.99 m [2H] 7.78 - 7.81 m [4H] C_6H_5.

$C_{14}H_{15}SbTe_2$ (560.21) MS	Calc.	C 30.03	H 2.70
	Found	C 29.71	H 2.77

Dimethyl(phenyltelluro)stibane (6).

0.53 g (0.0013 mole) Ph_2Te_2 were added to 0.39 g (0.0013 mole) Me_4Sb_2 and stirred at 0°C for 1h. There was a slightly exothermic reaction with quantitative formation of orange yellow liquid 6. MS 30 °C, 70 eV m/z (rel. int.) 358 (92) M^+, 343 (100) M^+ - Me, 328 (68), 251 (100). ^1H-NMR (δ C_6D_6) 1.00 s [6H] CH_3, 6.83 - 6.90 m, 6.95 - 7.00 m, 7.78 - 7.81 m [5H] C_6H_5.

$C_8H_{11}SbTe$ (356.52) MS	Calc.	C 26.94	H 3.11
	Found	C 25.31	H 3.34

Diethyl(phenyltelluro)stibane (7)

0.7 g (0.0017 mole) Ph_2Te_2 were added to 0.51 g (0.0017 mole) Me_4Sb_2 and stirred at 0°C for 1h. There was a slightly exothermic reaction with quantitative formation of orange yellow liquid 7. MS (30 °C, 70 eV) m/z (rel. int.) 386 (60) M^+, 357 (60) M^+ - Et, 251 (100). ^1H-NMR (δ C_6D_6), ABX_3 spin system with X 1.25 s [6H] CH_3, A 1.630, B 1.724 [4H] 6.83 - 6.90 m , 6.95 - 7.00 m ,7.78 - 7.81 m [5H] C_6H_5.

$C_{10}H_{15}SbTe$ (384.5) MS	Calc.	C 31.22	H 3.93
	Found	C 31.72	H 4.13

ACKNOWLEDGEMENT

We thank the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

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