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SYNTHESES OF DISTIBA-SELENANES, -TELLURANES AND A TELLUROSTIBANE

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Summary

Reactions of the distibanes R_4Sb_2 ($R = CH_3$, C_2H_5) with selenium or tellurium respectively produce the corresponding distiba-selenanes and -telluranes $R_2Sb–E–SbR_2$ (E = Se, Te). Selenium and $(C_6H_5)_4Sb_2$ react to form $(C_6H_5)_2Sb–Se–Sb(C_6H_5)_2$. *p*-Tolyltellurodiethylstibane is formed quantitatively from equimolar amounts of $(C_2H_5)_4Sb_2$ and $(p\text{-}CH_3C_6H_4Te)_2$.

Introduction

In the course of our investigations of the reactivity of tetraorganodistibanes [1], we studied their behaviour towards elemental selenium, tellurium and ditellurides. We now report the syntheses and spectra of the first compounds of the general formula $R_2Sb–E–SbR_2$ in which E is a selenium or tellurium atom, and also of a novel tellurostibane of the type $R_2Sb–TeR$.

Results and discussion

1,1,3,3-Tetraorganodistiba-selenanes and -telluranes

The compounds I–V are obtained in high yields according to eq. 1 when the corresponding distibanes are stirred with an excess of black selenium or tellurium in benzene at ambient temperature (I, II, IV, V) or in refluxing CS_2 (III). The reactions of the alkyl derivatives are slightly exothermic.

$$R_2Sb–SbR_2 + 1/x(E)_x \rightarrow \underset{(I–V)}{R_2Sb–E–SbR_2} \qquad (1)$$

I: $E = Se$, $R = CH_3$; orange-red liquid
II: $E = Se$, $R = C_2H_5$; yellow crystals
III: $E = Se$, $R = C_6H_5$; pale-yellow crystals
IV: $E = Te$, $R = CH_3$; brown liquid
V: $E = Te$, $R = C_2H_5$; red liquid.

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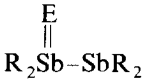
All the compounds I–V are soluble in common organic solvents. Dilute solutions of the alkyl derivatives I, II, IV and V are yellow, while those of III are colourless. When the alkyl compounds are exposed to the air they smell badly and decompose rapidly, but not with ignition like the parent distibanes. The phenyl derivative III is less sensitive towards oxygen than the alkyl analogues. All the compounds I–V are stable for weeks at 25°C when stored in sealed tubes.

A remarkable feature of the methyl derivatives I and IV is their thermochromism. At 5°C the orange-red liquid of I solidifies to form red crystals, which become yellow below −20°C. The tellurium compound IV is brown as a liquid but blue-violet in the solid phase below its melting point of 8°C. There is a striking similarity between IV and iodine. Thermochromic effects have also been observed in the case of several tetraorganodistibanes [2] and dibismutanes [3]. Thermochromic distibanes have unusual, short intermolecular contacts in the solid phase [2c,e]. We suggest that I and IV are associated in the solid, whereas the bulkier substituents in II, III and V prevent the close approach of the heavy atoms.

The composition of I–V has been confirmed by elemental analyses and mass spectroscopic molecular weight determinations. On this basis two isomeric constituents (**A**, **B**) are possible:

$$R_2Sb{-}E{-}SbR_2$$

(A)



$$R_2\overset{\overset{\displaystyle E}{\|}}{Sb}{-}SbR_2$$

(B)

The spectroscopic data for compounds I–V indicate that they have structure **A** as do the oxygen and sulfur analogues [1a]:

(1) The fragmentation pattern of the molecular ions of I–V favours **A** because there are no ions of the composition $[M-\mathrm{Se}]^+$ ($[M-\mathrm{Te}]^+$), which we would expect to be abundant for the isomers **B**. However, the fragmentation is not straightforward and ions of the type R_3SbE^+ and R_3Sb^+ are formed by rearrangements.

(2) The ^1H NMR spectra of I and IV show one sharp singlet for each compound. This is conclusive evidence for type **A** isomers unless there are dynamic processes operating. Structure **A** is also supported by the chemical shift of the signals, which is characteristic for Sb^{III} compounds of the general formula $(CH_3)_2SbX$ ($X = 1/2$ O, $1/2$ S, Cl, Br, I) [4].

(3) The frequencies of the strong signals in the vibrational spectra of I (230, 215 cm^{-1}) are significantly lower than in stibine selenides of the type $R_3Sb{=}Se$ (ν(Sb=Se) 300–270 cm^{-1} [5]), and so we assign them to Sb_2Se valence vibrations of the type **A** isomer of I. In the Raman spectrum of IV there is a strong emission at 180 cm^{-1} for the $\nu(Sb_2Te)$ vibration.

We must note, however, that the majority of the spectroscopic evidence concerns the methyl derivatives I and IV. Future work will involve further spectroscopic investigations and X-ray diffraction structures of the solids.

p-Tolyltelluro-diethylstibane (VI)

Tetraethyldistibane reacts with di-*p*-tolylditelluride at 25°C to form the tellurostibane VI in quantitative yield (eq. 2). VI is a orange, air-sensitive liquid. It is very soluble in non-polar solvents.

$$(C_2H_5)_2Sb\text{-}Sb(C_2H_5)_2 + p\text{-}CH_3C_6H_4Te\text{-}TeC_6H_4\text{-}p\text{-}CH_3 \rightarrow \underset{\text{(VI)}}{2(C_2H_5)_2Sb\text{-}TeC_6H_4\text{-}p\text{-}CH_3} \quad (2)$$

It is noteworthy that VI, like its methyl analogue $(CH_3)_2Sb\text{-}TeC_6H_4CH_3$ [6] is formed quantitatively. This presents a contrast to the reported equilibria involving dismutations between $(CH_3)_2P\text{-}P(CH_3)_2$ or $(CH_3)_2As\text{-}As(CH_3)_2$ and $CH_3Te\text{-}TeCH_3$ [7].

It seems that the formation of Sb–Te bonds is more favoured than the formation of P- or As–Te bonds. This may be due to a relative high ionic covalent resonance energy in the case of tellurostibanes.

Experimental

All experiments were carried out under Ar in dried solvents. ^1H NMR spectra: Varian EM 360, 60 MHz; IR spectra: Perkin–Elmer 577; mass spectra: CH 7 A, Varian MAT, MS data are given for the isotopes ^{121}Sb, ^{78}Se, ^{128}Te, the peak patterns correspond to theoretical values based on the natural abundance of isotopes; elemental analyses were carried out by Fa. Beller, Göttingen.

1,1,3,3-Tetramethyldistibaselenane (I)

A mixture of 1.25 g (15.8 mmol) of black Se powder and 3.03 g (10 mmol) $(CH_3)_4Sb_2$ [8] is stirred at 25°C for 1 h. Filtration and evaporation of the solvent gives 2.6 g (68%) I. IR (film): 505st $\nu(SbC_2)$, 230, 215st $\nu(SeSb_2)$ cm^{-1}. Raman: 508 (9) polarized (p), 235 (9) p, 225 (10) p $\nu(SeSb_2)$, 143 (4) p (cm^{-1}). ^1H NMR ($CDCl_3$): δ 1.30 ppm s. MS (30 eV, 20°C) m/z (rel. int. %): 380 (80) M^+, 365 (100) $M^+ - CH_3$, 350 (10) $M^+ - 2\ CH_3$, 335 (10) $M^+ - 3\ CH_3$, 320 (2) Sb_2Se^+, 229 (3) $(CH_3)_2SbSe^+$, 214 (3) CH_3SbSe^+, 199 (40) $SbSe^+$, 151 (30) $(CH_3)_2Sb^+$. Found: C, 12.85; H, 3.16. $C_4H_{12}Sb_2Se$ calcd.: C, 12.56; H, 3.16%.

1,1,3,3-Tetraethyldistibaselenane (II)

A mixture of 0.93 g (2.6 mmol) of $(C_2H_5)_4Sb_2$ [8] and 0.23 g (2.9 mmol) of black Se powder is stirred in 10 ml C_6H_6 for 3 h at 25°C. Filtration and evaporation at reduced pressure gives 0.9 g (79%) II as yellow needles, which readily become brown on the surface (m.p. 104°C, dec.). ^1H NMR ($CDCl_3$): δ 0.7–1.7 ppm (m). IR (Nujol suspension): 495st $\nu(SbC_2)$, 270m, 220w (cm^{-1}). MS (25 eV, 125°C) m/z (rel. int. %): 436 (20) M^+, 407 (30) $M^+ - C_2H_5$, 379 (20) $(C_2H_5)_2Sb_2Se^+$, 349 (20) $C_2H_5Sb_2Se^+$, 321 (10) HSb_2Se^+, 286 (15) $(C_2H_5)_3SbSe^+$, 257 (20) $(C_2H_5)_2SbSe^+$, 228 (30) $C_2H_5SbSe^+$, 208 (40) $(C_2H_5)_3Sb^+$, 179 (80), 150 (100). Found: C, 21.64; H, 3.16. $C_8H_{20}Sb_2Se$ calcd.: C, 21.90; H, 4.60%.

1,1,3,3-Tetraphenyldistibaselenane (III)

A mixture of 2.0 g (3.6 mmol) of $(C_6H_5)_4Sb_2$ [9] and 0.32 g (4 mmol) of black Se powder in 20 ml CS_2 is stirred under reflux for 4 h. Filtration, evaporation of the solvent, and recrystallisation from CH_3OH/C_6H_6 (1/1) gives 1.8 g (79%) pale yellow needles of III (m.p. 63°C). MS (35 eV, 90°C) m/z (rel. int. %): 628 (10) M^+, 430 (5) $(C_6H_5)_3SbSe^+$, 352 (100) $(C_6H_5)_3Sb^+$, 275 (100) $(C_6H_5)_2Sb^+$, 198 (100), 154 (80). Found: C, 46.17; H, 3.52. $C_{24}H_{20}Sb_2Se$ calcd.: C, 45.69; H, 3.20%.

1,1,3,3-Tetramethyldistibatellurane (IV)

A mixture of 3.03 g (10 mmol) of $(CH_3)_4Sb_2$ [8], 1.9 g (15 mmol) of Te and 20 ml C_6H_6 is stirred for 4 h. Filtration and evaporation of the solvent gives 3.4 g (79%) IV. IR (film): 505st $\nu(SbC_2)$ (cm^{-1}). Raman: 505 (2) p $\nu(SbC_2)$, 180 (10) p $\nu(TeSb_2)$, 130 (3) p (cm^{-1}). ^1H NMR ($CDCl_3$): δ 1.46 ppm s. MS (30 eV, 45°C) m/z (rel. int. %): 430 (90) M^+, 415 (100) $M^+ - CH_3$, 400 (30) $M^+ - 2CH_3$, 385 (40) $M^+ - 3CH_3$, 370 (20) Sb_2Te^+, 279 (10) $(CH_3)_2SbTe^+$, 249 (15) $SbTe^+$, 151 (60) $(CH_3)_2Sb^+$. Found: C, 10.93; H, 3.08. $C_4H_{12}Sb_2Te$ calcd.: C, 11.14; H, 2.80%.

1,1,3,3-Tetraethyldistibatellurane (V)

A mixture of 1.1 g (3.1 mmol) of $(C_2H_5)_4Sb_2$ [8], 1.0 g (7.8 mmol) of Te and 2 ml of C_6H_6 is stirred for 6 h. Filtration and evaporation of the solvent gives 1.0 g (66%) V. MS (30 eV, 60°C) m/z (rel. int. %): 486 (60) M^+, 457 (100) $M^+ - C_2H_5$, 430 (20) $(C_2H_5)_2Sb_2TeH^+$, 429 (20) $(C_2H_5)_2Sb_2Te^+$, 400 (90) $C_2H_5Sb_2Te^+$, 371 Sb_2TeH^+. Found: C, 20.28; H, 4.23. $C_8H_{20}Sb_2Te$ calcd.: C, 19.72; H, 4.14%.

p-Tolyltellurodiethylstibane (VI)

A mixture of 0.72 g (1.64 mmol) of ditolylditelluride [10] and 0.59 g (1.64 mmol) of $(C_2H_5)_4Sb_2$ [7] is stirred for 1 h at 25°C, to give a quantitative yield of VI. MS (20 eV, 75°C) m/z (rel. int. %): 398 (90) M^+, 369 (100) $M^+ - C_2H_5$, 341 (80) $M^+ - C_2H_5 - C_2H_4$. Found: C, 32.8; H, 4.46. $C_{11}H_{17}SbTe$ calcd.: C, 33.1; H, 4.3%.

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