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Complexes of Disulphoxides with Triphenyltin Chloride

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*Six new complexes have been prepared with Ph_3SnCl and the disulphoxides rac-$(PrSOCH_2)_2$, rac-*cis*-$PhSOCH{=}CHSOPh$, meso-$(PhSO)_2CH_2$, rac-$(PhSO)_2CH_2$, meso-$(PhSOCH_2)_2$, and rac-$(PhSOCH_2)_2$. The first of these complexes is a bridged 2:1 acid: base adduct, whereas the others seem to be 1:1 chelated compounds. Several features of the complexes were studied by IR spectroscopy, X-Ray crystallography and NMR spectroscopy.*

Experimental

Preparation of the Ligands

The literature describes several methods for the preparation of disulphides from thiols and halogenated hydrocarbons [1, 2] and the oxidation of the disulphides to the corresponding disulphoxides [2–6]. We tended to follow these methods with some variations. The products were identified by their elemental analyses, melting points, and IR spectra.

1) $(PrSCH_2)_2$

Equivalent amounts of 1-propanethiol and 1,2-dibromoethane were refluxed for 6 h with an excess of KOH in EtOH. The resulting mixture was filtered to eliminate the inorganic halide and distilled at reduced pressure. The fraction collected at 140–142 °C/5 torr was identified as the disulphide.

2) rac-$(PrSOCH_2)_2$

The product of 1 was mixed with a fourfold excess of Me_2SO and a few drops of HCl, and heated over a water bath for 20 h. A white solid was produced, which was recrystallized from a 3:2 benzene:hexane mixture (m.p. = 166–169 °C).

3) cis-$PhSCH{=}CHSPh$

The procedure was the same as in 1, using thiophenol and a *cis, trans* mixture of 1,2-dichloroethane containing approximately 20% of the *cis* isomer. At the end of the reaction the mixture was filtered and then chilled in an ice bath. The white precipitate obtained was recrystallized from EtOH and again in petroleum ether (m.p. = 31–32 °C). Further treatment of the residue also yielded the trans isomer (m.p. = 60–62 °C).

*4) rac-*cis-$PhSOCH{=}CHSOPh$

3 was refluxed for 2 h with a stoichiometric amount of 30% H_2O_2 in HOAc. The mixture was rotary-evaporated to an oil, which was dissolved in Et_2O and left in the refrigerator. Within 24 h white crystals deposited, and these were subsequently recrystallized from Et_2O (m.p. = 118–120 °C).

5) $PhSCH_2SPh$

This was prepared as 1, using PhSH and CH_2Br_2. After filtration, the mixture was chilled and a white precipitate formed, which was recrystallized from EtOH (m.p. = 35–36 °C).

6) meso- and rac-$PhSOCH_2SOPh$

The reaction was similar to 4, and after evaporation the mixture was dissolved in EtOH, which produced a white precipitate. This was recrystallized from EtOH and shown to be the meso isomer (m.p. = 188–190 °C). The remaining solution was then reduced to half its volume and another precipitate appeared. This was also recrystallized from EtOH and shown to be the racemic isomer (m.p. = 117–118 °C).

7) $PhSCH_2CH_2SPh$

The preparation was identical with 5 (with the use of $BrCH_2CH_2Br$), giving a white solid (m.p. = 68–70 °C).

8) meso- and rac-$PhSOCH_2CH_2SOPh$

The same procedure as in 6 was followed, but the mixture was stirred at room temperature for 24 h. Two products were obtained as before, and recrystal-

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lized from a 2:1 mixture of $CHCl_3$ and petroleum ether: meso-$PhSOCH_2CH_2SOPh$ (m.p. = 167–169 °C) and rac-$PhSOCH_2CH_2SOPh$ (m.p. = 121–123 °C).

Preparation of the Complexes

The general method consisted of dissolving equivalent amounts of both the acid and the base in $CHCl_3$, mixing, and stirring the solution under reflux for 3 h. The mixture was then evaporated under vacuum and recrystallized from a suitable solvent.

$(Ph_3SnCl)_2$·rac-$(PrSOCH_2)_2$, 1

Evaporation of the mixture to 1/3 of its initial volume produced a white precipitate; this was recrystallized from acetone, giving bright colourless crystals (found: C = 53.58, H = 5.65, Cl = 7.23, S = 6.02; calcd: C = 53.86, H = 4.90, Cl = 7.24, S = 6.53%; yield = 45%, m.p. = 131–134 °C).

Ph_3SnCl·$PhSOCH{=}CHSOPh$, 2

Evaporation of the mixture gave a colourless viscous mass; this was redissolved in CH_2Cl_2 and after very slow evaporation of the solvent, produced a white powder (found: C = 58.15; H = 4.22, Cl = 6.02, S = 9.37; calcd: C = 58.08, H = 4.08, Cl = 5.37, S = 9.68%; yield = 43%, m.p. = 74–76 °C).

Ph_3SnCl·meso-$(PhSO)_2CH_2$, 3

The mixture was evaporated to dryness and recrystallized twice in CH_2Cl_2, giving white crystals (found: C = 56.93, H = 4.45, Cl = 5.90, S = 8.52; calcd: C = 57.31, H, 4.16, Cl = 5.47, S = 9.86%; yield = 72%; m.p. = 107–109 °C).

Ph_3SnCl·rac-$(PhSO)_2SO$, 4

Evaporation of the mixture produced a viscous oil; this was dissolved in CH_2Cl_2 and slowly evaporated, giving again an oil. The oil was then dissolved in MeOH; addition of water immediately caused the precipitation of a white powder which was left to dry under vacuum in a desiccator. (Found: C = 56.22, H = 4.31, Cl = 6.28, S = 9.24; calcd: C = 57.31, H = 4.16, Cl = 5.47, S = 9.86; yield = 43%; m.p. = 109–111 °C).

Ph_3SnCl·meso-$(PhSOCH_2)_2$, 5

The mixture was evaporated to dryness and redissolved in a 1:1 mixture of MeOH and CH_2Cl_2, from which bright colourless crystals precipitated upon reduction of the volume (found: C = 57.24, H = 4.45, Cl = 5.21, S = 9.98; calcd: C = 57.91, H = 4.37, Cl = 5.35, S = 9.65%; yield = 39%; m.p. = 134–137 °C).

Ph_3SnCl·rac-$(PhSOCH_2)_2$, 6

The mixture was evaporated to dryness and recrystallized twice in CH_2Cl_2, giving white crystals (found: C = 56.93, H = 4.45, Cl = 5.90, S = 8.52%; calcd: C = 57.31, H = 4.16, Cl = 5.47, S = 9.86%; yield = 72%, m.p. = 107–109 °C).

Spectroscopy

Infrared spectroscopy was carried out on a PE 577 spectrophotometer using nujol mulls between CsBr windows. The spectra were calibrated with polystyrene film.

Proton NMR spectra were obtained from a Bruker WH 400 instrument using $CDCl_3$ as the solvent.

Results and Discussion

The analytical data and the NMR integration results suggest that, except for complex 1, all the compounds are 1:1 adducts between the Lewis acid Ph_3SnCl and the disulphoxides. Complex 1 is a 2:1 adduct between two Ph_3SnCl units whose Sn atoms occupy the centre of two trigonal bipyramids, as shown in Fig. 1 [7]. In the other five complexes the disulphoxide seems to act as a bidentate chelating agent containing a Sn atom in the centre.

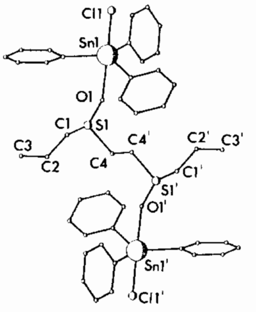

Fig. 1. The structure of $(Ph_3SnCl)_2$rac-$(PrSOCH_2)_2$.

Table I shows the infrared data. In all cases bonding occurred through the oxygen atom, as evidenced by the shift to lower wavenumbers of ν_{SO} after complexation. Except for complex 2, all the others showed a fairly constant $\Delta\nu_{SO}$ value (ranging from 43 to 46 cm^{-1}), whereas complex 2 showed a much greater value (70 cm^{-1}). Thus the ligand rac-1,2-*cis*-bis(phenylsulphynyl)ethene seems to be much more basic than the saturated disulphoxides. We interpret this as conjugation in the ring containing the metal atom, as well as the favoured geometry of this unsaturation-containing ring.

From the IR data we have calculated the SO bond distances using the Gillespie–Robinson method [8]. The results are shown in Table I, in which the experimental value for complex 1 is also given [7]. All estimated distances are longer than those of the free disulphoxides, and we can compare these results with the known SO bond distances for the free ligands meso-1,2-bis(phenylsulphynyl)ethane and rac-1,2-bis-(phensysulphynyl)ethane [6]. The method also allows an estimation of the bond orders. The decrease in bond order [Δ(b.o.)] caused by complexation is

TABLE I. Infrared and Calculated Data*.

Compound	ν_{SO} Ligand	ν_{SO} complex	$\Delta\nu_{SO}$	ν_{SnO}	ν_{SnC}	dSO ligand calcd.	dSO ligand exp.	dSO complex calcd.	dSO complex exp.	SO bond order in complex (b.o)	Δ(b.o)
1. $(Ph_3SnCl)_2 \cdot r\text{-}(PrSOCH_2)_2$	1013	970	43	450	270	1.516	–	1.534	1.491 [9] [a]	1.356	0.060
2. $Ph_3SnCl \cdot r\text{-}PhSOCH{=}CHSOPh$	1040	970	70	450	–	1.506	–	1.534	–	1.356	0.098
3. $Ph_3SnCl \cdot m\text{-}(PhSO)_2CH_2$	1038	985	43	451, 453	270	1.506	–	1.524	–	1.390	0.064
4. $Ph_3SnCl \cdot r\text{-}(PhSO)_2CH_2$	1040	995	45	452, 447	273	1.506	–	1.524	–	1.390	0.061
5. $Ph_3SnCl \cdot m\text{-}(PhSOCH_2)_2$	1035	990	45	450	273	1.508	1.487 [2] [b]	1.526	–	1.383	0.064
6. $Ph_3SnCl \cdot r\text{-}(PhSOCH_2)_2$	1035	989	46	452, 445	270	1.508	1.489 [6] [b] 1.494 [6]	1.528	–	1.377	0.070
7. Ph_3SnCl	–	–	–	–	275	–	–	–	–	–	–

*Absorptions in cm^{-1}, bond distances in pm. [a] Ref. 7. [b] Ref. 6.

some 50% greater for complex 2 compared to the others, reflecting the former's stronger interaction with the metal atom.

The Sn–C absorptions did not change appreciably with complexation, and a new band was observed around 450 cm^{-1}. This could be assigned to an SnO absorption [9] which is possibly raised to higher wavenumbers by resonance interaction with the SnCl absorption. The latter occurs at 340 cm^{-1} in Ph_3SnCl and was not observed by us for the complexes in the region studied. It is thus likely to have fallen below the transmittance range of CsBr.

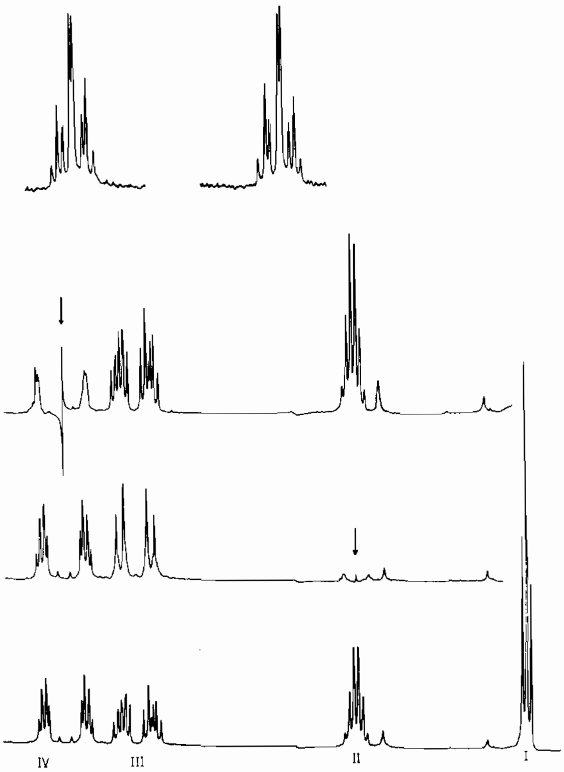

Fig. 2. (a) NMR spectrum of methylene protons in Ph_3SnCl rac-$(PhSOCH_2)_2$; (b) irradiated NMR spectrum of disulphide protons in $(Ph_3SnCl)_2$ rac-$(PrSOCH_2)_2$; (c) irradiated NMR spectrum of disulphoxide protons in $(Ph_3SnCl)_2$ rac-$(PrSOCH_2)_2$; (d) NMR spectrum of disulphoxide protons in $(Ph_3SnCl)_2$ rac-$(PrSOCH_2)_2$.

Figure 2-a shows the 400 MHz proton NMR spectrum of the methylene protons of $Ph_3SnCl \cdot$rac-$(PhSOCH_2)_2$ in $CDCl_3$. It consists of 16 lines, occurring at 2.6742, 2.6887, 2.6989, 2.7200, 2.7261, 2.7437, 2.7536, 2.7632, 3.3288, 3.3457, 3.3539, 3.3725, 3.3786, 3.9548, 3.4064, and 3.3417 ppm, respectively. The system is of the AA′ BB′ type, with four highly inequivalent protons; a similar spectral pattern, albeit in a simpler form, occurs again when propyl groups take the place of the phenyl groups in the disulphoxide and form complex 1. Figures 2-b to

2-d show the NMR spectra of the disulphoxide protons in $(Ph_3SnCl)_2$·rac-$(PrSOCH_2)_2$ in $CDCl_3$ in different conditions. Fig. 2-d is the full spectrum without irradiation, and the other figures show the irradiated cases, with irradiation applied where shown by the arrows. The 4 spectral patterns labelled I, II, III, and IV in Fig. 2-d are interpreted as follows:

I - this is a triplet absorbing at 1.0623, 1.0806, and 1.0989 ppm, respectively. It has been assigned to the CH_3 end of the propyl group. The two small absorptions between patterns I and II are impurities.

II - this is a very symmetrical sextet, as expected from the CH_2 unit directly bonded to the CH_3 unit of the propyl group. The absorptions occur at 1.7532, 1.7703, 1.7886, 1.8082, 1.8277, and 1.8460 ppm.

III - here we have what seems to be a pair of sextets, which could be assigned to the CH_2 unit of the propyl group directly bonded to the S atom. Fig. 2-c shows this to be the case, for upon irradiation of the group II protons, group III is decoupled and reduced to a much simpler pattern. Group III is of the AA′ BB′ type, with absorptions at 2.6199, 2.6407, 2.6529, 2.6602, 2.6724, 2.6919, 2.7505, 2.7664, 2.7701, 2.7823, 2.7859, and 2.7994 ppm.

IV - this must be due to the ‘internal’ methylene groups, *i.e.*, the methylene groups to be found between the two SO units. Indeed, irradiation of these protons did not affect the rest of the spectrum, as shown in Fig. 2-b, demonstrating that group IV protons do not belong to the propyl group. Group IV also represents an AA′ BB′ pattern, absorbing at 2.9129, 2.9275, 2.9458, 2.9581, 3.0972, 3.1094, 3.1277, and 3.1424 ppm.

The NMR spectrum of Ph_3SnCl·rac-*cis*-PhSOCH=CHSOPh in $CDCl_3$ showed a very symmetrical doublet of doublets absorbing at 6.7471, 6.7495, 6.7544, and 6.7568 ppm, indicating an AB pattern. In view of the discussion above it is noteworthy to say that in contrast, the spectrum of $PtCl_2$·rac-*cis*-PhSOCH=CHSOPh, an S-bonded five-membered chelate, only showed one absorption at 7.2532 ppm [10].

The complex Ph_3SnCl·rac-$(PhSO)_2CH_2$ also presented a doublet of doublets absorbing at 3.9627, 3.9944, 4.0555, and 4.0872 ppm. The two complexes containing meso-disulphoxides (namely Ph_3SnCl·meso-$(PhSO)_2CH_2$ and Ph_3SnCl·meso-$(PhSOCH_2)_2$) however, only showed one absorption each, at 3.9944 and 3.0289 ppm, respectively.

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