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EXCHANGE REACTIONS BETWEEN OXYGEN AND SULPHUR DERIVATIVES OF SILICON, GERMANIUM, TIN AND LEAD

D.A. ARMITAGE and A.W. SINDEN

Department of Chemistry, Queen Elizabeth College, Campden Hill, Kensington, London W8 7AH (Great Britain)

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Summary

The exchange of oxygen functional groups (—OR, —O— and —OCOMe) and sulphur functional groups (—SR, —S—) between R_3M (M = Si, Ge, Sn and Pb) and R_2M (M = Si, Sn) shows, in general, the heavier Group IV element to prefer sulphur. This supports the phenomenological rationalisation that the softness of the organometallic residue increases with the atomic weight of M, though germanium probably resembles silicon in its behaviour far more than it does tin.

The difference in the relative stability of oxygen and sulphur derivatives of silicon and tin is readily illustrated by the synthesis of thiosilanes and tin—sulphur compounds [1]. Silicon—sulphur compounds are moisture sensitive and have to be prepared under strictly anhydrous conditions [2], while the tin—sulphur bond can be synthesised in aqueous alkali [3]. This has been put on a thermochemical footing and the group trend described phenomenologically in terms of the increasing degree of softness of the Me_3M^+ group as the atomic weight of M increases. Indeed a steady increase in ΔH for reaction 1 is quoted, supporting the proposal that it is reasonable to prepare alkylthio derivatives of tin in aqueous solution but not those of silicon or germanium [4].

$$Me_3MOEt + n\text{-}BuSH \rightarrow Me_3MSBu\text{-}n + EtOH \qquad (1)$$

However, the position of germanium in this situation has not been definitely established. On the one hand, $(Me_2GeS)_3$ slowly hydrolyses in moist air [5a], while thiophenol reacts readily with both hexaethyldigermanium oxide and ethoxytrimethylgermane [5b]. Similarly, heating $(Me_3Ge)_2O$ with t-butanethiol readily gives the thiogermane [5a]. In addition, the equilibrium for the exchange reaction between thiosilanes and alkoxygermanes strongly favours the thiogermane and alkoxysilane [6]:

$Me_2Si(SMe)_2 + Me_2Ge(OMe)_2 \rightarrow Me_2Si(OMe)_2 + Me_2Ge(SMe)_2$

It is therefore interesting to note that over a long period of time (200 h) and with a catalyst (*p*-toluenesulphonic acid), an excess of ethanol will react completely with n-$Bu_2Sn(SPr\text{-}n)_2$ [7].

$$n\text{-}Bu_2Sn(SPr\text{-}n)_2 + 2EtOH \xrightarrow[\text{catalyst}]{200\ h} n\text{-}Bu_2Sn(OEt)_2$$

This paper describes exchange reactions involving sulphur (—S— and —SR) and oxygen functional groups (—O—, —OR, —OCOMe) between silicon, germanium, tin and lead. The reactions occur cleanly and involve migration of the thio group on to the heavier Group IV metalloid. Most of the exchanges involve silicon and tin, but a few reactions incorporating germanium and lead are included.

The exchange reactions between silicon—sulphur and tin—oxygen compounds are normally exothermic, though a few require gentle heating. Only when solid tin—oxygen compounds are used (e.g. dialkyltin oxides and tri-n-butyltin acetate) is strong heating required, in part, no doubt, to assist in deassociation.

Both mono- and bis-(alkylthio)silanes react with methoxytri-n-butyltin to give the expected alkylthiotri-n-butyltin:

$$Me_3SiSR + n\text{-}Bu_3SnOMe \rightarrow Me_3SiOMe + n\text{-}Bu_3SnSR \quad (R = Me, Et)$$
$$Me_2Si(SMe)_2 + 2n\text{-}Bu_3SnOMe \rightarrow Me_2Si(OMe)_2 + 2n\text{-}Bu_3SnSMe$$

Bis(ethylthio)di-n-butyltin can be prepared similarly from the dimethoxytin compound. However, tri-n-butyltin acetate had to be molten before the reaction with ethylthiotrimethylsilane would go to completion.

$$2Me_3SiSEt + n\text{-}Bu_2Sn(OMe)_2 \rightarrow 2Me_3SiOMe + n\text{-}Bu_2Sn(SEt)_2$$
$$Me_3SiSEt + n\text{-}Bu_3SnOCOMe \rightarrow Me_3SiOCOMe + n\text{-}Bu_3SnSEt$$

Hexamethyldisilthiane undergoes a strongly exothermic reaction with both methoxytri-n-butyltin and hexa-n-butylditin oxide, to give the ditin sulphide in very good yield in each case. The reaction of the oxide with ethylthiotrimethylsilane was less vigorous.

$$(Me_3Si)_2S \xrightarrow[\text{or } (n\text{-}Bu_3Sn)_2O]{n\text{-}Bu_3SnOMe} (n\text{-}Bu_3Sn)_2S$$

$$2Me_3SiSEt + (n\text{-}Bu_3Sn)_2O \rightarrow (Me_3Si)_2O + 2n\text{-}Bu_3SnSEt$$

Polymeric dialkyltin oxides react cleanly with thiosilanes and silthianes, but have to be heated strongly before any reaction occurs. Unlike the oxide, the tin sulphide can be distilled, with the ethyl compound melting sharply at 23-24°.

$$2Me_3SiSEt + n\text{-}Bu_2SnO \rightarrow (Me_3Si)_2O + n\text{-}Bu_2Sn(SEt)_2$$
$$(Me_3Si)_2S + R_2SnO \rightarrow (Me_3Si)_2O + R_2SnS \quad (R = Et, n\text{-}Bu)$$

The interaction of methoxytrimethylgermane and ethylthiotrimethylsilane supports the equilibration reported [6] for the bis-substituted silane and germane with the alkoxysilane and thiogermane forming after a period of heating.

$Me_3GeOMe + Me_3SiSEt \rightarrow Me_3GeSEt + Me_3SiOMe$

The alkoxysilane is the lowest boiling of the four components. It is therefore interesting to note that n-butylthiotrimethylsilane does not appear to react with methoxytrimethylgermane even after heating for 2 days under reflux.

Hexamethyldigermoxane and phenylthiotrimethylsilane underwent exchange after prolonged heating where again the siloxane is the lowest boiling constituent. The reaction of ethylthiotrimethylgermane with methoxytri-n-butyltin gives excellent yields of the alkoxygermane and tin—sulphur compound, supporting the soft acid characteristics of the tri-n-butyltin group.

$2Me_3SiSPh + (Me_3Ge)_2O \rightarrow 2Me_3GeSPh + (Me_3Si)_2O$
$Me_3GeSEt + n\text{-}Bu_3SnOMe \rightarrow Me_3GeOMe + n\text{-}Bu_3SnSEt$

This work supports the proposals that the softness of the R_3M^+ species increases with the atomic weight of M [4], with the OR/SR exchange providing an ideal system in which to study this. Consequently it is hardly surprising that ethylthiotrimethylsilane underwent a strongly exothermic reaction with trimethyllead methoxide to produce ethylthiotrimethyllead in excellent yield.

$Me_3SiSEt + Me_3PbOMe \rightarrow Me_3SiOMe + Me_3PbSEt$

However it would be premature to be too categorical about the relative softness of the R_3M^+ species. While exchange between silicon and tin is predictable on the basis of thermodynamic arguments (many of the reactions are exothermic, particularly those involving SR/OR exchange) the relative softness of R_3Ge^+ compared with silicon and tin analogues would have to be rationalised carefully. Such reactions involving germanium are not exothermic and have to be heated many hours before one of the products, the lowest boiling of all four components, is completely removed. Indeed, with n-butylthiotriethylsilane and methoxytrimethylgermane, no reaction appears to take place even after heating under reflux for 2 days.

Experimental

All reactions were carried out under strictly anhydrous conditions. Silicon— and germanium—sulphur compounds were prepared by standard methods [1], as were germanium— [5c], tin— [8], and lead—oxygen [9] compounds. Tri-n-butyltin acetate was obtained from Fluka AG. n-Butylthiotriethylsilane was prepared from the sodium salt of n-butanethiol and triethylchlorosilane as a colourless liquid, b.p. 56/0.1 mmHg, n_D^{21} 1.4710. (Found: C, 59.1; H, 11.89. $C_{10}H_{24}SSi$ calcd.: C, 58.9; H, 11.8%.)

Interaction of methoxytri-n-butyltin and methylthiotrimethylsilane (also ethylthiotrimethylsilane)

The silane (1.4 g, 1.0 mol) was added dropwise to the methoxide (3.7 g, 1.0 mol) with cooling. The mixture was heated giving methoxytrimethylsilane (1.2 g, 99%), b.p. 57°, n_D^{22} 1.3673 (lit. [10], b.p. 56°, n_D^{20} 1.3675) and methylthiotri-n-butyltin (3.9 g, 99%), b.p. 80°/0.001 mmHg, n_D^{23} 1.5035. (Found: C, 46.3; H, 8.94. $C_{13}H_{30}SSn$ calcd.: C, 46.2; H, 8.89%.)

A similar reaction with ethylthiotrimethylsilane (1.6 g, 1.0 mol) gave the methoxysilane (0.86 g, 70%), b.p. 56°, n_D^{20} 1.3667 and ethylthiotri-n-butyltin (3.0 g, 72%), b.p. 90°/0.01 mmHg, n_D^{25} 1.5010. (Found: C, 47.3; H, 9.66. $C_{14}H_{32}SSn$ calcd.: C, 47.8; H, 9.13%.)

Interaction of methoxytri-n-butyltin and bis(methylthio)dimethylsilane

The silane (2.15 g, 1.0 mol) was added to methoxide (9.1 g, 2.0 mol) without evolution of heat. Heating gave dimethoxydimethylsilane (1.05 g, 62%), b.p. 80°, n_D^{19} 1.3708 (lit. [10], b.p. 81°, n_D^{20} 1.3706) and subsequent vacuum distillation yielded methylthiotri-n-butyltin (9.4 g, 98%), b.p. 110-112°/0.1 mmHg, n_D^{23} 1.5055.

Interaction of dimethoxydi-n-butyltin and ethylthiotrimethylsilane

The silane (4.2 g, 2.7 mol) was added to the tin methoxide (3.4 g, 1.0 mol) producing a mildly exothermic reaction. After distilling off the methoxysilane (1.4 g, 58%), b.p. 56°, n_D^{25} 1.3668, vacuum distillation of the residue yielded bis(ethylthio)di-n-butyltin (2.4 g, 59%), b.p. 106°/0.01 mmHg, n_D^{24} 1.5350. (Found: C, 40.7; H, 8.19. $C_{12}H_{28}SnS_2$ calcd.: C, 40.6; H, 7.9%.)

Interaction of acetoxytri-n-butyltin with ethylthiotrimethylsilane

The silane (4.4 g, 1.0 mol) was added to the tin acetate (11.4 g, 1.0 mol) and the mixture strongly heated. Acetoxytrimethylsilane resulted (3.0 g, 70%), b.p. 103°, n_D^{23} 1.3890 (lit. [10], b.p. 103°) and vacuum distillation yielded ethylthiotri-n-butyltin (10.5 g, 91%), b.p. 124°/0.5 mmHg, n_D^{23} 1.5030.

Interaction of methoxytri-n-butyltin and hexamethyldisilthiane

The silthiane (1.83 g, 1.0 mol) was added dropwise to the tin methoxide (6.6 g, 2.0 mol) with cooling as the reaction was very exothermic. The methoxysilane was pumped off, trapped and redistilled (1.5 g, 69%), b.p. 57°, n_D^{25} 1.3664, and vacuum distillation of the residue gave hexa-n-butylditin sulphide (6.2 g, 97%), b.p. 130°/0.001 mmHg, n_D^{25} 1.5165 (lit. [1], b.p. 208°/1 mmHg, n_D^{21} 1.518).

Interaction of bis(tri-n-butyltin) oxide and hexamethyldisilthiane

Addition of the silthiane (2.2 g, 1.0 mol) to the tin oxide (7.4 g, 1.0 mol) was exothermic. After heating the mixture for 24 h, the hexamethyldisiloxane was distilled off (1.0 g, 50%), b.p. 100°, n_D^{20} 1.3780 (lit. [10], b.p. 100.4°, n_D^{20} 1.3772), followed by vacuum distillation of the tin sulphide (6.4 g, 84%), b.p. 130-132°/0.001 mmHg, n_D^{24} 1.5168.

Interaction of bis(tri-n-butyltin) oxide and ethylthiotrimethylsilane

The thiosilane (6.0 g, 2.0 mol) was added to the tin oxide (13.35 g, 1.0 mol) and the mixture heated to distil off the hexamethyldisiloxane (2.4 g, 66%), b.p. 100°, n_D^{25} 1.3685. The residue yielded ethylthiotri-n-butyltin (12.0 g, 77%), b.p. 84°/0.01 mmHg, n_D^{23} 1.5000.

Interaction of di-n-butyltin oxide and ethylthiotrimethylsilane

The thiosilane (6.0 g, 2.0 mol) was added to the oxide (5.55 g, 1.0 mol) and the mixture heated strongly. The reaction appeared to take place when the solid melted, and careful distillation over a 48 h period gave hexamethyldisiloxane (1.6 g, 44%), b.p. 100°, n_D^{19} 1.3801. The bis(ethylthio)di-n-butyltin was vacuum distilled (5.5 g, 70%), b.p. 100°/0.01 mmHg, n_D^{22} 1.5378.

Interaction of diethyltin oxide and hexamethyldisilthiane

The silthiane (3.8 g, 1.0 mol) was added to the tin oxide (4.1 g, 1.0 mol) and the mixture heated at 200° until the solid melted and a reaction took place. Hexamethyldisiloxane (2.7 g, 82%) was distilled off over 48 h, b.p. 100°, n_D^{21} 1.3785. The residual diethyltin sulphide solidified on standing but was vacuum distilled (3.3 g, 72%), b.p. 130-140°/0.01 mmHg, n_D^{23} 1.6394, m.p. 23-24°. (Found: C, 23.4; H, 4.95. $C_4H_{10}SSn$ calcd.: C, 23.0; H, 4.83%.) Di-n-butyltin sulphide was prepared by the same method (2.37 g, 66%), b.p. 190°/0.01 mmHg, n_D^{24} 1.5760. (Found: C, 36.5; H, 6.9. $C_8H_{18}SSn$ calcd.: C, 36.2; H, 6.8%.)

Interaction of methoxytrimethylgermane and ethylthiotrimethylsilane

The silane (3.8 g, 1.0 mol) was added to the germane (4.2 g, 1.0 mol) and heated over a period of 36 h, while methoxytrimethylsilane (1.2 g, 41%), b.p. 56-58°, n_D^{20} 1.3723 was distilled off. Raising the bath temperature gave ethylthiotrimethylgermane (2.9 g, 57%), b.p. 148°, n_D^{24} 1.4760 (lit. [1], b.p. 148°, n_D^{21} 1.4788).

Methoxytrimethylgermane and n-butylthiotriethylsilane

The germane (3.2 g, 1 mol) and silane (4.4 g, 1 mol) were heated under reflux for 2 days. Subsequent distillation of the mixture yielded methoxytrimethylgermane (1.8 g, 56%), b.p. 86°, n_D^{20} 1.4050 and n-butylthiotriethylsilane (3.9 g, 89%), b.p. 54°/0.1 mmHg, n_D^{20} 1.4710, indicating an apparent lack of reaction.

Interaction of hexamethyldigermoxane and phenylthiotrimethylsilane

The silane (4.45 g, 2.0 mol) was added to the germoxane (3.1 g, 1.0 mol) and heated for 1 week. Hexamethyldisiloxane slowly distilled off. This was then redistilled (1.6 g, 80%), b.p. 100°, n_D^{25} 1.3775. Vacuum distillation of the residue produced phenylthiotrimethylgermane (4.5 g, 82%), b.p. 38°/0.001 mmHg, n_D^{25} 1.5565 (lit. [1], b.p. 37°/0.001 mmHg, n_D^{23} 1.5560).

Interaction of ethylthiotrimethylgermane and methoxytri-n-butyltin

The germane (2.5 g, 1.0 mol) was added to the tin methoxide (4.46 g, 1.0 mol) and then heated to distil off the methoxygermane (1.7 g, 80%), b.p. 86°, n_D^{25} 1.4058 (lit. [11], b.p. 87-89°). The residue was vacuum distilled giving ethylthiotri-n-butyltin (4.7 g, 95%), b.p. 104°/0.1 mmHg, n_D^{21} 1.5020.

The interaction of trimethyllead methoxide with ethylthiotrimethylsilane

The thiosilane (3.83 g, 1 mol) was added dropwise to the lead methoxide

(8.1 g, 1 mol) with cooling. The reaction was very exothermic and after the addition was complete, the mixture was stirred for 1 h. The volatiles were pumped off and trapped (2.6 g), subsequent distillation yielding methoxytrimethylsilane, (2.0 g, 69%), b.p. 56°, n_D^{20} 1.3677, while vacuum distillation of the residue gave ethylthiotrimethyllead (7.7 g, 89%), b.p. 42°/0.1 mmHg, n_D^{21} 1.5863. (Found: C, 19.53; H, 4.56; S, 9.97. $C_5H_{14}PbS$ calcd.: C, 19.40; H, 4.47; S, 10.23%.)

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