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DESULPHURIZATION OF SULPHUR-CONTAINING ORGANOMETALLIC COMPOUNDS

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Summary

Desulphurization reactions of trialkyl- and dialkyl-tin sulfides with a variety of reagents such as acylic peroxides, salts and organic derivatives of some metals, halogen alkanes, as well as with sulphur acceptors such as copper powder or triphenylphosphine are discussed.

Introduction

In the past, insertion reactions of sulphur, selenium and tellurium in organometallic compounds through metal–metal coupling have been studied. Thus sulphur is inserted easily through M–H (M = Si,Ge) [1], Sn–Sn [2] and Ge–V coupling [3] with formation of the corresponding organometallic sulfides. These reactions are of interest from the theoretical as well as from the synthesis point of view. In this paper we shall discuss the reverse reaction of desulphurization of organometallic sulphides affected by a variety of reagents.

It is known that Sn–Sn bonds are cleaved in hexaalkyldistannane by acylic peroxide at room temperature [4], by 1,2-dibromomethane at 180°C [5] or by certain alkyl halides (methyl iodide at 180°C [6], benzyl chloride at 190–200°C or by triphenylchloromethane at 100°C [7]). It was of interest to elucidate the reactivity of organometallic sulfides to such reagents, i.e. compounds in which the metal–metal bond is cleaved by Group VI element, in particular by sulphur.

Results and discussion

Triethyltin sulfide and its analogues are easily desulphurized by benzoyl peroxide in benzene at room temperature. The reaction proceeds with release of elemental

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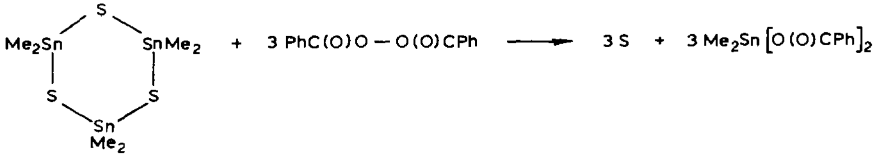
* Dedicated to Professor Calas on the occasion of his 70th birthday (April 8th, 1984) in recognition of his outstanding research in organometallic chemistry during more than 30 years.

sulphur (or other Group VI element) and with formation of triethyltin benzoate [8] (eq.1):

$$(Et_3M)_2E + PhC(O)O\text{–}O(O)CPh \rightarrow E + 2Et_3MO(O)CPh \qquad (1)$$

where M = Si, Ge, Sn; E = S, Se, Te

Trimeric dimethyltin sulfide reacts with benzoyl peroxide analogously. The reaction proceeds with cleavage of the six-membered ring, release of elemental sulphur and with the formation of dimethyltin dibenzoate (eq. 2):



(2)

It appears that the reactions proceed in a complex manner, kinetically independant free benzoate radicals being absent. Benzoate group attack is directed towards both metal atoms while decarboxylation is absent. This points to a molecular type of interaction in a complex. The elimination of sulphur from the organometallic sulfides can be successfully performed by the action of a suitable acceptor on the organotin sulfides, for example finely dispersed copper. The reaction between copper and sulphur atom yields copper sulfide (eq.3). The reaction of freshly precipitated powder-like copper with bis(triorganotin) sulfides, $(R_3Sn)_2S$, proceeds on the shaking vigorously in a medium of normal hydrocarbons at room temperature for R = Et,Bu [9] or at 65°C for R = Ph [10] (eq. 3):

(3)

Thus the above reaction is diametrically opposite to the reaction of sulfur insertion in distannane [2].

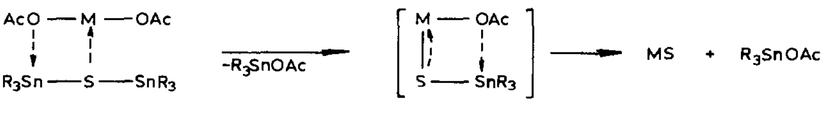
Reaction of trimeric dimethyltin sulfide with freshly precipitated copper takes place under more severe conditions. Thus, under heterogeneous conditions, without a solvent at 150–160°C, sulphur is eliminated with formation of CuS. If such a reaction is carried out with carefully mixed dry reagents while freezing out the volatile product in vacuum, it results in formation of copper sulfide, bis(trimethyltin) sulfide and metallic tin in molar ratio 2 : 1 : 1, which confirms eq. 4.

$$(Me_2SnS)_3 \xrightarrow{Cu,150°C} (Me_3Sn)_2S + 2CuS + Sn \qquad (4)$$

This reaction proceeds in a solvent (nonane) and is more complex, since bis(trimethyltin) sulfide, formed initially in conformity with eq. 4 undergoes further elimination of sulphur in the presence of copper in accordance with eq. 3. Hexamethyldistannane thus formed disproportionates on the copper at 150°C to tetramethyltin and dimethylstannylene. As a consequence, the ratio of the products changes in comparison with the reaction conducted without a solvent. The yield of CuS is increased and that of bis(trimethyltin) sulfide is decreased. The secondary products (tetramethyltin and dimethyltin oxide formed on oxidation of dimethylstannylene) make their appearance simultaneously.

Similarly to copper, triphenylphosphine abstracts sulphur from organic sulfides and disulfides, easily forming unreactive triphenylphosphine sulfide [11]. At the same time triphenylphosphine does not react with bis(tributyltin) sulfide even at 160°C in a medium of decane, benzene, tetrahydrofuran or acetonitrile [10]. Formation of Ph_3PS has been observed only at 20°C in CCl_4 solution [12]. The solvent is involved in this reaction. As this takes place the complex of triphenylphosphine with carbon tetrachloride $Ph_3P^+CCl_4Cl^-$ is initially formed which ten reacts with bis(tributyltin) sulfide along a heterolytic path. As a result tributyltin chloride, triphenylphosphine sulfide and a phosphorus-containing resin are formed [12].

Salts of copper and some other metals, forming covalent sulfides, also cleave the Sn–S bond in organotin sulfides in polar solvents. However, unlike the reaction with copper, this process is typically heterolytic in nature. Thus, mercury acetate reacts exothermically with trialkyltin sulfide in anhydrous acetone. Under these conditions cadmium, zink and copper acetates are less reactive and a refluxing reaction mixture is needed to complete the reaction. Mercury, cadmium, zink or copper sulfides and triethyltin acetate are formed in the course of such reactions in quantitative yields [13], (eq. 5).



(5)

In water, reaction of $(R_3Sn)_2S$ with zinç acetate at room temperature is completed in a few minutes while shaking. At the same time sodium acetate does not enter into reaction with trialkyltin sulfide at 90°C. Evidently formation of covalent and precipitating mercury, cadmium, zink or copper sulfides favours completion of the reactions. Similarly (eq.5), the reaction of Hg,Cd and Cu acetates with oxides of trialkyltin occurs. As this takes place, the corresponding metal oxides precipitate.

Bis(trimethyltin) sulfide has been exothermically alkylated or phenylated with diethyl- or diphenyl-zinc in benzene. As this takes place zinc sulfide is formed. In case of diphenyl zinc, trimethylphenyltin was obtained. When diethyl zinc was used the corresponding product, trimethylethyltin, disproportionates in the presence of ZnS to tetramethyltin and dimethyldiethyltin. Diphenylmercury is less reactive and enters into reaction only in the presence of hexamethylphosphorustriamide (HMPT). Diethylmercury under these conditions does not react with trimethyltin sulfide at all.

Grignard reagent enters into reaction with trimethyl or triethyltin sulfides exothermically in ether according to eq. 6 [13].

$$(R_3Sn)_2S + 2RMgX \rightarrow 2\ R_3SnR' + XMgSMgX \qquad (6)$$

where $R = Me$, $R' = Et$, CH_2Ph, Ph; $R = R' = Et$

Reaction of trialkyl and dialkyltin sulfides with alkyl halides with formation of sulfonium compounds are another example of heterolytic cleavage of Sn–S bonds. Thus CH_3I, CH_2I_2, C_2H_5I,CH_2BrCH_2Br cleave the Sn-S bond in trialkyl and dialkyltin sulfides. Reaction of bis(triorganostannyl) sulfide with excess alkyl iodide proceeds with formation of the corresponding organotin iodide and dialkyl sulfide, which precipitates out of the reaction mixture as an almost insoluble complex with RI (eq.7)

$$(R_3Sn)_2S + \underset{\text{excess}}{3R'I} \rightarrow 2\ Me_3SnI + R'_2S \cdot R'I \qquad (7)$$

Yields of products after refluxing reaction mixtures in pentene for 25 hours were almost stoichiometric. With R = Ph and R′ = Me no interaction was found under these conditions. When R = Me, Ph and R′ = Me, Et, CH_2I the reaction proceeds only on addition of hexamethylphosphorus triamide. Here triorganotin iodides form complexes (1 : 1) with this donor. In the reaction with CH_2I_2 both halogen atoms participitate and insoluble trimeric thioformaldehyde is formed.

Interaction of dimethyltin sulfide $(R_2SnS)_3$ with excess of CH_3I occurs on the prolonged (50 hours) refluxing of the reaction mixture (eq.8). This reaction is much faster after addition of HMPT. In this case the organotin product (dimethyltin diiodide) is formed quantitatively after 5 hours in the complex form, $(CH_3)_2SnI_2 \cdot 2$ HMPT (m.p. 164-165°C), out of hexane.

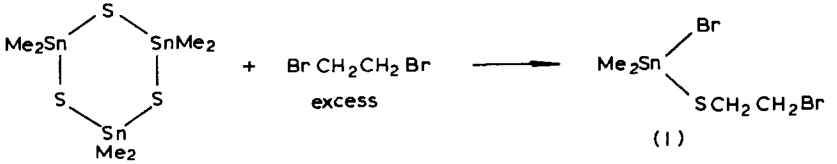
$$(Me_2SnS)_3 + \underset{\text{excess}}{9\ MeI} \xrightarrow{40°C} 3\ Me_2SnI_2 + 3Me_2S \cdot MeI \qquad (8)$$

Interaction of bis(trialkyltin) sulfide and trimeric dimethyltin sulfide with 1,2-dibromoethane proceeds in a variety of ways. Thus, bis(trialkyltin) sulfides react with 1,2-dibromoethane at 150°C releasing ethylene and elemental sulfur [14] (eq.9):

$$[(C_2H_5)_3M]_2X + BrCH_2CH_2Br \rightarrow 2(C_2H_5)_3SnBr + X + CH_2{=}CH_2 \qquad (9)$$

where M = Si,Ge,Sn; X = S,Se,Te

At the same temperature trimeric dimethyltin sulfide reacts with excess 1,2-dibromoethane, giving a new key compound, dimethyl(β-bromo)ethylsulfidotin bromide (I) in 60% yield (eq. 10).



(10)

Dimethyltin dibromide is obtained as a byproduct. I is characterized by high volatility and its fetid odour and gives involatile odourless 1 : 2 complexes with HMPT and pyridine. On alkaline hydrolysis of I, dimethyltin oxide and 1,4-ditiane are formed (eq.11)

(11)

The results considered here show that reactions of organometallic sulfides are varied and of importance not only from theoretical point of view, but also offer promise for synthesis.

Experimental

1. Interaction of trimeric dimethyltin sulfide with benzoyl peroxide

Dimethyltin sulfide (1 g, 0.0018 mol), benzoyl peroxide (1.34 g; 0.0054 mol) and 14 ml of benzene were placed in a flask. The mixture was allowed to stand for 70 hours. Elemental sulphur (0.17 g) was precipitated with a yield of 2.95 mol/mol of initial sulfide. Dibenzoatedimethyltin (2.13 g) was recovered from the solvent with a melting point 159–161°C ([15], melting point 160–162°C) and a yield 3.00 mol/mol of initial sulfide.

2. Interaction of trimeric dimethyltin sulfide with freshly precipitated copper with freezing-out of volatile products under vacuum

A carefully ground mixture of trimeric dimethyltin sulfide (3.87 g; 0.0071 mol) and 6.11 g of freshly precipitated copper was placed in one of the bends of a U-shaped evacuated sealed ampoule and heated at 170°C for 6 hours. The liquid reaction product was distilled into another bend, being cooled to −178°C. 2.41 g of the liquid product was collected with boiling point 122–123°C/21 mmHg, identified as trimethyltin sulfide; with a yield of 0.94 mol/mol of initial sulfide ([16], b.p. 118°C/21 mmHg). The black solid reaction residue (7.37 g) contained 5.25 g of copper, 1,30 g of copper sulfide (yield 1.92 mol/mol of initial sulfide) and 0.82 g of metallic tin (yield 0.97 mol/mol of initial sulfide).

3. Interaction of dimethyltin sulfide with copper in nonane solution

Dimethyltin sulfide (3.56 g;0.0066 mol), freshly precipitated copper (9.11 g) and 30 ml of nonane were heated in a sealed evacuated ampoule, 50 ml capacity, at 160°C for 40 hours. The liquid fraction was decanted off and the solid residue was washed with 5 ml of nonane. The solutions were combined and the solvent was removed at 30°C/1 mmHg into the trap, being cooled with liquid nitrogen. The residue (1.66 g) involatile under these conditions was identified as trimethyltin sulfide with a yield of 0.70 mol/mol of initial sulfide, b.p. 122°C/21 mmHg. The liquid from the trap was analysed by GLC (column 2 mm × 2 m, AP-L, carrier gas He,T_{column} 110°C). Tetramethyltin (0.30 g) was obtained, yield 0.25 mol/mol of initial sulfide. In the solid residue (11.06 g) 1.33 g of copper sulfide (yield 2.10 mol/mol of initial sulfide) 0.77 g of metallic tin (yield 0.98 mol/mol of initial sulfide) and dimethyltin oxide, recovered as dimethyltin dichloride (0.44 g) (yield 0.30 mol/mol of initial sulfide) were found.

4. Interaction of trimethyltin sulfide with copper in nonane solution

Trimethyltin sulfide (4.12 g; 0.0115 mol), freshly precipitated copper (7.40 g) and 30 ml of nonane were heated in a seaked evacuated ampoule, 50 ml capacity, at 160°C for 40 hours. The reaction mixture was treated as for the experiment 3. Tetramethyltin (2.68 g) was found (yield 1.30 mol/mol of initial sulfide as were copper sulfide (1.00 g), (yield 1 mol/mol of initial sulfide) metallic tin (0.55) (yield 0.40 mol/mol of initial sulfide) and dimethyltin oxide, recovered as dimethyltin dichloride (0.66 g) (yield 0.26 mol/mol of initial sulfide).

5. Interaction of hexamethyldistannane with copper in nonane solution

Hexamethyldistannane (2.98 g), freshly precipitated copper (5.5 g) and nonane (25 ml) were heated in a sealed evacuated ampoule, 50 ml capacity, at 160°C for 40 hours. The reaction solution was treated as above. 2.28 g of tetramethyltin (yield 1.40 mol/mol of initial distannane), 0.51 g of metallic tin (yield 0.47 mol/mol of initial distannane) and dimethyltin oxide, recovered as dimethyltin dichloride (0.26 g) (yield 0.13 mol of initial distannane) were obtained.

6. *Reaction of trimethyltinsulfide with methyl iodide*

Trimethyltin sulfide (7.19 g; 0.020 mol), methyl iodide (22.0 g) and pentane (10 ml) were heated with a backflow condenser for 25 hours. Filtration gave 2.86 g of sulfonium salt $Me_2S \cdot MeI$, yield 0.70 mol/mol of initial sulfide, decomposition temperature 218°C (a mixture with an authentic sample failed to give depression). GLC showed 0.30 g of trimethyltin iodide in the filtrate (yield 1.60 mol/mol of initial sulfide 0.67 g of thiomercaptide trimethyltin (yield 0.16 mol/mol of initial sulfide) and 0.21 g of tetramethyltin (yield 0.06 mol/mol of initial sulfide).

7. *Reaction of triethyltin sulfide with methyl iodide*

A mixture of 8.87 g (0.020 mol) of triethyltin sulfide, 22 g of methyl iodide and 10 ml of pentane was heated with a backflow condenser for 25 hours; 3.88 g of sulfonium salt $Me_2S \cdot MeI$ (yield 0.95 mol/mol of initial sulfide) and triethyltin iodide, released as triethyltin fluoride (7.64 g) (yield 1.70 mol/mol of initial sulfide) were collected.

8. *Reaction of trimethyltin sulfide with ethyl iodide*

A mixture of 7.19 g (0.020 mol) of trimethyltin sulfide, 4.00 g (0.16 mol) ethyl iodide, 7.16 g (0.040 mol) of HMPT and 10 ml of hexane were heated with a backflow condenser for 8 hours. Filtration gave 2.71 of sulfonium salt $Et_2S \cdot EtI$, yield 0.56 mol/mol of initial sulfide, m.p. 139°C (out of ether; a mixture with an authentic sample failed to give depression). The filtrate was vacuum evaporated at room temperature and under 40 mmHg vacuum, with a trap cooled with liquid nitrogen. GLC showed in the liquid from the trap 0.58 g of trimethyltin iodide (yield 0.10 mol/mol of initial sulfide) and 0.38 g of diethyl sulfide (yield 0.21 mol/mol of initial sulfide). The solid residue, involatile under the conditions, given above, was distilled at 104°C/0.5 mmHg and 15.41 g of the complex $Me_3SnI \cdot HMPT$ were obtained, yield 1.64 mol/mol of initial sulfide.

9. *Reaction of triphenyltin sulfide with methyl iodide*

Triphenyltin sulfide (3.0 g; 0.0041 mol), methyl iodide (47 g), HMPT (1.47 g; 0.0082 mol) and diethyl ether (10 ml) were heated with a backflow condenser for 10 hours. Filtration gave 0.82 g of sulfonium salt $Me_2S \cdot MeI$, yield 0.98 mol/mol of initial sulfide. The solvent was distilled of from the filtrate and the residue was recrystallized from heptane. The complex (5.11 g) $PhSnI \cdot HMPT$ was obtained, yield 1.98 mol/mol of initial sulfide, m.p. 125–127°C.

10. *Reaction of trimethyltin sulfide with methylene iodide*

Trimethyltin sulfide (5.0 g; 0.0139 mol); methylene iodide (19 g), HMPT (4.98 g; 0.0278 mol) and diethyl ether (10 ml) were heated with backflow condenser for 10 hours. Filtration gave 0.45 g of trimeric thioformaldehyde, yield 0.23 mol/mol of initial sulfide. The solvent was distilled off from the filtrate. Residue distillation at 104°C/0.5 mmHg gave 12.20 g of the complex $Me_3SnI \cdot HMPT$, yield 1.87 mol/mol of initial sulfide.

11. *Reaction of dimethyltin sulfide with methyl iodide*

Dimethyltin sulfide (2.76 g; 0.0051 mol), methyl iodide (8.69 g), HMPT (5.47 g; 0.0305 mol) and pentane (10 ml) were heated with a backflow condenser for 5 hours.

Filtration gave 3.12 g of sulfonium salt $Me_2S \cdot MeI$, yield 3.0 mol/mol of initial sulfide. The solvent was distilled off from the filtrate and the residue was recrystallized from hexane. The complex $Me_2SnI_2 \cdot 2HMPT$ (11.61 g) was collected with yield 3.00 mol/mol of initial sulfide, m.p. 164–165°C.

12. Reaction of dimethyltin sulfide with 1,2-dibromoethane

Dimethyltin sulfide (4.0 g; 0.0074 mol) and 1,2-dibromoethane (40 g) were heated at 140°C for 30 hours. The solvent was recovered under vacuum at 20–30°C/1 mmHg. From the residue by sublimation at 70°C/1 mmHg dimethyl[(β-bromo)ethylsulfido]tin bromide was isolated (4.91 g), yield 1.80 mol/mol of initial sulfide, m.p. 96–98°C/subl. Found: C, 12.11; H, 2.84; Br, 43.39; S, 8.60; Sn, 32.90. Calc. for $C_4H_{10}Br_2SSn$: C, 13.02; H, 2.74; Br, 43.30; S, 8.68; Sn, 32.19%.

Dimethyltin dibromide (1.37 g) was recovered as a by-product, yield 0.60 mol/mol of initial sulfide. The residue involatile under sublimation conditions (1.45 g) contained tin (0.35 g; 0.40 mol/mol of initial sulfide) determined by wet combustion in acids.

13. Formation of dimethyl[(β-bromo)ethylsulfide]tin bromide complex

A. Dimethyl[(β-bromo)ethylsulfido]tin bromide (0.37 g; 0.0010 mol) was mixed with dry pyridine (0.16 g; 0.0020 mol). The exothermic reaction yielded 0.53 g of the complex $Me_2Sn(Br)SCH_2CH_2Br \cdot 2C_5H_5N$,m.p.179–181°C(heptane). Found: C, 30.55; H, 3.80; N, 5.40; Sn, 22.47. Calc. for $C_{14}H_{20}Br_2N_2SSn$: C, 31.90; H, 3.80; N, 5.32; Sn, 22.53%. B. Dimethyl[(β-bromo)ethylsulfido]tin bromide (0.48 g; 0.0013 mol) was mixed with HMPT (0.72 g; 0.0040 mol). Exothermic formation of the complex was observed. The excess of HMPT was washed out with 10 ml of pentane and the residue was recrystallized from heptane. The complex $Me_2Sn(Br)SCH_2$-$CH_2Br \cdot 2HMPT$ (0.90 g; 0.0012 mol) was obtained, m.p. 141–143°C. Found: C, 25.39; H, 6.32; N, 12.55; Sn, 24.65. Calcd. for $C_{16}H_{46}Br_2N_6O_2P_2SSn$: C, 26.42; H, 6.33; N, 11.56; Sn, 24.86%.

14. Alkaline hydrolysis of dimethyl[(β-bromo)ethylsulfido]tin bromide

Dimethyl[(β-bromo)ethylsulfido]tin bromide (1.36 g; 0.0037 mol) was heated with 20 ml of 5% aqueous NaOH solution in a sealed ampoule at 50°C for 4 hours. Dimethyltin oxide (0.46 g) (yield 0.76 mol/mol of initial compound) and 1,4-dithiane (0.21 g) (yield 0.49 mol/mol of initial compound, m.p. 110–113°C) were recovered from reaction mixture (pentane, a mixture with an authentic sample failed to give depression). Bromide in the form of AgBr (1.39 g, yield 2.00 mol/mol of initial compound) was precipitated from the reaction solution.

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