GROUP IVB ORGANOMETALLIC SULPHIDES III*. CLEAVAGE OF THE GERMANIUM–SULPHUR BOND BY ELECTROPHILIC REAGENTS

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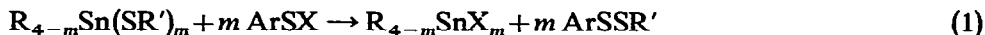
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SUMMARY

The germanium–sulphur bond in Bu_3GeSAr is cleaved by electrophilic reagents. Thus halogens and nitrosyl chloride react to give the disulphide, $ArSSAr$; sulphenyl chlorides, $Ar'SCl$, give $ArSSAr'$; sulphur chlorides, SCl_2 and S_2Cl_2, give tri- and tetrasulphides, $ArSSSAr$ and $ArSSSSAr$, respectively. Metathetic reactions also occur with triphenylmethyl chloride and phenylmercury chloride. The germanium sulphides appear to be less reactive than the corresponding tin sulphides.

INTRODUCTION

Reactions of organotin sulphides with divalent sulphur chlorides, sulphenyl halides and thiocyanates have been shown to give di- and polysulphide products[1,2].

$$R_{4-m}Sn(SR')_m + m\, ArSX \rightarrow R_{4-m}SnX_m + m\, ArSSR' \tag{1}$$

$$(R_3Sn)_2S + 2\, ArSX \rightarrow R_3SnX + ArSSSAr \tag{2}$$

$$\tfrac{1}{3}\,(R_2SnS)_3 + 2\, ArSX \rightarrow R_2SnX_2 + ArSSSAr \tag{3}$$

$$2\, R_3SnSAr + S_mCl_2 \rightarrow 2\, R_3SnCl + ArS_{m+2}Ar \tag{4}$$

$$X = Cl, Br\ or\ SCN;\ m = 1\ or\ 2;\ R' = alkyl\ or\ aryl$$

Symmetric disulphide products can also be produced from organotin sulphides on reaction with bromine[3] and iodine[2,4].

$$2\, R_3SnSR' + X_2 \rightarrow 2\, R_3SnX + R'SSR' \tag{5}$$
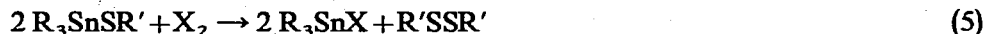
This reaction possibly occurs in two steps; the first of which leads to the formation of a sulphenyl halide:

$$R_3SnSR' + X_2 \rightarrow R_3SnX + R'SX \tag{6}$$

and the second step is the subsequent reaction of the sulphenyl halide [*i.e.* eqn. (1)].

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* For Part II see ref. 1.

The germanium–sulphur bond in germanium tetrakis(4-tolyl sulphide) is also cleaved by bromine to give di-4-tolyl disulphide[5]. We now wish to report on reactions of organogermanium sulphides with sulphur and sulphenyl chlorides. Reactions with other electrophilic reagents are also mentioned. A comparison of the reactivities of organotin and -germanium sulphides is attempted.

RESULTS AND DISCUSSIONS

The organogermanium sulphides used were of the type Bu_3GeSAr (Ar= 4-t-$C_4H_9C_6H_4$ and 4-$CH_3C_6H_4$). These sulphides reacted with sulphenyl chlorides (Ar′SCl), sulphur chlorides (SCl_2 and S_2Cl_2), and halogens (iodine and bromine) in a similar manner to the corresponding tin sulphides[1,2], Bu_3SnSAr [eqns. (1), (4) and (5)]. Smaller yields of sulphide products were however usually obtained from the organogermanium sulphide reactions. From the reactions in which obvious colour changes occurred, such as those between the organometallic sulphides and iodine (colour change violet to pale yellow) and 4-toluenesulphenyl chloride (red to pale yellow), it was found that the reaction times were equally short for both tin and germanium sulphides. Hence, at least in these particular reactions and most probably in all the halogen and sulphur halide reactions, it was impossible to distinguish the reactivities of the two organometallic sulphides. Even from the iodine and 4-toluene-sulphenyl chloride reactions—in which the electrophiles were obviously totally consumed—higher yields of isolated products were obtained from the organotin sulphide reactions; for example, the yields of di-4-tolyl disulphide from the reaction of 4-$CH_3C_6H_4SCl$ with 4-$CH_3C_6H_4SGeBu_3$ and 4-$CH_3C_6H_4SSnPr_3$ were 24 and 78 %[2] respectively. (The different alkyl groups attached to the two metals should have an insignificant effect on the product yields.) A factor contributing largely to such differences was the much greater difficulty in separating a sulphide product from a triorganogermanium halide than from a triorganotin halide.

Other electrophilic reagents were used to cleave the germanium–sulphur bond; these were nitrosyl chloride, triphenylmethyl chloride and phenylmercury chloride. The product isolated from the nitrosyl chloride reaction with 4-$CH_3C_6H_4SGeBu_3$ was the symmetric disulphide, (4-$CH_3C_6H_4S)_2$. This reaction in the first instance should have given 4-tolyl thionitrite, 4-$CH_3C_6H_4SNO$:

$$4\text{-}CH_3C_6H_4SGeBu_3 + NOCl \rightarrow Bu_3GeCl + 4\text{-}CH_3C_6H_4SNO \tag{7}$$

Aryl thionitrites, reported to be deeply coloured, are not thermally stable[6,7] and decompose to give the symmetric disulphide and nitric oxide, which can be oxidised to dinitrogen tetroxide under the reaction conditions.

$$2\,ArSNO \rightarrow ArSSAr + 2\,NO \tag{8}$$

The germanium sulphide reacted in tetrahydrofuran solution at $-78°$ with nitrosyl chloride to give a deep red coloured solution, which on warming to room temperature became paler in colour with evolution of brown dinitrogen tetroxide. The decomposition became most marked at temperatures above room temperature. Tri-n-butyltin 4-tert-butylphenyl sulphide[8], 4-t-$C_4H_9C_6H_4SSnBu_3$, and mercury bis(trifluoro-methyl sulphide)[9], $Hg(SCF_3)_2$, react similarly with nitrosyl chloride, each giving the appropriate disulphide.

Tertiary alkyl thionitrites, such as t-C$_4$H$_9$SNO and Ph$_3$CSNO, are more thermally stable[6]; t-C$_4$H$_9$SNO, for example, has been prepared by the reaction of nitrosyl chloride with both the thiol, t-C$_4$H$_9$SH, and its mercury salt[10]. An attempt to prepare and isolate triphenylmethyl thionitrite via a germanium sulphide reaction was aborted by the lack of thermal stability of Bu$_3$GeSCPh$_3$. The normal method of preparation, namely:

$$Bu_3GeCl + Ph_3CSH + Et_3N \xrightarrow{CCl_4} Et_3N \cdot HCl + Ph_3CSGeBu_3$$
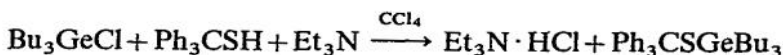
was used and the requisite amount of triethylamine hydrochloride was collected. On distilling under reduced pressure the oily product of this reaction, decomposition was evident. The distillate was initially blue in colour but slowly turned pale yellow and deposited a colourless crystalline material, shown to be triphenylmethane. This decomposition is being further investigated.

While it was not possible to distinguish between the reactivities of triorganotin and -germanium sulphides towards the halogens and sulphur electrophiles (and also towards nitrosyl chloride), the reactions of both phenylmercury chloride and triphenylmethyl chloride proceeded at different rates with tin[8] and germanium sulphide was less reactive.

$$R_3MSAr + PhHgCl \rightarrow R_3MCl + PhHgSAr \tag{10}$$

$$R_3MSAr + Ph_3CCl \rightarrow R_3MCl + Ph_3CSAr \tag{11}$$

M = Sn and Ge

The organotin sulphide, 4-t-C$_4$H$_9$C$_6$H$_4$SSnBu$_3$, reacted with PhHgCl within a few minutes to give an 84% yield of the phenylmercury aryl sulphide whereas the 4-CH$_3$C$_6$H$_4$SGeBu$_3$ reaction required 90 minutes to give a smaller yield (68%, based on the phenylmercury chloride taken) of the appropriate mercury sulphide. Some unreacted phenylmercury chloride was recovered from the germanium reaction. The yield of phenylmercury 4-tolyl sulphide based on the PhHgCl actually consumed was 82%. (In these reactions, separation of the phenylmercury aryl sulphide from both the organometallic chlorides was much more easily achieved than was the separation of the di- and polysulphides from the organometallic halides and especially from the organogermanium halides.)

No cleavage of the phenyl–mercury bond occurred in either of these reactions. Organogermanium sulphides can cleave carbon–mercury bonds[11] as shown by the production of mercuric sulphide and Pr$_3$GeCH$_2$CO$_2$Me from Hg(CH$_2$CO$_2$Me)$_2$ and (Pr$_3$Ge)$_2$S. In this case, the organic group cleaved is an activated one due to the proximity of the carboxymethyl group to the carbon–mercury bond. Mercuric chloride, a stronger Lewis acid than phenylmercury chloride, has been found to react with organogermanium sulphides[12] in a similar manner to PhHgCl with both chlorines being replaced by sulphide groups.

A report of the reaction of a germanium sulphide with a simple alkyl halide has been made[13]. Methyl iodide and R$_3$GeSCH$_3$ (R = Ph and CH$_3$) gave, over a period of one week at room temperature, R$_3$GeI and trimethylsulphonium iodide, Me$_3$S$^+$I$^-$. The formation of the sulphonium salt can be attributed to the small size of the alkyl substituents and the use of an excess of methyl iodide, and we found that use of a

controlled quantity of triphenylmethyl chloride caused cleavage of the germanium–sulphur bond in 4-$CH_3C_6H_4SGeBu_3$, to give the sulphide [eqn. (11)] rather than the sulphonium compound, the large size of the Ph_3C group no doubt playing a part. The corresponding tin reaction was a much faster one[8], indicating that tin sulphides are more reactive than germanium sulphides towards carbon halides.

The similarities between organotin and organogermanium sulphides in their reactions with disulphur dichloride and other electrophiles have been stressed. In each of these reactions, one sulphide product only was obtained. This should be contrasted with silicon-sulphide/disulphur-dichloride reactions, which give mixtures of polysulphide products[14].

EXPERIMENTAL

Materials

Tri-n-butylgermanium 4-tolyl and 4-t-butylphenyl sulphides (b.p. 170°/0.4 mm and 139°/0.02 mm respectively), were prepared from tri-n-butylgermanium chloride and the appropriate thiol in the presence of triethylamine in a similar manner to that described for the organotin sulphides[1,2]. Longer reaction times were however required. 4-Toluenesulphenyl chloride, sulphur dichloride and disulphur dichloride were purified samples from previous studies[1,2]. Nitrosyl chloride and triphenylmethyl chloride were commercial samples.

Phenylmercury chloride. Mercuric oxide (15 g) and trifluoroacetic acid (50 ml) were heated together until a colourless solution was obtained. Benzene (50 ml) was added with stirring to the cooled solution. The resulting homogeneous solution was gently refluxed for 1 h. Addition of sodium chloride (10 g) in water produced an immediate precipitate of phenylmercury chloride. The precipitate was collected, washed with water and recrystallised from ethanol; m.p. 252°; 14.2 g, 67%.

Reactions

1. *Triphenylmethyl chloride and tri-n-butylgermanium 4-tolyl sulphide.* 4-CH_3-$C_6H_4SGeBu_3$ (1.0 g) and Ph_3CCl (0.80 g) were refluxed in chloroform overnight. The solvent was removed and the residue was taken up in petroleum ether 60–80°. On cooling the solution in an acetone/CO_2 bath, triphenylmethyl 4-tolyl sulphide precipitated. It was recrystallised from acetone; m.p. 149–152° (lit.[15] m.p. 149°). Yield 0.91 g, 90%. (Found: C, 85.3; H, 5.9; S, 8.9. $C_{26}H_{22}S$ calcd.: C, 85.2; H, 6.1; S, 8.7%.)

2. *Phenylmercury chloride and tri-n-butylgermanium 4-tert-butylphenyl sulphide.* 4-t-$C_4H_9C_6H_4SGeBu_3$ (1.04 g) and PhHgCl (0.80 g) were refluxed in benzene for 1½ h. On cooling the clear solution, a solid (0.15 g; m.p. 253°)—unreacted PhHgCl—was obtained. The solvent was removed to leave an oily solid. The solid was collected (0.61 g; m.p. 129°) and washed with small volumes (1–2 ml) of hexane. The solvent was removed from the filtrate and the washings to leave an oil and solid. The solid was collected (0.16 g; m.p. 129–130°) and washed with 1-ml portions of hexane. The two solid samples of phenylmercury 4-tert-butylphenyl sulphide were combined and recrystallised from hexane; m.p. 129°. (Found: C, 43.2; H, 4.2; S, 7.4. $C_{16}H_{18}HgS$ calcd.: C, 43.4; H, 4.1; S, 7.2%.) The oil left at the end was shown to be tri-n-butylgermanium chloride.

3. *4-Toluenesulphenyl chloride and tri-n-butylgermanium 4-tolyl sulphide.* 4-CH$_3$C$_6$H$_4$SCl (0.43 g) was added to 4-CH$_3$C$_6$H$_4$SGeBu$_3$ (1.0 g) in carbon tetrachloride. The reaction was immediate as shown by the colour change from red to pale yellow. The solvent was removed, hexane added and the resulting solution cooled in an acetone/CO$_2$ bath to give a precipitate of di-4-tolyl disulphide. This was recrystallised from petroleum ether 60–80° ; m.p. 44–45° (lit.[16] m.p. 46°). Yield 0.16 g, 24%. The sample was identical with an authentic sample.

4. *Iodine and tri-n-butylgermanium 4-t-butylphenyl sulphide.* Iodine (0.31 g) and 4-t-C$_4$H$_9$C$_6$H$_4$SGeBu$_3$ (1.0 g) in carbon tetrachloride were gently heated for a few minutes to give a pale yellow solution. The reaction mixture was worked up as in (3) to give, after recrystallisation, di-4-tert-butylphenyl disulphide, m.p. 88° (lit.[17] m.p. 89°). Yield 0.15 g, 37%.

5. *Bromine and tri-n-butylgermanium 4-t-butylphenyl sulphide.* Bromine (0.20 g) and 4-t-C$_4$H$_9$C$_6$H$_4$SGeBu$_3$ (1.0 g) gave as in (4), di-4-tert-butylphenyl disulphide; m.p. 87°. Yield 0.10 g, 47.5%.

6. *Nitrosyl chloride and tri-n-butylgermanium 4-tolyl sulphide.* Solutions of 4-CH$_3$C$_6$H$_4$SGeBu$_3$ (1.0 g) and NOCl (0.18 g) in tetrahydrofuran were mixed at −78° to give a deep-red solution. On warming the solution, the colour changed to yellow and the brown gas, dinitrogen tetroxide, was observed. Evaporation of the solvent and work up of the residue as in (3), gave di-4-tolyl disulphide.

7. *Sulphur dichloride and tri-n-butylgermanium 4-tolyl sulphide.* 4-CH$_3$C$_6$H$_4$SGeBu$_3$ (1.0 g) and SCl$_2$ (0.14 g) in chloroform were left overnight at room temperature. The solvent was removed, hexane added to the residue and the solution cooled in an acetone/CO$_2$ bath to give di-4-tolyl trisulphide, which was recrystallised from hexane (0.11 g, 22%); m.p. 79° (lit.[18] m.p. 82°). (Found; C, 60.3; H, 5.2; S, 34.8. C$_{14}$H$_{14}$S$_3$ calcd.: C, 60.4; H, 5.0; S, 34.6%.)

8. *Disulphur dichloride and tri-n-butylgermanium 4-tolyl sulphide.* 4-CH$_3$C$_6$H$_4$SGeBu$_3$ (1.0 g) and S$_2$Cl$_2$ (0.20 g) were refluxed in chloroform for 3 h. The reaction mixture was worked up as in (7). Di-4-tolyl tetrasulphide; m.p. 68–70° (lit.[18] m.p. 75°). Yield crude 0.20 g, recrystallised 0.08 g, 18%. (Found; C, 54.3; H, 4.8; S, 41.4, C$_{14}$H$_{14}$S$_4$ calcd.: C, 54.0; H, 4.5; S, 41.3%.)

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