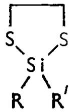
1307. *Preparations and Reactions of* 1,3-*Dithia*-2-*silacyclopentane Derivatives*

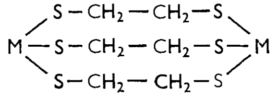
By E. W. Abel, D. A. Armitage, and R. P. Bush

New methods for the preparation of the 1,3-dithia-2-silacyclopentane ring system are reported. The silicon–sulphur bonds in this heterocyclic system undergo easy fission with a variety of covalent halides, thus providing an easy method for the formation of a wide variety of 1,3-dithiacyclopentanes with a metal or metalloid in the 2-position. Such rings containing boron, phosphorus, arsenic, antimony, and tin are reported.

Recent work on the properties of the 1,3-diaza-2-silacyclopentanes [1] has prompted a similar study of the 1,3-dithia-2-silacyclopentanes (I). 2,2-Dimethyl-1,3-dithia-2-silacyclopentane (I; R = R′ = Me) has been known for some time, and has been prepared by two methods involving reaction of dichlorodimethylsilane with either ethane-1,2-dithiol in the presence of triethylamine [2,3] or with the lead salt of ethane-1,2-dithiol.[4] Both methods involve either the reaction or production of solids, and we find that greatly improved yields of the ring system are obtained from completely homogeneous reactions.



(I)



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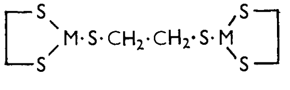
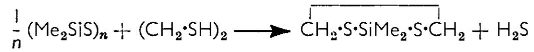


(III)

Reaction of ethane-1,2-dithiol with hexamethylcyclotrisilthiane gave a 92% yield of 2,2-dimethyl-1,3-dithia-2-silacyclopentane (equation 1). Although the starting material



$$\frac{1}{n}(Me_2SiS)_n + (CH_2{\cdot}SH)_2 \longrightarrow CH_2{\cdot}S{\cdot}SiMe_2{\cdot}S{\cdot}CH_2 + H_2S \qquad (1)$$

$(n = 2 \text{ and } 3)$

in this experiment was pure hexamethylcyclotrisilthiane, at the temperature of the reaction it is likely that some of this was converted into tetramethylcyclodisilthiane before reaction with the dithiol.[5]

Aminosilanes are reported to react with thiols, the reaction going to completion if the amine

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[1] E. W. Abel and R. P. Bush, *J. Organometallic Chem.*, 1965, **3**, 245; C. H. Yoder and J. J. Zuckermann, *Inorg. Chem.*, 1965, **4**, 116.

[2] F. P. Richter and B. A. Orkin, U.S.P. 2,590,039/1952 (*Chem. Abs.*, 1952, **46**, 5892).

[3] M. Wieber and M. Schmidt, *Z. Naturforsch.*, 1963, **18**b, 846.

[4] E. W. Abel, D. A. Armitage, and R. P. Bush, *J.*, 1965, 3045.

[5] T. Nomura, M. Yokoi, and K. Yamasaki, *Proc. Japan. Acad.*, 1953, **29**, 342 (*Chem. Abs.*, 1955, **49**, 12,274).

released has a lower boiling point than the thiol and can be distilled from the reaction mixture.[6,7] Ethane-1,2-dithiol thus reacted with bis(diethylamino)-dimethylsilane and -methylphenylsilane, to evolve diethylamine and form, respectively, 2,2-dimethyl-1,3-dithia-2-silacyclopentane and 2-methyl-2-phenyl-1,3-dithia-2-silacyclopentane (I; R = Me, R′ = Ph) (equation 2). By a similar reaction, the removal of ethylamine from a mixture of

$$\underset{(R = Me\text{ and }Ph)}{(Et_2N)_2SiRMe} + (CH_2\cdot SH)_2 \longrightarrow \overline{CH_2\cdot S\cdot SiMeR\cdot S\cdot CH_2} + 2Et_2NH \qquad (2)$$

tri-*N*-ethylhexamethylcyclotrisilazane and ethane-1,2-dithiol gave 2,2-dimethyl-1,3-dithia-2-silacyclopentane (equation 3).

$$(EtN\cdot SiMe_2)_3 + 3(CH_2\cdot SH)_2 \longrightarrow 3\overline{CH_2\cdot S\cdot SiMe_2\cdot S\cdot CH_2} + 3EtNH_2 \qquad (3)$$

The reactions of (I; R = R′ = Me) with boron trichloride and phenylboron dichloride have already been reported to yield the corresponding boracyclopentanes: $\overline{CH_2\cdot S\cdot SiMe_2\cdot S\cdot CH_2} + RBCl_2 \longrightarrow Me_2SiCl_2 + \overline{CH_2\cdot S\cdot BR\cdot S\cdot CH_2}$ (R = Ph or Cl).[4] Varying this experiment (R = Cl), by a change in the molar ratio of the reactants, has produced a different product (equation 4). Two possible structures can be considered for this product

$$2BCl_3 + 3\overline{CH_2\cdot S\cdot SiMe_2\cdot S\cdot CH_2} \longrightarrow B_2S_6(C_2H_4)_3 + 3Me_2SiCl_2 \qquad (4)$$

as depicted by (II; M = B) and (III; M = B). The proton magnetic resonance spectrum consists of two sharp singlets, τ 6·70 and 6·90, with relative intensities in the ratio 2 : 1. This evidence strongly favours structure (III) in which eight protons are in an identical (ring) environment, and the other four are in a different (chain) environment, thus accounting for the two peaks of 2 : 1 intensity. In (II), all the protons would be expected to be in identical environment, giving rise to a single proton resonance. Further, the infrared spectrum of the compound suggests the presence of the five-membered dithiaboracyclopentane ring system.[8]

Phenylphosphorus and phenylarsenic dichlorides react with 2,2-dimethyl-1,3-dithia-2-silacyclopentane to give good yields of the corresponding phospha- and arsa-dithiacyclopentanes (equation 5). The methyl analogue of this 2-phenyl-1,3-dithia-2-phospha(III)-

$$\underset{(M = P\text{ and }As)}{PhMCl_2} + \overline{CH_2\cdot S\cdot SiMe_2\cdot S\cdot CH_2} \longrightarrow Me_2SiCl_2 + \overline{CH_2\cdot S\cdot MPh\cdot S\cdot CH_2} \qquad (5)$$

cyclopentane has been recently reported, and is oxidised to the corresponding phosphorus(V) compound by sulphur.[9] We have obtained the phosphorus(V) heterocyclic system by the direct interaction of phenylphosphoryl chloride with 2,2-dimethyl-1,3-dithia-2-silacyclopentane (equation 6). This ring system of 1,3-dithia-2-phospha(V)cyclopentane has been previously mentioned but not characterised.[10]

$$PhP(O)Cl_2 + \overline{CH_2\cdot S\cdot SiMe_2\cdot S\cdot CH_2} \longrightarrow Me_2SiCl_2 + \overline{CH_2\cdot S\cdot P(O)Ph\cdot S\cdot CH_2} \qquad (6)$$

The trichlorides of phosphorus, arsenic, and antimony react in a manner similar to boron, in that each reaction produces two products depending upon the ratio of the reactants (equations 7 and 8). The products of the equimolar reactions (equation 7) are the monocyclic phospha-, arsa-, and stiba-dithiacyclopentanes. In the case of the reactions represented by equation (8), analyses and molecular weight measurements confirm the product in

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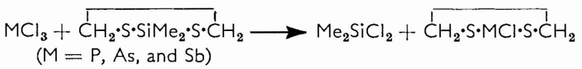
[6] E. W. Abel, *J.*, 1960, 4406; 1961, 4933.

[7] E. Larsson and R. Marin, Swed. Pat. 138,357/1952 (*Chem. Abs.*, 1954, **48**, 2761).

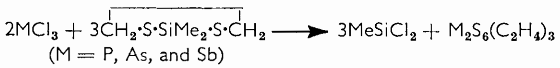
[8] A. Finch, personal communication.

[9] M. Wieber, J. Otto, and M. Schmidt, *Angew. Chem.*, 1964, **76**, 648.

[10] A. E. Arbuzov and V. M. Zoroastrova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim Nauk*, 1952, 453.



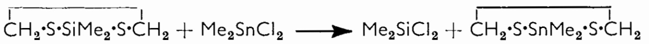
$$MCl_3 + CH_2{\cdot}S{\cdot}SiMe_2{\cdot}S{\cdot}CH_2 \longrightarrow Me_2SiCl_2 + CH_2{\cdot}S{\cdot}MCl{\cdot}S{\cdot}CH_2 \quad (M = P,\ As,\ and\ Sb) \qquad (7)$$



$$2MCl_3 + 3CH_2{\cdot}S{\cdot}SiMe_2{\cdot}S{\cdot}CH_2 \longrightarrow 3MeSiCl_2 + M_2S_6(C_2H_4)_3 \quad (M = P,\ As,\ and\ Sb) \qquad (8)$$

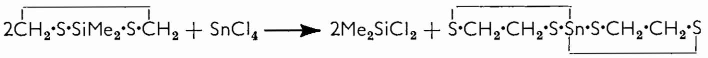
each case to be $M_2S_6(C_2H_4)_3$ (M = P, As, or Sb). As in the case of boron, above, the possibility of two structures, (II) and (III), for these compounds arises. In the case of the phosphorus and arsenic products, the proton resonance spectra, as with the boron compounds, strongly suggests structure (III). The two main resonance absorptions are not simple singlets, owing to ^{31}P coupling and what appears to be an A_2B_2 structure of the ring protons. This latter effect may be caused by the non-planarity of the ring, or stereostability about the phosphorus and arsenic atoms. However, the relative 2 : 1 gross intensities of the two well separated absorptions support structure (III). The points concerning ring geometry are being further investigated and findings will be reported later. In the case of the antimony compound of formula $Sb_2S_6(C_2H_4)_3$, however, the proton resonance spectrum only contains one absorption, τ 6·50. This strongly suggests, though does not prove, that the antimony compound, unlike the others takes up structure (II). The broadness of the absorption centred at τ 6·50 suggests considerable steric crowding of the six methylene groups in this molecule, and it is of interest to note that to make a molecular model of (II; M = Sb) requires considerable crowding. Experimental efforts to make the antimony derivative of structure (III), by first making 2-chloro-1,3-dithia-2-stibacyclopentane reported above, and then treating this with further dithiasilacyclopentane has resulted only in the formation of intractable yellow glasses.

Dimethyltin dichloride reacted with 2,2-dimethyl-1,3-dithia-2-silacyclopentane on warming, to form the 2,2-dimethyl-1,3-dithia-2-stannacyclopentane (equation 9), which was identified with the products of previous preparations of this ring system.[3,11]



$$CH_2{\cdot}S{\cdot}SiMe_2{\cdot}S{\cdot}CH_2 + Me_2SnCl_2 \longrightarrow Me_2SiCl_2 + CH_2{\cdot}S{\cdot}SnMe_2{\cdot}S{\cdot}CH_2 \qquad (9)$$

The reaction of 2,2-dimethyl-1,3-dithia-2-silacyclopentane with stannic chloride was very vigorous at room temperature and produced 1,4,6,9-tetrathia-5-stannaspiro[4,4]-nonane (equation 10), identified with the products of previous preparations of this compound.[11,12]



$$2CH_2{\cdot}S{\cdot}SiMe_2{\cdot}S{\cdot}CH_2 + SnCl_4 \longrightarrow 2Me_2SiCl_2 + S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}Sn{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S \qquad (10)$$

EXPERIMENTAL

In the numerous reactions involving the evolution of dichlorodimethylsilane, this product was characterised in each case by boiling point and refractive index. All reactions were carried out under anhydrous conditions and all solvents were dried before use.

Hexamethylcyclotrisilthiane,[5] tri-*N*-ethylhexamethylcyclotrisilazane,[13] phenylboron dichloride,[14] and phenylarsenic dichloride [15] were obtained by known methods. Other reactants, except those mentioned below, were obtained from commercial sources.

Bis(diethylamino)dimethylsilane.—Dichlorodimethylsilane (193 g., 1 mol.) was slowly added to a stirred solution of diethylamine (438 g., 4 mol.) in ether (2000 ml.) at room temperature. The mixture was heated to reflux and stirred for 6 hr., and after filtration, continuous washing of the precipitate, and removal of ether, distillation gave bis(diethylamino)dimethylsilane (250 g., 82%), b. p. 36°/0·5 mm., n_D^{20} 1·4340, d_4^{16} 0·815.

Bis(diethylamino)methylphenylsilane.—To a solution of phenyl-lithium in ether [prepared from bromobenzene (84 g., 2 mol.) and lithium (14 g., 4 mol.)] was added diethylamine (73 g., 2 mol.). After stirring for 3 hr., dichloromethylphenylsilane (96 g., 1 mol.) was carefully

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[11] E. W. Abel and D. B. Brady, *J.*, 1965, 1192.

[12] H. J. Backer and W. Drenth, *Rec. Trav. chim.*, 1951, **70**, 559.

[13] E. W. Abel and R. P. Bush, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1685.

[14] J. E. Burch, W. Gerrard, M. Haworth, and E. F. Mooney, *J.*, 1960, 4916.

[15] I. L. Knunyants, V. Ya. Pil'skaya, *Izvest. Akad. Nauk. S.S.S.R., Otdel. khim Nauk*, 1955, 472.

added, and the solution stirred and refluxed for 2 hr. After removal of the precipitated lithium salts, and ether, distillation gave *bis(diethylamino)methylphenylsilane* (91 g., 69%), b. p. 78°/0·05 mm., n_D^{20} 1·4960 (Found: C, 68·1; H, 10·8. $C_{15}H_{28}N_2Si$ requires C, 68·2; H, 10·6%).

Reaction of Ethane-1,2-*dithiol with Bis(diethylamino)dimethylsilane*.—The dithiol (46 g., 1 mol.) was added to bis(diethylamino)dimethylsilane (98·2 g., 1 mol.) and the mixture heated. Diethylamine (95%), b. p. 56°, n_D^{23} 1·3833, was evolved during 2 hr.; subsequent distillation of the residual oil yielded 2,2-dimethyl-1,3-dithia-2-silacyclopentane (66·7 g., 91%), b. p. 188°, n_D^{20} 1·5534 (Found: C, 32·2; H, 6·5. Calc. for $C_4H_{10}S_2Si$: C, 32·0; H, 6·7%).

Reaction of Ethane-1,2-*dithiol with Hexamethylcyclotrisilthiane*.—The dithiol (19·0 g., 3 mol.) and trisilthiane (18·2 g., 1 mol.) were heated together under reflux. Hydrogen sulphide was evolved during 4 days, and subsequent distillation of the residue gave 2,2-dimethyl-1,3-dithia-2-silacyclopentane (28·0 g., 92%), b. p. 188—189°, n_D^{20} 1·5536.

Reaction of Ethane-1,2-*dithiol with Bis(diethylamino)methylphenylsilane*.—Heating together of the dithiol (5·33 g., 1 mol.) and the aminosilane (14·94 g., 1 mol.) caused the evolution of diethylamine (6·56 g., 79%), b. p. 56°, n_D^{20} 1·3850. Distillation of the residue gave 2-*methyl*-2-*phenyl*-1,3-*dithia*-2-*silacyclopentane* (6·0 g., 50%), b. p. 98°/0·05 mm., n_D^{20} 1·6180 (Found: C, 50·9; H, 5·5%; *M*, 202. $C_9H_{12}S_2Si$ requires C, 51·0; H, 5·6%; *M*, 212).

Reaction of Ethane-1,2-*dithiol with Tri*-N-*ethylhexamethylcyclotrisilazane*.—The dithiol (50·5 g., 3 mol.) was added to cyclosilazane (47 g., 1 mol.) at room temperature, and the mixture heated under reflux. When no further ethylamine was evolved (*ca*. 3 days), the resulting oil was fractionally distilled, to give 2,2-dimethyl-1,3-dithia-2-silacyclopentane (44 g., 59%), b. p. 188°, n_D^{20} 1·5531.

Interaction of Boron Trichloride and 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane* (*Equation* 4).—The dithiasilacyclopentane (11·3 g.) was added slowly, with constant shaking, to boron trichloride (5·9 g.) at −78°. The reaction was extremely vigorous and constant cooling was necessary. After warming the resulting mixture to 20°, dichlorodimethylsilane (80%) was removed under reduced pressure and trapped. Recrystallisation of the residual solid from toluene–light petroleum (b. p. 80—100°) yielded 1,2-*di*-(1,3-*dithia*-2-*boracyclopent*-2-*ylthio*)*ethane* (4·2 g., 56%), m. p. 88—91° (Found: C, 24·0; H, 4·2. $C_6H_{12}B_2S_6$ requires C, 24·2; H, 4·0%).

Interaction of Phenylphosphorus Dichloride and 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane*.—The dichloride (13·32 g., 1 mol.) and the dithiasilacyclopentane (11·18 g., 1 mole.) were heated together, to evolve dichlorodimethylsilane (77%), and subsequent distillation of the residue yielded 2-*phenyl*-1,3-*dithia*-2-*phosphacyclopentane* (8·6 g., 58%), b. p. 136—137°/0·2 mm., n_D^{23} 1·6880 (Found: C, 47·6; H, 4·1%; *M*, 210. $C_8H_9PS_2$ requires C, 48·0; H, 4·5%; *M*, 200). Similar reactions with phenylarsenic dichloride and phenylphosphoryl dichloride gave, respectively, 2-*phenyl*-1,3-*dithia*-2-*arsacyclopentane* (13·5 g., 83%), b. p. 154°/0·05 mm. (the solid distillate was recrystallised from hexane–benzene to give well formed crystals, m. p. 43—45°) (Found: C, 39·1; H, 3·6%; *M*, 243. $C_8H_9AsS_2$ requires C, 39·3; H, 3·7%; *M*, 244), and a small yield of 2-*oxo*-2-*phenyl*-1,3-*dithia*-2-*phospha*(v)*cyclopentane* (2·0 g.), b. p. 180°/0·001 mm. This latter compound remained as a viscous oil for some months and then crystallised. It was recrystallised from toluene–light petroleum, to give well formed crystals, m. p. 70° (Found: C, 41·5; H, 4·20%; *M*, 240. $C_8H_9OS_2P$ requires, C, 44·4; H, 4·19%; *M*, 216). The proton resonance specrum consists of two well separated complex multiplets of relative intensity 5 : 4. This is exactly the result to be expected from such a compound with 5 aromatic and 4 aliphatic protons, with numerous causes for the complex splittings, which will be discussed in a later publication.

Interaction of Phosphorus Trichloride and 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane* (Equation 7; M = P).—The trichloride (6·73 g.) and the dithiasilacyclopentane (7·35 g.) were warmed together to eliminate dichlorodimethylsilane (84%). Distillation of the residue gave 2-chloro-1,3-dithia-2-phosphacyclopentane [10] (5·8 g., 75%), b. p. 67°/1 mm., n_D^{25} 1·6850 (Found: C, 15·2; H, 2·5. Calc. for $C_2H_4ClS_2P$: C, 15·2; H, 2·5%). Similar reactions with arsenic and antimony trichlorides in these proportions gave, respectively, 2-chloro-1,3-dithia-2-arsacyclopentane [16] (3·2 g., 45%), b. p. 94°/0·05 mm., which soldified upon cooling (recrystallisation from chloroform gave white crystals, m. p. 38°) (Found: C, 12·5; H, 2·0; As, 37·0; S, 31·4%; *M*, 199. Calc. for $C_2H_4AsClS_2$: C, 11·9; H, 2·0; As, 37·0; S, 31·7%; *M*, 203), and 2-chloro-1,3-dithia-2-stibacyclopentane [17] (7·4 g., 94%), m. p. 122—123° (Found: C, 9·7; H, 1·9; S, 25·7; Sb, 49·2%; *M*, 261. Calc. for $C_2H_4ClS_2Sb$: C, 9·7; H, 1·6; S, 25·8; Sb, 48·9%; *M*, 249).

[16] W. H. C. Rueggeberg, A. Ginsberg, and W. A. Cook, *J. Amer. Chem. Soc.*, 1946, **68**, 1860.

[17] R. E. D. Clark, *J.*, 1932, 1826.

Interaction of Phosphorus Trichloride and 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane* (Equation 8; M = P).—The dithiasilacyclopentane (6·4 g.) and the trichloride (3·92 g.) were heated together, to evolve dichlorodimethylsilane (69%). The residual solid mass was recrystallised from chloroform, to yield the crude product (3·8 g., 79%). A further recrystallisation from benzene gave white crystals of 1,2-di-(1,3-dithia-2-phosphacyclopent-2-ylthio)ethane,[10] m. p. 130° (Found: C, 22·2; H, 3·9; P, 17·3%; *M*, 348. Calc. for $C_6H_{12}P_2S_6$: C, 21·3; H, 3·6; P, 18·3%; *M*, 338). Similar reactions with arsenic and antimony trichlorides in these proportions gave the corresponding arsa-compound [15] (2·5 g., 63%) as white crystals, m. p. 82—83° (Found: C, 17·4; H, 3·1; S, 46·5%; *M*, 429. Calc. for $C_6H_{12}As_2S_6$: C, 16·9; H, 2·8; S, 45·1%; *M*, 426), *stiba-compound* (5·0 g., 80%), m. p. 132—133° (Found: C, 13·9; H, 2·0; S, 37·0%; *M*, 545. $C_6H_{12}S_6Sb_2$ requires C, 13·9; H, 2·3; S, 37·0%; *M*, 520).

Interaction of 2-*Chloro*-1,3-*dithia*-2-*stibacyclopentane and* 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane*.—The dithiasilacyclopentane (2·30 g., 1 mol.) was added to the dithiastibacyclopentane (7·60 g., 2 mol.) in di-n-butyl ether (20 cc.), and the mixture heated under reflux, to evolve dichlorodimethylsilane (64%). Removal of solvent and other volatile materials at 20°/0·01 mm. left a yellow glass-like *solid* which softened on warming but was insoluble in common organic solvents (Found: C, 14·5; H, 2·4. $C_6H_{12}S_6Sb_2$ requires C, 13·9; H, 2·3%).

Interaction of Dimethyltin Dichloride and 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane*.—Addition of the dichloride (7·6 g., 1 mol.) to the dithiasilacyclopentane (5·2 g., 1 mol.) produced a marked warming effect, and subsequent heating caused evolution of dichlorodimethylsilane (68%). The residue was recrystallised from ethanol, to give 2,2-dimethyl-1,3-dithia-2-stannacyclopentane [3,11] (5·0 g., 60%), m. p. 80—81° (Found: C, 20·0; H, 4·3. Calc. for $C_4H_{10}S_2Sn$: C, 20·0; H, 4·2%).

Interaction of Stannic Chloride and 2,2-*Dimethyl*-1,3-*dithia*-2-*silacyclopentane*.—The addition of the chloride (5·2 g., 1 mol.) to the dithiasilacyclopentane (6·0 g., 2 mol.) results in a vigorous reaction, and the precipitation of a yellow solid. Dichlorodimethylsilane (40%) was trapped on subsequent heating, and recrystallisation of the solid residue gave 1,4,6,8-tetrathia-5-stannaspiro[4,4]nonane [11,12] (4·2 g., 70%), m. p. 181—182° (Found: C, 16·3; H, 2·6. Calc. for $C_4H_8S_4Sn$: C, 15·9; H, 2·7%).

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