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CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

II*. PREPARATION AND PROPERTIES OF DITHIACYCLOPENTANE AND DITHIACYCLOHEXANE DERIVATIVES OF SILICON, GERMANIUM AND TIN

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Summary

The preparation and properties of dithiacyclopentane and dithiacyclohexane derivatives of silicon, germanium and tin are described and general mass spectral features of these heterocycles are discussed.

The availability of lead salts of dithiols has been known for some time [2,3] but unlike lead thiolates [4] their use as synthetic intermediates for the preparation of organometallic and organometalloid sulphur compounds has been almost completely ignored.

The value of lead dithiolates as intermediates in organometallic reactions can be summarised as follows:

(*a*) They are obtained by the almost instantaneous reaction of a dithiol and an aqueous-ethanol solution of lead acetate in a near quantitative yield and high purity and can be used without further purification once dried.

(*b*) They are stable solids and can be stored for long periods and handled without the necessity of special precautions employed for volatile dithiols.

(*c*) They can be easily added to reaction mixtures and the progress of the reaction can then be followed as the yellow lead dithiolate is converted to white lead chloride. Once the reaction is complete the lead chloride, and any excess lead dithiolate, can be filtered off rendering a complete separation of the products.

By comparison with the thiol derivatives of Group IV elements those of dithiols have been almost ignored. Dithiol derivatives of silicon have been ob-

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tained from the reaction of a dithiol with the corresponding dichlorosilane in the presence of triethylamine [5] and those of tin from the interaction of a dichlorostannane, dithiol and sodium [6].

The interaction of lead dithiols and Group IV organometallic dichlorides was found to be a very convenient method for the synthesis of the corresponding dithiacyclopentane and dithiacyclohexane derivatives. The highly insoluble lead chloride, produced in the reaction, was easily separated by filtration from the reaction mixture and on removal of the solvent the dithiacyclopentane and

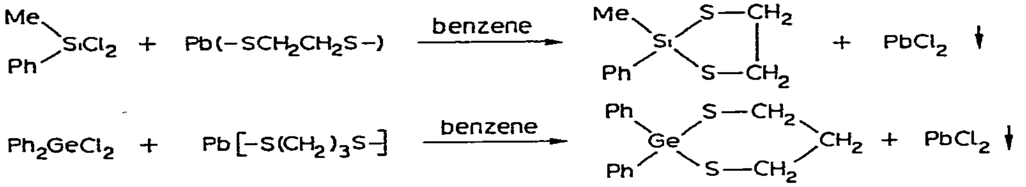


TABLE 1

PHYSICAL CONSTANTS AND ANALYTICAL DATA OF DITHIACYCLOPENTANE AND DITHIACYCLOHEXANE DERIVATIVES OF SILICON, GERMANIUM AND TIN

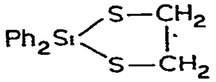
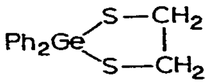
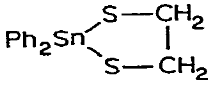
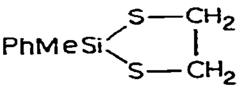
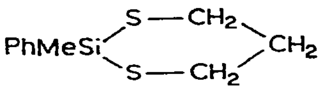
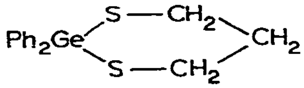
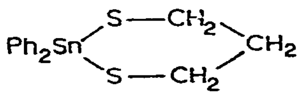
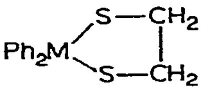
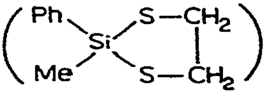
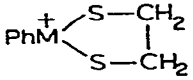
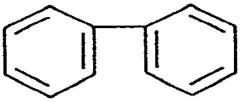
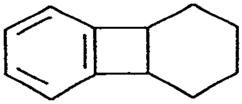
Compound	Yield (%)	B.p./m.p. (°C)	Analysis found (calcd.) (%)	
			C	H
	52	64-66	61.85 (61.4)	5.91 (5.1)
	45	74-78	52.71 (52.8)	4.56 (4.4)
	43	93-94	45.94 (46.0)	3.78 (3.45)
	69	117-119/0.3	51.59 (50.9)	5.54 (5.66)
	71	180-181/0.7	55.79 (53.1)	7.77 (6.2)
	46	65-66	54.1 (54.2)	5.29 (4.82)
	55	90-92	48.12 (47.5)	3.86 (4.22)

TABLE 2

PRINCIPAL IONS IN THE MASS SPECTRA OF DITHIACYCLOPENTANE DERIVATIVES

Ion	M		
	Si	Ge	Sn
 	88.8 (46.4)	77.7	16.7
Ph_2MSH	14.1	5.3	
	100 (100)	100	100
PhMS	22.2 (20)	36.1	26.7
	20.0	11.1	13.3
	5.9	5.3	3.7
PhM	11 (20)	26	33.3
Ph	34 (36.6)	100	60
$PhSCH_2CH_2^+$	22.2 (20)	16.6	86.7
PhS	8.9 (15)	26.4	56.7

hexane derivatives were obtained by distillation or recrystallization of the residue.

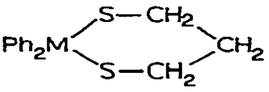
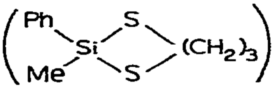
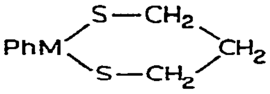
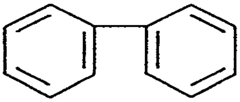
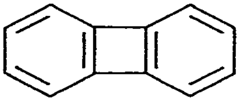
The analysis details and physical constants of the compounds prepared by this method are given in Table 1.

Mass spectra

The mass spectra of the dithiacyclopentane and dithiacyclohexane derivatives showed that they are all monomeric in the gaseous phase. The major ions of interest are listed in Tables 2 and 3 and the general mode of fragmentation of the dithiacyclopentane derivatives is represented in Fig. 1. It is of interest to note that the base peak in all the diphenyl compounds is due to the P—Ph$^+$ ion and that both the dithiacyclopentane and dithiacyclohexane derivatives undergo a common mode of fragmentation resulting in the formation, in high abundance,

TABLE 3

PRINCIPAL IONS IN THE MASS SPECTRA OF DITHIACYCLOHEXANE DERIVATIVES

Ion	M		
	Si	Ge	Sn
 	(57.1)	77.7	26.3
	(100)	100	34.6
Ph_2M		94	4.6
PhMS	(14.3)	27.7	26.3
PhM	(6.6)	38.5	100
		10	7.7
		7	7.3
$C_7H_7^+$	(8.0)	3.6	9.2

of biphenyl$^+$, biphenylene$^+$, PhM$^+$, PhMS$^+$ ions. In the case of the former heterocycles the sulphur containing ions $PhSCH_2CH_2^+$ and PhS$^+$ are also observed in high abundance.

Experimental

Lead dithiolates were obtained from the interaction of a dithiol and lead acetate in aqueous ethanol. After washing with water the dithiolates were dried in a vacuum dessicator. As the experimental details for the preparation of the dithiacyclopentane and dithiacyclohexane derivatives was essentially the same only one example is fully described and the physical constants and analytical data for all compounds are given in Table 1. The mass spectra were recorded, using an AEI MS902 mass spectrometer, at 70 eV. The source was maintained at 170°C and the compounds were introduced as neat liquids or solids using a cooled direct-insertion probe.

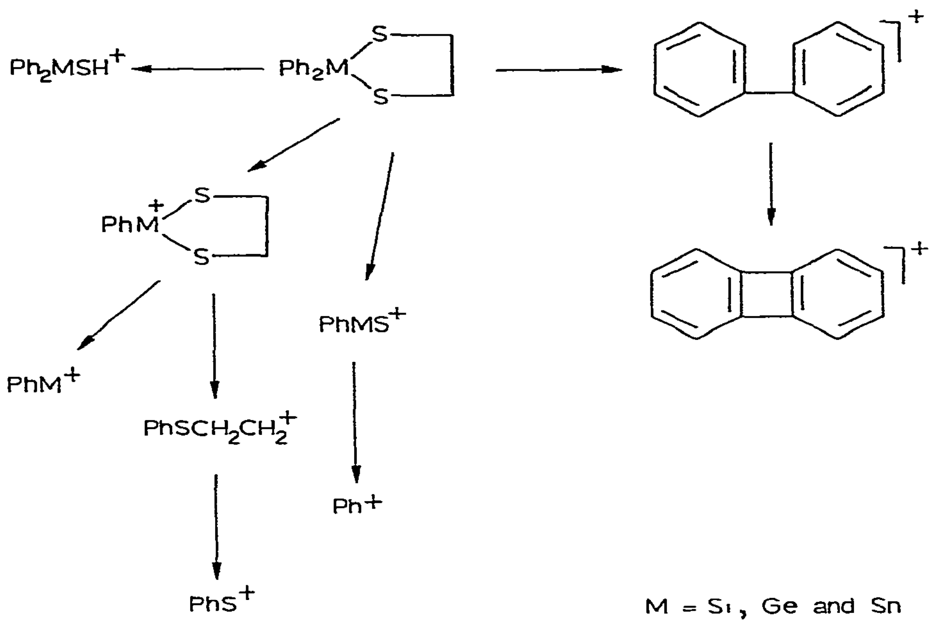


Fig. 1. General fragmentation pattern for 2,2′-diphenyl-1,3-dithiacyclopentane derivatives of Si, Ge and Sn.

Preparation of 2,2′-methylphenylsiladithiacyclopentane

Dichloromethylphenylsilane (3.5 g, 0.018 mol) in benzene (50 ml) was slowly added to lead ethanedithiolate (5.4 g, 0.018 mol) in benzene (50 ml) and the mixture was refluxed for 5 h. The lead chloride was filtered off and the filtrate, freed from solvent, afforded on distillation 2,2′-methylphenylsiladithiacyclopentane (2.7 g, 69%) b.p. 117-119°C/0.3 mmHg. (Found C, 51.59; H, 5.54%; mol. wt. 212. $C_9H_{12}SiS_2$ calcd.: C, 50.91; H, 5.66%; mol. wt. 212).

Acknowledgement

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References

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