

GROUP IV ORGANOMETALLIC SULFUR COMPOUNDS

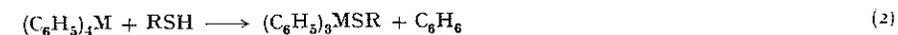
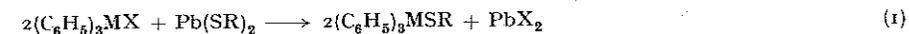
THIO DERIVATIVES OF PHENYL-GERMANES, -STANNANES AND -PLUMBANES

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(Received August 11th, 1964)

In previous communications from these laboratories, the syntheses of thio-triphenyl-germanes^{1,2} and -plumbanes³, $(C_6H_5)_3MSR$, were described. This work has been continued and some of the little known bithiodiphenyl derivatives, $(C_6H_5)_2M(SR)_2$, have been isolated. Heterocyclic compounds containing germanium, tin or lead atoms in the ring, similar to those reported by Schmidt⁴ and by Poller⁵ were also prepared.

THIOTRIPHENYL DERIVATIVES

Several possible methods for the synthesis of thiotriphenyl-germanes, -stannanes and -plumbanes were investigated.



(M = Ge, Sn or Pb; X = Cl or Br).

Thiotrialkylsilanes⁶ and thiotriphenylplumbanes³ have been obtained in good yields (70–100%) by route (1), when R was a simple alkyl or aryl group. Thiotriphenyl-germanes could also be prepared by this method. With more complex thiols containing a second functional group, we were seldom able to isolate the thiotriphenylplumbanes, presumably owing to the insolubility or instability of the divalent lead thio salts.

Little reaction was observed when tetraphenyl-germane, -stannane, or -plumbane were treated with simple aliphatic or aromatic thiols (route 2). Certain thioacids were sufficiently acidic to cleave the metal-carbon bonds of tetraphenyl-stannane and -plumbane. Tetraphenylgermane, however, was resistant to acid attack and could be recrystallized from thioacetic acid. No reaction occurred when the triphenylmetal halides were treated with thiols in boiling benzene. Abel⁶ also has shown that chlorotrimethylsilane did not react with aliphatic thiols.

Good yields of the thio derivatives were obtained when the triphenylmetal chlorides or bromides were allowed to react at room temperature with thiols in the presence of a tertiary organic base (route 3). Reaction of halotriphenylplumbanes

with thiols in the presence of pyridine were slow. Similar reactions in triethylamine were noticeably faster and gave greater yields of product. Base catalyzed hydrolysis of the triphenyl metal halides was not usually observed and no special precautions to exclude moisture were necessary. Slight hydrolysis did occur with the halotriphenylgermanes in the presence of triethylamine but not in pyridine.

Aminothiols, $\text{HS}(\text{CH}_2)_x\text{NH}_2$, reacted with halotriphenylgermanes to give, as the main product, bis(triphenylgermanium) oxide. The Ge-N bond, which apparently formed at a faster rate than the Ge-S bond, was readily hydrolyzed to the oxide.

The thiotriphenylgermanes, -stannanes and -plumbanes prepared in this work are listed in Tables 1, 2 and 3. The germanium derivatives are thermally and hydrolytically stable. The thiotriphenylplumbanes are also hydrolytically stable, but in contrast

TABLE 1
THIOTRIPHENYLGERMANES, $(\text{C}_6\text{H}_5)_3\text{GeSR}$

R	M.p.	Analyses Calculated Found				Solvent for recryst., etc.
		C	H	Ge	S	
$(\text{CH}_2)_{10}\text{CH}_3$	56°	70.92	7.78	14.78	6.50	$\text{C}_6\text{H}_6/\text{CH}_2\text{OH}$
$\text{CH}_2\text{CH}_2\text{OH}$	oil	70.63	7.60	15.50	6.59	Chrom. on SiO_2
$\text{CH}_2\text{CH}=\text{CH}_2$	62°	63.10	5.25	19.95	8.40	Elute with C_6H_6
CH_2COOH	149-50°	62.31	5.12	19.95	7.38	P.E. 30-60/hexane
$\text{C}(\text{O})\text{CH}_3$	105°	67.00	5.34	19.28	8.51	Hexane/ C_6H_6
$\text{CH}_2\text{C}(\text{O})\text{OCH}_3$	44-5°	66.45	5.33	19.20	8.81	Hexane/ C_6H_6
$\text{CH}_2\text{C}(\text{O})\text{NH}_2$	151°	60.81	4.59	18.37	8.11	Chrom. on SiO_2
C_6H_5	96°	61.07	4.78	17.86	8.13	Elute with CH_2Cl_2
C_6F_5	96-7°	63.40	4.76	19.15	8.44	C_6H_6
<i>p</i> - ClC_6H_4	101-2°	63.23	4.69	19.48	8.57	Hexane/ C_6H_6
2- C_{10}H_7	88-9°	61.75	4.93	17.77	7.85	Hexane
17- β -mercapto-testosterone	188°	61.43	4.99	18.19	8.06	Hexane/ C_6H_6
		60.16	4.85	18.56	8.54	Hexane
		69.80	4.87	17.60	7.74	Hexane/ C_6H_6
		69.80	4.78	17.70	8.14	Hexane
		57.30	3.00	14.43	6.37	Hexane/ C_6H_6
		57.08	3.12	14.47	6.37	Hexane
		64.40	4.28	16.22	7.15	Hexane/ C_6H_6
		64.60	4.47	15.99	7.07	Hexane
		72.60	4.78	15.68	6.92	Hexane
		72.70	5.00	15.55	6.93	Hexane/ C_6H_6
		73.10	6.97	11.95	5.28	Hexane/ C_6H_6
		73.12	7.03	11.94	5.51	Hexane/ C_6H_6

to the germanium derivatives, which were often purified by distillation, none of the lead compounds can be distilled without decomposition. It has been shown that the thiotrialkylsilanes are thermally stable, but readily hydrolyzed⁶. The thermal stability of the metal-sulfur bond in the thiotrialkyl (-aryl) derivatives decreases in the series Si, Ge, Sn and Pb, while the hydrolytic stability increases.

Mercaptotriphenylgermane, $(\text{C}_6\text{H}_5)_3\text{GeSH}$, could be prepared by treating the halotriphenylgermanes with hydrogen sulfide in the presence of pyridine or triethylamine². The corresponding reactions with halotriphenylstannanes or -plumbanes gave quantitative yields of the sulfides, $[(\text{C}_6\text{H}_5)_3\text{M}]_2\text{S}$.

TABLE 2
THIOTRIPHENYLPLUMBANES, $(\text{C}_6\text{H}_5)_3\text{PbSR}$

R	M.p.	Analyses Calculated Found			Solvent for recryst., etc.
		C	H	Pb	
$\text{CH}_2\text{CH}_2\text{OH}$	78-9°	46.57	3.91	40.18	$\text{CHCl}_3/\text{hexane}$
$\text{CH}_2\text{CH}_2\text{NH}_2$	40°	46.59	3.92	40.02	Chrom. on SiO_2
$\text{CH}_2\text{CH}=\text{CH}_2$	45°	46.66	4.12	40.26	yield 25%
$\text{CH}_2\text{C}(\text{O})\text{OCH}_3$	87-8°	47.58	4.12	40.06	Chrom. on SiO_2
$\text{CH}_2\text{C}(\text{O})\text{NH}_2$	124-5°	49.30	3.94	40.50	unstable
C_6F_5	91°	49.40	3.99	40.23	$\text{CHCl}_3/\text{C}_6\text{H}_6$
<i>p</i> - ClC_6H_4	102°	46.40	3.71	38.13	Hexane/ C_6H_6
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	111°	46.36	3.69	38.30	Hexane
<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4$	135-6°	45.43	3.62	39.21	Hexane/ C_6H_6
17- β -mercapto-testosterone	152°*	45.39	3.58	38.93	Hexane
	125°	45.22	2.37	32.50	Hexane/ C_6H_6
		45.86	2.68	32.14	Hexane/ C_6H_6
		49.53	3.29	35.60	Hexane/ C_6H_6
		49.55	3.29	35.54	EtOH
		48.66	3.23	34.96	EtOH
		48.64	3.22	34.74	EtOH
		51.25	3.76	36.83	Hexane/ C_6H_6 *
		51.27	3.76	36.68	Hexane/ CHCl_3
		59.90	5.71	27.93	Hexane/ C_6H_6 *
		59.92	5.73	27.85	Hexane/ CHCl_3

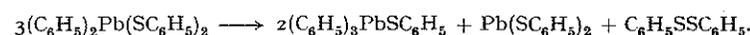
* Two melting points were observed, depending on the solvent used for recrystallization. The IR spectra of the two samples were identical.

TABLE 3
THIOTRIPHENYL- AND BISTHIODIPHENYL-STANNANES

R	M.p.	Analyses Calculated Found				Solvent for recryst., etc.
		C	H	Sn	S	
$(\text{C}_6\text{H}_5)_3\text{SnSR}$						
C_6H_5	102-3°	62.78	4.39	25.85	6.98	Hexane
$\text{CH}_2\text{C}_6\text{H}_5$	84°	63.07	4.60	25.82	6.97	Benzene/hexane
<i>p</i> - ClC_6H_4	96-7°	63.44	4.69	25.09		Hexane
$\text{SC}(\text{O})\text{C}_6\text{H}_5$	108-9°	63.61	4.53	25.37	6.49	Hexane
		58.34	3.88	24.04	6.32	EtOH; Lit. ¹³ m.p. 108
		58.66	3.94	24.07	6.58	turns yellow on standing
		61.63	4.13	24.37	6.49	
		61.50	4.32	24.87	6.49	
$(\text{C}_6\text{H}_5)_2\text{Sn}(\text{SR})_2$						
C_6H_5	65°	58.20	4.10	24.17		Lit. ¹² m.p. 65-65.5
		58.09	4.54	24.37		

BISTHIODIPHENYL DERIVATIVES

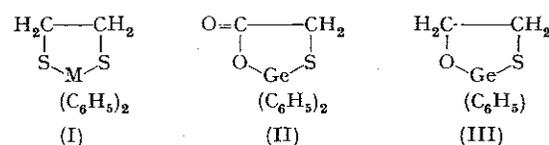
In reactions of lead(II) thio salts with chlorotriphenylplumbane, trace amounts of diphenyllead compounds were often formed and could be detected by thin layer chromatography. Although a small quantity of bis(2-benzothiazolythio)diphenylplumbane was isolated from the reaction of chlorotriphenylplumbane, from reactions of dichlorodiphenylplumbane with several divalent lead thio salts, $[\text{Pb}(\text{SR})_2]$, where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{CH}_2\text{C}_6\text{H}_5]$ only the thiotriphenylplumbanes were isolated. Bisthiodiphenylgermanes were prepared readily from dihalodiphenylgermanes by route 3, using two moles of thiol. Significant quantities of thiotriphenylplumbanes, lead(II) mercaptides and disulfides, RSSR , were found from reactions of dichlorodiphenylplumbane with thiols in the presence of base. Apparently the bisthiodiphenylplumbanes are thermally unstable. Only three such compounds were synthesized under carefully controlled reaction conditions. A quantitative study showed that the decomposition of bis(phenylthio)diphenylplumbane occurred mainly by the following route:



The bisthiodiphenylgermanes are colorless and thermally stable. Many of them can be distilled without change. It was necessary during the preparations to add the base and thiol simultaneously to the dihalophenyldigermanes in order to prevent formation of oxides, since base catalyzed hydrolysis was significant. The bisthiodiphenylplumbanes are yellow crystalline solids, similar in appearance to the divalent lead mercaptides.

HETEROCYCLIC DERIVATIVES

Dithiobis(triphenylgermanes and -plumbanes), $(\text{C}_6\text{H}_5)_3\text{MS-R-SM}(\text{C}_6\text{H}_5)_3$, were prepared from ethanedithiol and 1,3,4-thiadiazole-2,5-dithiol. The reaction of ethanedithiol with dihalodiphenylgermanes, -stannanes and -plumbanes in the presence of base gave heterocyclic compounds containing metal atoms in the ring (I).



M = Ge, Sn or Pb

Reactions of dihalodiphenylgermanes with thioglycolic acid and 2-hydroxyethanethiol also gave ring compounds (II and III). High melting ($> 300^\circ$) solids were isolated in low yield from reactions of thioglycolic acid with dihalodiphenylstannanes and -plumbanes. These materials were insoluble in most organic solvents and were probably polymeric.

(Carboxymethylthio)triphenylgermane, $(\text{C}_6\text{H}_5)_3\text{GeSCH}_2\text{COOH}$, and (2-hydroxyethylthio)triphenylplumbane, $(\text{C}_6\text{H}_5)_3\text{PbSCH}_2\text{CH}_2\text{OH}$ were prepared, but no bisthio-

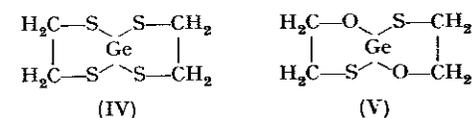
diphenyl derivatives containing free OH or COOH groups were isolated. It is believed that such compounds were formed but readily cyclized with elimination of thiol.

A number of similar heterocyclic compounds containing germanium or tin in the ring have recently been reported. From reactions of dimethyldichlorogermane with ethanedithiol, thioglycolic acid or 2-hydroxyethanethiol in the presence of triethylamine, Schmidt⁴ has prepared the dimethyl analogues of (I), (II) and (III). Other dimethylgermanium ring compounds were derived in the same way from substituted thiophenols or phenols⁷.

Poller⁵ has prepared 2,2-diphenyl-2-stanna-1,3-dithiacyclopentane and the dimethyl⁴ compound has also been reported. Reaction of 1,3-propanedithiol with dimethyldichlorogermane and -stannane in the presence of base gave six-membered heterocycles⁸. Dimeric and trimeric cyclic alkyl (aryl) sulfides of germanium⁹ and tin¹⁰ are known with alternating sulfur and metal atoms.

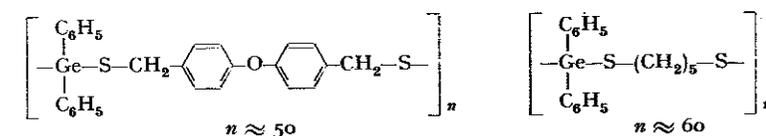
From the reaction of germanium tetrachloride and ethanedithiol in the presence of pyridine, we have isolated the compound with spirane type structure (IV).

These compounds were first reported by Backer and Drenth¹¹ who reacted ethanedithiol with the tetrachloride in the presence of sodium ethoxide. A similar compound (V) was prepared from germanium tetrachloride and 2-hydroxyethanethiol either in the presence of base or via the disodium salt.



POLYMERIC DERIVATIVES

p,p'-Oxybis(α -toluenethiol) and 1,5-pentanedithiol reacted with dihalodiphenylgermanes at room temperature to give gums which were soluble in most organic solvents. Both had an approximate molecular weight, in benzene, of 23,000.



Germanium tetrachloride reacted with these dithiols giving insoluble white solids, which did not melt below 300° .

EXPERIMENTAL

General

The organometallic halides used in these experiments were prepared from the tetraphenyl derivatives by published procedures. The thiols were the purest commercial samples available and were not usually purified further. Pyridine and triethylamine were purified by distillation. Chromatographic separations were carried out on a column (30×2.5 cm) containing about 45 g of silica gel or alumina. Compounds

containing the sulfur-carbonyl groupings tended to decompose on the column and could not be chromatographed. The separation and purification of the organometallic compounds were controlled by thin layer chromatography (T.L.C.) using microscope slides and silica gel G. The plates were eluted with benzene/methanol (9:1) and the spots were developed in an iodine vapor bath (Ge, Sn, Pb) or with dithizone spray (Pb). The T.L.C. separations with the germanium derivatives were essentially reproducible on an alumina column. A molecular distillation apparatus operating at 0.05 mm was used to purify many of the germanium derivatives. A Mechrolab vapor pressure osmometer Model 301A was used to determine molecular weights (benzene solvent). Qualitative infrared spectra were recorded on a Perkin-Elmer Model-Spectrophotometer. Melting points, obtained on a Thomas Hoover melting point apparatus were uncorrected.

Lead salts of thiols were prepared from the thiol and lead acetate in aqueous alcohol and after washing with water were dried in a vacuum desiccator.

Preparation of thiotriphenylplumbanes (Route 1)

A benzene or methanol solution (100 ml) of chlorotriphenylplumbane (4.7 g, 10 mmole) and lead(II) thio salt (10 mmole) was boiled under reflux until the yellow precipitate was replaced by white lead chloride (1-24 h). The insolubles were filtered off and the filtrate evaporated. The thiotriphenylplumbanes were readily obtained in 80-95% yield from the residue by crystallization. No reaction was observed using lead(II) thio salts, $Pb(SR)_2$, $R = CH_2CH_2OH$, $CH_2CH_2NH_2$, and $CH_2CH=CH_2$. From the reaction of lead(II) benzothiazolethiolate, the bithiodiphenylplumbane (12%) was separated from the thiotriphenylplumbane (51%) by fractional crystallization from benzene.

Attempted preparation of bithiodiphenylplumbanes (Route 1)

A benzene or methanol suspension (100 ml) of dichlorodiphenylplumbane (5 mmole) and lead(II) mercaptide (10 mmole) was boiled under reflux. The yellow precipitate of the lead(II) mercaptides remained even after 24 h. The reaction mixture was treated as before. Only varying amounts of the thiotriphenylplumbanes were isolated. Several reactions were attempted with the lead(II) mercaptides, $Pb(SR)_2$ ($R = CH_3$, C_2H_5 , C_6H_5 , $CH_2C_6H_5$, $CH_2CH=CH_2$, CH_2COOCH_3).

Preparation of thiotriphenyl compounds (Route 3)

A typical example for the preparation of the thiotriphenyl derivatives is given. Bromotriphenylgermane (3.84 g, 10 mmole) in benzene (100 ml) was added to a mixture of thiophenol (1.10 g, 10 mmole) and pyridine or triethylamine (~10% excess) in benzene (50 ml). An immediate precipitate of amine hydrobromide was formed. The reaction mixture was stirred at room temperature for one hour and the quantitative amount of hydrobromide was filtered off. The filtrate was washed with 1% sulphuric acid, water and dried ($MgSO_4$). Removal of the solvent gave an oil from which (phenylthio)triphenylgermane (3.6 g, 82%) was isolated by crystallization from benzene/hexane, m.p. 96°. The tin and lead compounds were prepared in the same way from either the chloride or bromide, although longer reaction time (~6 h) was necessary with lead. All of the compounds listed in tables 1, 2 and 3 could be obtained by this method, usually in 70-90% yield.

A mole ratio of triphenylmetal halides to dithiol of 2:1 was used in the preparation of the dithiobis(triphenylmetal) compounds, $(C_6H_5)_3MS-R-SM(C_6H_5)_3$, (Table 6).

The bithio derivatives, $(C_6H_5)_2M(SR)_2$, were prepared in an identical manner from the dihalodiphenyl-germanes, -stannanes and -plumbanes, and two molar equivalents of the thiols in benzene. A reaction time of 24 h was necessary in the preparations of the bithiodiphenylplumbanes since the diphenyllead dihalides were only sparingly soluble in benzene. Owing to the thermal instability of the lead products, the temperature was kept below 30° during the reaction and the recrystallization procedures. (See Tables 3, 4 and 5.)

TABLE 4
BITHIODIPHENYLGERMANES, $(C_6H_5)_2Ge(SR)_2$

R	M.p. or n_D	Analyses	Calculated Found				Solvent for recryst., etc.
			C	H	Ge	S	
$(CH_2)_{10}CH_3$	$n_D^{28.5}$ 1.5343	67.90 68.60	9.39 9.74	12.07 11.51	10.66 10.29	Distil.	
$CH_2CH=CH_2$	$n_D^{28.5}$ 1.6229	58.00 57.35	5.40 5.48	19.46 19.62	17.20 17.26	Distil.	
$CH_2C(O)NH_2$	140°	47.15 46.84	4.45 4.43	17.83 18.06	15.71 15.97	CH_3COCH_3	
C_6H_5	n_D^{22} 1.6776	64.75 64.61	4.52 4.71	17.01 17.01	14.40 13.97	Distil.	
<i>p</i> -ClC ₆ H ₄	n_D^{22} 1.6751	56.10 56.37	3.53 3.83	14.13 14.51	12.47 12.19	Distil.	
<i>p</i> -NO ₂ C ₆ H ₄	114-5°	53.86 53.65	3.39 3.42	13.57 13.35	11.99 12.35	C_6H_6 /EtOH	
<i>p</i> -NH ₂ C ₆ H ₄	115°	60.60 60.82	4.66 4.87	15.25 15.48	13.48 13.56	Low yield (15%) Hexane/ C_6H_6	
$CH_2C_6H_5$	50-1°	66.10 65.87	5.11 5.23	15.35 15.79	13.55 13.71	Distil. Solidified after some days	
$C(O)C_6H_5$	150-1°	62.37 62.46	4.01 4.31	14.48 14.80	12.79 12.57	Hexane/ C_6H_6	
<i>z</i> -C ₁₀ H ₇	90-1°	70.49 70.15	4.43 4.52	13.31 12.89	11.76 11.80	Solidified after distillation	

TABLE 5
BITHIODIPHENYLPLUMBANES $(C_6H_5)_2Pb(SR)_2$

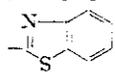
R	M.p.	Analyses	Calculated Found			Solvent for recryst., etc.
			C	H	Pb	
C_6H_5	75°	49.72 49.74	3.48 3.54	35.73 35.45	Hexane/ C_6H_6	
<i>p</i> -ClC ₆ H ₄	71-2°	44.44 44.46	2.80 2.72	31.93 32.27	Hexane/ C_6H_6	
	148-50°	45.01 45.87	2.61 2.58	29.86 29.66	C_6H_6	

TABLE 6

DITHIOBIS(TRIPHENYL-GERMANES AND -PLUMBANES), $(C_6H_5)_3MS-R-SM(C_6H_5)_3$

R	M.p.	Analyses				Mol. wt.	Solvent for recryst., etc.
		Calculated	Found				
		C	H	M	S		
<i>M = Ge</i>							
CH ₂ CH ₂	152°	65.30	4.90	20.15	9.15	700	Hexane/C ₆ H ₆
		65.48	4.90	21.00	9.25	698	
CH ₂ C ₆ H ₄ OC ₆ H ₄ CH ₂		69.20	4.87	16.73	7.39	868	Chrom. on SiO ₂ .
	syrup	69.65	4.92	17.10	7.16	750	Elute with C ₆ H ₆
C(O)C ₆ H ₄ C(O)	255-7°	65.72	4.26	18.07	7.96	804	C ₆ H ₆
		64.95	4.72	17.18	7.93	826	
<i>M = Pb</i>							
CH ₂ CH ₂	141-2°	47.10	3.54	42.76	—	969	Hexane/C ₆ H ₆
		47.51	3.53	42.22	—	962	
N—N	205°	44.53	2.95	40.43	—	1025	Hexane/C ₆ H ₆
	dec.	44.55	2.96	40.19	—	1008	

Decomposition of bis(phenylthio)diphenylplumbane

A benzene/ethanol (1/1) solution of bis(phenylthio)diphenylplumbane (0.7 g, 1.2 mmole) was boiled under reflux for 8 h. The yellow precipitate of bis(phenylthio)lead (0.18 g, 0.42 mmole) was filtered off and the filtrate evaporated. Extraction of the yellow oil with diethyl ether gave the insoluble (phenylthio)triphenylplumbane (0.41 g, 0.76 mmole) and a yellow soluble oil. A G.L.C. study showed that diphenyl disulfide was the major constituent of this oil. No diphenyl sulfide was found.

Preparation of (carbamoylmethylthio)triphenylgermane, (C₆H₅)₃GeSCH₂C(O)NH₂

Dry ammonia was passed through a well-stirred methanol solution of (methoxycarbonylmethylthio)triphenylgermane for 2 h at room temperature. Removal of the solvent gave (carbamoylmethylthio)triphenylgermane in 90% yield, m.p. 151°, recrystallized from benzene/hexane. The corresponding lead compound was prepared by the same method.

Bis(methoxycarbonylmethylthio)diphenylgermane was an oil which decomposed on attempted distillation. It was not isolated in a pure state, but the bis(thioglycolamide) was a solid and readily purified.

Neither the acid nor the amide derivatives could be prepared from dichlorodiphenylplumbane.

Preparation of 2,2-diphenyl-2-germa-1,3-dithiacyclopentane (I)

A solution of dibromodiphenylgermane (3.83 g, 10 mmole) in benzene (50 ml) was added to ethanedithiol (0.94 g, 10 mmole) and pyridine (excess) in benzene (25 ml). The mixture was stirred at room temperature for 1 h, and the hydrobromide and solvent removed. 2,2-Diphenyl-2-germa-1,3-dithiacyclopentane (I), m.p. 87-8°, was obtained from the residue by crystallization from benzene/hexane (2.9 g, 93%). (Found C, 52.53; H, 4.50; Ge, 23.22; S, 20.62; mol. wt., 320. C₁₄H₁₄GeS₂ calcd.: C, 52.70; H, 4.33; Ge, 22.80; S, 20.15%; mol. wt., 319.)

The corresponding tin and lead compounds were prepared in the same way, although longer reaction times were necessary. 2,2-Diphenyl-2-stanna-1,3-dithiacyclopentane had m.p. 108°, (lit.⁵ m.p. 108-9°). 2,2-Diphenyl-2-plumba-1,3-dithiacyclopentane, m.p. 132-3°, slowly decomposed. (Found C, 37.42; H, 3.10; Pb 45.19; mol. wt., 472. C₁₄H₁₄PbS₂ calcd.: C, 37.09; H, 3.11; Pb, 45.66%; mol. wt., 454.)

2,2-Diphenyl-2-germa-1-oxa-3-thiacyclopentane-5-one (II) was isolated from the reaction of dibromodiphenylgermane (3.87 g, 10 mmole) and thioglycolic acid (1.84 g, 20 mmole) in ether in the presence of pyridine. The compound had a m.p. 143-5° (0.5 g, 16.7%, recryst. from benzene/hexane). (Found: C, 53.14; H, 3.92; Ge, 22.62; S, 10.06; mol. wt., 332. C₁₄H₁₄GeO₂S calcd.: C, 53.06; H, 3.82; S, 10.12; Ge, 22.91%; mol. wt., 349.)

Reaction of dichlorodiphenylstannane (3.43 g, 10 mmole) and sodium thioglycolate (2.28 g, 20 mmole) in pyridine gave a solid product which was insoluble in most organic solvents. It was purified by dissolving in dimethyl sulfoxide and reprecipitating with benzene, m.p. > 300°. (Found C, 45.06; H, 3.22; S, 9.03; Sn, 32.94. C₁₄H₁₂O₂SSn calcd.: C, 46.32; H, 3.33; S, 8.83; Sn, 32.70%.)

The product isolated from an analogous reaction with dichlorodiphenylplumbane was also high melting and insoluble in organic solvents. It decomposed in dimethyl sulfoxide to give divalent lead compounds. (Found C, 35.66; H, 2.56; Pb, 47.36. C₁₄H₁₂O₂PbS calcd.: C, 37.25; H, 2.68; Pb, 45.89%.)

Preparation of 2,2-diphenyl-2-germa-1-oxa-3-thiacyclopentane (III)

Dichlorodiphenylgermane (5.3 g, 1.8 mmole) was treated with 2-hydroxyethanethiol (2.8 g, 3.6 mmole) in ether in the usual manner in the presence of pyridine. Removal of the amine hydrochloride and solvent gave an oil. Molecular distillation gave an oil and a higher boiling fraction which solidified. Recrystallization of the latter from methanol/benzene gave (III) (0.5 g, 11%); m.p. 80-81°. (Found C, 54.95; H, 4.62; Ge, 23.91; S, 10.81; mol. wt., 305. C₁₄H₁₄GeOS calcd.: C, 55.51; H, 4.66; Ge, 23.96; S, 10.58%; mol. wt., 303.)

The lower boiling oil when freshly distilled showed a strong absorption band in its infrared spectrum in the OH stretching frequency region at 3330 cm⁻¹. It was probably the bithio compound, (C₆H₅)₂Ge(SCH₂CH₂OH)₂. No elemental analysis was obtained since it readily cyclized to give the ring compound (III), showing no OH absorption peak.

Compound (III) was also obtained in good yield (80%) by reaction of dichlorodiphenylgermane with the disodium salt of 2-hydroxyethanethiol in toluene.

Reaction of ethanedithiol with germanium tetrachloride

Germanium tetrachloride (3.72 g, 17 mmole) was treated in the usual manner with ethanedithiol (3.26 g, 35 mmole) in benzene in the presence of excess triethylamine. The spirane (IV) (3.9 g, 57%) was recrystallized from benzene; m.p. 165°; lit.¹² m.p. 164°. (Found C, 18.76; H, 3.14; Ge, 28.84; S, 50.06; mol. wt., 472. C₄H₈GeS₄ calcd.: C, 18.71; H, 3.13; Ge, 28.25; S, 49.90%; mol. wt., 454.)

Reaction of germanium tetrachloride with 2-hydroxyethanethiol in the same manner gave the spirane compound V (20%). Recrystallized from benzene it melted at 181°. (Found C, 21.72; H, 3.74; Ge, 32.22; S, 28.53; mol. wt., 255. C₄H₈GeS₂O₂ calcd.: C, 21.32; H, 3.58; Ge, 32.50; S, 28.36%; mol. wt., 225.)

Infrared spectra (CCl_4 soln.) of compounds (I) and (III) showed two bands of medium intensity at 925 cm^{-1} and 860 cm^{-1} , which appear to be characteristic of these compounds. Similar absorption peaks appeared in the spectra of the spirans (IV) and (V), although the thioglycolic acid derivative (II) shows weak absorption at 940 cm^{-1} and 890 cm^{-1} (KBr disc).

ACKNOWLEDGEMENTS

The authors are indebted to the International Lead Zinc Research Organization (Dr. SCHRADER F. RADTKE) and to the Germanium Research Committee (Mr. ROBERT J. SEARLS, JR.) for financial support. We thank Mr. CARMINE DIPIETRO of these Laboratories for the microanalyses.

SUMMARY

A number of thio derivatives of the types $(\text{C}_6\text{H}_5)_3\text{MSR}$ and $(\text{C}_6\text{H}_5)_2\text{M}(\text{SR})_2$, $\text{M} = \text{Ge}, \text{Sn}$ or Pb , have been synthesized by reactions of thiols with the triphenyl- or diphenyl-metal halides in the presence of a tertiary organic base. The thermal and hydrolytic stabilities of these compounds are discussed. Heterocyclic derivatives with metal atoms in the ring were isolated from reactions of the dihalodiphenylmetal compounds with ethanedithiol, thioglycolic acid and 2-hydroxyethanethiol.

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