

10,10'-bi(phenoxasilin), melting range 206–225°. Recrystallization from benzene-petroleum ether (b.p. 60–70°) and from petroleum ether (b.p. 80–110°) gave 2.20 g. (56.5%) of pure product, m.p. 231–233°.

*Anal.* Calcd. for  $C_{38}H_{26}O_2Si_2$ : Si, 10.28. Found: Si, 10.15, 10.22. The infrared spectrum as a carbon disulfide solution was superimposable with that of 10,10-diphenylphenoxasilin except for the band at 14.45  $\mu$ , which is smaller and not split into a doublet.

*2-Trimethylsilyl-10,10-diphenylphenoxasilin* (XVI). To 10.0 g. (0.041 mole) of 4-trimethylsilylphenyl phenyl ether dissolved in 60 ml. of tetrahydrofuran and cooled to ice-bath temperature was added slowly an ether solution containing 0.092 mole of *n*-butyllithium. The light yellow solution gave a positive Color Test II. The ice-bath was removed, and, after the solution had stirred at room temperature for 1 hr., mild warming was applied for 15 hr. Color Test II was then negative, but Color Test I was positive. The reaction mixture after it had been poured jet-wise through a glass wool plug into a dried, nitrogen swept addition funnel, was added dropwise to a flask with the simultaneous addition of 10.4 g. (0.041 mole) of dichlorodiphenylsilane dissolved in 50 ml. of tetrahydrofuran. Spontaneous refluxing occurred, and Color Test I was negative upon completion of addition. Following hydrolysis with dilute aqueous ammonium chlo-

ride solution, the usual work-up was carried out to yield a brown oil. This was distilled at reduced pressure to give 8.05 g. of oil boiling over the range 185–198° (0.05 mm.). Treatment of the oil with methanol gave 3.15 g. (18.2%) of a white solid, melting range 114–120°. After several recrystallizations from methanol, the melting point of the 2-trimethylsilyl-10,10-diphenylphenoxasilin was raised to 123–124°, 2.95 g. (16.9%).

*Anal.* Calcd. for  $C_{27}H_{26}OSi_2$ : C, 76.70; H, 6.20. Found: C, 76.85, 77.00; H, 5.75, 5.83.

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## Studies in Organosilicon Chemistry. XLIV. Synthesis and Infrared Studies of Analogous Heterocyclic Compounds of Periodic Column IV-B

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The synthesis of five compounds, 1,1-diphenylcyclohexane and its 1,1-analogs of silicon, germanium, tin, and lead, has been completed. Their infrared patterns are presented, together with a critique. Bromination of cyclopentamethylene-diphenylstannane yields cyclopentamethylenedibromostannane. Iodination removes only one phenyl group. Similar action by anhydrous hydrogen bromide gas yields cyclopentamethylenedibromostannane.

In a paper published by Oshesky and Bentley,<sup>1</sup> the use of infrared absorption data for the identification of a series of silacyclohexane compounds was based on a group of absorption bands appearing characteristically in both the rock salt and cesium bromide regions of the infrared. Tentatively these were assigned as being attributable to the heterocyclic system. A cursory investigation was undertaken to test the hypothesis that a similar set of correlations would hold for the identification of a hetero-ring system involving the remaining Group IVB elements, germanium, tin, and lead.

Our investigation, limited only to the rock salt region (4000–650  $cm^{-1}$ ) was carried out on the six-membered, heterocyclic system shown in Fig. 1.

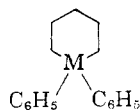


Fig. 1. M = C, Si, Ge, Sn, Pb

In addition to the characteristic metal-phenyl absorptions<sup>2</sup> between 1125 and 1050  $cm^{-1}$ , there occurred a series of three absorption bands at 2650, 990–965, and 910  $cm^{-1}$  which very favorably agreed with those observed for the silacyclohexane system (Table I). It is interesting to note that 1,1-diphenylcyclohexane, with the exception of the weak absorption band at 2650  $cm^{-1}$ , showed no

TABLE I  
ABSORPTION DATA

Compound	Frequency, Absorption, $cm^{-1}$		
$(CH_2)_5C(C_6H_5)_2$	2640 (w) <sup>a</sup>	—	905 (m)
$(CH_2)_5Si(C_6H_5)_2$	2640 (w)	987 (s)	908 (s)
$(CH_2)_5Ge(C_6H_5)_2$	2640 (w)	987 (s)	913 (s)
$(CH_2)_5Sn(C_6H_5)_2$	2640 (w)	970 (s)	907 (s)
$(CH_2)_5Pb(C_6H_5)_2$	2650 (w)	965 (s)	909 (s)
$(CH_2)_5SnBr_2$	2650 (w)	970 (s)	910 (s)
$(CH_2)_5Sn(I)C_6H_5$	2650 (w)	970 (s)	910 (s)
$(CH_2)_5SnCl_2$	2650 (w)	990 (s)	910 (s)

<sup>a</sup> w = weak, m = medium, s = strong.

(1) G. D. Oshesky and F. F. Bentley, *J. Am. Chem. Soc.*, 79, 2057 (1957).

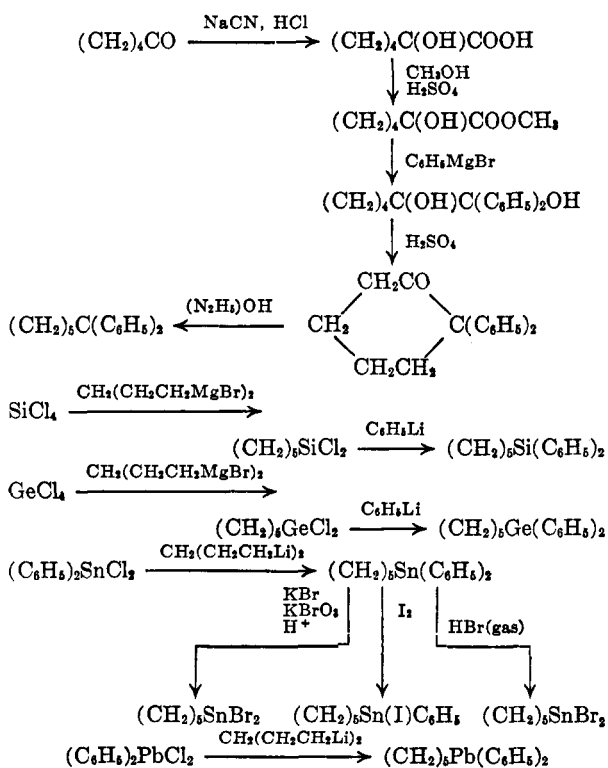
(2) J. G. Noltes, M. C. Henry, and M. J. Janssen, *Chem. & Ind.*, 298 (1959).

absorption bands of comparable strength in the other two regions of the spectrum.

Based on the assumption that these particular absorption bands may be characteristic of the heterocyclic, six-membered structural unit, a series of reactions was carried out in particular with the tin-containing heterocycle in view of the fact that this material had undergone bromination and hydrobromination reactions with the preferential cleavage of the phenyl group. Spectral analysis of the resultant products showed the total elimination of the phenyl group as phenyl bromide, while the other nonvolatile material maintained the strong absorption pattern attributable empirically to the hetero-ring system. Titration data substantiated the formation of a cyclic tin bromide.

As a result of the preliminary evidence, work is currently being continued along these lines to determine the reliability of this set of absorption bands for other hetero-ring systems of the fourth group elements.

The compounds were prepared by methods described in the Experimental, generally in accordance with procedures already published. Five new compounds are listed in Table II. Over-all procedures are listed below.



#### EXPERIMENTAL

1-Hydroxycyclopentyl-1 carboxylic acid,<sup>3</sup> methyl 1-hydroxycyclopentyl-1 carboxylate,<sup>4</sup> diphenyl-(1-hydroxycyclopentyl-1)-

TABLE II  
PHYSICAL PROPERTIES<sup>a</sup>

	M.P.	B.P.	Mm.	<i>n</i>
1,1-Diphenylcyclohexane	43-44			
Cyclopentamethylenediphenylgermane		125-128	0.08	1.5873
Cyclopentamethylenediphenylstannane		138-140	0.10	1.6007
Cyclopentamethylenetin dibromide		166 <sup>b</sup>	0.40-0.45	
Cyclopentamethylenephanyltin iodide		219 <sup>b</sup>	0.45-0.85	

<sup>a</sup> New compounds only. <sup>b</sup> Wax bath temperature of the microdistilling assembly.

carbinol,<sup>4</sup> and 2,2-diphenylcyclohexanone<sup>5,6</sup> were prepared by methods in the literature, as indicated.

1,1-Diphenylcyclohexane was prepared by a method outlined by Huang and Minlon.<sup>7</sup> To a 200-cc. flask, fitted with a reflux condenser and containing 5 g. (0.13 mole) of sodium hydroxide, 80 cc. of diethylene glycol, and 5 cc. of 85% hydrazine hydrate solution, was added 10 g. (0.04 mole) of 2,2-diphenylcyclohexanone.

The system was refluxed for 1 hr. The temperature was allowed to increase slowly to 195°. After equipping the flask with an air condenser, refluxing was continued for 4 more hr. On cooling, a small layer of oil was found on the surface of the glycol. Acidification of the mixture with 14 cc. of hydrochloric acid and 100 cc. of water led to crystallization of this oil. The resultant solid was suction-filtered yielding 8 gr. (85% yield) of 1,1-diphenylcyclohexane. Recrystallization from hot ethanol gave a white crystalline material, m.p. 43°-44°.

Anal. Calcd. for C<sub>18</sub>H<sub>20</sub>, C, 91.45, H, 8.55. Found: C, 91.05, H, 8.58.

Cyclopentamethylenedichlorosilane<sup>8</sup> and cyclopentamethylene diphenylsilane<sup>9,10</sup> were prepared according to recorded methods.

Cyclopentamethylenedichlorogermane was prepared by the method of Schwarz and Reinhardt.<sup>11</sup>

Cyclopentamethylenediphenylgermane was synthesized by dissolving 25.6 g. of crude cyclopentamethylenedichlorogermane in 50 cc. of anhydrous ether and slowly adding, with vigorous stirring, to a solution of phenyllithium, prepared from 47.1 g. of bromobenzene in 150 cc. of anhydrous ether and 4.7 g. of lithium shot suspended in 150 cc. of anhydrous ether. This addition took 10 min. during which time the reflux temperature was slowly attained. After refluxing for 2.5 hr., the system was allowed to stand overnight.

Heating was resumed the next day for 4.5 hr. and the mixture then hydrolyzed with 200 cc. of 3% hydrochloric acid. The ether and water were separated and the water layer washed with 100 cc. of ether, followed by two 50-cc. portions of the same solvent. The combined ether extracts were dried over calcium chloride.

(5) A. Burger and W. B. Bennett, *J. Am. Chem. Soc.*, **72**, 5414 (1915).

(6) H. E. Zaugg, M. Freifelder, and B. W. Horron, *J. Org. Chem.*, **15**, 1191 (1950).

(7) M. Huang and H. Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(8) G. D. Oshesky and F. F. Bentley, *J. Am. Chem. Soc.*, **79**, 2057 (1957).

(9) C. Tamborski and H. Rosenberg, *J. Org. Chem.*, **25**, 246 (1960).

(10) G. D. Oshesky and F. F. Bentley, *WADC Tech. Rep.*, **56**, 434 (1957).

(11) R. Schwarz and W. Reinhardt, *Ber.*, **65**, 1743 (1932).

(3) J. Wislicenus, *Ann.*, **275**, 333 (1892).

(4) H. Meerwein and W. Unkel, *Ann.*, **376**, 156 (1910).

After distillation of solvent, 27.0 g. of residue remained which was fractionated giving cyclopentamethylenediphenylgermane, b.p. 125–128° (0.08 mm.),  $n_D^{20}$  1.5873.

*Anal.* Calcd. for  $C_{17}H_{20}Ge$ ; C, 68.75; H, 6.80, Ge, 24.45. Found: C, 68.99, H, 6.75, Ge, 24.15.

*Cyclopentamethylenediphenylstannane.* To 72.5 g. (0.211 mole) of diphenyltin dichloride dissolved in 200 cc. of anhydrous ether, was added, dropwise, 1,5-dilithiopentane. The lithium compound was prepared from 9.5 g. of lithium in accordance with the method of West and Rochow.<sup>12</sup> The reaction vessel was equipped in the usual manner and an atmosphere of pure nitrogen was used throughout this preparation. The rate of addition was such that a constant ether reflux was maintained. After the addition of the lithium compound had been completed, the reaction mixture was allowed to stand overnight.

Hydrolysis was accomplished by slowly adding 200 cc. of cold water and stirring. The two-phase system was transferred to a large separatory funnel and the aqueous layer separated. The ether layer was gravity filtered. The filtrate was washed with 50 cc. of *N* sodium hydroxide solution and the ether layer again separated and filtered. This filtrate was dried over calcium chloride. Distillation of the ether left 41.6 g. of a crude milky oil. On distillation the oil yielded 9 g. of a clear colorless liquid, cyclopentamethylene-diphenylstannane, b.p. 138°–140° (0.10 mm.),  $n_D^{20}$  1.6007.

(12) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

*Anal.* Calcd. for  $C_{17}H_{20}Sn$ : C, 59.51, H, 5.89, Sn, 34.60. Found: C, 60.03, H, 6.15, Sn, 34.85.

*Cyclopentamethylenediphenylplumbane.* This compound was prepared in the same manner as was the analogous tin compound described above. Infrared analysis of the product indicated the formation of cyclopentamethylenediphenylplumbane but on standing and exposure to light and air, the product rapidly colored and after several days a resinous solid was observed forming. No physical properties are therefore reported.

*Cyclopentamethylenebromostannane* was prepared by the action of a standardized potassium bromide-potassium bromate solution on cyclopentamethylenediphenylstannane in carbon tetrachloride, b.p. 166° (wax bath temperature) (0.40 mm.–0.45 mm.). Quantitative data on the bromination and infrared data supported the structure. The action of anhydrous hydrogen bromide gave rise to the same product. The by-product in this reaction was benzene.

*Cyclopentamethylenephenyltin iodide* was prepared by the treatment of the cyclopentamethylenediphenylstannane with iodine in carbon tetrachloride solution. Iodination data and infrared figures confirmed the structure, b.p. 219°<sup>13</sup> (0.45 mm.–0.85 mm.).

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(13) Wax bath temperature.

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## Polymeric Ligands. I. Some Salicylic Acid Derivatives

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The preparation and properties of a salicylic acid-formaldehyde copolymer are described. The preparation of the zinc(II), nickel(II), uranyl, iron(III), and aluminum(III) chelates is described. The thermal and spectral properties of the chelates are discussed.

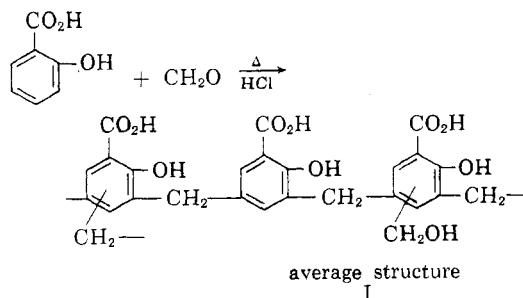
Salicylic acid chelates have been known for many years.<sup>1</sup> However, a number of these materials are water-soluble, and therefore, salicylic acid often cannot be used as a metal precipitant. If a polymer could be fashioned from salicylic acid, a highly water-insoluble ligand should be produced, which would be useful as a metal precipitant. We also wished to find out if the polymeric metal chelates were more stable, thermally, in air, than the parent polymer.

Salicylic acid polymers have been prepared before.<sup>2</sup> However, none of these systems have been

fully characterized and no polymeric chelates have ever been prepared from such systems.

We have prepared a fully characterized polymeric salicylic acid and prepared several different metal chelates from the polymeric ligand.

When salicylic acid was condensed with formaldehyde, a water-insoluble polymer was obtained which had an average molecular weight of  $6700 \pm 15\%$ . The analyses and neutral equivalents



compare favorably with the structure (I) shown above. The polymer was soluble in ethanol, acetone, dimethylformamide, and dimethyl sulf-

(1) F. J. Welcher, "Organic Analytical Reagents," D. VanNostrand Co., Inc., New York, 1947, Vol. II, p. 118.

(2) W. H. Butler (to Bakelite Corp.), U. S. Patent 2,144,101 (1939); M. VanLoon (to Bataafische Petroleum Maatschappij), Dutch Patent 65,636 (1950); E. C. Yokel (to Eastman Kodak Co.), U. S. Patent 2,565,418 (1951); G. Baumhardt, *Eng. e quim* (Rio de Janeiro), **4**, No. 25 (1932). *Chem. Abstr.*, **48**, 2012a (1954). K. Ashida, "Chem. High Polymers," *Japan*, **9**, 397 (1952); *Chem. Abstr.*, **48**, 7817h (1954). H. Kawabe and M. Yanagita, *Rept. Sci. Res. Inst.* (Japan), **28**, 264 (1952); M. Sugihara, *Sci. Ind. Japan*, **27**, 236 (1953); S. Umezawa and U. Ohtsuka, *Japan* 1598/1953. *Chem. Abstr.*, **48**, 2290 (1954). S. Matsumura and T. Komiya, *Japan* 1693/1953. *Chem. Abstr.*, **48**, 3596 (1954).