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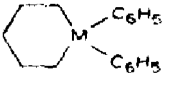
NOTE

Studies in organosilicon chemistry
XLVII. The synthesis and infrared study of heterocyclic compounds of silicon, germanium and tin

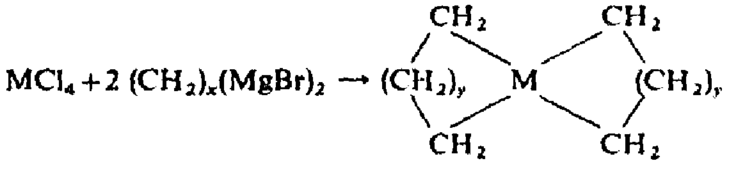
Previous investigations[1,2] have shown that certain infrared spectra structure correlations can be drawn and related to the congeneric series of six-membered heterocyclic compounds incorporating one or more of the main Group IV elements. Similarly Oshesky and Bentley[3] have shown that useful correlations that are helpful in identifying the six-membered silicon containing ring can be extracted from an examination of a series of silacyclohexane compounds. Particularly interesting and of diagnostic value were absorption bands centering about 910 and 1000 cm^{-1}. In further studies along these lines, compounds of the type shown below have demonstrated that a similar extension of this absorption pattern is possible for other six-membered ring systems within this group.



M = Ge, Sn, Pb

In continuing studies, a series of spirocyclic compounds was chosen for examination as being useful in further reaffirming these spectral correlations and possibly assigning new ones. This paper describes the synthesis and spectral examination of a series of five- and six-membered heterocyclic ring systems containing silicon, germanium and tin.

The germanium- and tin-containing compounds were prepared by reaction between the tetrachlorides and a small excess of the appropriate di-Grignard reagents.



$$MCl_4 + 2\,(CH_2)_x(MgBr)_2 \rightarrow (CH_2)_y(CH_2)_2M(CH_2)_2(CH_2)_y$$

M = Ge; $x = 4$ or 5, $y = 2$ or 3
M = Sn; $x = 5$, $y = 3$

The over-all yields were not high (~30%) and were particularly low for the six-membered tin spirocycle (~10–15%).

In contrast to the instability of the tin compounds, the five- and six-membered cyclic compounds of silicon and germanium were found to be quite stable.

Discussion

On the basis of a careful, comparative study made on these and other heterocycles within the group (*e.g.* ref. 1,2), further verification is possible of the fact that six-membered ring systems of this type persist in showing a characteristic infrared band pattern consisting particularly of two strong absorption bands with maxima centered at 990 and 910 cm^{-1} respectively. While the latter band is relatively invariant (± 5 cm^{-1}), the absorption band at 990 cm^{-1} shows both an increased intensity and a shift to lower frequency of approximately 20 cm^{-1} most noticeable for the tin-containing heterocycle.

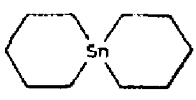
It is important to point out that this spectral correlation is limited to those compounds in which there is only one heteroatom in the ring and in which the carbocyclic portion is unsubstituted. Alkyl or aryl substitution on the hetero-atom however does not appear to significantly alter this band pattern[3].

Although only eight compounds were studied in which a five-membered ring was featured, a similar spectra-to-structure correlation was apparent. A more exhaustive investigation by Nametkin *et al.*[4] seems to strengthen the reliability of this assignment. The five-membered heterocycles show a particularly characteristic pair of bands at approximately 1080 cm^{-1} and 1025 cm^{-1} respectively. In the case of silicon-containing rings, the latter absorption shows a tendency of splitting, with band maxima located at 1030 cm^{-1} and 1020 cm^{-1}. A closely similar pattern holds for the germanium-containing rings.

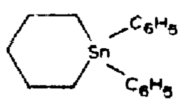
It should be noted that in cases involving both types of ring systems, as for example with the silicon spirocycle 5-silaspiro[4.5]decane (I), both pairs of absorption band patterns are clearly observed.

The facile reactivity of the six-membered tin heterocycles prompted a study of cleavage reactions which could either lead to ring cleavage or proceed with ring retention. For this study, 6-stannaspiro[5.5]undecane (II) and 1,1-diphenyl-1-stannacyclohexane (III) were chosen. These compounds were treated with hydrogen bromide, bromine and iodine. Fig. 1 summarizes the overall results of these reactions. Cleavage reactions of (III) are described in our previous paper[1]. Although iodination of alkyl- and aryl-substituted organotin compounds is generally reported to yield monoiodinated products[1,5,6], this study indicates that reactions carried out in the absence of solvent and at higher temperatures (80–85°) result in formation of the cyclic tin diiodide. The spirocyclic tin compound offers two possible courses of reaction, either complete loss of ring structure or partial retention, as shown below.

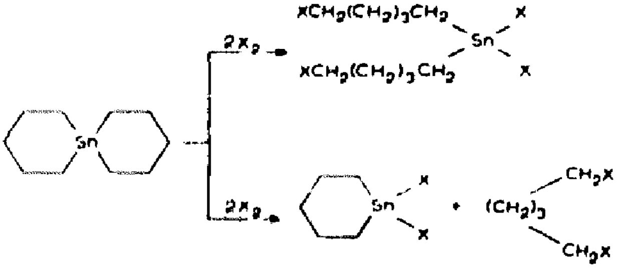
(I)



(II)



(III)



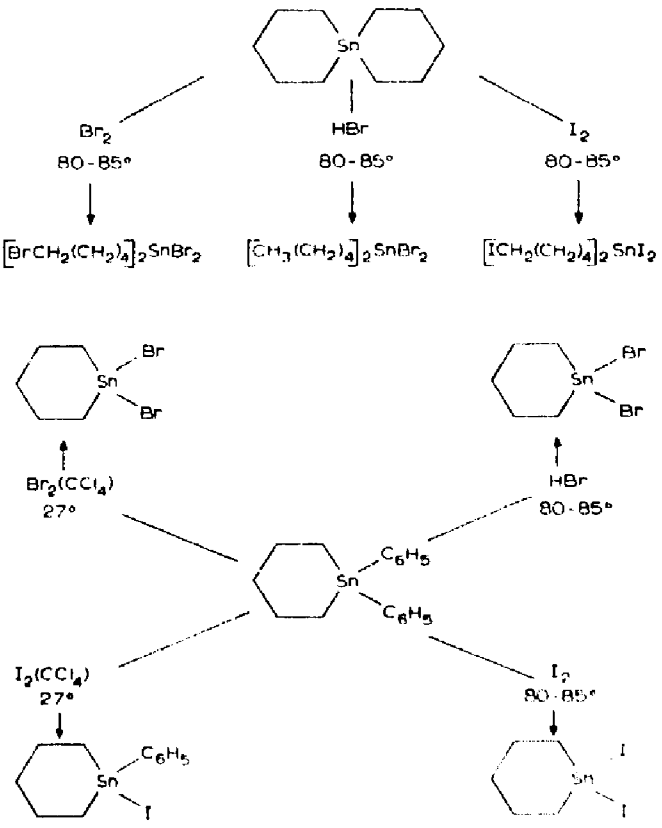
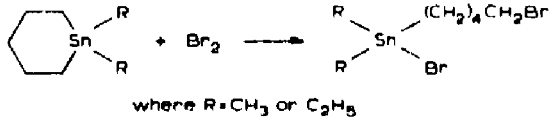


Fig. 1.

Experimentally it has been found that both ring systems are ruptured and that the reaction does not go beyond the utilization of two moles of halogen or hydrogen bromide per mole of organotin spirane. The infrared spectra of the resulting organotin dihalides showed complete loss of band character at 910 and 970 cm^{-1}.

These results are in agreement with those obtained by Polster who reported complete ring cleavage in the bromination of 3,3,9,9-tetramethyl-6-stannaspiro[5.5]-undecane[7]. Earlier bromination studies by Grüttner and Krause on cyclic organotin compounds of the type shown below also resulted in ring rupture[8].



Since the organotin dihalides were, for the most part, oils and difficult to distill in the small quantities in which they were synthesized, it was found convenient to prepare crystalline complexes through coordination with either 2,2'-bipyridine or 1,10-phenanthroline. As reported elsewhere[9,10], such derivatives are stable and can easily be recrystallized and analyzed. The melting points and elemental analyses of these complexes are listed in Table 1.

TABLE 1

MELTING POINTS AND ELEMENTAL ANALYSES OF COMPLEXES

	Compound	*M.p.* (°*C*)	*C* (%) *found* (*calcd.*)	*H* (%) *found* (*calcd.*)	*N* (%) *found* (*calcd.*)	*X* (%) *found* (*calcd.*)
2,2'-Bipyridine complexes						
(a)	$\overline{(\mathrm{CH_2})_5\mathrm{Sn}}\mathrm{Br_2}$	207–210	35.35 (35.69)	4.03 (3.59)	6.00 (5.55)	
(b)	$[\mathrm{BrCH_2(CH_2)_4}]_2\mathrm{SnBr_2}$	157–9	32.51 (32.69)	4.18 (3.84)		41.98 (43.50)
(c)	$[\mathrm{ICH_2(CH_2)_4}]_2\mathrm{SnI_2}$	145–7	26.34 (26.03)	3.22 (3.06)	3.38 (3.04)	54.85 (55.01)
1,10-Phenanthroline complexes						
(a)	$\overline{(\mathrm{CH_2})_5\mathrm{Sn}}\mathrm{Br_2}$	218–20	38.73 (38.61)	3.23 (3.43)	4.88 (5.30)	
(b)	$[\mathrm{BrCH_2(CH_2)_4}]_2\mathrm{SnBr_2}$	149–51	34.62 (34.82)	3.82 (3.72)	3.90 (3.69)	
(c)	$[\mathrm{ICH_2(CH_2)_4}]_2\mathrm{SnI_2}$	172–74	28.88 (27.91)	2.80 (2.98)	2.78 (2.96)	51.89 (53.62)

Experimental part

Spirocyclic silicon compounds. 5-Silaspiro[4.4]nonane, 5-silaspiro[4.5]decane and 6-silaspiro[5.5]undecane were all prepared via previously published procedures[11].

6-Germaspiro[5.5]*undecane.* The di-Grignard reagent of 1,5-dibromopentane was prepared with modifications according to the method of Kreuchunas[12]. To the freshly prepared di-Grignard solution (based on 0.32 mole of dibromide), 21.4 g (0.10 mole) of germanium tetrachloride was added after dilution with 50 ml of ethyl ether. After a reflux period of over 7 h, the reaction mixture was hydrolyzed with 200 ml of 1% hydrochloric acid. Separation of the ether layer, drying over anhydrous calcium chloride and flash evaporation of the solvent, left 21.9 g of a distillable oil. Fractional distillation yielded 5.6 g of purified product, 6-germaspiro[5.5]undecane, b.p. 99–101°/10 mm; n_D^{25} 1.5005. (Found: C, 56.81; H, 9.65. $C_{10}H_{20}Ge$ calcd.: C, 56.41; H, 9.49%.)

5-Germaspiro[4.4]*nonane.* In a similar manner, the five-membered germanium spirocycle was prepared by reaction of the Grignard reagent prepared from 71.3 g of 1,4-dibromobutane with 23.0 g (0.10 mole) of germanium tetrachloride. Fractional distillation yielded 6.3 g of 5-germaspiro[4.4]nonane, b.p. 70–72°/10 mm; n_D^{25} 1.5033. (Found: C, 52.06; H, 8.94. $C_8H_{16}Ge$ calcd.: C, 51.98; H, 8.74%.)

6-Stannaspiro[5.5]*undecane.* A di-Grignard reagent, prepared from 73.6 g (0.32 mole) of 1,5-dibromopentane, was used in reaction with 26.1 g (0.10 mole) of tin tetrachloride diluted with 100 ml of dry n-pentane. After the usual extraction and drying procedures, fractional distillation of 28.9 g of crude liquid product yielded only 3.9 g of the tin heterocycle, 6-stannaspiro[5.5]undecane, b.p. 119–120°/10 mm;

n_D^{25} 1.5362. (Found: C, 46.64; H, 7.64. $C_{10}H_{20}Sn$ calcd.: C, 46.37; H, 7.80%.)

Cleavage reactions. Cleavage reactions were carried out with the six-membered tin spirocycle and 1,1-diphenyl-1-stannacyclohexane prepared according to previously published procedure[1].

Bromination reactions were carried out using 1 g quantities of the respective tin compounds dissolved in 2 ml of carbon tetrachloride, by the slow addition of liquid bromine until a persistence of color was registered. The resulting solution was then evaporated under a stream of nitrogen while being warmed over a steam bath. The remaining oils were examined spectroscopically and subsequently converted to stable coordination complexes with 2,2'-bipyridine and 1,10-phenanthroline according to the method of Alleston and Davies[9].

Iodination reactions were carried out similarly using iodine crystals.

Hydrobromination was accomplished by passing a slow stream of anhydrous hydrogen bromide through the reagents while maintaining the temperature at 80–85°.

Microanalyses for carbon, hydrogen and nitrogen were carried out by Dr. G. WEILER and Dr. F. B. STRAUSS, Microanalytical Laboratory, 164 Banbury Road, Oxford, England, and ALFRED BERNHARDT, Mikroanalytisches Laboratorium in Max-Planck Institut, 433 Mülheim (Ruhr), Germany.

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1 F. J. BAJER AND H. W. POST, *J. Org. Chem.*, 27 (1962) 1422.
2 F. J. BAJER AND H. W. POST, *J. Org. Chem.*, 28 (1963) 1941.
3 G. D. OSHESKY AND F. F. BENTLEY, *J. Am. Chem. Soc.*, 79 (1957) 2057.
4 N. S. NAMETKIN, V. D. OPPENGEIM, V. I. ZAV'YALOV, K. S. PUSHCHEVAYA AND V. M. VDOVIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1965) 1547.
5 R. K. INGHAM, S. D. ROSENBERG AND H. GILMAN, *Chem. Rev.*, 60 (1960) 459.
6 J. G. A. LUIJTEN AND G. J. M. VAN DER KERK, *Investigations in the Field of Organotin Chemistry*, Institute for Organic Chemistry TNO, Utrecht, Holland, 1955.
7 R. POLSTER, *Ann. Chem.*, 654 (1962) 20.
8 G. GRÜTTNER AND E. KRAUSE, *Ber.*, 50 (1917) 1549.
9 D. L. ALLESTON AND A. G. DAVIES, *J. Chem. Soc.*, (1962) 2050.
10 T. TANAKA, M. KOMURA, Y. KAWASAKI AND R. OKAWARA, *J. Organometal. Chem.*, 1 (1964) 484.
11 R. WEST, *J. Am. Chem. Soc.*, 76 (1954) 6012.
12 A. KREUCHUNAS, *J. Am. Chem. Soc.*, 75 (1953) 3339.

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