

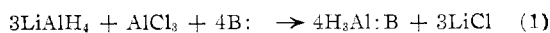
that of the mixed bis-adduct. On the other hand, when excess diethyl ether is added to a solution of mono-(diethyl ether) alane in benzene, the molecular weight only increases to 126, *vs.* a theoretical value of 178 for a bis-ether complex. This indicates that a second molecule of ether does not actually coordinate with the  $\text{AlH}_3$ . It also is interesting to note that in benzene monotetrahydrofuran alane shows a greater degree of association than diethyl ether alane, again indicating that the steric requirements of diethyl ether are greater than those of tetrahydrofuran and molecular association of diethyl ether alane is thereby inhibited.

The behavior of monotrimethylamine alane in ether and tetrahydrofuran also is best explained by these steric considerations. As previously noted, the spectrum of monotrimethylamine alane in diethyl ether shows two Al-H absorptions, with the stronger being at the higher frequency, indicating that a mixture of tetra- and pentacoordinate complexes has been formed in which the former is the major component. Trimethylamine alane in tetrahydrofuran, however, shows the Al-H absorption at the lower frequency, suggesting a small steric interference between tetrahydrofuran and trimethylamine.

These results show that the Lewis bases studied fall in the following order in their tendency to form bis-complexes with alane: tetrahydrofuran > trimethylamine > diethyl ether. This order is the reverse of that given by the steric requirements of these bases, using the degree of association of monotetrahydrofuran alane, monotrimethylamine alane, and diethyl ether alane in benzene (1.55, 1.42, and 1.21, respectively) as a criterion of the steric requirements. The order does not correspond to the expected order of basicity of the Lewis bases toward alane, *i.e.*, trimethylamine > tetrahydrofuran > diethyl ether. That tetrahydrofuran is actually a weaker base toward alane than trimethylamine is demonstrated by the fact that trimethylamine is not displaced from its 1:1 complex when the latter is dissolved in tetrahydrofuran. Data which would unequivocally relate the basicities of diethyl ether and tetrahydrofuran toward alane are presently incomplete, although the preponderant evidence shows that tetrahydrofuran is the stronger base. Molecular weight data could provide additional proof of the strength of a particular base which is used as the solvent. Thus, if a Lewis base (B) is displaced from its alane complex when it is dissolved in a second Lewis base (B'), the apparent molecular weight of the complex will approach one-half of the formula weight of the original alane-Lewis base complex.

#### Experimental

**Alane-Lewis Base Complexes.**—The alane complexes with the various Lewis bases were prepared in the appropriate solvent by the basic method of Finholt, *et al.*<sup>7</sup> (eq. 1). The lithium chlo-



(7) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

ride was removed by filtration and the alane-Lewis base ratios were determined by quantitative hydrolyses and standard wet chemical analyses on the residues. Molecular weights were determined cryoscopically in benzene and ebullioscopically in the ethers. Infrared spectra were determined as differentials in solution using a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. In the case of diethyl ether alane in diethyl ether the infrared spectrum had to be determined immediately upon filtration, since the insoluble  $(\text{AlH}_3)_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  generally started to precipitate within 20 min. after removal of the lithium chloride.

**Acknowledgment.**—We wish to acknowledge the assistance of Mr. Raymond Storey in the determination and interpretation of the infrared spectra.

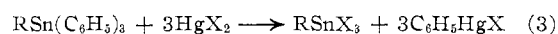
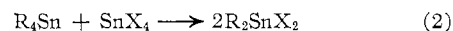
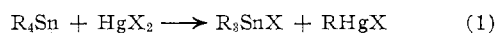
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF  
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### Cyclopropyltin Halides and Related Compounds

BY DIETMAR SEYFERTH<sup>1a</sup> AND HARVEY M. COHEN<sup>1b</sup>

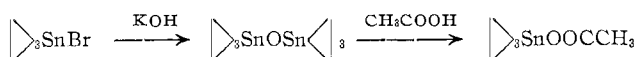
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Recently we have reported the synthesis of a number of cyclopropyltin compounds by the Grignard procedure.<sup>2</sup> Using these compounds as starting materials, we have prepared mono-, di-, and tricyclopropyltin chlorides and bromides by the reactions listed below (R = cyclopropyl, X = Cl and Br)



Reaction 1 appears to be a good route to cyclopropylmercuric chloride and bromide as well as to tricyclopropyltin halides. Reaction 3 suggests that the phenyl group is cleaved from tin much more readily than is the cyclopropyl group. This observation is of some interest when compared with the finding that hydrogen chloride in dimethyl sulfoxide solution cleaves a cyclopropyl group from dicyclopropylmercury at a rate ten times greater than the cleavage of a phenyl group from diphenylmercury.<sup>3</sup> In connection with reaction 2, which was carried out at *ca.* 220°, it was desirable to establish the thermal stability of tetracyclopropyltin. It was found that this compound was stable for at least 2 hr. at 230° in a nitrogen atmosphere.

Tricyclopropyltin iodide, dicyclopropyltin diiodide, tricyclopropyltin fluoride, and dicyclopropyltin dithiocyanate were prepared by standard methathetical reactions. Tricyclopropyltin acetate resulted from the sequence



(1) (a) Alfred P. Sloan Research Fellow; (b) Allied Chemical Corporation Fellow, 1960-1961.

(2) D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **1**, 913 (1962).

(3) R. E. Dessy, G. F. Reynolds, and J.-Y. Kim, *J. Am. Chem. Soc.*, **81**, 2683 (1959).

The biocidal activity of a number of these compounds is under investigation.

### Experimental

Throughout this section R = cyclopropyl.

**Thermal Stability of Tetracyclopropyltin.**—To a small flask fitted with a nitrogen inlet tube and thermometer was added 1.0 ml. of  $R_4Sn$ . The contents of the flask were heated to  $215^\circ$  by an oil bath. The temperature was raised to  $230^\circ$  over the course of 1 hr. and the contents of the flask were maintained at this temperature for an additional 2 hr. During the entire heating period, no gas evolution was noted. The originally colorless  $R_4Sn$  had become very faint yellow. Gas chromatography (Dow Corning 710 silicone fluid 35% on 80–100 mesh Chromosorb P, jacket at  $236^\circ$ , preheater at  $204^\circ$ , postheater at  $228^\circ$ , 14 p.s.i. He) indicated quantitative recovery. Thus a 40.0- $\mu$ l. aliquot of the sample which had been heated to  $230^\circ$  produced a single peak of the identical area as that found for a 40.0- $\mu$ l. aliquot of an unheated sample.

**Dicyclopropyltin Dichloride.**—To a 25-ml. three-necked flask fitted with a water condenser topped with a nitrogen inlet tube and thermometer was added 4.85 g. (0.0171 mole) of  $R_4Sn$ . The flask was cooled by an ice bath and 2.00 ml. (0.0171 mole) of  $SnCl_4$  added by pipet. After the originally exothermic reaction (temperature to  $110^\circ$  with cooling) had subsided, the flask was heated to  $220^\circ$  over the course of 1 hr. (solution color dark brown) and maintained at  $220$ – $225^\circ$  for 4.5 hr. longer. Volatiles were removed *in vacuo*. Distillation gave 7.9 g. (86%) of material of b.p.  $105$ – $106^\circ$  (0.1 mm.), which crystallized in the receiving vessel (needles), m.p.  $59$ – $60^\circ$ . An analytical sample was obtained by recrystallization from hexane, m.p.  $60$ – $60.5^\circ$ .

*Anal.*<sup>4</sup> Calcd. for  $C_6H_{10}SnCl_2$ : C, 26.52; H, 3.71; Cl, 26.06. Found: C, 26.87; H, 3.95; Cl, 26.27.

**Dicyclopropyltin Dibromide.**—This reaction was carried out in a similar manner using 5.00 ml. (0.0226 mole) of  $R_4Sn$  and 3.00 ml. (0.0229 mole) of  $SnBr_4$ . Volatiles were removed *in vacuo*. Redistillation gave 14.9 g. (91%) of material, b.p.  $113^\circ$  (0.2 mm.), m.p.  $52$ – $53.5^\circ$ . Recrystallization from hot hexane yielded analytically pure material, m.p.  $53$ – $54^\circ$  (needles).

*Anal.* Calcd. for  $C_6H_{10}SnBr_2$ : C, 20.00; H, 2.79; Br, 44.32. Found: C, 20.14; H, 3.06; Br, 44.37.

**Tricyclopropyltin Chloride.**—For this and the following reactions of cyclopropyltin compounds with mercuric halides, the method of Seyferth<sup>5</sup> was used. To a three-necked flask fitted with a Soxhlet extraction apparatus topped with a condenser with a nitrogen inlet tube was added 14.14 g. (0.05 mole) of  $R_4Sn$  and 200 ml. of diethyl ether. To the thimble of the extractor was added 13.37 g. (0.05 mole) of  $HgCl_2$ . The ether was cycled for 3 days. Shiny platelets were filtered, m.p.  $186^\circ$ . Recrystallization of the solid from diethyl ether gave highly reflective plates of  $RH_3SnCl$ , m.p.  $186.5$ – $187^\circ$  (lit.<sup>6</sup> m.p.  $186$ – $187^\circ$ ). Fractional distillation of the filtrate, followed by filtration and redistillation, gave 9.2 g. (66%) of  $R_3SnCl$ , b.p.  $84$ – $85^\circ$  (0.4 mm.),  $n_D^{25}$  1.5415.

*Anal.* Calcd. for  $C_9H_{15}SnCl$ : C, 38.97; H, 5.43; Cl, 12.78. Found: C, 38.63; H, 5.44; Cl, 12.17.

**Tricyclopropyltin Bromide.**—This reaction was carried out in the same manner as the previous one with 14.15 g. (0.05 mole) of  $R_4Sn$ , 18.02 g. (0.05 mole) of mercuric bromide, and 250 ml. of diethyl ether. Cycling of the ether was continued for 4 days. The solid (shiny platelets) was filtered off and the ether evaporated using a rotary evaporator. The residual liquid was allowed to stand overnight, then filtered and distilled to give 11.9 g. (74%) of  $R_3SnBr$ , b.p.  $80.5^\circ$  (0.2 mm.),  $n_D^{25}$  1.5600.

*Anal.* Calcd. for  $C_9H_{15}SnBr$ : C, 33.59; H, 4.70; Br, 24.83. Found: C, 33.47; H, 4.57; Br, 24.82.

Recrystallization of 4.0 g. of the 15.2 g. of solid obtained gave 3.45 g. of material, m.p.  $196$ – $197.5^\circ$  (from ether), a total yield of 13.1 g. (82%) of pure cyclopropylmercuric bromide, a new compound. A second recrystallization gave material, m.p.  $196.5$ – $197.5^\circ$ .

*Anal.* Calcd. for  $C_3H_5HgBr$ : C, 11.20; H, 1.55. Found: C, 11.40; H, 1.84.

**Cyclopropyltin Trichloride.**—This reaction was carried out in the same manner as the above reactions with 25.0 g. (0.0638 mole) of  $R_3Sn(C_6H_5)_3$  in 250 ml. of diethyl ether and 52.0 g. (0.1914 mole) of  $HgCl_2$  to give after 3 days 13.9 g. (82%) of  $R_3SnCl_3$ , b.p.  $59$ – $61^\circ$  (1 mm.),  $n_D^{25}$  1.5447.

*Anal.* Calcd. for  $C_9H_9SnCl_3$ : C, 13.54; H, 1.89; Cl, 39.97. Found: C, 13.66; H, 2.22; Cl, 39.77.

In addition 58.7 g. (98%) of  $C_6H_5HgCl$  (m.p.  $245$ – $251^\circ$ ) was obtained. Recrystallization from benzene gave pure material, m.p.  $256$ – $258^\circ$ .

**Cyclopropyltin Tribromide.**—This reaction was carried out as above with 25.0 g. (0.0638 mole) of  $R_3Sn(C_6H_5)_3$  in 300 ml. of diethyl ether and 69.0 g. (0.1914 mole) of  $HgBr_2$ . After the ether had been cycled for 3 days,  $C_6H_5HgBr$  was filtered off and the ether removed. Distillation yielded 12.7 g. (50%) of  $R_3SnBr_3$ , b.p.  $56$ – $57^\circ$  (0.15–0.10 mm.),  $n_D^{25}$  1.6282.

*Anal.* Calcd. for  $C_9H_9SnBr_3$ : C, 9.02; H, 1.26; Br, 60.01. Found: C, 9.16; H, 1.44; Br, 59.84.

**Tricyclopropyltin Iodide.**—To a solution of 5.62 g. (0.0203 mole) of  $R_3SnCl$  in 10 ml. of acetone was added a solution of 3.05 g. (0.0203 mole) of NaI in 15 ml. of acetone. The precipitated NaCl was filtered off. After removal of acetone at atmospheric pressure, distillation of the residual liquid gave 6.3 g. (84%) of  $R_3SnI$ , b.p.  $97.5$ – $98^\circ$  (0.4 mm.),  $n_D^{25}$  1.5908.

*Anal.* Calcd. for  $C_9H_{15}SnI$ : C, 29.31; H, 4.10; I, 34.41. Found: C, 29.06; H, 4.27; I, 34.37.

**Dicyclopropyltin Diiodide.**—To a solution of 2.0 g. (0.074 mole) of  $R_2SnCl_2$  in about 10 ml. of acetone was added a solution of 2.4 g. (0.0148 mole) of NaI in 10 ml. of acetone. The insoluble NaCl was filtered and the acetone removed from the filtrate at reduced pressure using a rotary evaporator. The remaining solid was crystallized from pentane to afford a yellow solid. Recrystallization gave 2.35 g. (70%) of  $R_2SnI_2$  (small clusters of needles), m.p.  $37.5$ – $38^\circ$ .

*Anal.* Calcd. for  $C_6H_{10}SnI_2$ : C, 15.86; H, 2.22; I, 55.86. Found: C, 16.13; H, 2.54; I, 56.05.

**Tricyclopropyltin Fluoride.**—To 1.5 g. (0.0041 mole) of tricyclopropyltin iodide was added 5 ml. of a 10% solution of KF in 1:1 water–methanol. The resulting solid was filtered off, washed with a 1:1 water–methanol solution, and recrystallized from hot tetrahydrofuran to give 1.1 g. (95%) of  $R_3SnF$  in the shape of small needles. The pure material sublimates at  $175^\circ$  at atmospheric pressure.

*Anal.* Calcd. for  $C_9H_{15}SnF$ : C, 41.43; H, 5.80. Found: C, 41.31; H, 5.84.

**Tricyclopropyltin Acetate.**—A solution of 7.0 g. (0.022 mole) of  $R_3SnBr$  in 20 ml. of diethyl ether was shaken with 8 ml. of a solution of 2.2 g. (0.033 mole) of KOH (85%) in 12 ml. of water. The water layer was drawn off and the ether layer shaken with the remaining 4 ml. of KOH solution. The solid material which had separated into the ether layer (1.5 g.) was filtered off and the ether layer dried briefly over  $MgSO_4$  and evaporated to dryness to yield 4.6 g. of a somewhat oily solid. This solid was dissolved in 40 ml. of ether (the additional material which may have been crude  $R_3SnOH$  was ether-insoluble), and 1.1 g. (0.018 mole) of glacial acetic acid was added. Solid settled out (4.0 g., m.p.  $157$ – $158^\circ$ ) in small fluffy white needles. Concentration of the ether solution yielded an additional 0.5 g., m.p.  $155$ – $156^\circ$ . The total yield was 4.5 g. (88% based on what was presumably the oxide). Recrystallization of a portion of the  $R_3SnOOCCH_3$  gave an analytically pure sample, m.p.  $157.5$ – $158^\circ$ .

*Anal.* Calcd. for  $C_{11}H_{18}SnO$ : C, 43.90; H, 6.02. Found: C, 44.25; H, 6.12.

**Dicyclopropyltin Dithiocyanate.**—A solution of 0.8 g. (0.01 mole) of sodium thiocyanate (dried *in vacuo*) in 10 ml. of absolute

(4) All halogen analyses were performed by Dr. S. M. Nagy (M.I.T.) by precipitation of the halide from ethanolic solution with silver nitrate and weighing the resulting silver halide.

(5) D. Seyferth, *J. Org. Chem.*, **22**, 478 (1957).

(6) E. Tobler and D. J. Foster, *Z. Naturforsch.*, **17b**, 135 (1962).

ethanol was added to 1.33 g. (0.0049 mole) of  $R_3SnCl_2$  in about 5 ml. of ethanol. The solution was warmed on a steam bath for a few minutes to coagulate the insoluble NaCl. The solid was filtered off and the solvent removed at 1 mm. with gentle warming (about 40°). The residue was crystallized by dissolving it in hot benzene and slowly evaporating on a rotary evaporator to give 1.0 g. (64%) of  $R_3Sn(SCN)_2$ , m.p. 184–187° dec.

*Anal.* Calcd. for  $C_3H_{10}N_2S_2Sn$ : C, 30.30; H, 3.19; SCN, 36.63. Found: C, 30.57; H, 3.40; SCN,<sup>7</sup> 36.58.

**Acknowledgments.**—The authors are grateful to the National Science Foundation for support of this work under Grant NSF G-21051.

(7) Determined by Dr. S. M. Nagy by precipitation of silver thiocyanate with silver nitrate in ethanol.

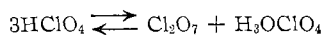
CONTRIBUTION FROM THE  
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## Raman Spectrum of Solid Perchloric Acid and the Nature of the Solid Phase

BY A. J. DAHL, J. C. TROWBRIDGE, AND R. C. TAYLOR

Received December 14, 1962

Anhydrous perchloric acid is a well characterized compound in the gaseous and liquid phases. Recently, however, the phase diagram for the system  $Cl_2O_7-H_2O$  has been studied<sup>1</sup> and the results of the investigation interpreted as indicating that no compound exists in the solid for a 1:1 ratio of the heptoxide to water. Instead, the equilibrium



was postulated to exist at the 1:1 composition with the position of the equilibrium being shifted almost completely to the right at low temperatures. The solid material corresponding to a 1:1 mole ratio of  $H_2O$  and  $Cl_2O_7$  was considered to be a mixture of two phases, most likely  $Cl_2O_7$  and  $H_3OCIO_4$ , although the possibility of a hydrate of  $Cl_2O_7$  also was mentioned.

Recent infrared investigations of solid anhydrous perchloric acid<sup>2</sup> and solid  $Cl_2O_7$ <sup>3</sup> do not appear to support this interpretation.

The possibility of such an equilibrium was not considered in the infrared papers, however, and since most of the strong infrared bands of  $Cl_2O_7$  are overlapped by those of perchloric acid, it was felt that a Raman spectrum of the solid might be of interest. A Raman spectrum of crystalline perchloric acid has not been reported previously.

### Experimental

Anhydrous perchloric acid was prepared in a vacuum line having no joints or stopcocks using the general procedure of

(1) A. A. Zinov'ev and V. Ya. Rosolovskii, *Zh. Neorgan. Khim.*, **10**, 2383 (1958).

(2) P. A. Giguère and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

(3) R. Savoie and P. A. Giguère, *ibid.*, **40**, 991 (1962).

TABLE I  
OBSERVED RAMAN BANDS OF SOLID  $HClO_4$  (IN  $cm^{-1}$ )

This research	Raman		Infrared $HClO_4(s)^2$	Assignments
	$HClO_4(l)^4$	284		
			346	
436 ± 8 w	424		371	Sym. $OCIOH$ def.
			428	Asym. $OCIOH$ def.
			478	OH torsion
			566	Sym. $OCIO$ def.
585 m	577		585	Asym. $OCIO$ def.
			603	
738 s	740		740	
			760	In-phase $HOCIO_3$ str.
1038 vs	1031		1033	Out-of-phase $HOCIO_3$ str.
	1210 v br		1200	(478 + 760 = 1238)
1243 w			1245	OH def.
			1283	Sym. $ClO_3$ str.
			1315	Asym. $ClO_3$ str.
1550 ± 3 vvw				
2329 w				( $N_2$ , gas value = 2330.7)
3040 ± 4 vvw				
3336 ± 5 w	3350 v br	3260		OH str.

Smith,<sup>4</sup> A calorimetric determination of its melting point<sup>5</sup> gave a value of  $-102^\circ$ , which agrees with the Russian value<sup>1</sup> but is appreciably higher than the figure of  $-112^\circ$  previously accepted. Details will be published elsewhere. The spectroscopic sample was distilled three times, the last time directly into a small 7-mm. diameter glass tube which served as the cell. After freezing the material in liquid nitrogen, the tube was carefully sealed off to prevent exposure to the atmosphere. Prior to taking the Raman spectrum, the sample was melted three times, the liquid being kept at a temperature just above its melting point to ensure that the equilibrium, if such did exist, would be attained. The spectrum was obtained with the sample tube immersed in liquid nitrogen.

The experimental procedure for obtaining the Raman spectrum was similar to that described by Schrader.<sup>6</sup> The sample was illuminated on one side with spectrally pure Hg 4358 radiation and the light scattered from the opposite side, after four reflections from multilayer interference filters to reduce the intensity of the exciting line, was focused on the slit of the spectrograph. The exposure time was 24 hr. using a heat sensitized Eastman IIA-O plate.

The observed frequencies are listed in Table I together with the Raman values for liquid perchloric acid and infrared data for the solid. Uncertainties in the experimental values are about 2  $cm^{-1}$  except where noted.

### Discussion

Inspection of the values given in Table I shows good agreement between the data obtained in the present case and those recorded in the literature for liquid perchloric acid,<sup>7</sup> the principal difference being in the OH bands which were much sharper in the solid.

No indication was obtained of the presence of the very intense  $921\text{ cm}^{-1}$  vibration of  $H_3OCIO_4$ <sup>8</sup> nor of the  $501$  and  $695\text{ cm}^{-1}$  vibrations of  $Cl_2O_7$ .<sup>9</sup> Interference with any of these bands in the Raman spectrum is unlikely and their absence indicates that

(4) G. F. Smith, *J. Am. Chem. Soc.*, **75**, 184 (1953).

(5) J. C. Trowbridge, Dissertation, The University of Michigan, Nov., 1962.

(6) B. Schrader, F. Nerdel, and G. Kresze, *Z. physik. Chem. (Frankfurt)*, **12**, 132 (1957).

(7) A. Simon and M. Weist, *Z. anorg. allgem. Chem.*, **268**, 301 (1952).

(8) R. C. Taylor and G. L. Vidale, *J. Am. Chem. Soc.*, **78**, 5999 (1956).

(9) R. Fonteyne, *Natuurw. Tijdschr. (Ghent)*, **20**, 275 (1938).