the transition state two limiting cases are considered: (1) the reacting hydrogen atoms are completely free, the frequencies therefore being zero, and (2) the bond between the reacting hydrogen atoms is essentially that in a gaseous hydrogen molecule, the frequencies being taken[21] as HH = 4405, HD = 3817, HT = 3598 and DT = 2846. Substitution of the appropriate frequencies in equation 2, using $T = 298°$K., gives for case (1), $k_{\mathrm{SiH}}/k_{\mathrm{SiD}} = 4.1$, $k_{\mathrm{SiH}}/k_{\mathrm{SiT}} = 7.8$. The assumptions for case (2) lead to values of $k_{\mathrm{SiH}}/k_{\mathrm{SiD}} = 1.00$ and $k_{\mathrm{SiH}}/k_{\mathrm{SiT}} = 1.12$. The experimental values of 1.15 for $k_{\mathrm{SiH}}/k_{\mathrm{SiD}}$ for the one reaction studied and 1.29, 1.40 and 1.49 for $k_{\mathrm{SiH}}/k_{\mathrm{SiT}}$ for three reactions, are in much better agreement with the values calculated for case (2) than with those for case (1).

For oxygen–hydrogen bond rupture the calculated values of $k_{\mathrm{SH}}/k_{\mathrm{ST}}$ are for case (1) 21.5, and for case (2) 3.1 or 2.1 for hydrolysis of a protium or deuterium silane, respectively. The experimental values (Table IV) are 4.0 for tripropylsilane, 7.0 for triphenylsilane and 7.2 for triphenylsilane-*d*.

Although the calculations are only approximate, for reasons already mentioned, the experimental results are sufficiently close to the values calculated for case (2) to support the hypothesis of considerable hydrogen–hydrogen bonding in the transition state.

That the calculated value of $k_{\mathrm{SH}}/k_{\mathrm{ST}}$ for the deuterosilane is considerably smaller than that for the protium compound, while the experimental values are nearly equal, is probably attributable to the crudeness of the calculations. In particular, if instead of a free hydrogen molecule in the transition state there is some residual bonding of hydrogen to silicon, the theoretical values for the two compounds would be considerably closer. Taking into account the pre-exponential factors of equation 1 might also help resolve the discrepancy.

Acknowledgment.—We are indebted to Dr. D. A. Hutchison and Mr. L. G. Pobo for mass spectrometric analyses.

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Organotin Halides with Diazomethane

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Halomethyl derivatives of tin have been prepared in good yield by the reaction of diazomethane with six organotin halides, and the fully alkylated derivatives of the type R_3SnCH_2X have been prepared. The adverse physiological effects of compounds of the type $(CH_3)_2(CH_2X)SnX$ are pointed out. The properties of 14 new organotin compounds are reported.

While side-chain chlorination and bromination of methylsilicon compounds are well known preparative methods for halomethylsilanes, such procedures cannot be applied to the preparation of halomethyltin compounds because the halogens, even under the mildest possible conditions, cause cleavage of the carbon–tin bond.[2] For example, chlorination of tetramethyltin gives methyltin chlorides and methyl chloride. Recent attempts to prepare chloroethyltin compounds by photochemical chlorination and by treatment of tetraethyltin with sulfuryl chloride in the presence of a peroxide catalyst similarly were unsuccessful, and only carbon–tin bond cleavage was observed.[3]

Recent work on the reaction of diazoalkanes with halides of tin[4,5] showed that an α-haloalkyl group may be introduced by this method

$$\gt\mathrm{Sn{-}Cl} + \mathrm{CH_2N_2} \longrightarrow \gt\mathrm{Sn{-}CH_2Cl} + \mathrm{N_2}$$

However, only tin tetrahalides and their α-haloalkyl derivatives were treated in this manner before our study.

We have extended the application of the diazomethane reaction to five alkyltin halides and one aryltin halide. Treatment of dimethyltin dichloride, dibromide, or diiodide with slightly more than one equivalent of diazomethane in ether at 5° accompanied by *extremely vigorous stirring* during the addition gave the corresponding halomethyldimethyltin halides in yields of 70–80, 73 and 78%, respectively. The liquid products are all powerful lachrymators and vesicants, decreasing somewhat in potency as the atomic weight of the halogen increases. They are extremely irritating to the eyes, nose and throat, and cause very painful irritations of sensitive areas of the skin, particularly on the eyelids. In direct contact with the skin, even in solution, they cause painful blisters similar to those caused by alkylmercuric halides. Some irritating effects were even noticed during recrystallization of solid, high-melting halomethyltin fluorides. The trialkyltin halides in general are known to be decidedly toxic as well as irritating.[6,7] It is strongly recommended that great caution be exercised in handling the halogenated trialkyltin halides described in this report.

The physiological properties of the halomethyldimethyltin halides do *not* seem to be due to the presence of the halomethyl groups; rather they seem to be a function of the trialkyltin group. This is dem-

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onstrated by the pleasant odor and lack of irritating effect of chloromethyltrimethyltin, in high contrast to the effect of chloromethyldimethyltin chloride. This peculiarity of the trialkyltin halides is under extensive study elsewhere.[6,7] We have found butyltin compounds containing the chloromethyl group to be less irritating than methyltin compounds.

It was impossible to isolate bromomethyldiphenyltin bromide from the reaction of diphenyltin dibromide with diazomethane. The product and unchanged starting material could not be separated by fractional distillation at very low pressure. It has been reported, however, that diorganotin difluorides are soluble in excess of potassium fluoride solution, while triorganotin fluorides are not,[8] which should make possible a separation by treatment of the distillate with a large excess of neutral aqueous-alcoholic potassium fluoride solution. We found that bromomethyldiphenyltin fluoride precipitated as an amorphous white solid which could be purified by recrystallization from a methanol–95% ethanol mixture. Iodomethyldimethyltin fluoride similarly was prepared from iodomethyldimethyltin iodide.

The methylenation of triorganotin halides could not be effected in ether solution at 5–10°. When triphenyltin chloride, triphenyltin iodide and tri-*n*-butyltin chloride were treated with excess diazomethane under these conditions, only the starting materials were recovered. It should be noted that Yakubovich and his co-workers[4,5] prepared tetrakis-(halomethyl)-tin compounds in good yield by treating tin tetrahalides with diazomethane in benzene solution. Furthermore, in the reactions of chlorosilanes, it was found[9] that the presence of a halomethyl group seems to offer less hindrance to further methylenation than an unsubstituted methyl group. It seems possible that this effect operates, though more weakly, in the alkyltin halides. It is also possible that the triorganotin halides that we attempted to methylenate were too hindered to permit ready access of the attacking diazomethane molecule.

We have prepared chloromethyltrimethyltin, bromomethyltrimethyltin and chloromethyl-tri-*n*-butyltin in yields of 73, 71 and 80%, respectively, by the action of the Grignard reagent on halomethyldialkyltin halides. In addition iodomethyltrimethyltin was obtained by the reaction of chloromethyltrimethyltin with sodium iodide in anhydrous acetone.

All three halomethyltrimethyltin compounds form Grignard reagents in about 90% yield, and these should make possible the study of the almost unknown field of aliphatic organofunctional tin chemistry.

Thiocyanomethyltrimethyltin was prepared by adding a mixture of chloromethyltrimethyltin and bromomethyltrimethyltin to a warm solution of sodium thiocyanate.[10] Sodium halide precipitated immediately; the yield of thiocyanomethyltrimethyltin was 69%.

Experimental

1. **Organotin Halides.**—Dimethyltin dichloride prepared as described elsewhere[11] was purified by recrystallization from benzene. *Anal.* Calcd. for $C_2H_6SnCl_2$: C, 11.34; H, 2.84; Cl, 32.28. Found: C, 11.15; H, 3.00; Cl, 32.21. Dimethyltin diiodide (m.p. 43–45°) was prepared in 77.5% yield by reaction of dimethyltin dichloride with an equivalent amount of sodium iodide in acetone solution and was recrystallized from anhydrous ether. Dimethyltin dibromide was obtained in 54% yield by treatment of dimethyltin oxide[12] with 48% aqueous hydrobromic acid, concentration of the aqueous solution, extraction with ether and evaporation of the ether extracts.[13] Recrystallization from 30–60° petroleum ether to which a small amount of anhydrous ethyl ether had been added gave pure dimethyltin dibromide, m.p. 75°. Diphenyltin dibromide was prepared by bromination of tetraphenyltin.[14]

2. **Diazomethane.**—The diazomethane solutions were prepared as described in our previously reported methylenations of germanium and silicon chlorides.[15]

3. **Reaction of Diazomethane with Alkyltin Halides.**—The preparation of chloromethyldimethyltin chloride is given as an example of the procedure used.

A solution of 50 g. (0.228 mole) of dimethyltin dichloride in 750 ml. of anhydrous ether in a three-liter, three-necked flask equipped with a mechanical stirrer, a reflux condenser and a one-liter dropping funnel was cooled to 5°. A solution of 0.35 mole of diazomethane in 500 ml. of ether at −5° was added slowly with *vigorous stirring.* The diazomethane solution was decolorized immediately on contact with the dimethyltin dichloride solution, and evolution of nitrogen was observed. After the addition was completed the reaction mixture was light yellow in color. Stirring was continued and the reaction mixture was allowed to warm up to room temperature. The now colorless reaction mixture smelled strongly of a trialkyltin compound. The ether was removed by distillation at atmospheric pressure. The residue was transferred to a 100-ml. round-bottomed flask and fractionation was continued using a 12-inch Vigreux column equipped with a reflux head. A single fraction, b.p. 76–79° at 10.5 mm., chloromethyldimethyltin chloride, 38.7 g., a yield of 72.8%, was obtained. In similar runs yields ranging from 65 to 80% were obtained.

Methylenations of the other alkyltin compounds mentioned in the discussion above were carried out using the same procedure, except that in the attempted methylenations of the triorganotin halides copper powder was added as a catalyst. The new compounds so prepared, together with their physical properties and their analyses, are listed in Table I.

4. **Chloromethyltrimethyltin.**—A Grignard reagent was prepared from 36.6 g. (1.5 g. atom) of Mg turnings and 150 g. (1.58 moles) of methyl bromide in 400 ml. of anhydrous ether. Chloromethyldimethyltin chloride, 120 g. (0.513 mole), dissolved in an equal volume of ether, was added at such a rate that a moderate reflux was maintained. The reaction mixture was refluxed for 18.5 hours after the addition was completed. The reaction mixture subsequently was cooled to 0° and hydrolyzed by adding 180 ml. of saturated ammonium chloride solution. Separation of the ether layer, removal of the ether and fractionation of the residue through a 12-inch Vigreux column at reduced pressure gave 80.0 g. of chloromethyltrimethyltin, b.p. 44–48° at 15 mm., a yield of 73%. In subsequent runs yields ranging from 65 to 75% were obtained. Chloromethyltrimethyltin was fractionated at reduced pressure, although its boiling point is relatively low (146° by the micro-method), since during fractionation at atmospheric pressure some decomposition seemed to occur.

Bromomethyltrimethyltin was obtained from bromomethyldimethyltin bromide, and chloromethyl-tri-*n*-butyltin from chloromethyl-di-*n*-butyltin chloride, using procedures identical with that outlined above. The properties of the products are listed in Table I.

5. **Iodomethyltrimethyltin.**—Chloromethyltrimethyltin, 15.0 g. (0.07 mole), was added to 15 g. (0.1 mole) of sodium

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Table I

Organotin Compounds Prepared by the Diazomethane Method Together with Some of their Derivatives

Compound	Yield, %	B.p. °C.	B.p. Mm.	n^{25}_{D}	d^{25}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Other, % Calcd.	Other, % Found
$(CH_3)_2(CH_2Cl)SnCl$	70–80	76.7	11	1.5263		15.42	14.97	3.45	3.35		
$(CH_3)_2(CH_2Br)SnBr$	73	75–79	3.5–4	1.5683		11.17	11.72	2.50	2.66		
$(CH_3)_2(CH_2I)SnI$	78	111–111.2	5	1.6690		8.6	8.76	1.92	1.98		
$(CH_3)_2(CH_2I)SnF$	..	*d*				11.67	11.24	2.61	2.93	38.45	38.78[a]
$(n\text{-}C_4H_9)_2(CH_2Cl)SnCl$	74.5	106–110	0.3	1.5095	1.378	33.9	34.01	6.32	6.30		
$m\text{-}C_4H_9(CH_2Cl)_2SnCl$	57.9	82–87	0.18–0.2	1.5394	1.649	23.22	23.34	4.22	4.21	38.26	38.06[a]
$(C_6H_5)_2(CH_2Br)SnF$	..	*e*				40.50	41.66	3.14	3.37		
$(CH_3)_3SnCH_2Cl$	73	44–48	15	1.4860	1.556	22.52	22.65	5.20	5.35	16.62	17.61[b]
$(CH_3)_3SnCH_2Br$	71	46.2–50	11	1.5070	1.722	18.64	18.79	4.30	4.42		
$(CH_3)_3SnCH_2I$	78	53–54.5	6.5	1.5510		15.78	15.92	3.65	3.70		
$(n\text{-}C_4H_9)_3SnCH_2Cl$	80	108–112	0.5	1.4801	1.135	45.99	47.03	8.61	8.89[c]		
$(CH_3)_3SnCH_2SCN$	69	104–105	4	1.5247	1.491	25.45	25.52	4.70	4.81		

[a] Tin. [b] Chlorine. [c] Repeated fractionation did not improve the C, H values. [d] Dec. ~290°. [e] M.p. >260°.

iodide dissolved in 100 ml. of anhydrous acetone. Sodium chloride precipitated immediately. The mixture was refluxed for 22 hours, cooled and filtered. Distillation of the acetone at atmospheric pressure and fractionation of the residue gave 16.6 g. of iodomethyltrimethyltin, a yield of 78%. The product, originally colorless, changed to yellow in color on standing in daylight and the odor of a trialkyltin halide became apparent. Carbon-tin bond cleavage by the liberated iodine is thus indicated.

6. **Thiocyanomethyltrimethyltin.**—To a hot solution of 5.7 g. (0.7 mole) of sodium thiocyanate in 36 ml. of 95% ethanol was added 6.1 g. (0.0285 mole) of chloromethyltrimethyltin and 10.7 g. (0.0415 mole) of bromomethyltrimethyltin. Sodium halide precipitated immediately. After the mixture had been shaken intermittently for two hours it was filtered. The filtrate was shaken with twice its volume of distilled water and the organic layer was separated. The aqueous layer was extracted twice with ether. After drying of the combined organic layer and ether extracts the ether was removed by distillation and the residue was fractionated to give 11.4 g. of thiocyanomethyltrimethyltin. The originally colorless product turned red on standing in a stoppered vial in the dark.

This method also was successfully applied to the preparation of organotin compounds in which the thiocyanate group is linked to the tin atom. Dimethyltin dithiocyanate and di-*n*-butyltin dithiocyanate were prepared from the respective chlorides in this manner in good yield. In these preparations the filtrate was not washed with water, but was evaporated to leave the crude, crystalline thiocyanates which were purified by recrystallization. Dimethyltin dithiocyanate $(CH_3)_2Sn(SCN)_2$, fine white needles from benzene, m.p. 198.6–199.4° (dec. to a red liquid). *Anal.* Calcd. for $C_4H_6S_2N_2Sn$: C, 18.15; H, 2.28. Found: C, 18.31; H, 2.50. Dibutyltin dithiocyanate $(n\text{-}C_4H_9)_2Sn(SCN)_2$, fine white needles from chloroform, m.p. 144–145°. *Anal.* Calcd. for $C_{10}H_{18}S_2N_2Sn$: Sn, 34.00. Found: Sn, 34.02.

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[Contribution from the Chemistry Division, Oak Ridge National Laboratory]

The Low Temperature Heat Capacity and Entropy of Cadmium Iodide

By A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen

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The heat capacity of crystalline cadmium iodide has been measured between 15 and 300°K. At 298.16°K. C_p = 19.11 cal./mole deg. and S^0 = 38.5_0 e.u. of which 1.5 e.u. has been obtained by extrapolation below 15°K. Heat capacity, entropy and certain derived thermodynamic quantities are tabulated at 10° intervals up to 300°K. The heat capacity of cadmium iodide rises so rapidly at very low temperatures that near 15°K. it varies approximately as $T^{1.4}$. Nowhere above 15°K. does the heat capacity follow either the Debye T^3 law or the T^2 relationship shown by certain substances which have layer lattice structure.

A number of recent studies of crystalline substances with so-called "layer structure" have shown that, where this structure is sufficiently pronounced, the heat capacity follows a T^2 dependence and does not follow the usual Debye T^3 law in the approximate range 15 to 60°K. Thus, graphite,[1] gallium[2] and boron nitride[3] have been shown to obey the T^2 relationship and suggestions have been made[4] concerning similar behavior in other compounds.

Crystalline cadmium iodide, CdI_2, has a so-called "layer structure"[5] but with less marked anisotropy than is the case with graphite or boron nitride. The iodines form a nearly perfect hexagonal close packed array with cadmiums occupying octahedral holes of alternate layers, so that the lattice of cadmium iodide is rather like a stack of sandwiches. Thus, it was of considerable interest to learn whether cadmium iodide is sufficiently layer-like to cause the low-temperature heat capacity to follow a T^2 dependence. Furthermore, we were interested in determining thermodynamic constants

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