wires to prevent contact with the block at any other place except the very ends, which are twisted together.

Lamps of suitable resistance are placed in parallel. One ampere with 230 volts is sufficient to weld the common wires employed as thermocouples. However, wires of larger gage may be welded by decreasing the resistance.

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STUDIES RELATING TO ALKYL TIN COMPOUNDS. I. SOME STANNOETHANES. II. TRIMETHYLBENZYL STANNANE

BY CHARLES A. KRAUS AND RALPH H. BULLARD[1]

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I. Some Stannoethanes

Introduction.—The elements of the fourth group of the periodic system (not including titanium) form compounds of the type $R_3M.MR_3$, where M is an element of the fourth group and R is an organic group or hydrogen. In these compounds the stability of the bond between the atoms of the element M depends upon the nature of the central element as well as upon that of the substituent groups R. In general, the more electronegative the central element M, the more stable is the bond between the atoms of that element. Thus, tin atoms are bonded much more loosely than are atoms of germanium or silicon. The bond between carbon atoms is extremely stable with the exception of compounds in which the substituents R are aryl or very heavy alkyl groups. The stability of a bond between two carbon atoms in these compounds is the weaker the heavier the substituent groups.

In the case of carbon, these compounds are spoken of as methyls as, for example, triphenylmethyl, the idea being that these compounds consist actually of the free substituted methyl groups. Here there is an attempt to differentiate between the C—C bond as it occurs in the methyls on the one hand and carbon-chain compounds on the other. Such differentiation appears somewhat arbitrary, particularly in the case of other elements of the fourth group, such as lead, tin, germanium and silicon. Little is known with regard to the stability of the Pb—Pb bond. In the case of tin compounds, the Sn—Sn bond is fairly stable, particularly when phenyl groups are the substituents. The Ge—Ge bond appears to be very stable. Probably the stability of the Si—Si bond is even higher than that of germanium.

In view of the gradation in the strength of the bonds of the type M—M

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in the case of the elements of the fourth group, it is not possible to draw a sharp line of distinction between true chain compounds and free radicals such as triphenylmethyl. It appears logical, therefore, to classify these compounds as chains rather than as unsaturated groups. While it is true that, under suitable conditions, certain of these compounds dissociate into their constituent radicals in varying degree, we cannot well utilize this property as a basis for a system of classification.

The free valences of the groups are, in fact, mutually satisfied. The tendency for groups of this type to combine is strictly analogous to that of the atoms of the electronegative elements to polymerize in the free state. While, for example, iodine is dissociated into its atoms at higher temperatures, under ordinary conditions it exists in the dimolecular form in the vapor state and in solution it may have even more complex molecules.

It is an interesting fact that in the case of tin the Sn—Sn bond is much more stable when the substituents are aryl than when they are alkyl groups. In the case of carbon the reverse is true. It seems not unlikely that steric hindrance is involved here. It might be expected that such effects would play a diminishing role as the effective area of the atom increased.

The present investigation was undertaken for the purpose of preparing a number of compounds involving the Sn—Sn bond and gaining some notion with regard to their stability.

A number of compounds of the type $R_3'Sn\cdot SnR_3''$ have been prepared in the present investigation and it has been shown that in benzene at higher temperatures these compounds undergo reaction with the formation of the compounds $(R'_3Sn)_2$ and $(R''_3Sn)_2$. Incidentally, compounds between groups containing different substituents may be made according to two distinct reactions, namely

$$R'_3SnNa + BrSnR''_3 = NaBr + R'_3Sn\cdot SnR''_3 \qquad (1)$$
$$R''_3SnNa + BrSnR'_3 = NaBr + R''_3Sn\cdot SnR'_3 \qquad (2)$$

The two reactions lead to the formation of the same compound but it is of interest to note that, in the case of reactions involving the trimethyltin and triphenyltin groups, one proceeds quantitatively while the other leads to a mixture of stannoethanes.

Hexamethyl Stannoethane, $(CH_3)_3Sn\cdot Sn(CH_3)_3$.—This compound was prepared according to the method of Kraus and Sessions[2] by the reduction of trimethyltin bromide with sodium in liquid ammonia.

Since hexamethyl stannoethane is appreciably volatilized by ammonia vapor, the supernatant solvent layer was siphoned off when the reaction was completed. The stannoethane was then washed with water, separated from the water layer and dried by filtering through sodium sulfate in an atmosphere of nitrogen. Finally, the liquid was transferred to small weighed tubes in an atmosphere of nitrogen and sealed; yield 84% of pure material.

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[2] Kraus and Sessions, This Journal, **47,** 2361 (1925).

Anal. Subs., 0.5260 g.: SnO_2, 0.4833. Calcd. for $[(CH_3)_3Sn]_2$: Sn, 72.48. Found: 72.37.

Mol. wt. Subs., 0.3268, 0.6592; in benzene, 22.28, 22.28: Δt, 0.225, 0.450. Calcd. for $[(CH_3)_3Sn]_2$: mol. wt., 327.6. Found: 326.0, 328.7, av., 327.4.

These results show clearly that even at fairly low concentrations trimethyltin exists in benzene near its freezing point in the dimolecular form.

Trimethyltriethyl Stannoethane, $(CH_3)_3Sn \cdot Sn(C_2H_5)_3$.—This compound was prepared according to Reactions 1 and 2. It is a liquid at ordinary temperatures and the method of manipulation was identical with that used in the case of hexamethyl stannoethane.

So far as could be determined, the products of Reactions 1 and 2 were identical. Compounds of this type are so difficultly volatile that no test of identity is possible by comparison of their boiling points. Both products remained liquid at temperatures as low as —60°. That the product of this reaction did not consist of a mixture of hexamethyl and hexa-ethyl stannoethanes was shown by comparing the properties of the compound with those of mixtures of the two stannoethanes. Hexamethyl stannoethane melts at 23.3° and, according to Sessions[3] and Towne,[4] hexa-ethyl stannoethane is liquid at the temperature of boiling ammonia. In the present investigation, it failed to solidify at —75°. According to Towne,[4] the melting point of hexamethyl stannoethane is lowered on addition of the corresponding ethyl derivative. While Towne's melting-point curve is incomplete, it is clear from his observations that these two stannoethanes form neither compounds nor solid solutions. In view of the very low melting point of the ethyl derivative, the eutectic evidently lies very near to the axis of the methyl compound at a temperature somewhere below —75°. Towne found that in an equimolecular mixture of the two stannoethanes, crystals of hexamethyl stannoethane appear at about —5°. In the present investigation a mixture containing 49.62 mole % of hexamethyl stannoethane and 50.38 mole % of hexa-ethyl stannoethane was found to precipitate crystals of the first compound at —5° which, on warming, disappeared at —3.5°. At —33°a large fraction of the methyltin derivative was precipitated from solution. In view of the fact that the products obtained by Reactions 1 and 2 showed no signs of a solid precipitate at temperatures as low as —60°, we must conclude that the product of the two reactions is a compound between the trimethyltin and triethyltin groups.

Since hexamethyl and hexa-ethyl stannoethane, according to Kraus and Sessions[2] and Rügheimer,[5] are dissociated in benzene at its boiling point, it was to be expected that, if a mixture of these compounds was dissolved in benzene at higher temperatures, reaction would occur with the

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[3] Sessions, Dissertation, Clark University, 1924.

[4] Towne, Thesis, Clark University, 1924.

[5] Rügheimer, *Ann.*, **364**, 53 (1910).

formation of a compound between the trimethyl- and triethyltin groups. To test this point, a mixture containing 44.98 mole % of the former and 50.12 mole % of the latter compound was dissolved in benzene and the solution was concentrated by boiling for 17 minutes, after which the last traces of benzene were removed with a high-vacuum pump. On cooling the resulting product, crystals appeared at —20° which, on slowly warming, disappeared at —19.1°. Since in the original mixture the solid phase (hexamethyl stannoethane) disappeared at —3.5°, it follows that reaction must have taken place in boiling benzene. It may be stated in this connection that the properties of the original pure compounds are uninfluenced as a result of solution in benzene; the pure liquid mixture retains its original properties after standing for some months.

Triphenyltrimethyl Stannoethane, $(C_6H_5)_3Sn{\cdot}Sn(CH_3)_3$.—This compound was prepared according to Reactions 1 and 2.

On treating sodium triphenyltin with trimethyltin bromide in liquid ammonia, a solid was immediately precipitated. This product was repeatedly washed with ammonia, after which the last traces of ammonia were removed with a pump. The final product melted rather sharply to a clear, colorless liquid at 106°. It showed no tendency to oxidize in air.

Anal. Subs., 0.2299, 0.3186: SnO_2, 0.1345, 0.1863. Calcd. for $(C_6H_5)_3Sn_2(CH_3)_3$: Sn, 46.24. Found: 46.09, 46.05.

Mol. wt. Subs., 1.1411, 1.9080; in benzene, 28.038, 28.038: Δt, 0.398, 0.666. Calcd. for $(C_6H_5)_3Sn_2(CH_3)_3$: mol. wt., 513.4. Found: 511.3, 511.0, av., 511.2.

In preparing the material by washing with liquid ammonia, practically no tin was carried over with the washings. In other words, the only product removed in this process is sodium bromide. Since the product was not otherwise purified and since the melting point of the product was sharp, the inference is that the reaction as carried out proceeded quantitatively.

A reaction was also carried out between sodium trimethyltin and triphenyltin bromide in liquid ammonia. A precipitate was immediately formed on introduction of the bromide. After washing with liquid ammonia, the product failed to yield a definite melting point. In most instances it began to soften at about 100°, but the solid did not completely disappear until a temperature of 150° or more was reached. This result suggested that the reaction, in this case, did not proceed quantitatively with the formation of triphenyltrimethyl stannoethane. Presumably hexamethyl and hexaphenyl stannoethane were also formed.

On dissolving the product of this reaction in ether and carrying out a series of recrystallizations, a compound was finally obtained which melted at 103°. From the residue was obtained a compound melting at 223–225°. This appeared to be impure hexaphenyl stannoethane, whose melting point is 232°.

A mixture of the product of the first reaction with the purified product of the second reaction showed the same melting point as the constituent materials. This shows that in the main the second reaction leads to the same product as the first, but while the first proceeds quantitatively, the second does not. Evidently the course of the reaction depends, in a measure, on the sign of the charge on the two groups. It is interesting to note that while trimethyltin is readily oxidized, the compound between the trimethyltin and triphenyltin groups is stable with respect to oxygen. In this respect it resembles hexaphenyl stannoethane.

II. Trimethylbenzyl Stannane, $(CH_3)_3Sn{\cdot}CH_2{\cdot}C_6H_5$

Preparation.—Sodium trimethyl stannide was treated with an equivalent quantity of benzyl chloride in liquid ammonia. Reaction takes place according to the equation

$$(CH_3)_3SnNa + C_7H_7Cl = (CH_3)_3SnC_7H_7 + NaCl \qquad (3)$$

The compound is precipitated in the form of fine drops which coalesce on stirring. This liquid was washed with water, filtered and dried. It cannot be purified readily by distillation since it decomposes when heated to 215°. The reaction proceeds quantitatively and the product obtained appeared to be quite pure.

Anal. Subs., 0.4337: SnO_2, 0.2308. Calcd. for $(CH_3)_3SnC_7H_7$: Sn, 46.60. Found: 46.56.

Mol. wt. Subs., 0.5655, 1.0157; in benzene, 23.189, 23.189: Δt, 0.4715, 0.875. Calcd. for $(CH_3)_3SnC_7H_7$: mol. wt., 254.7. Found: 258.6, 250.3, av., 254.6.

Bromination of Trimethylbenzyl Tin.—According to Grüttner and Krause,[6] when a quaternary organic tin compound is brominated at low temperatures, the lightest group is substituted. An attempt was made to carry out such bromination in the case of the monobenzyl derivative. It was found that the benzyl rather than a methyl group is replaced on bromination.

A weighed quantity of trimethylbenzyl tin was dissolved in ether and to this was added the equivalent quantity of bromine dissolved in ether, the solution being cooled to liquid ammonia temperatures. This method is recommended by Grüttner and Krause.[7] After evaporation of the ether the resulting product was distilled, the distillate coming over between 174° and 200° being collected. Such change of boiling point, alone, shows that the reaction did not proceed as was expected.

Mol. wt. Subs., 0.6057, 1.1372; in benzene, 23.786, 23.786: Δt, 0.637, 1.172. Calcd. for $(CH_3)_3SnBr + C_7H_7Br$: mol. wt., 208. Found: 199.9, 204.0, av., 202.0.

According to molecular-weight determinations, then, the product obtained on brominating trimethylbenzyl tin consists of a mixture of trimethyl tin bromide and benzyl bromide in equimolar proportions. Apparently in this instance the heavier rather than the lighter group is substituted on bromination.

Summary

1. The molecular weight of hexamethyl stannoethane in benzene by the cryoscopic method corresponds to the formula $[(CH_3)_3Sn]_2$.

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[6] Grüttner and Krause, (a) *Ber.*, **49**, 1128 (1916); (b) **50**, 203, (c) 1804 (1917).

[7] Ref. 6 a, p. 1419. Ref. 6 c.

2. An equimolecular liquid mixture of hexamethyl and hexa-ethyl stannoethane is in equilibrium with solid hexamethyl stannoethane at —3.5°. A mixture of the two compounds in boiling benzene solution gives evidence of interaction between the trimethyl- and triethylstannyl groups.

3. The mixed stannoethanes, $(CH_3)_3Sn\cdot Sn(C_2H_5)_3$ and $(CH_3)_3Sn\cdot Sn(C_6H_5)_3$, have been prepared and some of their properties studied. The compounds were prepared by two reactions in which the charges on the interacting groups were, respectively, reversed. The same compounds were formed in the two cases, but one reaction in the case of the phenyl derivative led to the formation of the pure compound and the other to a mixture of this compound with hexamethyl and hexaphenyl stannoethanes.

4. Trimethylbenzyl tin has been prepared. On brominating this compound in ether solution at liquid ammonia temperatures, the benzyl group is substituted.

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[CONTRIBUTION FROM THE PROTEIN INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE ROLE OF THE PROTEOLYTIC ENZYMES IN THE DECOMPOSITION OF THE HERRING[1]

BY L. H. ALMY

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The immature herring, *Clupea harengus*, is canned as the sardine in Maine. According to the usual procedure, the fish are caught in weirs, transferred to the hold of the sardine boat, treated there with salt, and transported to the factory, where they are washed, held in brine for one to two hours, removed therefrom and steamed for ten or fifteen minutes, dried somewhat in a current of warm air, and packed in cans. Mustard or oil is added, and the cans are capped, sealed and processed.[2]

Ordinarily the fish decompose very little before they are canned, as the interval between their removal from the water and their steaming is comparatively short. When caught, the fish are usually in search of food; occasionally a large proportion of the herring taken from a weir have feed in their digestive tracts. Such "feedy" fish decompose rapidly, and

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[2] For details of the canning process see Weber, "The Maine Sardine Industry," *U. S. Dept. of Agriculture Bull.*, No. 908 (1921).