Summary

Some crystalline complex compounds of cobalt and thioglycolic acid have been prepared and on the basis of chemical analysis and oxygen consumption their possible constitutions have been discussed. The bearing of these constitutions on the heavy metal catalysis of the oxidation of thiol acids has been pointed out.

New York, N. Y.

[Contribution from the Chemical Laboratory of Brown University]

STUDIES RELATING TO METHYL TIN DERIVATIVES. VI. THE REACTION BETWEEN CHLOROFORM AND SODIUM TRIMETHYL STANNIDE IN LIQUID AMMONIA

By Charles A. Kraus and Arthur M. Neal

Received July 11, 1930 Published November 5, 1930

As was shown in an earlier paper[1] sodium trimethyl stannide reacts with methylene chloride in liquid ammonia with the formation of di-trimethyl stannyl methane. It might, therefore, be expected that a corresponding reaction would take place between chloroform and sodium trimethyl stannide according to the equation

$$3(CH_3)_3SnNa + CHCl_3 = [(CH_3)Sn]_3CH + 3NaCl \qquad (I)$$

Indeed, when chloroform is added to a solution of sodium trimethyl stannide in liquid ammonia, reaction takes place immediately with the formation of a white precipitate which, in part at least, is solid. On evaporation of the ammonia, an oily liquid is left behind, which might be expected to be tri-trimethyl stannyl methane. A closer investigation of this liquid, however, showed that it consisted of at least two substances and it was found necessary to examine the product at length in order to establish the nature of the substances in question. The various experiments relating to this study are described below.

Preliminary Experiments.—A quantity of sodium trimethyl stannide was treated with chloroform in liquid ammonia. When the reaction was completed, the ammonia was allowed to evaporate and the oily liquid left behind was washed several times, first with ammonia water and, finally, with distilled water. The liquid was separated from the water layer and dried by filtering through anhydrous sodium sulfate in an atmosphere of nitrogen. Samples were sealed in weighed tubes from which the air had been displaced by nitrogen.

Samples of the product were analyzed for tin by the Carius method.

Anal. Subs., 0.3403, 0.3841: SnO_2, 0.3046, 0.3433. Calcd. for $[(CH_3)_3Sn]_3CH$: Sn, 70.64. Found: Sn, 70.73, 70.40.

The molecular weight of the compound was determined by the cryoscopic method with benzene as solvent.

---

[1] Kraus and Neal, This Journal, **52**, 695 (1930).

Mol. wt. Solvent, 33.25, 33.25; solute, 0.8495, 0.7541; Δt, 0.400, 0.335°; mol. wt., 319.1, 338.5. Calcd. for $[(CH_3)_3Sn]_3CH$: mol. wt., 504.1.

While the results of analysis correspond fairly well with those required for tri-trimethyl stannyl methane, the mean molecular weight of the substance in benzene is clearly incompatible with this formula. A re-examination of the product initially formed in liquid ammonia showed that it was partly liquid and partly solid at liquid ammonia temperatures and that the solid disappeared at 0°.

It was suspected that the product was a mixture, one constituent of which was trimethyl tin. The latter compound combines readily with iodine and the trimethyl tin iodide formed may be precipitated from most solvents by means of gaseous ammonia. Accordingly, known weights of the original preparation were treated with a standard solution of iodine in carbon tetrachloride. In four experiments, from 1.7 to 1.8 atoms of tin in the original mixture reacted with one atom of iodine. In other words. approximately four-sevenths of the original mixture consisted of trimethyl tin. It is difficult to account for this ratio except by assuming a loss of trimethyl tin in the process of purification. This is borne out by the variation observed in this ratio.

The solutions, after iodination, were treated with ammonia. Any trimethyl tin iodide present was precipitated and recovered. Samples of the precipitated product were analyzed for iodine and tin.

Anal. Subs., 0.2332, 0.3757: AgI, 0.1760, 0.2852. Calcd. for $(CH_3)_3SnI \cdot NH_3$: I, 41.25. Found: I, 40.79, 41.03. Subs., 0.1682: SnO_2, 0.0838. Calcd. for $(CH_3)_3SnI \cdot NH_3$: Sn, 38.59. Found: Sn, 39.24.

The analyses, as well as the properties of the compound, show clearly that trimethyl tin iodide is one of the products of iodination of the original mixture. Nearly all the iodine concerned in the reaction is converted to trimethyl tin iodide. In one experiment, 2.716 g. of iodine was required for iodination and 2.566 g. was recovered as trimethyl tin iodide.

Seemingly, one constituent of the original product of reaction between sodium trimethyl stannide and chloroform is trimethyl tin. The second constituent of this product appears to be resistant to the action of iodine and, even, as later experiments have shown, to bromine at ordinary temperatures. The original reaction proceeds smoothly and, seemingly, quantitatively, except for losses that seem to be due chiefly to trimethyl tin. We may account for the products of the reaction by assuming that tri-trimethyl stannyl methane is formed as an intermediate product according to Equation I, and that this, in turn, breaks down according to the reaction equation

$$2[(CH_3)_3Sn]_3CH = 2[(CH_3)_3Sn]_2 + (CH_3)_3SnCH{=}CHSn(CH_3)_3 \qquad \text{(II)}$$

The second constituent of this reaction. di-trimethyl stannyl ethylene, is an unsaturated aliphatic derivative and might be expected to add halogens. This, however, is not the case. Nevertheless, the experiments which we have carried out seem to indicate that this compound is, in fact, formed as one of the products of interaction between sodium trimethyl stannide and chloroform.

Properties of Di-trimethyl Stannyl Ethylene.—The second constituent of the product formed by the interaction of chloroform and sodium trimethyl stannide was isolated by evaporating the ethereal solution after removal of the trimethyl tin by means of iodine and ammonia, as described above. The last traces of ether were removed by means of a vacuum pump. The resulting product appeared to be a substantially pure compound which is quite stable and which boils at 194–195° under atmospheric pressure. It does not solidify at liquid ammonia temperatures.

The molecular weight of the compound was determined by the cryoscopic method, using benzene as solvent. The following results were obtained.

Mol. wt. Solvent, 35.60, 18.72, 19.49; solute, 1.7447, 0.2169, 0.9320; Δt, 0.704, 0.166, 0.692°; mol. wt., found, 348.0, 349.0, 345.6; calcd. for $[(CH_3)_3SnCH]_2$, 353.4.

The last experiment was carried out with a sample specially purified, as will be described below.

The compound was analyzed for tin by the Carius method.

Anal. Subs., 0.2521, 0.2038, 0.1952: SnO_2, 0.2153, 0.1729, 0.1665. Calcd. for $[(CH_3)_3SnCH]_2$: Sn, 67.17. Found: Sn, 67.27, 66.83, 67.19: mean, 67.10.

Carbon and hydrogen determinations were also made on the compound but it was difficult to obtain entirely satisfactory results, owing chiefly to the fact that it was very difficult to obtain an even combustion of the material.[2] The following results were obtained.

Anal. Subs., 0.2672, 0.4356, 0.1910: H_2O, 0.1444, 0.2368, 0.3901; CO_2, 0.2604, 0.3901, 0.1779. Calcd. for $[(CH_3)_3SnCH]_2$: H, 5.70; C, 27.15. Found: H, 6.05, 6.09, 6.19, mean, 6.11; C, 26.58, 24.43, 25.39, mean, 25.47.

While the results of these analyses are somewhat variable, when taken in connection with the analyses for tin and the molecular weight of the compound, there seems little doubt but that the formula assigned to it is correct. It seems strange, however, that a compound having a pair of doubly bonded carbon atoms should be so stable, generally, toward the halogens.

If di-trimethyl stannyl methane is one of the primary products of the original reaction, then, in order to account for the results obtained on iodination, it is necessary to assume that some trimethyl tin is lost prior to iodination. It seems that the difference in the tin content of a mixture corresponding to the formula $[(CH_3)_3Sn]_3CH$ and one in which three parts of the ethylene derivative are mixed with four parts of trimethyl tin, might be detected by analysis. Accordingly, careful analyses for tin were carried out by the Carius method with the following results.

Anal. Subs., 0.4761, 0.1698: SnO_2, 0.4238, 0.1511. Found: Sn, 70.12, 70.10; mean, 70.11.

For a mixture corresponding to the formula of tri-trimethyl stannyl methane, 70.64% of tin is required, while for a mixture containing three moles of the ethylene compound to four moles of trimethyl tin, $[(CH_3)_3Sn]_2$, 70.20% is required.

Bromination of $[(CH_3)_3SnCH]_2$.—Although di-trimethyl stannyl ethylene is inactive toward bromine at ordinary temperatures, bromination takes place slowly in boiling carbon tetrachloride. A known weight of the ethylene derivative was accordingly treated with bromine and, when the reaction was completed, the mixture was allowed to cool and ammonia was passed through the solution. A precipitate was formed which, on analysis, was shown to be diammino dimethyl tin dibromide, $(CH_3)_2SnBr_2\cdot 2NH_3$. The precipitate was thrown on a filter, washed, dried and analyzed.

Anal. Subs., 0.1914, 0.3170: AgBr, 0.2128, 0.3484. Calcd. for $(CH_3)_2SnBr_2\cdot 2NH_3$: Br, 46.66. Found: Br, 47.34, 46.78. Subs., 0.1461: SnO_2, 0.0632. Calcd. for $(CH_3)_2SnBr_2\cdot 2NH_3$: Sn, 34.66. Found: Sn, 34.07.

The amount of tin recovered in the form of dimethyl tin dibromide was 1.1 g., while the amount of tin present in the original compound was 1.17 g. It seems that, on bromination, the following reaction occurs

$$(CH_3)_3SnCH{=}CHSn(CH_3)_3 + 4Br_2 = 2(CH_3)_2SnBr_2 + 2CH_3Br + 2C_2H_2Br_2 \quad \text{(III)}$$

Action of Sodium on Di-trimethyl Stannyl Ethylene in Liquid Ammonia.—To gain some further knowledge as to the constitution of the above compound, it was introduced

---

[2] For these determinations we are indebted to Mr. E. Alison Flood of this Laboratory.

into a reaction tube and treated with metallic sodium in liquid ammonia. As reaction proceeded, gas was evolved, the solution acquired a yellow color and a fine granular precipitate was formed. This precipitate was doubtless sodium amide. The evolved gas proved to be methane. On adding ammonium bromide to the reaction products in the tube, the precipitate disappeared and a gas was evolved which proved to be hydrogen. After disappearance of the sodium amide, further addition of ammonium bromide resulted in the precipitation of an oily liquid which was highly volatile. The reactions appeared to be similar to those previously studied in the case of di-trimethyl stannyl methane.[1]

Weighed samples of di-trimethyl stannyl ethylene in sealed bulbs were introduced into the reaction tube, in which they were then broken. The compound in question had previously been prepared in considerable quantity and was subjected to fractional distillation under a pressure of 17 mm., under which condition it boiled at 85–86.5°. No sign of decomposition was observable. The product was analyzed for tin, the results of which analyses have already been given. The results of these reduction experiments are tabulated.

TABLE I

REDUCTION OF DI-TRIMETHYL STANNYL ETHYLENE

Compound, g.	Sodium, g.	Gas evolved, cc.	Mol. wt. evolved gas	M. moles compound	M. atoms sodium	Atoms sodium per mole of compound	Mole of gas per mole of compound
2.5221	0.5979	133.4	16.1	7.13	26.00	3.65	0.84
2.2803	.5979	136.6	17.7	6.45	26.00	4.03	.95

As may be seen from the table, approximately four atoms of sodium were required to reduce the compound completely. In general, an excess of metal was added, which excess was determined by titrating back with ammonium bromide. This method is not precise, as there is a tendency for particles of ammonium bromide to adhere in the colder portions of the reaction tube, which, in general, leads to values for the reacted sodium that are too low. The evolved gas was passed through a concentrated solution of sodium in liquid ammonia to remove volatile tin compounds. Any loss in the tin compounds leads to low values for the amount of gas evolved. In the two experiments for which the data are given, the compound was dropped slowly into a concentrated solution of sodium in liquid ammonia. Under these conditions, reaction takes place immediately and there is less chance for loss of the compound. The relative amount of gas obtained in these experiments was markedly higher than that obtained in earlier experiments, in which the metal was dropped into a solution of the compound in liquid ammonia.

Samples of gas were analyzed by the explosion method. The results of three such analyses are given below.

Assuming the gas to be methane, the following reaction occurs on explosion

$$CH_4 + 2O_2 = CO_2 + H_2O \text{ (liquid)}$$

TABLE II

ANALYSIS OF EVOLVED GAS

	Cubic centimeters		
Vol. gas taken	20.4	13.8	24.3
Vol. oxygen added	61.4	75.0	67.2
Total vol.	81.8	88.8	91.5
Vol. after explosion	41.0	62.4	42.8
Contraction of vol. on explosion	40.8	26.4	48.6
Vol. after absorbing CO_2	21.0	49.2	18.8
Vol. CO_2 absorbed	20.0	13.2	24.1

The contraction on explosion, should be equal to twice the volume of methane and the contraction of volume, on absorption of carbon dioxide, should be equal to the original volume of methane. As may be seen, the results of analyses are in excellent agreement with the reaction equation for methane. There can be no doubt, therefore, that when di-trimethyl stannyl ethylene is reduced by means of sodium in liquid ammonia, one mole of methane is evolved per mole of compound. The reaction equation may be written as follows

$$(CH_3)_3SnCH{=}CHSn(CH_3)_3 + 4Na + 2NH_3 = (CH_3)_3SnNa + CH_2{=}CHSn(CH_3)_2Na + 2NaNH_2 + CH_4 \quad (IV)$$

Actually, the reaction takes place in two stages. First, the linkage between a trimethyl tin group and an ethylenic carbon atom is broken down according to the reaction equation

$$(CH_3)_3Sn{=}CHSn(CH_3)_3 + 2Na + NH_3 = (CH_3)_3SnNa + CH_2{=}CHSn(CH_3)_3 + NaNH_2 \quad (V)$$

Trimethyl vinyl tin in turn is reduced by sodium, a methyl group being split off according to the equation

$$CH_2CH{=}Sn(CH_3)_3 + 2Na + NH_3 = CH_2{=}CHSn(CH_3)_2Na + CH_4 + NaNH_2 \quad (VI)$$

Thus, as a net result of the reaction, there is obtained an equimolar mixture of sodium trimethyl tin and sodium dimethyl vinyl tin.

Preparation of Trimethyl Vinyl Tin.—According to the above reaction equations, the liquid ammonia solution, on completion of the reaction, contains sodium trimethyl stannide and sodium dimethyl vinyl stannide. It is difficult to separate the trimethyl tin from the dimethyl vinyl derivative. The final product of the reaction, after evaporation of the ammonia, had a markedly different appearance from pure sodium trimethyl tin. The mixture seemed to be much more stable at ordinary temperatures and was of a bright yellow color.

It was thought that some information might be gained as to the existence of the vinyl compound by treating the reaction mixture with methyl iodide, which would lead to the formation of tetramethyl tin and trimethyl vinyl tin. This reaction was accordingly carried out. Since both tetramethyl tin and trimethyl vinyl tin are highly volatile compounds and in order to avoid loss, alcohol was added to the reaction products in the reaction tube and then water. The reaction tube was then removed from the ammonia bath and water was added until the tube was nearly filled. The supernatant aqueous solution was siphoned off and the light oil in the bottom was washed several times with fresh water. The bottom of the reaction tube was then cut off, traces of water were removed with filter paper, the tube was suspended in liquid ammonia to freeze the last drops of water and, while it was still cold, the liquid was transferred to a second tube through a fine capillary. In this tube the liquid was washed several times with liquid ammonia in order to remove traces of water. The tube was then sealed and evacuated. The molecular weight of the vapors of this liquid was then determined by the vapor density method. In general, the temperature of the tube containing the liquid was kept at least several degrees below room temperature. The pressure was read on a specially constructed closed-end manometer, the limbs of which had a diameter of 18 mm. The difference in level of the mercury columns was read by means of a cathetometer and the readings were reproducible within 0.05 mm. Appropriate corrections were applied for the temperature of the mercury, etc.

In a first series of measurements, the density varied from 184.7 initially to 194.2 at the end. There was a small amount of liquid left in the bottom of the tube at the end of these experiments which was much more difficultly volatile than the remainder. The more volatile constituents were accordingly condensed and a second series of density determinations was carried out. As may be seen from Table III, the molecular weight of the vapor increased continuously from 181.1 to 190.9. The molecular weight of tetramethyl tin is 178.8 and that of trimethyl vinyl tin is 190.8.

TABLE III

MEAN MOLECULAR WEIGHT OF VAPOR MIXTURES OF TETRAMETHYL TIN AND TRIMETHYL VINYL TIN

Volume of density bulb = 345.7 cc.

Vapor, g.	Pressure, cm.	Temp. of vapor, °C.	Mol. wt.
0.1351	4.028	26.1	181.1
.1298	3.862	25.9	181.3
.1756	5.188	26.5	183.0
.1895	5.599	26.8	183.1
.1487	4.385	27.1	183.8
.1295	3.805	27.0	184.3
.1475	4.314	27.0	186.0
.1372	3.988	27.4	186.1
.1380	4.014	27.5	186.5
.0873	2.488	28.4	190.9

The determinations of molecular weights by the vapor density method show clearly that the material consisted of a mixture of two substances whose molecular weights correspond closely to those of tetramethyl tin and trimethyl vinyl tin. Further work will be required in order to definitely establish the existence of trimethyl vinyl tin. The results support the experiments previously described as indicating the formation of di-trimethyl stannyl ethylene when sodium trimethyl tin reacts with chloroform.

An attempt was made to prepare di-trimethyl stannyl ethylene by the action of sodium trimethyl tin on acetylene chloride. It was found that, while reaction took place readily, the tin derivative was all converted to trimethyl tin.

Action of Carbon Tetrachloride on Sodium Trimethyl Tin and Sodium Triethyl Tin.—Carbon tetrachloride reacts readily with sodium trimethyl tin, the chief product of the reaction being trimethyl tin or hexamethyl stanno-ethane. The trimethyl tin separates as the reaction proceeds. A sample of the product gave a molecular weight of 319.5 in benzene, which is in good agreement with 327.4, the molecular weight of the stanno-ethane. On analysis, it was shown that the compound contained 72.65% of tin, while that required for hexamethyl stanno-ethane is 72.48.

All the tin originally present in the reacting materials was recovered as stanno-ethane. In one experiment 0.155 cc. of carbon tetrachloride was allowed to react with sufficient sodium trimethyl tin to complete the reaction. The carbon tetrachloride used was equivalent to 0.2208 g. of chlorine. The chlorine was recovered in the form of silver chloride at the end of the reaction. The silver chloride weighed 0.8706 g., which is equivalent to 0.2154 g. of chlorine. This shows that the chlorine was completely removed from the carbon tetrachloride. What happens to the carbon atom of the tetrachloride has not, as yet, been determined. It probably reacts with the solvent.

Sodium triethyl tin reacts with carbon tetrachloride in the same way as does sodium trimethyl tin. The chief product of the reaction is hexaethyl stanno-ethane. The molecular weight (in benzene) of the product obtained was 413.1, as against 411.4 required for the stanno-ethane.

Summary

The reaction between chloroform and sodium trimethyl stannide in liquid ammonia has been investigated. A tertiary substitution product is not formed but there is produced a mixture of trimethyl tin and di-trimethyl stannyl ethylene. The latter compound is a liquid boiling at 194–195° and having a normal molecular weight in benzene. The halogens do not add readily to the ethylenic group. At higher temperatures bromine reacts with the formation of dimethyl tin dibromide.

On reducing di-trimethyl stannyl ethylene with sodium in liquid ammonia

there is formed an equimolar mixture of sodium trimethyl stannide and sodium dimethyl vinyl stannide, along with methane and sodium amide. On adding methyl iodide to this mixture there is produced a mixture of tetramethyl tin and trimethyl vinyl tin. Trimethyl vinyl tin has not as yet been obtained in the pure state.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

THE FRIEDEL AND CRAFTS REACTION WITH 8-HYDROXYQUINOLINE

BY KONOMU MATSUMURA

RECEIVED JULY 14, 1930 PUBLISHED NOVEMBER 5, 1930

On adopting the method of Behn and Rosenmund,[1] the Friedel and Crafts reaction was found to be applicable to 8-hydroxyquinoline and this paper deals with the preparation of 5-acetyl-, 5-benzoyl- and 5-chloro-acetyl-8-hydroxyquinoline. That the acyl radicals which have been introduced occupied position 5 could be ascertained by converting these compounds into the known substances either by a Beckmann rearrangement of their oximes or by reduction, respectively.

Experimental

5-Acetyl-8-hydroxyquinoline.—On introducing acetyl chloride (25 g.) into the solution of 8-hydroxyquinoline (43.5 g.) in nitrobenzene (400 g.), yellow precipitates separated. On the addition of aluminum chloride to it 100 g. at a time under shaking, the precipitates disappeared and a clear solution resulted. It was kept at 70° for twelve hours in a flask fitted with a calcium chloride tube. On cooling, some crushed ice and 100 cc. of hydrochloric acid (10%) were added to it and the separated nitrobenzene was driven off with steam. On standing overnight, the separated hydrochloride of 5-acetyl-8-hydroxyquinoline was filtered. It was dissolved in water and on the addition of sodium acetate to it, the free base separated out. It was recrystallized from hot water; yield, 25.5 g. (45% of the theoretical) after recrystallization.

It forms in colorless hair-like needles from hot water, m. p. 112–112.5°. It is fairly easily soluble in the usual organic solvents, dilute mineral acid or alkali. It gives a green color with ferric chloride and a deep red color with diazotized sulfanilic acid and alkali.

Anal. Subs., 5.043 mg.: CO_2, 13.029; H_2O, 2.111. Subs., 6.715: N_2, 0.421 (15°, 769 mm.). Calcd. for $C_{11}H_9O_2N$: C, 70.59; H, 4.81; N, 7.49. Found: C, 70.46; H, 4.65; N, 7.42.

Beckmann Rearrangement of its Oxime.—A mixture of the oxime (0.2 g.), glacial acetic acid (1.6 g.) and acetic anhydride (0.4 g.) was saturated with hydrogen chloride gas in the cold and was kept at 100° for three hours in a sealed tube. On cooling, the contents were made alkaline with sodium carbonate and shaken with chloroform. On concentrating the solvent, colorless crystals were obtained; yield, 0.18 g. It formed in colorless flat needles from chloroform, m. p. 216–217.5°. The mixed melting point with an authentic specimen of 5-acetamino-8-hydroxyquinoline (m. p. 217–218°) which had

---

[1] Behn, German Patent 95,901 (1897); Rosenmund and Schulz, *Arch. Pharm.*, **265**, 308 (1927).