588. *Sodium Derivatives of Dimethylstannane.*

By S. F. A. Kettle.

Conductimetric titration of a solution of sodium in liquid ammonia with dimethylstannane shows the formation of dimethylstannylenedisodium, $SnMe_2Na_2$, dimethylstannylsodium, $SnMe_2HNa$, and *sym*-tetramethyldistannyldisodium, $(SnMe_2Na)_2$. Under suitable conditions aminodimethylstannylsodium, $Me_2(NH_2)SnNa$, is also formed. Dimethylstannylenedisodium reacts with ammonia above 0° to give aminodimethylstannylsodium. With methyl iodide it gives tetramethyltin [1] and with ammonium bromide, dimethylstannane. Dimethylstannylsodium, which has not been prepared pure, decomposes at 20° to give *sym*-tetramethyldistannyldisodium. *sym*-Tetramethyldistannyldisodium, which can be prepared pure and is stable at room temperature, reacts with ammonium bromide to give a mixture of dimethylstannane and dimethyltin, $(SnMe_2)_n$. With methyl iodide, hexamethyldistannane, Sn_2Me_6, is formed. Aminodimethylstannylsodium, which is stable at room temperature and can be prepared pure, reacts with ammonium bromide to give dimethyltin.

Kraus and Greer reported that the reaction between dimethyltin dichloride and sodium in liquid ammonia proceeds with the successive formation of the yellow, insoluble dimethyltin, $(SnMe_2)_n$, the red soluble *sym*-tetramethyldistannyldisodium, $(SnMe_2Na)_2$, and ultimately the intensely red and soluble dimethylstannylenedisodium, $SnMe_2Na_2$.[1] In the work reported here the same compounds were obtained, but the last two have been found to be lime-green, the red colours reported by Kraus and Greer probably being caused by aminodimethylstannylsodium, $Me_2(NH_2)SnNa$.

The method of simultaneous measurement of conductivity and evolution of hydrogen in the titration of a solution of sodium in liquid ammonia with a volatile hydride was used to study the reaction between sodium and dimethylstannane.[2]

A typical variation of conductivity as successive portions of dimethylstannane were added to a solution of sodium in liquid ammonia at the temperature of melting chloroform (—63·5°) is shown in Fig. 1. The conductivity is a minimum when the $Na : SnMe_2H_2$ ratio is rather less than 2 : 1; at this point the blue colour of the solution was discharged, showing that the principal reaction is between two atoms of sodium and one molecule of dimethylstannane. The hydrogen evolution confirms that dimethylstannylenedisodium is formed:

$$SnMe_2H_2 + 2Na = SnMe_2Na_2 + H_2 \quad \quad (1)$$

In a competing reaction dimethylaminostannylsodium is formed, but this reaction is negligible under the conditions of the run. The conductivity becomes constant at an

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[1] Kraus and Greer, *J. Amer. Chem. Soc.*, 1925, **47**, 2568.
[2] Emeléus and Kettle, *J.*, 1958, 2444.

Na : $SnMe_2H_2$ ratio of just less than 1 : 1, showing that the reaction between dimethylstannylenedisodium and dimethylstannane involves one molecule of each.

The evolution of hydrogen throughout the same titration is shown in Fig. 2. Up to Na : $SnMe_2H_2$ = 2 : 1 it is that required by eqn. (1) for the formation of dimethylstannylenedisodium. In Fig. 2 the broken line (1) is the plot expected if the reaction between dimethylstannylenedisodium and dimethylstannane proceeded with the formation of dimethylstannylsodium, $SnMe_2HNa$:

$$SnMe_2Na_2 + SnMe_2H_2 = 2SnMe_2HNa \quad \ldots \quad (2)$$

The broken line (2) is the plot expected if the reaction gave *sym*-tetramethyldistannyldisodium, $(SnMe_2Na)_2$:

$$SnMe_2Na_2 + SnMe_2H_2 = (SnMe_2Na)_2 + H_2 \quad \ldots \quad (3)$$

The experimental plot lies between (1) and (2), yet shows the abrupt cessation of hydrogen evolution required by equation (3) at Na : $SnMe_2H_2$ = 1 : 1 (when all of the dimethylstannylenedisodium formed as an intermediate has reacted); it is concluded that reactions (2) and (3) proceed simultaneously.

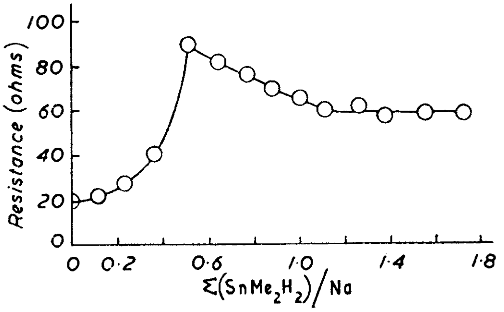

FIG. 1. *Variation of resistance in the titration of sodium in liquid ammonia with dimethylstannane.*

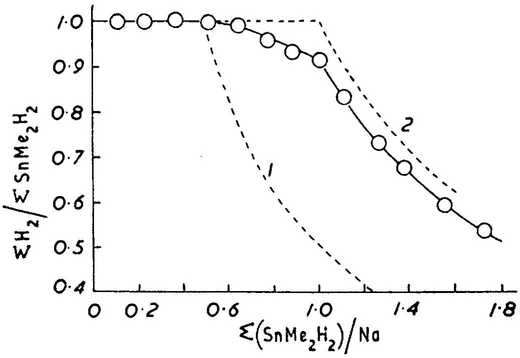

FIG. 2. *Evolution of hydrogen in the titration of sodium in liquid ammonia with dimethylstannane.*

When dimethylstannane and twice the equivalent amount of sodium, as a concentrated solution in liquid ammonia, are allowed to react rapidly at —45° the solution contains " excess " of sodium and more hydrogen is evolved than could have come from the dimethylstannane taken. The excess of hydrogen is equimolar with the excess of sodium. This clearly demonstrates that the solvent is participating in the reaction, an amino-group replacing a hydrogen atom in dimethylstannane, aminodimethylstannylsodium being formed:

$$SnMe_2H_2 + Na + NH_3 = Me_2(NH_2)SnNa + \tfrac{3}{2}H_2 \quad \ldots \quad (4)$$

Solid dimethylstannylenesodium evolved ammonia and hydrogen on warming to room temperature to give pure aminodimethylstannylsodium: $SnMe_2Na_2 + NH_3 = Me_2(NH_2)SnNa + NaH$. This reaction provides a convenient way of preparing pure aminodimethylstannylsodium. The composition of the product has been confirmed by analysis. Dimethylstannylenedisodium had presumably been left as an ammine at —63·5°; on warming, reaction occurred to give aminodimethylstannylsodium and sodium hydride. The hydrogen evolved came from the reaction between sodium hydride and ammonia giving hydrogen and sodamide.[3]

The aminodimethylstannylsodium dissolved in liquid ammonia to form an intensely red solution which gave only dimethyltin $(SnMe_2)_n$ on addition of ammonium bromide.

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[3] Hurd, " Chemistry of the Hydrides," Wiley, 1952, p. 31. A subsidiary experiment has shown that this reaction proceeds slowly at room temperature between sodium hydride and gaseous ammonia.

Ammonium bromide also reacted with the remaining sodium hydride, giving hydrogen: $NaH + NH_4Br = NaBr + NH_3 + H_2$. The sum of this hydrogen and that liberated earlier by the reaction between sodium hydride and ammonia was equimolar with the dimethylstannylenedisodium taken, as required by the above reaction series.

When the solvent ammonia was removed at —63·5° from a mixture of dimethylstannylsodium and *sym*-tetramethyldistannyldisodium no hydrogen was evolved until the solid residue was warmed to 0°; at room temperature dimethylstannylsodium decomposed rapidly, one mole of hydrogen being evolved from two of the hydride. The solid residue completely dissolved in liquid ammonia giving a solution with the properties expected of pure *sym*-tetramethyldistannyldisodium, suggesting that this is the product of the decomposition of dimethylstannylsodium. This conclusion was confirmed by analysis: $2Me_2SnHNa = (SnMe_2Na)_2 + H_2$. *sym*-Tetramethyldistannyldisodium is stable at room temperature in the absence of air.

The reaction between dimethylstannylenedisodium and ammonium bromide in liquid ammonia at —63·5° regenerates dimethylstannane, identified by its molecular weight and infrared spectrum. Ammonia and dimethylstannane are best separated chemically by washing with 10% sulphuric acid.

When dimethylstannane and sodium react at —45° to give a high yield of aminodimethylstannylsodium, the addition of ammonium bromide gives dimethyltin in addition to dimethylstannane. The dimethyltin was characterised as described below.

sym-Tetramethyldistannyldisodium would be expected to give the unknown *sym*-tetramethyldistannane, $(SnMe_2H)_2$, with ammonium bromide in liquid ammonia. The products isolated from this reaction were dimethyltin and dimethylstannane; presumably *sym*-tetramethyldistannane is first formed but rapidly decomposes: $(SnMe_2H)_2 = SnMe_2 + SnMe_2H_2$. Dimethylstannane was removed with the ammonia and separated as described above. Dimethyltin, left in the solid residue, was extracted with methylene dichloride, centrifuged, and obtained pure by removing the methylene dichloride under vacuum. The yellow residue was identified by analysis and by a characteristic reaction with aqueous silver nitrate in which the particles of the insoluble tin compound turn black.

Methyl iodide and *sym*-tetramethyldistannyldisodium react in liquid ammonia to give hexamethyldistannane; after removal of the solvent the product remains in the solid residue. Dimethylstannylenedisodium and methyl iodide react to give tetramethyltin.[1]

In many of the reactions discussed above solid residues were obtained. In all cases an infrared spectrum of the solid was taken and in no case was Sn–H absorption found.

The chemistry of dimethylstannylsodium was not investigated since it was impossible to prepare it pure or in good yield.

EXPERIMENTAL

Dimethylstannane was prepared by the reduction of dimethyltin dichloride with lithium aluminium hydride in dioxan and purified by fractionation through a melting-toluene bath (—95°).[4] Dimethyltin dichloride (20·1 g.) and lithium aluminium hydride (5·1 g.) in 100 ml. of sodium-dry dioxan gave 9·0 g. of pure dimethylstannane (96% on $LiAlH_4$). The purity of the product was checked by vapour-pressure and molecular-weight measurements. The vapour pressure of dimethylstannane is given by the equation $\log_{10} p$ (cm.) $= 6·64 - (1473/T)$, which gives b. p. 36° and Trouton constant 21·6.

The measurements of conductivity and hydrogen take-off were made at the temperature of melting chloroform (—63·5°),[2] the cell constant being 1·54. In this cell at —63·5° the conductivity of the solvent ammonia was $6·85 \times 10^{-5}$ ohm^{-1} and the conductivity of a saturated solution of dimethylstannane in ammonia was $1·45 \times 10^{-4}$ ohm^{-1}, both negligible compared with the conductivities measured in the run. Resistances were measured in a conventional bridge arrangement at 1000 c./sec. with oscilloscope display.[5] The typical run shown in Figs.

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[4] Finholt, Bond, Wilzbach, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 2692.

[5] Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544.

1 and 2 was made with 0·0165 g. of sodium in 3·13 g. of ammonia. The ammonia used was dried over sodium and the sodium was freshly cut reagent grade stored without oil.

Preparation and Properties of Dimethylstannylenedisodium.—Pure dimethylstannylenedisodium is made by adding small portions of dimethylstannane to sodium in liquid ammonia until a 1 : 2 ratio of hydride to sodium has been reached. Addition of the requisite amount of dimethylstannane in one portion invariably leads to the formation of a considerable amount of aminodimethylstannylsodium.

To sodium (0·352 mmole) in *ca.* 3 g. of ammonia frozen in liquid nitrogen, dimethylstannane (0·177 mmole) was added in portions and allowed to react at −63·5°. Hydrogen (0·177 mmole) was evolved. To sodium (0·943 mmole) in *ca.* 3 g. of ammonia frozen in liquid nitrogen, dimethylstannane (0·475 mmole) was added. The reaction vessel was warmed with the hand until all the ammonia had liquefied and then plunged into a bath of melting chlorobenzene (−45°). 0·615 mmole of hydrogen was evolved and the solution was still deep blue. After addition of just enough dimethylstannane to react with the remaining sodium the solution was reddish-brown. The hydrogen evolved indicates 59% formation of aminodimethylstannylsodium. The molecular weight of the hydrogen evolved in this reaction was 1·8 and its infrared spectrum showed no C–H adsorption, showing that no methane had been evolved, so that fission of a Sn–CH$_3$ bond had not taken place and the solvent must have participated in the reaction.

If sodium and dimethylstannane in an exact 2 : 1 ratio are allowed to react rapidly, then for every atom of hydrogen evolved in excess of that required by eqn. (1) there should also be one atom of sodium in excess [see eqn. (4)]. It is possible to determine the excess of sodium by adding ammonium bromide (by the rotating-arm technique) when for every atom of sodium one atom of hydrogen is liberated: $2NH_4Br + 2Na = 2NH_3 + 2NaBr + H_2$. In one run sodium (0·466 mmole) reacted with dimethylstannane to give hydrogen (0·252 mmole)—an " excess " of 0·019 mmole—and a dark blue solution which, with ammonium bromide, gave 0·018 mmole of hydrogen. In a second run sodium (0·391 mmole) reacted with dimethylstannane (0·196 mmole) to give hydrogen (0·209 mmole), an " excess " of 0·014 mmole, and a dark blue solution which with ammonium bromide gave 0·014 mmole of hydrogen.

After removal of the solvent ammonia by pumping at −63·5° for 2 3 hr., dimethylstannylenedisodium remains as a lime-green solid. On warming to room temperature it becomes dark red-brown, and ammonia and hydrogen are evolved. The ammonia evolved is not in a fixed ratio to the dimethylstannylenedisodium, varying from run to run. The hydrogen must have come from ammonia so a reaction between dimethylstannylenedisodium and the solvating ammonia is indicated: $SnMe_2Na_2 + NH_3 = Me_2(NH_2)SnNa + NaH$; $NaH + NH_3 = NaNH_2 + H_2$. The colour of the product suggests that it is aminodimethylstannylsodium. The hydrogen evolved is not equimolar with the dimethylstannylenedisodium taken, so sodium hydride must remain unchanged. This will react with ammonium bromide in liquid ammonia to give hydrogen: $NaH + NH_4Br = NaBr + NH_3 + H_2$, and the total hydrogen evolved should then be equimolar with the dimethylstannylenedisodium taken. Dimethylstannylenedisodium (0·146 mmole) liberated hydrogen (0·032 mmole) on warming to room temperature. Addition of ammonia and ammonium bromide caused the evolution of hydrogen (0·115 mmole). The total hydrogen liberated (0·147 mmole) is equimolar with the dimethylstannylenedisodium taken, confirming the above reaction scheme.

Kraus and Greer reported on the chemistry of (impure) dimethylstannylenedisodium but did not mention its reaction with ammonium halides.[1] In a previous paper a method of chemically separating stannane and the monoalkylstannanes from ammonia by use of a solution of copper sulphate in 10% sulphuric acid was described.[2] Dimethylstannane reacts very rapidly with copper sulphate to give a brown precipitate, so in the separation of dimethylstannane from ammonia, 10% sulphuric acid was used alone. A solution of pure dimethylstannylenedisodium (0·196 mmole) was prepared as described above and excess of ammonium bromide added by the rotating-arm technique. The volatile material was separated and ammonia removed from this chemically. After fractionation through a bath at −78° to remove water, the product was pure dimethylstannane (Found: *M*, 152. Calc. for $SnMe_2H_2$: *M*, 151), confirmed by its infrared spectrum and vapour pressure (5·4 mm. at −63·5°. $SnMe_2H_2$ has 5·2 mm. at −63·5°). Yield, 0·0097 g. (30%).

Preparation and Properties of Aminodimethylstannylsodium.—As described in the preceding section aminodimethylstannylsodium is made by the thermal decomposition of dimethylstannylenedisodium in the presence of ammonia. The product is contaminated by sodium hydride and amide; if in the preparation the ammonia is removed slowly it is found that aminodimethylstannylsodium is left as a hard film on the sides of the reaction vessel and the contaminants are left as a white residue at the bottom. Prepared and separated in this way a specimen of aminodimethylstannylsodium was analysed (Found: C, 13·1; H, 4·5; N, 7·6. Calc. for SnC_2H_8NNa: C, 12·8; H, 4·3; N, 7·5%).

With ammonium bromide in liquid ammonia, aminodimethylstannylsodium gave a yellow precipitate of dimethyltin. The volatile material could not be resolved into fractions and was completely absorbed by 10% sulphuric acid. The yellow residue was partially soluble in water giving a solution which contained sodium and ammonium bromides. The particles of yellow, water-insoluble precipitate, when added to neutral silver nitrate solution, turned black, a reaction characteristic of dimethyltin. Dimethyltin dissolved in methylene dichloride to give a yellow solution which was freed from ionic halides by centrifuging. Aminodimethylstannylsodium (0·226 mmole), after reaction with ammonium bromide in liquid ammonia, gave 0·0256 g. of methylene dichloride-soluble material (Found: C, 16·5; H, 3·8. Calc. for SnC_2H_6: C, 16·1; H, 4·0%).

Aminodimethylstannylsodium is best stored in a vacuum. When opened in a nitrogen-flushed dry-box a specimen turned dark-green in 15 min. and was black after ½ hr. After two days the black residue was analysed (Found: C, 6·4; H, 3·7; N, 5·3. Calc. for SnC_2H_8NNa: C, 12·8; H, 4·3; N, 7·5%).

Preparation and Properties of sym-*Tetramethyldistannyldisodium.*—*sym*-Tetramethyldistannyldisodium is the major product of the reaction between equimolar quantities of dimethylstannylenedisodium and dimethylstannane. Dimethylstannylsodium, which is also formed, decomposes on warming to give *sym*-tetramethyldistannyldisodium and hydrogen. Dimethylstannylenedisodium (0·278 mmole) reacted with dimethylstannane (0·281 mmole) in liquid ammonia to give hydrogen (0·226 mmole), indicating the 81% formation of *sym*-tetramethyldistannyldisodium. On standing at −63·5° for ½ hr. no more hydrogen was liberated, showing that the decomposition of dimethylstannylsodium does not occur at this temperature. After removal of the solvent ammonia the solid product was slowly warmed. At −10° hydrogen evolution commenced and at 20° was rapid. In the decomposition 0·065 mmole of hydrogen was evolved, a total of 0·281 mmole, equimolar with the dimethylstannylenedisodium taken. After removal of ammonia the product was analysed (Found: C, 14·2; H, 3·8. Calc. for $Sn_2C_4H_{12}Na_2$: C, 14·0; H, 3·5%). The product was deposited as a thin hard film on the walls of the reaction vessel, difficult to remove with a spatula.

With methyl iodide, *sym*-tetramethyldistannyldisodium gave hexamethyldistannane. Excess of methyl iodide was condensed on a frozen solution of *sym*-tetramethyldistannyldisodium (0·302 mmole). A white precipitate of sodium iodide was formed on warming. Removal of the volatile material at −45° followed by methylene dichloride extraction of the solid residue, centrifuging, and removal of the solvent *in vacuo*, gave a white oily solid, m. p. 22° (lit.,[6] Sn_2Me_6, m. p. 23°) (Found: C, 21·8; H, 5·2. Calc. for $Sn_2C_6H_{18}$: C, 22·0; H, 5·5%).

sym-Tetramethyldistannyldisodium reacted with ammonium bromide in liquid ammonia to give dimethyltin and dimethylstannane, separated as described above. *sym*-Tetramethyldistannyldisodium (0·222 mmole) gave 0·0353 g. of dimethyltin (Found: C, 16·3; H, 3·4. Calc. for SnC_2H_6: 0·0330 g. containing C, 16·1; H, 4·0%), and 0·0060 g. (18%) of dimethylstannane [*M*, 154 (calc., 151)], confirmed by its infrared spectrum and vapour pressure (5·3 mm. at −63·5°; $SnMe_2H_2$ has 5·2 mm. at −63·5°). The low yield of dimethylstannane is attributed to the difficulty of separation from ammonia.

sym-Tetramethyldistannyldisodium does not react with dimethylstannane; in liquid ammonia the latter separates as a liquid (sometimes colloidal) and can be recovered.

sym-Tetramethyldistannyldisodium is best stored in a vacuum; it rapidly decomposes in a nitrogen-flushed dry-box, presumably by reacting with traces of oxygen.

Infrared Spectra.—The infrared spectra of all the stable compounds made above were recorded. Aminodimethylstannylsodium and dimethylstannylenedisodium appeared to react with all the media used (hexachlorobutadiene, Nujol, potassium bromide—with the last two because of traces of water and air). The spectra recorded, while perhaps not those of the compounds, showed the expected absorption, *i.e.*, N–H, C–H. The infrared spectrum of dimethylstannane showed the following peaks in the range 4000—600 cm.$^{-1}$: 3666 cm.$^{-1}$ (w),

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[6] Kraus and Bullard, *J. Amer. Chem. Soc.*, 1926, **48**, 2132.

3070 (m), 3014 (s), 2938 (s), 2838 (m), 2622 (vw), 2395 (w), 2204 (w), 1993 (vw), 1856 (vs), 1738 (w), 1727 (w), 1531 (w), 1430 (w), 1348 (vw), 1304 (vw), 1212 (w), 1204 (w), 1195 (w), 1140 (vw), 1063 (vw), 773 (vs), 755 (vs), 744 (vs), 721 (vs), 708 (vs).

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