124. *Some Reactions of Tributyl- and Triphenyl-stannyl Derivatives of Alkali Metals.*

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Tri-n-butylstannyl-lithium reacts with chlorotrimethylsilane and with carbon dioxide as if it contained butyl-lithium in equilibrium with dibutyltin. Triphenylstannylsodium, which can be prepared from sodium–naphthalene and tetraphenyltin, hexaphenyldistannane, or triphenyltin bromide, reacts normally with ethyl bromide and benzyl chloride, but as a reducing agent with benzophenone, benzoyl chloride, oxygen, carbon dioxide, and sulphur dioxide.

Alkali-metal derivatives of trialkyl- and triaryl-stannanes (R_3SnM) are readily prepared by well-known reactions in liquid ammonia solution, but their scope as synthetic reagents is limited by the reactivity of the solvent. Solutions or suspensions of these substances in diethyl ether were later prepared from organolithium reagents and organotin(II) compounds, the latter being prepared either separately [1] or from tin(II) chloride: [2]

$$SnCl_2 + 3RLi = R_3SnLi + 2LiCl$$

Wishing eventually to use reagents R_3SnM for the synthesis of compounds containing bonds between tin and other metals, we found it necessary first to investigate some of the already reported reactions of R_3SnM, many of which appeared unexpected and difficult to understand. For example, in their first paper [2] on triphenylstannyl-lithium, Gilman and Rosenberg obtained the following products on reaction with halides: EtI gave Ph_4Sn,

[1] Wittig, Meyer, and Lange, *Annalen*, 1951, **571**, 195.
[2] Gilman and Rosenberg, *J. Amer. Chem. Soc.*, 1952, **74**, 531.

27%, and Ph_3EtSn, 36%; $Ph{\cdot}CH_2Cl$ gave Ph_4Sn, 60%, and $Ph_3Sn{\cdot}CH_2Ph$, 22%; Ph_3SnCl gave Ph_6Sn_2, 53%; and Ph_3SiCl gave $Ph_3Si{\cdot}SnPh_3$, 71%. They also detected no reaction with benzophenone. In their first paper they found that carbonation yielded no benzoic acid, this result being confirmed in their second [3] and third [4] papers in which they reported the isolation of tetraphenyltin (4·7%) and then both this product (24%) and hexaphenyldistannane (Ph_6Sn_2, 16%).

We confirmed the formation of triphenylsilyltriphenyltin from chlorotriphenylsilane, and that of hexaphenyldistannane from triphenyltin halides, but obtained different results in respect of the other reactions.

Trialkylstannyl Derivatives.—Triethylstannyl-lithium [5] and its n-butyl analogue [2] have also been described, but their only reported reactions are those with ethyl and butyl halides forming the tetra-alkyl compound. We did not investigate the reactions of triethylstannyl-lithium formed from ethyl-lithium, $SnCl_2 + 3EtLi = Et_3SnLi + 2LiCl$, since Gilman and Rosenberg [5] found that free ethyl-lithium was present in the reaction mixture (colour test [6] based on halogen exchange with *p*-bromodimethylaniline) when only 2·5 mol. had been added. Consequently the addition of ethyl-lithium to diethyltin is reversible: $Et_2Sn + EtLi \rightleftharpoons Et_3SnLi$. The reagent would not be useful for the preparation of triethylstannyl derivatives of, for example, reactive metal halides, since the ethyl-lithium present would also react—possibly faster than the Et_3SnLi. Since it was stated [2] that the same colour test indicates the absence of free butyl-lithium until just over 3 mol. have been added to tin(II) chloride, the formation of tri-n-butylstannyl-lithium did not appear to be reversible and the use of this reagent seemed to be promising.

We found, however, that reagents which react rapidly with butyl-lithium react with tri-n-butylstannyl-lithium as if it were a mixture of dibutyltin and butyl-lithium. For example, chlorotrimethylsilane gave butyltrimethylsilane, and carbonation gave dibutyltin

$$Bu_3SnLi \rightleftharpoons Bu_2Sn + BuLi$$
$$BuLi + Me_3SiCl \longrightarrow BuMe_3Si$$

and a mixture of valeric acid and dibutyl ketone. We were unable to find any satisfactory synthetic use for tri-n-butylstannyl-lithium.

Reactions of Triphenylstannyl Alkali-metal Derivatives.—Triphenylstannyl-sodium or -lithium was prepared in practically quantitative yield, as judged by recovery of ethyltriphenyltin after subsequent reaction with ethyl bromide, either from triphenyltin bromide and sodium in liquid ammonia (followed by replacement of ammonia by ether or dimethylformamide) or by Gilman and Rosenberg's method [2] using phenyl-lithium and tin(II) chloride. The liquid-ammonia method gave better yields except in those instances in which the reagent subsequently used is sensitive to ammonia. We found that triphenylstannylsodium, prepared in liquid ammonia, tenaciously retains ammonia even when boiled in diethyl ether.

Triphenylstannylsodium can also be prepared by reaction between sodium–naphthalene and hexaphenyldistannane, triphenyltin bromide, or even tetraphenyltin, in tetrahydrofuran or in 1,2-dimethoxyethane:

$$Ph_3Sn{\cdot}SnPh_3 + 2C_{10}H_8Na \longrightarrow 2Ph_3SnNa + 2C_{10}H_8$$
$$Ph_3SnBr + 2C_{10}H_8Na \longrightarrow Ph_3SnNa + NaBr + 2C_{10}H_8$$
$$Ph_4Sn + 2C_{10}H_8Na \longrightarrow Ph_3SnNa + C_6H_6 + 2C_{10}H_8$$

These reactions are accompanied by vivid colour changes. In the third reaction, which represents a very easy route to triphenylstannylsodium, it is probable that phenylsodium

[3] Gilman and Rosenberg, *J. Org. Chem.*, 1953, **18**, 680.
[4] Gilman and Rosenberg, *J. Org. Chem.*, 1953, **18**, 1554.
[5] Gilman and Rosenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 2507.
[6] Gilman and Swiss, *J. Amer. Chem. Soc.*, 1940, **62**, 1847.

is formed as a transitory intermediate and reacts at once with solvent. Addition of ethyl bromide to triphenylstannylsodium prepared by these three methods gave ethyltriphenyltin in 75%, 60%, and 65% yield respectively (of purified product).

Gilman and Rosenberg found that tetraphenyltin was commonly a major product of reactions between triphenylstannyl-lithium and alkyl halides. We obtained only insignificant amounts of this product in most of our reactions; for example, ethyl bromide gave 99% of ethyltriphenyltin (by the liquid ammonia method, replacing ammonia by ether) and benzyl chloride gave 88% of benzyltriphenyltin. Reaction with triphenyltin bromide was almost quantitative (95% yield of hexaphenyldistannane).

When an ethereal solution of benzophenone is added to triphenylstannylsodium a bright greenish-blue colour develops at once. This must be due to an electron transfer to the ketone, forming the blue diphenyl ketyl, the greenish tinge being due to the presence of some of the tan-coloured triphenylstannylsodium: $Ph_3Sn^-Na^+ + Ph_2CO \rightleftharpoons \frac{1}{2}Ph_6Sn_2 + Ph_2CO^-Na^+$. Addition of water immediately discharges the colour, and from the reaction mixture were isolated not only benzophenone, as found by Gilman and Rosenberg, but also about an equal weight of diphenylmethanol, a trace of benzpinacol, and hexaphenyldistannane in quantity equivalent to a 75% tin recovery. A similar blue colour, also attributed to ketyl formation, was noted in the complicated reaction between triphenylsilylpotassium and benzophenone.[7] Triphenylgermyl-lithium reacts normally with benzophenone, giving triphenylgermyldiphenylmethanol.[8]

Reaction with benzoyl chloride was more complex, and was accompanied by the transient development of a bright red colour which lasted a few seconds after each addition of benzoyl chloride. This may have been due to the formation of benzoyl radicals or anions. The tin again appeared as hexaphenyldistannane, but no benzil could be detected though it was sought because the reaction mixture was yellow. Instead, the dibenzoate of *cis*-stilbenediol was isolated:

$$Ph{\cdot}COCl + Ph_3SnNa \longrightarrow Ph_6Sn_2 + Ph{\cdot}C(O^-){:}C(O^-)Ph$$

$$Ph{\cdot}C(O^-){:}C(O^-)Ph + 2Ph{\cdot}COCl \longrightarrow Ph{\cdot}C(OBz){:}C(OBz)Ph + 2Cl^-$$

In the last two reactions discussed, triphenylstannylsodium acts only as an electron source, itself being converted into hexaphenyldistannane. This is in contrast to reactions with alkyl halides, in which the distannane is not formed to an appreciable extent. We found a borderline case in reaction with diphenyl disulphide, in which both hexaphenyldistannane and triphenyl(phenylthio)tin are formed:

$$Ph_3SnNa + PhS{\cdot}SPh \longrightarrow Ph_6Sn_2 + Ph_3SnSPh + PhSNa$$

These products were obtained irrespective of the order of mixing of the reactants.

Finally, we report some reactions with simple inorganic compounds, in which triphenylstannylsodium acts only as a reducing agent, hexaphenyldistannane having been the only product containing tin that was isolated. Reaction with gaseous oxygen yields hexaphenylstannane and sodium peroxide (detected only in 50% yield): $2Ph_3SnNa + O_2 \longrightarrow Ph_6Sn_2 + Na_2O_2$.

Carbon dioxide is reduced to oxalate anions, recovered in 98% yield as calcium oxalate, most of the tin again appearing as hexaphenyldistannane: $2Ph_3SnNa + 2CO_2 = Ph_6Sn_2 + Na_2C_2O_4$. Similarly sulphur dioxide gives the distannane (75%) and sodium dithionite (96% by reaction with silver nitrate): $2Ph_3SnNa + 2SO_2 = Ph_6Sn_2 + Na_2S_2O_4$. Alkali-metal amalgams reduce carbon dioxide and sulphur dioxide in a similar way.[9]

Triphenylstannyl-sodium or -lithium is not indefinitely stable in contact with diethyl

[7] Brook and Schwartz, *J. Amer. Chem. Soc.*, 1960, **82**, 2435.
[8] Gilman and Gerow, *J. Amer. Chem. Soc.*, 1955, **77**, 5740.
[9] Hohn, Fitzer, and Nedwed, *Z. anorg. Chem.*, 1953, **274**, 297; Hohn, Fitzer, Chizzola, and Nedwed, *ibid.*, 1954, **275**, 32.

ether or tetrahydrofuran: hexaphenyldistannane is slowly formed and ethanol (or butanol) was also detected.

Experimental

Microanalyses are by Mr. A. Wiper, of these laboratories. Preparations involving alkali metals or their organic derivatives were carried out in an inert atmosphere.

Triphenyltin bromide was prepared in about 90% yield by heating tetraphenyltin and tin(IV) bromide together for 15 hr. at 220°; propan-1-ol was a convenient solvent for its crystallization, diphenyltin dibromide being freely soluble and tetraphenyltin virtually insoluble in this solvent.

Reactions of Tri-n-butylstannyl-lithium.—Chlorotrimethylsilane. Tri-n-butylstannyl-lithium was prepared by Gilman and Rosenberg's method [2] from tin(II) chloride (17·4 g., 0·092 mole) and n-butyl-lithium in diethyl ether. To this was added, with stirring at −40°, chlorotrimethylsilane (11·5 c.c., 0·092 mole) in ether (100 c.c.). There was no apparent colour change. After removal of ether, volatile products were separated by vacuum-distillation. Fractionation then yielded n-butyltrimethylsilane (6·4 g., 54%), b. p. 116—116·5°, $n_D^{19·5}$ 1·4032 (lit.,[10] b. p. 115·5°, n_D^{20} 1·4030) (Found: C, 65·2; H, 13·75. Calc. for $C_7H_{18}Si$: C, 64·6; H, 13·9%). The involatile residue was orange-red, suggesting the presence of dibutyltin, and extraction by benzene followed by vacuum-distillation gave tetra-n-butyltin (4·3 g.), b. p. 122·5—123·5°/2·9 mm., possibly formed by disproportionation of dibutyltin.

Carbon dioxide. Tri-n-butylstannyl-lithium (0·093 mole) in ether (100 c.c.) was poured on ether and solid carbon dioxide. Oxalate could not be detected in the product, which yielded valeric acid, b. p. 185—187° (3·6 g.; *p*-toluidide, m. p. 71—71·5°), and di-n-butyl ketone, b. p. 185—187° (2·1 g.; semicarbazone, m. p. 89°). The red involatile residue remaining after separation of valeric acid and di-n-butyl ketone contained dibutyltin, since oxidation with 4% aqueous hydrogen peroxide followed by addition of concentrated hydrochloric acid gave di-n-butyltin dichloride, m. p. 39—39·5° (after crystallization from pentane and sublimation; 3·5 g.).

Preparation of Triphenylstannyl-sodium and Reaction with Alkyl Halides.—(A) *The liquid-ammonia method.* Sodium (1·2 g., 0·05 g.-atom) was added, in small pieces, to dry liquid ammonia (100 c.c., distilled from sodium) at −78°. With continuous stirring a suspension of triphenyltin bromide (10·7 g., 0·025 mole) in ether (100 c.c.) was added, quickly at first and later quite slowly to avoid passing appreciably beyond the equivalence point, which is marked by a change from the blue of dissolved sodium through a bright blood-red colour to the pale tan colour of triphenylstannylsodium. The cooling bath was then removed, and most of the ammonia allowed to boil away. More ammonia was removed by pumping at about 20 mm. and then ether (100 c.c.) was added to the yellow-brown residue. Ethyl bromide (2·7 g., 0·025 mole) in ether (50 c.c.) was slowly added with brisk stirring, the mixture being kept at about −60°. Then the mixture was allowed to warm to room temperature and stirred for an hour. Addition of an equal volume of water, separation of the ether phase, and crystallization from methanol of the residue after removal of ether yielded ethyltriphenyltin (8·5 g., 94%), m. p. 55—56° (lit.,[11] m. p. 56°). In similar reactions benzyl chloride yielded benzyltriphenyltin, 80 and 88%, m. p. 90—90·5° from ethanol (lit.,[2] m. p. 90—91°). Ethyltriphenyltin was also prepared in 98% yield by using dimethylformamide instead of diethyl ether as reaction medium.

(B) *The phenyl-lithium method.* Triphenylstannyl-lithium was prepared as previously described.[2]

(C) *The sodium–naphthalene method.* A solution of sodium–naphthalene in 1,2-dimethoxyethane containing 0·027 g.-atom of sodium was added, at 0°, to a stirred suspension of hexaphenyldistannane (0·0135 mole) in the same solvent. The dark green colour of the sodium–naphthalene was rapidly discharged, and the reaction mixture was a deep violet colour when half the sodium–naphthalene had been added. At the equivalence point the colour faded to the pale tan of triphenylstannyl-sodium. Addition of ethyl bromide, removal of naphthalene by steam-distillation, and crystallization of the residue from ethanol gave ethyltriphenyltin (75%).

In a similar but more exothermic reaction using triphenyltin bromide the colour changed from deep green to the final colour through an intermediate magenta. When tetraphenyltin

[10] Bygden, *Ber.*, 1911, **44**, 2640.
[11] Krause and Schmitz, *Ber.*, 1919, **52**, 2150.

was used initially the colour changed from deep green to blood-red and this persisted even at the equivalence point.

Reactions of Triphenylstannylsodium, etc.—With benzophenone. Benzophenone (4·6 g., 0·025 mole) in ether (50 c.c.) was added to triphenylstannylsodium (0·025 mole) in ether (*ca.* 50 c.c.) at room temperature. The colour changes have already been mentioned. After hydrolysis, filtration yielded hexaphenyldistannane (6·6 g., 75%), and from the yellow ether phase were isolated benzophenone (1·5 g., 33%), diphenylmethanol (1·5 g., 32%), and a trace of benzpinacol (tetraphenylethylene glycol).

With benzoyl chloride. Benzoyl chloride (0·08 mole) in ether (50 c.c.) was slowly added at room temperature to triphenylstannyl-lithium (0·08 mole; prepared by Gilman and Rosenberg's method [2]) in ether (100 c.c.). After hydrolysis, hexaphenyldistannane (20 g., 72%) was recovered, together with a much more soluble product (2·5 g.), identified as the dibenzoate of *cis*-1, 2-stilbenediol (mixed m. p. with authentic specimen prepared by Gomberg and Bachmann's method [12]).

With diphenyl disulphide. Diphenyl disulphide (0·016 mole) in 1,2-dimethoxyethane (22 c.c.) was added to triphenylstannylsodium (0·016 mole, from triphenyltin bromide and sodium–naphthalene) in the same solvent (50 c.c.) at 0°. During the addition the colour changed from light brown through red to a very pale yellow. Next morning the mixture was steam-distilled to remove naphthalene, acidified, and again steam-distilled, yielding thiophenol (2·0 g., identified as 2,4-dinitrophenyl phenyl sulphide, m. p. 120—121°). Extraction of the insoluble residue from the steam-distillation with ethanol gave triphenyl(phenylthio)tin (3·0 g.; m. p. and mixed m. p. 102—103°), and the ethanol-insoluble material when crystallized from benzene gave hexaphenyldistannane (3·4 g., m. p. 229—232°).

In another experiment in which triphenylstannyl-lithium in ether (from phenyl-lithium [2]) was added to an equimolar quantity of diphenyl disulphide in ether, the same products were isolated together with a small amount of unreacted disulphide.

With oxygen. A slow stream of oxygen was passed through triphenylstannylsodium (0·025 mole) in ether (100 c.c.) for 3 hr. A solid product was filtered off (under nitrogen), washed with warm benzene to remove organic matter, and hydrolyzed, giving oxygen (45 c.c. at N.T.P.). A small test sample taken before hydrolysis liberated iodine when added to aqueous potassium iodide. Hexaphenyldistannane (7·0 g.) was recovered from the benzene extract.

With carbon dioxide. Dry carbon dioxide was bubbled through triphenylstannylsodium (0·025 mole) in ether (100 c.c.) during 3 hr. at room temperature; the mixture quickly became colourless. After addition of water, oxalate was determined in the aqueous phase (gravimetrically as calcium oxalate dihydrate, 98%) and hexaphenyldistannane, m. p. 231—232° (7·0 g., 80%), was recovered.

With sulphur dioxide. Dry sulphur dioxide was passed through triphenylstannylsodium (0·01 mole) in 1,2-dimethoxyethane at room temperature for 15 min. The mixture was stored for several hours and then filtered under nitrogen. The residue was washed with ether until there was no trace of sulphur dioxide in the filtrate; it was then washed with warm water into ammoniacal silver nitrate, and the precipitated silver collected, dried, and weighed (1·0533 g., equiv. to 96% of sodium dithionite). Hexaphenyldistannane (2·6 g., 75%) was recovered.

Triphenyl(phenylthio)tin, $Ph_3Sn{\cdot}SPh$.—Thiophenol (12 g.) in dry methanol (20 c.c.) was added to sodium methoxide (5·4 g.) in dry methanol (20 c.c.). Triphenyltin bromide (42 g.) in tetrahydrofuran (50 c.c.) was then added slowly. The mixture was boiled with reflux for 30 min. and filtered; the product crystallized from the filtrate. Recrystallization from ethanol gave colourless *product*, m. p. 103° (37 g., 82%) (Found: C, 62·8; H, 4·5. $C_{24}H_{20}SSn$ requires C, 62·7; H, 4·4%).

Diphenyldi(phenylthio)tin, $Ph_2Sn(SPh)_2$.—This was similarly prepared from diphenyltin dibromide, and crystallized from ethanol as colourless needles, m. p. 66—67° (Found: C, 58·3; H, 4·3. $C_{24}H_{20}S_2Sn$ requires C, 58·6; H, 4·1%).

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SOUTH ROAD, DURHAM. [*Received, September 1st*, 1960.]

[12] Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 2587.