tween −30 and −35° for 35 min. rather than between −25 and −30°. In this run the yield of 4-dibenzofurancarboxylic acid was 1.32 g. (25%).[11]

From the neutral organic layer there was isolated 2.51 g. (60%) of starting dibenzofuran.

Metalation of dibenzofuran in diethyl ether at 0°. Twenty milliliters of a diethyl ether solution containing 0.028 mole of butyllithium was added rapidly to a stirred solution of 4.2 g. (0.025 mole) of dibenzofuran in 35 ml. of dry diethyl ether cooled to *ca* −10°. The reaction mixture was stirred in an ice bath for 1 hr., cooled to −20° and carbonated. Work-up in the usual manner afforded 0.26 g. (4.9%) of 4-dibenzofurancarboxylic acid, m.p. 210–212°.

The organic layer, after drying and distilling the ether, gave 3.32 g. (79%) of starting dibenzofuran.

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[11] The low yield of acid obtained when using butyl bromide may be due in part to the tendency of butyl bromide to couple in tetrahydrofuran. Butyllithium can be prepared only in very small yields from butyl bromide and lithium in tetrahydrofuran; B. Gaj, unpublished studies.

Reaction of Triphenyltin-Lithium with Some Esters

HENRY GILMAN AND LEWIS A. GIST, JR.[1]

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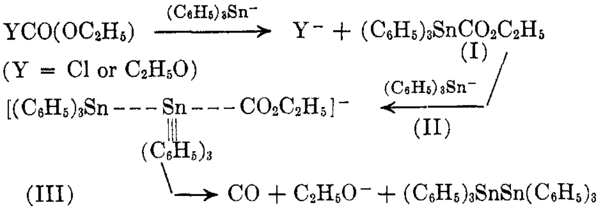
In the course of investigations in this laboratory, the reactions of triphenyltin-lithium with diethyl carbonate and with ethyl chloroformate have been explored as a possible route for preparing ethyl triphenylstannylcarboxylate and bistriphenyltin ketone. The products obtained, however, were not the desired ester and ketone. Instead, carbon monoxide was vigorously evolved, and hexaphenylditin was obtained as the principle product along with a lesser amount (*ca.* 20%) of tetraphenyltin.

The mechanism of this reaction was not determined. It is believed, however, that ethyl triphenylstannylcarboxylate was first formed, then decarbonylated in a manner similar to that proposed earlier for esters of triphenylsilanecarboxylic acid,[2] and for methyl triphenylgermanecarboxylate.[3] The proposed mechanism would involve the attack of the triphenyltin anion (II) on the tin atom of the intermediate ethyl triphenylstannylcarboxylate (I) with the formation of a transition state (III), which leads to the products obtained.



$$YCO(OC_2H_5) \xrightarrow{(C_6H_5)_3Sn^-} Y^- + \underset{(I)}{(C_6H_5)_3SnCO_2C_2H_5}$$

$$(Y = Cl \text{ or } C_2H_5O)$$

$$[(C_6H_5)_3Sn---\underset{(C_6H_5)_3}{\underset{|||}{Sn}}---CO_2C_2H_5]^- \xleftarrow[(II)]{(C_6H_5)_3Sn^-}$$

$$(III) \longrightarrow CO + C_2H_5O^- + (C_6H_5)_3SnSn(C_6H_5)_3$$

It is reasonable to expect the intermediate ethyl triphenylstannylcarboxylate to be rather unstable in the presence of a base. The electropositive triphenyltin radical attached directly to a pseudopositive carbon atom should be highly susceptible to an anionic attack of this type. Furthermore, the large atomic radius of the tin atom coupled with its low electron density renders it vulnerable to nucleophilic attack. It is also possible that a radical mechanism might be proposed for this reaction.

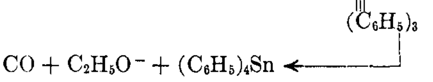
After carbonation of the product obtained from the reaction of triphenyltin-lithium with fluorene, d'Ans and co-workers[4] obtained approximately a 20% yield of 9-fluorenecarboxylic acid. These investigators[4] concluded, therefore, that triphenyltin-lithium was approximately 20% dissociated according to the equation:

$$(C_6H_5)_3Sn^-\,Li^+ \rightleftarrows (C_6H_5)_2Sn + C_6H_5Li$$

Conversely, the reactions of triphenyltin-lithium with gaseous carbon dioxide, Dry Ice, benzophenone, and benzalacetophenone were investigated in this laboratory earlier,[5,6] and no evidence of such an equilibrium could be found.

The reaction of triphenyltin-lithium with diethyl carbonate and with ethyl chloroformate offered an opportunity to investigate again the possibility of this equilibrium. None of the compounds which might be expected from the reaction of phenyllithium with diethyl carbonate or with ethyl chloroformate could be found among the products of the reaction.

The presence of tetraphenyltin in these reaction mixtures could conceivably have resulted from the reaction of ethyl triphenylstannylcarboxylate (I) with phenyllithium as follows:



$$C_6H_5^-Li^+ + \underset{(I)}{(C_6H_5)_3SnCO_2C_2H_5} \longrightarrow$$

$$[(C_6H_5)---\underset{(C_6H_5)_3}{\underset{|||}{Sn}}---CO_2C_2H_5]^- + Li^+$$

$$CO + C_2H_5O^- + (C_6H_5)_4Sn \longleftarrow$$

However, tetraphenyltin is believed to have resulted as a by-product in the preparation of triphenyltin-lithium, and not from a reaction of the type proposed above, since it is invariably obtained

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[1] General Education Board Fellow at Iowa State College, 1952–1954.

[2] A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **77**, 2322 (1955).

[3] H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 4675 (1955).

[4] J. d'Ans, H. Zimmer, E. Endrulat, and K. Lübke, *Naturwissenschaften*, **39**, 450 (1952).

[5] H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, **18**, 680 (1953).

[6] H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, **18**, 1554 (1953).

in yield of 15–20% in the hydrolysis of triphenyltin-lithium.[6] Furthermore, the reaction of phenyllithium (as well as phenylmagnesium bromide) with methyl triphenylgermanecarboxylate has been investigated,[7] and the product obtained was triphenylgermyldiphenylcarbinol, rather than tetraphenylgermane.

It has been concluded, therefore, that the ability of triphenyltin-lithium to act as a metalating agent cannot be precluded in interpreting the results obtained by d'Ans and co-workers[4] since no evidence of an equilibrium has been obtained in any of the reactions of triphenyltin-lithium with carbonyl systems.

EXPERIMENTAL

All melting points reported here are uncorrected. For compounds melting below 250°, the determinations were made in a silicone-oil bath with a 250° thermometer. For high melting compounds a copper block equipped with a 520° thermometer was employed.

Triphenyltin-lithium. Triphenyltin-lithium was prepared through the reaction[8] of phenyllithium with anhydrous tin (II) chloride. A typical 0.045 mole preparation of triphenyltin-lithium was treated with a solution of 13.3 g. (0.045 mole) of triphenylchlorosilane in 100 ml. of ether according to the method previously described.[5,6] After hydrolysis, 19.6 g. (73%) of crude triphenylsilyltriphenyltin was obtained, melting over the range of 277–285°. This compound was recrystallized from benzene to produce 17.7 g. (65%) of pure triphenylsilyltriphenyltin, melting at 287–289°. A mixture melting point with an authentic specimen was not depressed. This experiment indicates the presence of triphenyltin-lithium in a minimum yield of 65%.

Triphenyltin-lithium with diethyl carbonate. Run I. A solution of 2.36 g. (0.02 mole) of diethyl carbonate in 10 ml. of ether was added rapidly to an ethereal suspension of 0.01 mole of triphenyltin-lithium at −10°. Immediately after this addition, a gas was evolved vigorously which blackened a piece of filter paper moistened with a dilute solution of palladium chloride,[9] thus indicating that the gas was carbon monoxide. The stirred reaction mixture was allowed to come to room temperature, and then stirred at room temperature for 1 hr. The mixture was then poured slowly into aqueous ammonium chloride, the insoluble product was removed by filtration, and the two layers were separated. The insoluble product removed after hydrolysis was recrystallized from benzene to obtain 0.55 g. (14%) of tetraphenyltin, melting at 224°. The ethereal layer was dried, then concentrated to obtain 2.01 g. of amorphous material melting over the range 194–207°. Fractional crystallization of this mixture from carbon disulfide, followed by recrystallization of the fractions from benzene gave 1.40 g. (40%) of hexaphenylditin, melting at 231–232°, and 0.32 g. (8%) of additional tetraphenyltin, melting at 222–223°. The total yield of tetraphenyltin was 22%. Mixture melting points with authentic specimens in each case were not depressed.

No evidence of ethyl benzoate, benzophenone or benzoic acid could be found.

Run II. This reaction did not differ essentially from the one described above except in the size of the run. From the reaction of 0.045 mole of triphenyltin-lithium with 10.6 g. (0.09 mole) of diethyl carbonate essentially the same results were obtained. Carbon monoxide was evolved vigorously (palladium chloride test). After hydrolysis and purification of the products, 7.8 g. (50%) of hexaphenylditin, melting at 230–231°, and 3.46 g. (19.5%) of tetraphenyltin, melting at 221–223° were obtained.

No evidence of ethyl benzoate, benzophenone, or benzoic acid could be found.

Triphenyltin-lithium with ethyl chloroformate. Run I. A solution of 9.7 g. (0.09 mole) of freshly distilled ethyl chloroformate in 25 ml. of ether was added all at once to an ethereal suspension containing 0.045 mole of triphenyltin-lithium at room temperature. Carbon monoxide was vigorously evolved (palladium chloride test). The reaction mixture was stirred at room temperature for a period of 2 hr., then hydrolyzed with water, and the products were isolated in the same manner as was described in the reaction of triphenyltin-lithium with diethyl carbonate. After first separating the products by fractional crystallization from carbon disulfide, they were recrystallized from benzene, to produce 1.3 g. (9.2%) of tetraphenyltin and 8.1 g. (51%) of hexaphenylditin. The products obtained melted at 220–222° and 226–227° respectively, and mixture melting points with authentic specimens were not depressed.

No other products were found in the reaction mixture.

Run II. This reaction was carried out under exactly the same conditions as the reaction described in *Run I,* with the single exception that the reversed order of addition was used; *i.e.,* the 0.045 mole of triphenyltin-lithium suspended in ether was added gradually to 9.7 g. (0.09 mole) of ethyl chloroformate in 25 ml. of ether. After hydrolysis, fractional crystallization, and recrystallization as described above, 1.6 g. (11%) of tetraphenyltin and 8.6 g. (54%) of hexaphenylditin were obtained. These products melted at 220–222° and 228–230° respectively.

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Polynitrogen Systems from the Hydrazinocarbonic Acids. Part VIII.[1] The Synthesis and Estimation of Some Nitroguanylhydrazones

F. L. SCOTT,[2] W. N. MORRISH, AND J. REILLY

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The use of nitroaminoguanidine as a reagent for the characterization of carbonyl compounds[3] has been extended in this present note. In addition an effort was made to utilize the Jamieson iodate technique[4] to estimate some nitroguanylhydrazones.

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[2] To whom inquiries concerning reprints are to be sent. Present address, Department of Chemistry, University of California, Los Angeles 24, Calif.

[3] Compare (a) R. A. Henry and G. B. L. Smith, *J. Am. Chem. Soc.,* **74,** 278 (1952); (b) W. F. Whitmore, A. J. Revukas, and G. B. L. Smith, *J. Am. Chem. Soc.,* **57,** 706 (1935); (c) G. B. L. Smith and E. P. Shoub, *J. Am. Chem. Soc.,* **59,** 2077 (1937); (d) W. D. Kumler and P. P. T. Sah, *J. Am. Pharm. Assoc.,* **41,** 375 (1952).

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