saturated ammonium chloride solution. The ether layer was then separated, dried over anhydrous sodium sulfate and vacuum distilled to yield 31.0 g. (79%) of dibutyl phosphite, b.p. 89–91° (3 mm.), $n^{19.5}\text{D}$ 1.4246.

Diethyl 2-Hydroxypropane-2-phosphonate.—To 0.1 mole of the bromomagnesium derivative of diethyl phosphite, 5.8 g. (0.1 mole) of acetone in 25 ml. of anhydrous ether was added. The reaction mixture was then refluxed for three hours and after standing overnight at room temperature was decomposed in the manner previously indicated. After separation of the ether layer and drying over anhydrous sodium sulfate, vacuum distillation yielded 8.0 g. (41%) of product, b.p. 145–148° (20 mm.), m.p. 14–16°, literature[10] b.p. 145° (20 mm.), m.p. 14–15°.

Diethyl Ester of α-Hydroxybenzylphosphonic Acid.—To 0.1 mole of the bromomagnesium derivative of diethyl phosphite, 10.6 g. (0.1 mole) of benzaldehyde in 25 ml. of anhydrous ether was added. The reaction mixture was refluxed for three hours and then worked up as previously indicated. After removal of some unreacted phosphite and benzaldehyde by vacuum distillation, the residue in the still flask was recrystallized from benzene–petroleum ether to give 15 g. (61.5%) of crude product. After several recrystallizations, pure product, m.p. 83–84°, was obtained; lit.[11] m.p. 83–84°.

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DEPARTMENT OF CHEMISTRY
DUQUESNE UNIVERSITY
PITTSBURGH, PA.

Reaction of Triphenyltin Hydride with Methyllithium

BY HENRY GILMAN AND SANDERS D. ROSENBERG

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Triethylsilane has been treated with methyllithium,[1] *n*-propyllithium, *n*-butyllithium, phenyllithium and lithium ethoxide.[2] In each reaction the products were lithium hydride and the corresponding substituted triethylsilane. This type

$$(C_2H_5)_3SiH + RLi \longrightarrow (C_2H_5)_3SiR + LiH$$
$$(C_2H_5)_3SiH + C_2H_5OLi \longrightarrow (C_2H_5)_3SiOC_2H_5 + LiH$$

of reaction was extended to the aromatic series when triphenylsilane was treated with methyllithium and phenyllithium to form lithium hydride and triphenylmethylsilane and tetraphenylsilane, respectively,[3] and appeared to be general for hydrides of Group IV-B elements when it was shown that triphenyltin hydride[3] and triphenylgermane[4] yielded lithium hydride and tetraphenyltin and tetraphenylgermanium, respectively, when reacting with phenyllithium. Benkeser and Riel[5] treated four substituted triarylsilanes with methyllithium to form, in each case, the triarylmethylsilane and lithium hydride.

Recently it was reported that when triphenyltin hydride reacts with methyllithium the products are triphenyltin-lithium and methane.[6] The reactive intermediate, triphenyltin-lithium, was identified by reaction with triphenyltin bromide to form hexaphenylditin in 49% yield.

$$(C_6H_5)_3SnH + CH_3Li \longrightarrow (C_6H_5)_3SnLi + CH_4$$

It may not be valid to generalize that the reaction of trisubstituted tin hydrides with methyllithium will be the same as that of trisubstituted silanes. The latter when treated with methyllithium form trisubstituted methylsilanes.[1,3,5] But because of this apparent anomalous result[6] and our interest in the organometallic complex, triphenyltin-lithium,[7] the reaction was repeated in this Laboratory.

It was found that triphenyltin hydride and methyllithium react to form triphenylmethyltin (18%), tetraphenyltin (25%) and lithium hydride in accordance with results cited previously.[1–5] In a check run the yield of triphenylmethyltin was 15% and of tetraphenyltin, 25%. No gas evolution was noted in either run and the characteristic yellow-tan color, denoting triphenyltin-lithium, was not evident. It is interesting to note the formation of tetraphenyltin, possibly as a consequence of disproportionation, even under these mild conditions.[3]

$$(C_6H_5)_3SnH + CH_3Li \longrightarrow (C_6H_5)_3SnCH_3 + (C_6H_5)_4Sn + LiH$$

We are also presenting at this time a method for the quantitative analysis of tin in organotin compounds.[8]

Experimental

Triphenyltin Hydride.—This preparation was carried out as described by Wittig and co-workers[6] except that triphenyltin iodide was used in place of triphenyltin bromide. Two runs were made and in both the yield of triphenyltin hydride, distilling at 151° (0.05 mm.), was 1.8 g. (51.6%). It was found that if triphenyltin chloride was substituted for triphenyltin iodide no reaction took place under corresponding conditions.

Reaction of Triphenyltin Hydride with Methyllithium.—The methyllithium used in this reaction was prepared[9] by refluxing for one hour, 1.42 g. (0.01 mole) of freshly opened methyl iodide (Eastman Kodak Co., white label) with 0.08 g. (0.01 g. atom plus 10%) of lithium metal in 100 ml. of ether. The lithium iodide thus formed was allowed to settle out and the clear methyllithium solution was used.

A 250-ml. flask was equipped with a magnetic stirrer, a 100-ml. graduated dropping funnel, a nitrogen inlet tube and a gas outlet tube. The gas outlet tube was attached to a gas bubble counter filled with concentrated sulfuric acid; the counter was, in turn attached to a Dumas tube filled with fine cupric oxide; this tube was attached to water- and carbon dioxide-absorption tubes used in micro carbon and hydrogen quantitative analysis.[10]

About 50 ml. of ether was placed in the flask, gentle stirring was begun, and a very slow stream (*ca.* one bubble every three seconds) of nitrogen gas was passed through the entire system for one hour. The long burner under the Dumas tube was turned on during the sweep-through of the gas. The absorption tubes were then weighed.

After the absorption tubes were returned to their positions 1.6 g. (0.0046 mole) of triphenyltin hydride was added to the reaction flask and 0.0046 mole of methyllithium in 35 ml. of ether was placed in the dropping funnel. The same rate of nitrogen sweep-through and stirring as before were

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maintained while the methyllithium solution was added dropwise. There was no discernible increase in the bubble rate during the addition of the methyllithium solution and a white solid precipitated. No yellow-tan colored precipitate or yellow solution indicative of triphenyltin-lithium formed. The system was swept with nitrogen for 0.5 hour after the addition was completed. The absorption tubes were then reweighed and, within limits of allowable error, there was no change in weight for either tube. A Color Test I,[11] made one hour after the addition was completed, was negative.

The ethereal solution was filtered from the white solid, extracted with 50 ml. of water, and dried over sodium sulfate. This white solid was analyzed as lithium hydride by the method outlined previously.[3] The ether layer yielded an oil which was digested with 50 ml. of methanol, and the mixture was allowed to cool slowly. On cooling, 0.4 g. of solid melting over the range 170–225° was recovered. This solid was recrystallized from 25 ml. of petroleum ether (b.p. 77–120°) to yield 0.35 g. (25.0% calculated on the number of phenyl groups available) of tetraphenyltin melting at 222–225°. A mixed melting point with an authentic specimen showed no depression. The methanol was removed by distillation leaving an oil. Thorough cooling in a Dry Ice-bath yielded an oily solid. This mass was extracted twice with 5-ml. portions of cold ethanol to yield 0.5 g. of crude triphenylmethyltin melting over the range 48–54°. This crude solid was recrystallized from 5 ml. of ethanol to yield 0.3 g. (18.1%) of triphenylmethyltin melting at 59–61°.[12] A mixed melting point determination with an authentic specimen prepared in essential accordance with the procedure of Bullard and Robinson[12] showed no depression.

Run 2.—This run was carried out precisely as was the first. Once again no gas evolution was noted, the characteristic yellow-tan color of triphenyltin-lithium was not observed and the weight of the gas absorption tubes remained constant. In this experiment 0.35 g. (25%) of tetraphenyltin melting at 224–225° and 0.25 g. (15.0%) of triphenylmethyltin melting at 60–61° was obtained. Both compounds were identified by the method of mixed melting points.

A Method for the Quantitative Analysis for Tin in Organotin Compounds.—Tin in organotin compounds usually is determined as stannic oxide. Pfeiffer[13] introduced a method which involves decomposition of the sample by the use of fuming nitric acid in a sealed tube, followed by evaporation of the product with concd. sulfuric acid and ignition to stannic oxide. A more convenient method[14] uses fuming nitric plus fuming sulfuric acid in a covered porcelain crucible to decompose the sample, followed by ignition to stannic oxide. Concentrated sulfuric acid plus 30% hydrogen peroxide has been used in place of fuming nitric plus fuming sulfuric acid.[15] Volatile organotin compounds usually give low results by the fuming acid procedure. A method has been introduced whereby the volatile organotin compound is first decomposed with bromine in carbon tetrachloride, followed by treatment with concd. nitric plus sulfuric acid and finally ignition to stannic oxide.[16]

It has been found that organotin compounds can be completely decomposed simply by treatment with concd. sulfuric acid followed by ignition to stannic oxide. This method can be applied to volatile as well as non-volatile compounds. Vycor crucibles have been used in place of porcelain crucibles because of the greater visibility afforded by the former.

In a 30-ml. Vycor crucible (Corning Glass Works, Corning, N. Y., code word GIKYN) was weighed approximately 0.2 g. of the organotin compound to be analyzed. To this was added, with caution, 20 drops (1.0 ml.) of concd. sulfuric acid (sp. gr. 1.84), and the crucible was placed on a Rogers ring burner. The sample usually turned jet black almost immediately. The excess acid was then cautiously removed by heating the uncovered crucible at its top. The ring was then raised at intervals, thereby gradually lowering the position of the flame on the sides of the crucible until the flame was directed to the bottom, and the carbonaceous material formed by the action of the acid was completely ignited leaving a white solid. The uncovered crucible was then ignited on a Bunsen burner for 0.5 hour to insure complete conversion to stannic oxide, cooled and weighed in the usual manner. A complete analysis requires about two hours to run. Some representative results follow.

(1) Triphenyl-*o*-methoxyphenyltin, a solid; calcd. for $C_{25}H_{22}OSn$: Sn, 25.97. Found: Sn, 26.10, 26.21.

(2) Tri-*n*-butylphenyltin, a liquid; calcd. for $C_{16}H_{32}Sn$: Sn, 32.33. Found: Sn, 32.37, 32.47.[17]

(3) Triphenyl-*m*-dimethylaminophenyltin, a solid; calcd. for $C_{26}H_{25}NSn$: Sn, 25.24. Found: Sn, 25.28, 25.41.

(4) Triphenyl-3-dimethylamino-6-(4′-bromophenylazo)-phenyltin, a solid; calcd. for $C_{32}H_{28}N_3BrSn$: Sn, 18.01. Found: Sn, 18.10, 18.17.

DEPARTMENT OF CHEMISTRY
THE IOWA STATE COLLEGE
AMES, IOWA

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Some Glyoxylic Steroids

BY DAVID GOULD AND E. B. HERSHBERG

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The acid-catalyzed rearrangement of cortisone acetate has been shown to lead to a glyoxal side chain.[1] Some related results on glyoxylic steroids stem from our attempt to hydrolyze cortisone acetate by the Freudenberg[2] conditions. This reaction failed to give cortisone, but instead gave the product of Mattox and Kendall,[3] 21,21-dimethoxy-4-pregnene-3,11,20-trione (I). We obtained the same product from free cortisone, using the same procedure. These hydrolytic conditions were then applied to pregnane-17α,21-diol-3,11,20-trione 21-acetate which, according to infrared analysis, also gave a product with a saturated ether bond but without acetate or hydroxyl groups. This is presumably 21,21-dimethoxypregnane-3,11,20-trione (II), in analogy with the structure of the product obtained from cortisone acetate.

These structures were not then known, and we felt that possible formulations of I and II were those also considered by Mattox to be 16,21-dimethoxypregnantriones.[1] Since we had successfully cleaved methanol from 16α-methoxy-5-pregnen-3β-ol-20-one to give 5,16-pregnadien-3β-ol-20-one acetate,[4] we similarly treated the dimethoxy trione I obtained from cortisone, with acetic anhydride and *p*-toluenesulfonic acid, expecting to obtain the corresponding Δ^{16}-20-ketone. The isolated product, however, did not contain hydroxyl, methoxyl or conjugated carbonyl, according to infrared spectra. It did show infrared bands corresponding to acetate and enol acetate, conjugated diene, carbonyl (*e.g.*, at C_{11}), and interacting 21-acetate and 20-carbonyl. This evidence applied to the correct formulation of I[1] and combined with the negative rotatory shift and the analysis, indicates that the material is 3,5-pregnadiene-3,21,21-triol-11,20-dione triacetate (III).

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