amine hydrochloride was filtered off, and the triamide recovered from the ether solution and purified as described in the previous paragraph. Twelve and four-tenths grams of a pale yellow oil was obtained from which 9.4 g. of crystalline material, m.p. 52–53° was obtained. Recrystallization from petroleum ether raised the melting point to 54°. The addition of this amide to the product obtained from dibutylamine and phosphorus pentasulfide did not depress its melting point.

$(C_4H_9NH)_3PS$, m.p. 54°. *Anal.* Calcd. for $C_{12}H_{30}N_3PS$: C, 51.58; H, 10.82; N, 15.04; P, 11.09. Found: C, 51.63; H, 10.92; N, 14.95; P, 11.72.

$(C_6H_5CH_2NH)_3PS$, m.p. 122–123°. The addition of the triamide, m.p. 123–125°, prepared from benzylamine and phosphorus pentasulfide,[2] to this substance did not lower its melting point.

CLEVELAND, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Preparation of Triphenyltin-lithium and Some of Its Reactions

BY HENRY GILMAN AND SANDERS D. ROSENBERG

The preparation of triphenyltin-lithium from stannous chloride and phenyllithium is described together with an account of some of its chemical properties. Tetraphenyltin, triphenylbenzyltin, triphenylethyltin, hexaphenylditin and triphenylsilyl-triphenyltin have been prepared by the reaction of triphenyltin-lithium with appropriate halides. In addition, some other reactions are described.

Investigations in this Laboratory have shown[1] that lead dichloride reacts with three equivalents of phenyllithium in the cold to form triphenyllead-lithium, and that treatment of this intermediate with appropriate halides gives organolead derivatives of the type $(C_6H_5)_3PbR$ in good yields. Similar reactions have been carried out with dihalides of other Group IV-B elements. The results obtained from the reaction of phenyllithium with germanium diiodide, GeI_2, will be reported later.[2]

In a recent article[3] Wittig and co-workers reported that triphenyltin-lithium has been prepared by treating diphenyltin with one equivalent of phenyllithium. It has been found in this Laboratory that triphenyltin-lithium can be prepared directly by treating finely ground, anhydrous stannous chloride[4] with three equivalents of phenyllithium in the cold, thereby eliminating the preparation of diphenyltin. A series of color changes takes place as the addition of the phenyllithium progresses. When the first equivalent of phenyllithium has been added the reaction mixture is orange in color; the addition of the second equivalent changes the color to deep red[5]; the third equivalent turns the color to light tan.

Triphenyltin-lithium has been treated with a series of halides in order to form some unsymmetrical organotin compounds of the type $(C_6H_5)_3SnR$, and to explore the procedure for the introduction of water-solubilizing groups. The path of the reactions has been postulated as

$$SnCl_2 + 2C_6H_5Li \longrightarrow (C_6H_5)_2Sn + 2LiCl \quad (1)$$

$$(C_6H_5)_2Sn + C_6H_5Li \longrightarrow (C_6H_5)_3SnLi \quad (2)$$

$$(C_6H_5)_3SnLi + RX \longrightarrow (C_6H_5)_3SnR + LiX \quad (3)$$

In the reactions of triphenyltin-lithium with benzyl chloride and ethyl iodide a considerable amount (60.0 and 26.9%, respectively) of tetraphenyltin was isolated; reactions with iodobenzene, triphenyltin chloride and triphenylchlorosilane yielded only the expected products in good yields.

It has been shown[1] that equation (2) applied to the lead series

$$(C_6H_5)_2Pb + C_6H_5Li \rightleftarrows (C_6H_5)_3PbLi \quad (4)$$

represents an equilibrium system with the equilibrium displaced 80% toward the triphenyllead-lithium. It has not yet been rigorously established whether triphenyltin-lithium is involved in a related equilibrium system. Carbonation of triphenyltin-lithium by passing carbon dioxide gas over the surface of the reaction mixture for five hours yielded no benzoic acid or addition products of benzoic acid. Addition of benzophenone to triphenyltin-lithium yielded no detectable amounts of triphenylcarbinol and led only to recovery of benzophenone. Color Test I[6] remains negative until slightly more than three equivalents of phenyllithium have been added.[7]

Further experiments designed to explain the formation of the tetraphenyltin and elucidate the exact nature of the triphenyltin-lithium intermediate are now being carried out.

Experimental

Triphenyltin-lithium.—To a well-stirred suspension of 8.54 g. (0.045 mole) of finely ground, anhydrous stannous chloride in 50 ml. of ether maintained at −10°, was added, dropwise, 0.135 mole (3 equivalents) of phenyllithium dissolved in 137 ml. of ether. When one equivalent (0.045 mole, 46 ml.) had been added, the reaction mixture was orange-colored; with two equivalents (0.09 mole, 91 ml.) the color was deep red; with three equivalents (0.135 mole, 137 ml.) the color was light tan. Color Test I[6] was negative upon completion of the addition of all (137 ml.) of the phenyllithium solution.

General Procedure for the Reaction of Triphenyltin-lithium with a Halide.—To a well-stirred suspension of triphenyltin-lithium in ether was added an ether solution of the appropriate halide. Unless otherwise stated the reaction mixture was then refluxed for 1.5 hours and hydrolyzed by pouring into a saturated ammonium chloride solution.

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[1] H. Gilman, L. Summers and R. W. Leeper, THIS JOURNAL, **74**, in press (1952); see also E. Bindschadler and H. Gilman, *Proc. Iowa Acad. Sci.*, **48**, 273 (1941) [*C. A.*, **36**, 1595 (1942)].

[2] H. Gilman, L. Summers and S. D. Rosenberg, THIS JOURNAL, **74**, in press (1952).

[3] G. Wittig, F. J. Meyer and G. Lange, *Ann.*, **571**, 167 (1951); see also G. Wittig, *Angew. Chem.*, **62**, 231 (1950).

[4] "Stannochlor" purchased from Metal and Thermit Corporation.

[5] See E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Gebruder Borntraeger, Berlin, 1937, p. 355, for a discussion of the color of solutions of diaryltin compounds in organic solvents.

[6] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

[7] In the lead series Color Test I becomes positive between 2.8 and 3.0 equivalents of phenyllithium.

The solids which remained suspended in the ether layers on hydrolysis were filtered off and dried. The ether layers were separated and dried over anhydrous sodium sulfate. Ether was removed by distillation. The products were identified by mixed melting point with an authentic specimen unless otherwise stated. All melting points are uncorrected.

Iodobenzene; Tetraphenyltin.—To 0.045 mole of triphenyltin-lithium was added 10.1 g. (0.0495 mole, 10% excess 0.045 mole) of iodobenzene dissolved in 40 ml. of ether. The reaction mixture was refluxed and hydrolyzed. The yellow solid recovered on hydrolysis was combined with the solid residue from the ether layer and crystallized from petroleum ether (b.p. 77–120°) to yield 12.7 g. (66.2%) of tetraphenyltin melting at 224–225°.

Benzyl Chloride; Triphenylbenzyltin.—To 0.045 mole of triphenyltin-lithium was added 5.7 g. (0.0495 mole) of benzyl chloride dissolved in 30 ml. of ether while the temperature of the reaction mixture was maintained at −35° in order to minimize possible side reactions. The suspension was stirred for 30 minutes at −35°, then for an additional 30 minutes while the temperature was permitted to rise to −10°. It was then hydrolyzed. The yellow solid recovered on hydrolysis was crystallized from petroleum ether (b.p. 77–120°) to yield 8.7 g. (60.0%) of tetraphenyltin melting at 224–225°. The ether layer yielded a yellow oil which partially solidified on cooling in an ice-bath. The solid was crystallized from ethanol to yield 4.6 g. (21.7%) of triphenylbenzyltin melting at 90–91°.

Ethyl Iodide; Triphenylethyltin.—To 0.045 mole of triphenyltin-lithium was added 7.7 g. (0.0495 mole) of ethyl iodide dissolved in 40 ml. of ether. The reaction mixture was refluxed and hydrolyzed. The yellow solid recovered on hydrolysis was crystallized from petroleum ether (b.p. 77–120°) to yield 3.9 g. (26.9%) of tetraphenyltin melting at 224–225°. The ether layer yielded a deep yellow solid which was extracted with 100 ml. of petroleum ether (b.p. 60–70°). On cooling the petroleum ether solution in an ice-bath a yellow solid precipitated. The solid was crystallized from a minimum amount of ethanol to yield 6.2 g. (36.4%) of triphenylethyltin melting at 56–58°.

Triphenyltin Chloride; Hexaphenylditin.—To 0.023 mole of triphenyltin-lithium was added 8.86 g. (0.023 mole) of triphenyltin chloride dissolved in 250 ml. of ether. The reaction mixture was refluxed and hydrolyzed. The white solid recovered on hydrolysis was combined with the solid residue from the ether layer and crystallized from an excess of petroleum ether (b.p. 77–120°) to yield 7.7 g. (52.8%) of hexaphenylditin melting at 229–231°.

Triphenylchlorosilane; Triphenylsilyl-triphenyltin.—To 0.045 mole of triphenyltin-lithium was added 13.3 g. (0.045 mole) of triphenylchlorosilane dissolved in 100 ml. of ether. The reaction mixture was refluxed for three hours and then hydrolyzed. The yellow solid recovered on hydrolysis was crystallized twice from a minimum amount of benzene to yield 19.5 g. (71.3%) of triphenylsilyl-triphenyltin melting at 289–291°. From the ether layer, 2.2 g. of unreacted triphenylchlorosilane was recovered.

Anal. Calcd. for $C_{36}H_{30}SiSn$: Si, 4.61; Sn, 19.48. Found: Si, 5.09; Sn, 19.61.

A mixed melting point with a specimen prepared by the reaction of triphenylsilyl-potassium with triphenyltin chloride showed no depression.[8]

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[8] Unpublished work of T. C. Wu.

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[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

The Synthesis of Pimelic Acid from Cyclohexene-4-carboxylic Acid and its Derivatives

BY FRANK X. WERBER, J. E. JANSEN AND T. L. GRESHAM

Optimum reaction conditions for the alkaline isomerization and cleavage of cyclohexene-4-carboxylic acid to pimelic acid are presented. Evidence has been obtained showing that the intermediate cyclohexene-1-carboxylic acid undergoes attack by hydroxyl ion with displacement of a hydride ion to give cyclohexanone-2-carboxylic acid as a further intermediate; the latter is cleaved to pimelic acid or decarboxylated to cyclohexanone in relative amounts depending upon the reaction conditions. Hydrogen is formed in equivalent amounts, and hydrogenation is a side reaction. 3,6-Endomethylenecyclohexene-4-carboxylic acid does not undergo the new cleavage reaction. Cyclohexene-4-carboxaldehyde is partly cleaved to pimelic acid, and partly undergoes hydrogenolysis and aromatization.

Reports on a novel synthesis of pimelic acid and substituted pimelic acids, by cleavage of various cyclohexene derivatives, have recently appeared in the literature.[1,2] A study of this cleavage reaction was begun independently in this Laboratory prior to receipt of the German and U. S. publications, and the course of the reaction has been partly elucidated.

Unsaturated aliphatic acids are cleaved in fused alkali to acetic acid and a second saturated acid with two fewer carbon atoms than the starting material.[3,4] Extension of this reaction to cyclic unsaturated acids would lead one to expect cleavage to a single dibasic acid. Fusion of cyclohexene-4-carboxylic acid (I) in potassium hydroxide indeed gave pimelic acid in a yield of 33%. The reaction was further examined in aqueous solution under pressure and under a variety of conditions. Under the best conditions found, pimelic acid could be obtained in 78% yield. Complete conversions could be effected above 300° with reaction times up to 10 hours.

The gain of one carboxyl group in the reaction points to an oxidative process. Since oxygen is not freely available when the reaction is carried out in a sealed autoclave one would suspect dehydrogenation; actually, 0.85 mole of hydrogen per mole of I was found in the off-gases in one experiment (Burrell gasometric technique). Cyclohexanone (V) was a by-product of the reaction under all conditions; it was formed in yields varying from 3 to 24%.[5] This ketone is known to be the product of the "ketonic cleavage" of cyclohexanone-2-carboxylic acid (III), whereas pimelic acid is formed from III by the "acid cleavage," which usually required alkaline conditions.[6] It thus becomes rea-

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[1] H. J. Pistor and H. Plieninger, *Ann.*, **562**, 239 (1949); see also USPB 25616, pp. 472–476 (U. S. Department of Commerce).

[2] H. deV. Finch, S. A. Ballard and T. W. Evans, U. S. Patent 2,454,047 to Shell Development Company; *C. A.*, **43**, 5416 (1949).

[3] F. G. Edmed, *J. Chem. Soc.*, **73**, 627 (1898); F. Varrentrap, *Ann.*, **35**, 196 (1840).

[4] F. Becker, *Ber.*, **11**, 1413 (1878).

[5] Cyclohexanone could also be formed by pyrolysis of disodium pimelate. In the presence of little water (5 moles per mole disodium pimelate) this became a serious reaction; however, under the conditions discussed above—large excess of water (22 moles per mole I)—the amount formed from disodium pimelate on heating at 350° was too small to be measured.

[6] H. R. Snyder, L. A. Brooks and S. H. Shapiro, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 531.