Synthesis of Triaryltin Hydrides[1,2]

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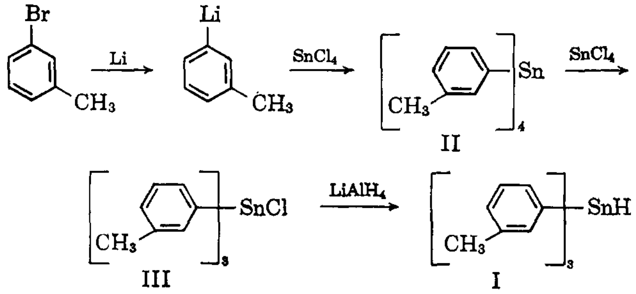
Three new triaryltin hydrides have been synthesized: tris(*m*-tolyl)tin, tris(*o*-tolyl)tin, and tris(*o*-biphenylyl)tin hydrides. The attempted syntheses of tris(*p*-chlorophenyl)tin and tris(*m*-trifluoromethylphenyl)tin hydrides failed. The course of the reactions is discussed and several new organotin intermediates are described.

Triphenyltin hydride, whose preparation[5] was first described in 1926, remained until recently the only known member of the triaryltin hydride series. The synthesis of new triaryltin hydrides has become important in light of the emerging interest in the hydrogenolysis reactions of alkyl[6-12] and aryl[6-8,13,14] halides with triphenyltin hydride. Recently the syntheses of tris(*p*-tolyl), tris(*p*-fluorophenyl), and trimesityltin hydrides were reported from our laboratories.[14] We would like at this time to report the successful syntheses of three additional new hydrides and the attempted, but unsuccessful, synthesis of two others.

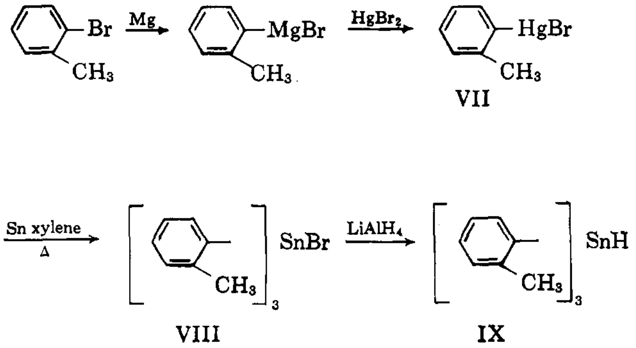
Using the conventional synthetic route, tris(*m*-tolyl)tin hydride (I) was prepared by first treating *m*-tolyllithium with stannic chloride giving tetrakis-(*m*-tolyl)tin (II) in 75% yield.[15] Redistribution of II with stannic chloride afforded tris(*m*-tolyl)tin chloride (III), whose reduction with lithium aluminum hydride proceeded smoothly to I.



An analogous synthetic scheme was thought applicable to the preparation of the *o*-tolyl analog of I. Treatment of *o*-tolyllithium with stannic chloride gave tetrakis(*o*-tolyl)tin (IV). However, in our hands, contrary to claims in the literature,[16] IV would not undergo the redistribution reaction with stannic chloride. Iodine in carbon tetrachloride likewise failed to cleave IV.

The procedure reported by Krause and Becker[15] yielded tris(*o*-tolyl)tin chloride (V) in poor, unreliable yields. This was then accomplished by treating *o*-tolylmagnesium bromide with stannic chloride, converting the mixture of tris(*o*-tolyl)tin chloride and bromide so obtained to the hydroxide with aqueous hydrochloric acid. V was converted to tris(*o*-tolyl)tin hydroxide (VI) by titration with aqueous base as a further proof of structure.

On the other hand, the little used procedure of Nad and Kocheshkov[17] was successful. In this method an arylmercuric halide is treated with powdered tin in boiling xylene to give the triaryltin halide directly in 41% yield. Thus, *o*-tolylmercuric bromide (VII) was obtained from the Grignard and mercuric bromide. Reaction of VII with powdered tin in refluxing xylene gave tris(*o*-tolyl)tin bromide (VIII), which in turn yielded tris(*o*-tolyl)tin hydride (IX) on reduction with lithium aluminum hydride.



Tris(*o*-biphenylyl)tin hydride (X) was readily obtained from the corresponding bromide by reduction with lithium aluminum hydride. The one-step synthesis of tris(*o*-biphenylyl)tin bromide (XI) from *o*-biphenylylmagnesium bromide and stannic bromide had previously been reported.[18] The structure of X was confirmed by conversion to tris(*o*-biphenylyl)tin chloride (XII) with carbon tetrachloride. Bis(*o*-biphenylyl)tin dibromide (XIII) was inadvertently obtained when impure *o*-bromobiphenyl (found to contain considerable amounts of *o*-aminobiphenyl) was used in the synthesis of XI.

In order to place electron-withdrawing substituents into triaryltin hydrides, tetrakis(*m*-trifluoromethyl-

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[3] Taken from a portion of the dissertation submitted to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, 1964.

[4] To whom inquiries should be sent.

[5] R. F. Chambers and P. C. Scherer, *J. Am. Chem. Soc.*, **48**, 1054 (1926).

[6] J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind.* (London), **9**, 294 (1959).

[7] H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962).

[8] H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Org. Chem.*, **28**, 2165 (1963).

[9] (a) E. J. Kupchik and R. J. Kiesel, *Chem. Ind.* (London), **37**, 1654 (1962); *J. Org. Chem.*, **29**, 764 (1964).

[10] D. H. Lorenz and E. I. Becker, *J. Org. Chem.*, **27**, 3370 (1962).

[11] E. J. Kupchik and T. Lanigan, *ibid.*, **27**, 3661 (1962).

[12] D. Seyferth, H. Yamazaki, and D. L. Alleston, *ibid.*, **28**, 703 (1963).

[13] L. A. Rothman and E. I. Becker, *ibid.*, **24**, 294 (1959); *ibid.*, **25**, 2203 (1960).

[14] D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *ibid.*, **28**, 2332 (1963).

[15] This compares with the 29% yield previously reported by E. Krause and R. Becker [*Ber.*, **53**, 173 (1920)] using the Grignard reagent and stannic chloride.

[16] K. A. Kocheshkov, M. M. Nad, and A. P. Aleksandrov, *ibid.*, **67**, 1348 (1934).

[17] M. M. Nad and K. A. Kocheshkov, *J. Gen. Chem. USSR*, **8**, 42 (1938); *Chem. Abstr.*, **32**, 5387 (1938).

[18] G. Bähr and R. Gelius, *Ber.*, **91**, 812 (1958).

phenyl)tin[19] (XIV) and tetrakis(*p*-trifluoromethylphenyl)tin (XV) were synthesized from the corresponding arylmagnesium bromides and stannic chloride. Attempted redistribution of XIV with stannic chloride was unsuccessful as was the attempted cleavage with iodine in carbon tetrachloride.

The unsuccessful cleavage of XIV by either stannic chloride or iodine in carbon tetrachloride may be related to the recent studies concluded on the effect of substituents of varying electronic character of the rates of cleavage of aryltin bonds by electrophilic reagents.[20,21]

Tris(*m*-trifluoromethylphenyl)tin bromide (XVI) was obtained by refluxing a solution of *m*-trifluoromethylphenylmercuric bromide (XVII) in xylene in the presence of powdered tin. However, reduction of XVI with lithium aluminum hydride gave only hexakis-(*m*-trifluoromethylphenyl)ditin (XVIII) and not the expected hydride. A complex reaction was indicated in view of a series of colors which developed upon hydrolysis of the reaction mixture, which may in part be due to oxygen (see Experimental). However, these were not investigated further.

Tris(*p*-chlorophenyl)tin chloride (XIX) was obtained by the redistribution of tetrakis(*p*-chlorophenyl)-tin (XX) with stannic chloride. Reduction of XIX with lithium aluminum hydride again failed to yield the expected hydride; only hexakis(*p*-chlorophenyl)-ditin (XXI) could be isolated.

It has previously been reported[14] that the reduction of tris(*p*-fluorophenyl)tin chloride did yield the corresponding hydride (33% yield) accompanied, however, by the formation of considerable amounts of hexakis-(*p*-fluorophenyl)ditin (50% yield). The accompaniment of tin–hydride formation by such large amounts of hexa compound had not previously been observed.

The difficulties in the attempted syntheses of tris-(aryl)tin hydrides in which the aryl group contains electron-withdrawing groups may be related to the ease of attack of the tin atom by halide ions in solution. Such assisted reactions leading to formation of hydrogen or even cleavage of tin–aryl bonds have been recently reported.[22,23]

Experimental

Materials.—All the substituted bromobenzenes (except where indicated) used in synthesis were washed with concentrated sulfuric acid until the sulfuric acid layer remained colorless. The organic halide was then separated, washed twice with water and twice with 5% sodium bicarbonate solution, followed by a final wash with water. The organic halide was then separated, dried over calcium chloride, and distilled from calcium hydride.

Lithium metal ribbon (contaminated with 0.6–1.0% sodium) from Lithium Corporation of America was used. Finest powdered, purified tin metal from Fisher Laboratory Chemicals, was used. Ingots of Nelco magnesium were milled into turnings using a Carboloy cutting tool.

All metalation reactions and reductions with lithium aluminum hydride were carried out under dry nitrogen in apparatus protected by a calcium chloride tube.

Melting points were determined in capillary tubes and are corrected. Analyses were carried out by Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y., and by one of the authors, A. S.

Preparation of Tetrakis(*m*-tolyl)tin(II).—A solution of 50 g. (0.29 mole) of *m*-bromotoluene in a mixture of 150 ml. of ether and 50 ml. of benzene (distilled from calcium hydride) was added dropwise to 5.1 g. (0.71 g.-atom) of finely cut lithium ribbon. After the completion of addition, the reaction mixture was refluxed for a period of 1 hr.; it was cooled and then filtered in an inert atmosphere. A solution of 14.1 g. (0.054 mole, 6.3 ml.) of stannic chloride in 25 ml. of dry benzene was added dropwise to the reaction mixture. Upon completion of addition, the reaction mixture was refluxed for 1.5 hr. and then carefully hydrolyzed with 10% hydrobromic acid. The organic layer was separated, washed with water, and finally dried over anhydrous sodium sulfate.

Distillation of the mixed solvent at reduced pressure afforded a yellow oil, which crystallized on the addition of a few milliliters of ethanol. Recrystallization of the yellow solid from ethanol afforded 20.0 g. (0.041 moles, 77%) of feathery, slightly yellow needles, m.p. 126.0–128.0° (lit.[15] m.p. 128.5°). One more recrystallization from ethanol yielded 16.5 g. (0.034 mole, 58%) of white needles, m.p. 128.4–129.6°.

Preparation of Tris(*m*-tolyl)tin Hydride (I).—Tris(*m*-tolyl)-tin chloride was prepared according to the method of Kocheshkov, *et al.*[16] A solution of 3.4 g. (7.9 mmoles) of tris(*m*-tolyl)tin chloride in 60 ml. of ether was added dropwise to 2.0 g. (0.053 mole) of lithium aluminum hydride suspended in 40 ml. of ether in a three-necked, round-bottomed flask equipped with a reflux condenser, stirrer, nitrogen-inlet tube, addition funnel, and calcium chloride drying tube. After addition was complete (0.5 hr.), the reaction mixture was stirred for 3.5 hr. at room temperature. Water was then carefully added until there was no further evidence of gas evolution. The contents of the flask were then poured into a dilute aqueous solution of sodium potassium tartrate. The ether layer was separated, washed several times with water, and finally dried over anhydrous sodium sulfate. Distillation of the solvent under reduced pressure gave a white, viscous oil, which was distilled affording 2.0 g. (5.1 mmoles, 65%) of colorless liquid, b.p. 194–195° (1.3 mm.). For analysis a small sample of the above was redistilled without any change in boiling point.

Anal. Calcd. for $C_{21}H_{22}Sn$: C, 64.16; H, 5.64; Sn, 30.20. Found: C, 64.38; H, 5.88; Sn, 29.85.

Preparation of Tetrakis(*o*-tolyl)tin (IV).—A solution of 100 g. (0.58 moles) of *o*-bromotoluene in a mixture of 300 ml. of ether and 100 ml. of benzene (distilled from calcium hydride) was added dropwise to 10 g. (1.4 g.-atoms) of finely cut lithium ribbon. After completion of addition, the reaction mixture was stirred at room temperature for a period of 1 hr. and it was then filtered under an inert atmosphere. A solution of 28.1 g. (0.11 mole, 12.6 ml.) of stannic chloride in 50 ml. of dry benzene was then added dropwise to the reaction mixture. Upon completion of addition, the reaction mixture was refluxed for 7 hr. and then allowed to stir at room temperature overnight. The reaction mixture was then carefully hydrolyzed with 10% hydrobromic acid, and the organic layer was separated, washed with water, and finally dried over anhydrous sodium sulfate. Distillation of the ether–benzene solution under reduced pressure left a yellowish solid, which was recrystallized from benzene–ethanol to give 27.5 g. of product, m.p. 211–220°. Further recrystallization from benzene-ethanol gave 20.0 g. (0.041 mole, 38%) of white crystalline solid, m.p. 217.5–219.5° (lit.[24] m.p. 216–217°).

Attempted Synthesis of Tris(*o*-tolyl)(tin Chloride (IV).—The procedure of Kocheshkov[16] for the preparation of this compound was essentially followed. Stannic chloride (5.4 g., 2.42 ml., 0.021 mole) was added to 30 g. (0.062 mole) of tetrakis(*o*-tolyl)tin in a round-bottomed flask equipped with a reflux condenser, calcium chloride drying tube, and magnetic stirrer. The reaction mixture was heated at 205° for 3 hr. and an additional 3 hr. at 160°. On cooling, the solid obtained was extracted with boiling methanol, filtered hot, concentrated, and then allowed to cool. The material obtained was found to be only starting material as shown by mixture melting point and the Beilstein test for halogen.

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[19] This compound was obtained in 57% yield. This compares with a 12% yield previously reported by O. Fuchs and H. W. Post [*Rec. trav. chim.*, **78**, 566 (1959)]. Their procedure consisted of preparing *m*-trifluoromethylphenyllithium by exchanging butyllithium with *m*-trifluoromethylbromobenzene and then treating with stannic chloride to give XIV.

[20] E. Eaborn and J. A. Waters, *J. Chem. Soc.*, 542 (1961).

[21] R. W. Bott, C. Eaborn, and J. A. Waters, *ibid.*, 681 (1963).

[22] R. D. Chambers and T. Chivers, *Proc. Chem. Soc.*, 208 (1963).

[23] R. E. Dessy, T. Hieber, and F. Paulik, *J. Am. Chem. Soc.*, **86**, 28 (1964).

[24] R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

Attempted Synthesis of Tris(*o*-tolyl)tin Iodide.—The procedure described for the preparation of triphenyltin iodide from tetraphenyltin by Chambers and Scherer[5] was followed. To 2.0 g. (4.1 mmoles) of tetrakis(*o*-tolyl)tin dissolved in 100 ml. of chloroform in a round-bottomed flask equipped with a reflux condenser and addition funnel was added 5 ml. of a solution of 1.04 g. (4.1 mmoles) of iodine dissolved in 200 ml. of chloroform. After the addition of the 5-ml. aliquot, the solution was refluxed for 3 hr. without any observable uptake of iodine.

Preparation of Tris(*o*-tolyl)tin Chloride (V).—The compound was prepared according to the method of Krause and Becker[15] and purified by recrystallization from methanol, m.p. 115.0–115.7°. Krause and Becker report a melting point of 99.5° from absolute ethanol.

Anal. $C_{21}H_{21}ClSn$: C, 58.99; H, 4.95; Cl, 8.29; Sn, 27.76. Found: C, 59.11; H, 5.18; Cl, 8.11; Sn, 27.75.

Preparation of Tris(*o*-tolyl)tin Hydroxide (VI).—Tris(*o*-tolyl)tin chloride (0.43 g., 1.0 mmole) dissolved in ethanol was titrated with 0.2 *N* aqueous sodium hydroxide to a thymol blue end point. On allowing the solution to stand overnight, crystals deposited which were filtered and dried, affording 0.39 g. (0.96 mmole, 95%) of white solid, melting at 213.8–215.5°.

Anal. $C_{21}H_{22}OSn$: C, 61.65; H, 5.42; Sn, 29.01. Found: C, 61.76; H, 5.43; Sn, 28.81.

Preparation of *o*-Tolylmercuric Bromide (VII).—A solution of 50 g. (0.29 mole) of *o*-bromotoluene in 200 ml. of ether was added dropwise to 8.0 g. (0.33 mole) of magnesium; then, after the completion of addition, the reaction mixture was allowed to stir overnight and it was then filtered in an inert atmosphere. At this point, 129.7 g. (0.36 mole) of mercuric bromide was added in small portions under a nitrogen atmosphere, after which the reaction mixture was allowed to stir overnight. A solution of 85.7 g. (0.72 mole) of potassium bromide dissolved in 200 ml. of 1% aqueous hydrobromic acid was added dropwise with stirring. The reaction mixture was filtered, and the ether layer was separated from the aqueous phase, washed several times with water, and dried over anhydrous sodium sulfate.

The ether solution was distilled and the solid that remained was combined with the solids previously obtained. The combined solids were recrystallized twice from benzene to give 55 g. (0.15 mole, 51%) of white crystalline solid, m.p. 165–167° (lit.[25] m.p. 168°).

Preparation of Tris(*o*-tolyl)tin Bromide (VIII). Procedure A.—To 100 ml. of xylene in a two-necked, round-bottomed flask equipped with a stirrer and a reflux condenser were added 18.6 g. (0.050 mole) of *o*-tolylmercuric bromide and 41.5 g. (0.35 mole) of powdered tin. The reaction mixture was refluxed for 18 hr., then filtered and distilled under reduced pressure.

The remaining white solid was extracted with hot methanol, filtered, concentrated, and allowed to cool to give 3.2 g. (6.7 mmoles, 41%) of white crystalline solid, m.p. 100.5–101.5°.

Procedure B.—Tris(*o*-tolyl)tin chloride (4.3 g., 0.010 mole) dissolved in 50 ml. of ether was washed twice with 20% aqueous sodium hydroxide, washed with water, washed twice with 10% hydrobromic acid, washed again with water, separated, and dried over anhydrous sodium sulfate.

The ether solution was distilled and the remaining solid was recrystallized from methanol, affording 3.5–4.0 g. (8.2–9.4 mmoles, 74–85%) of tris(*o*-tolyl)tin bromide, m.p. 101.4–101.9° (lit.[15] m.p. 99.5°).

Anal. $C_{21}H_{21}BrSn$: C, 53.44; H, 4.48; Br, 16.93; Sn, 25.14. Found: C, 53.74; H, 4.48; Br, 16.81; Sn, 25.36.

Preparation of Tris(*o*-tolyl)tin Hydride (IX).—A solution of 1.4 g. (3.0 mmoles) of tris(*o*-tolyl)tin bromide in 25 ml. of ether was added dropwise to 2.0 g. (0.053 mole) of lithium aluminum hydride which was suspended in 40 ml. of ether; then, after addition was complete (0.5 hr.), the reaction mixture was stirred for 3 hr. at room temperature. Water was then carefully added until there was no further evidence of gas evolution. The contents of the flask were then poured into a dilute aqueous solution of sodium potassium tartrate. The ether layer was separated, washed several times with water, and then dried over anhydrous sodium sulfate.

The ether solution was then distilled under reduced pressure, leaving a white solid which was sublimed at 90° (0.2 mm.) to give 1.0 g. (2.5 mmoles, 85%) of colorless product, m.p. 97.5–99.5°. Recrystallization from methanol gave 0.9 g. (2.3 mmoles, 77%) of white needles, m.p. 98.6–99.4° (evacuated melting point tube).

Anal. $C_{21}H_{22}Sn$: C, 64.16; H, 5.64; Sn, 30.20. Found: C, 64.06; H, 5.58; Sn, 30.20.

Preparation of Tris(*o*-biphenylyl)tin Hydride (X).—Tris(*o*-biphenylyl)tin bromide was prepared according to the procedure of Bähr and Gelius.[18] A solution of 10.5 g. (0.016 mole) of tris(*o*-biphenylyl)tin bromide in 300 ml. of ether was added dropwise to 2.0 g. (0.053 mole) of lithium aluminum hydride suspended in 25 ml. of ether. After addition was complete, the reaction mixture was refluxed for 1.5 hr.

At this time 100 ml. of dry benzene was added and the reaction mixture was refluxed for an additional 1.5 hr. After cooling, the reaction mixture was hydrolyzed carefully with water. The contents of the flask were then poured into a dilute aqueous solution of sodium potassium tartrate, the organic phase was separated, washed several times with water, and finally dried over anhydrous sodium sulfate.

After concentrating the ether–benzene solution under reduced pressure to about 50 ml., ethanol was then added to the hot solution to incipient turbidity, and the solution was allowed to cool. Filtration of the white glimmering crystals afforded 5.0 g. (8.6 mmoles, 54%) of product, m.p. 171.5–173.0° (evacuated melting point tube). An analytical sample, m.p. 171.9–172.6°, was prepared by recrystallizing a small sample of the above material from butanol.

Anal. Calcd. for $C_{36}H_{28}Sn$: C, 74.64; H, 4.87; Sn, 20.49. Found: C, 74.34; H, 4.73; Sn, 20.01.

Preparation of Tris(*o*-biphenylyl)tin Chloride (XII).—A solution of 1.5 g. (2.6 mmoles) of tris(*o*-biphenylyl)tin hydride in 50 ml. of carbon tetrachloride was evaporated to dryness on a steam bath over a period of 0.5 hr. On the addition of a few drops of cyclohexane the remaining oil crystallized. The white solid obtained was recrystallized from cyclohexane to yield 0.9 g. (1.5 mmoles, 56%) of product, m.p. 156.9–158.0°. The product no longer showed a band at the characteristic frequency for tin–hydride absorption in the infrared region and furthermore gave a positive Beilstein test.

Anal. Calcd. for $C_{36}H_{27}ClSn$: C, 70.45; H, 4.43; Cl, 5.78; Sn, 19.34. Found: C, 70.87; H, 4.51; Cl, 5.79; Sn, 19.26.

Isolation of Bis(*o*-biphenylyl)tin Dibromide (XXII).—On attempting to prepare tris(*o*-biphenylyl)tin bromide according to the procedure of Bähr and Gelius,[18] *o*-bromobiphenyl (Pierce Chemical Co.) was initially used without further purification.

The product obtained was recrystallized two times from butanol, once from ethanol–benzene and finally from hexane–benzene to yield 5.0 g. (8.6 mmoles, 20%) of white product, m.p. 174.5–175.8°.

Anal. $C_{24}H_{18}Br_2Sn$: C, 49.28; H, 3.10; Br, 27.32; Sn, 20.29. Found: C, 49.43; H, 3.21; Br, 27.56; Sn, 20.29.

Subsequent infrared analysis of the starting material showed that considerable amounts of *o*-aminobiphenyl were present as impurity in the *o*-bromobiphenyl.

The filtrate obtained (above) from the first recrystallization deposited colorless square platelets on standing for several days. The white solid obtained after filtering and drying melted at 165–169° and gave a superimposable infrared spectrum for tris(*o*-biphenylyl)tin bromide.

The filtrate obtained from the second recrystallization likewise deposited crystals on standing for several days. The white crystals collected melted at 67.6–68.6°. Superimposable infrared spectrum and no depression on admixture with an authentic sample showed the material to be biphenyl.

Preparation of Tetrakis(*p*-trifluoromethylphenyl)tin (XV).—A solution of 50 g. (0.22 mole) of *p*-trifluoromethylbromobenzene in 150 ml. of ether was added dropwise to 8.1 g. (0.33 mole) of magnesium ribbon; then, after the completion of addition, the reaction mixture was refluxed for 0.5 hr. and then a solution of 7.2 g. (0.027 mole, 3.2 ml.) of stannic chloride in 100 ml. of dry benzene was added dropwise. Upon the completion of addition, the reaction mixture was again refluxed for 4 hr. and then hydrolyzed by the dropwise addition of 10% hydrobromic acid. The organic layer was separated, washed with water, and then dried over anhydrous sodium sulfate.

The ether–benzene solution was distilled under reduced pressure, leaving behind a red-orange solid. The solid was taken up in a minimum of chloroform and passed through an acidic Wöelm alumina column. The column was eluted with chloroform, leaving a dark yellow band on the column. The light yellow eluate was distilled under reduced pressure leaving a light yellow solid,

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(25) E. L. Hill, *J. Am. Chem. Soc.*, **50**, 167 (1928).

which after recrystallization from carbon tetrachloride, followed by another recrystallization from ethanol, afforded white feathery needles weighing 8.2 g. (0.013 mole, 43%), m.p. 150.0–150.7°.

Anal. $C_{28}H_{16}F_{12}Sn$: C, 48.10; H, 2.31; Sn, 16.98. Found: C, 47.78; H, 2.07; Sn, 17.10.

Preparation of Tetrakis(*m*-trifluoromethylphenyl)tin (XIV).—A solution of 50 g. (0.22 mole) of *m*-trifluoromethylbromobenzene in 150 ml. of ether was added dropwise to 8.1 g. (0.33 g.-atom) of magnesium ribbon; then, after the completion of addition, the reaction mixture was refluxed for 0.5 hr. and then a solution of 10.0 g. (0.038 mole, 4.5 ml.) of stannic chloride in 100 ml. of dry benzene was added dropwise. After completion of this addition, the reaction mixture was refluxed for 4 hr. and then hydrolyzed by the dropwise addition of 10% hydrobromic acid. The organic layer was separated, washed with water and finally dried over anhydrous sodium sulfate.

The ether–benzene solution was distilled under reduced pressure, leaving an orange-yellow solid, which was recrystallized twice from chloroform, yielding 15.0 g. (0.021 mole, 57%) of white needles, m.p. 142.7–144.0° (lit.[19] m.p. 143–144°).

Attempted Synthesis of Tris(*m*-trifluoromethylphenyl)tin Chloride.—Stannic chloride (2.2 g., 0.84 mole, 1.0 ml.) was added to 18 g. (0.026 mole) of tetrakis(*m*-trifluoromethylphenyl)tin in a round-bottomed flask equipped with a reflux condenser, calcium chloride drying tube, and magnetic stirrer. The reaction mixture was heated at 210° for 3.5 hr. and for an additional 3 hr. at 155°. After cooling the reaction mixture, no product other than starting material could be isolated.

Attempted Synthesis of Tris(*m*-fluoromethylphenyl)tin Iodide.—A solution of 2.5 g. (0.010 mole) of iodine in 150 ml. of carbon tetrachloride was added to 7.0 g. (0.010 mole) of tetrakis(*m*-trifluoromethylphenyl)tin in a round-bottomed flask equipped with a reflux condenser. The solution was refluxed for 4 days without any visible change in the color of the solution. The solution was cooled, shaken with a dilute solution of sodium bisulfite, washed twice with water, and dried over anhydrous sodium sulfate.

The carbon tetrachloride was distilled, leaving behind only starting material.

Preparation of *m*-Trifluoromethylphenylmercuric Bromide (XVII).—A solution of 25 g. (0.11 mole) of *m*-trifluoromethylbromobenzene in 100 ml. of ether was added dropwise to 4.0 g. (0.16 g.-atom) of magnesium ribbon; then, after the completion of addition, the reaction mixture was allowed to stir for 0.5 hr. and then filtered under nitrogen. To the filtered Grignard solution was added 40 g. (0.11 mole) of mercuric bromide in small portions, under a nitrogen atmosphere. The reaction mixture was allowed to reflux overnight, hydrolyzed by the addition of water, and then filtered.

The solid obtained was refluxed with 200 ml. of a 1% aqueous hydrobromic acid solution and again filtered hot. This process was repeated twice more, and the solid was collected and thoroughly dried. Recrystallization from ethanol afforded 30.4–35.0 g. (0.071–0.082 mole, 65–75%) of nearly white solid, m.p. 178–180°. An analytical sample, m.p. 178.5–180.0°, was prepared by subliming a small portion of the above material at 150° (40 mm.).

Anal. $C_7H_4BrF_3Hg$: C, 19.75; H, 0.95; Br, 18.78. Found: C, 19.81; H, 1.15; Br, 18.70.

Preparation of Tris(*m*-trifluoromethylphenyl)tin Bromide (XVI).—To a mixture of 124.5 g. (1.1 mole) of powdered tin and 63.0 g. (0.015 mole) of *m*-trifluoromethylphenylmercuric bromide in a two-necked, round-bottomed flask equipped with a reflux condenser and stirrer, were added 500 ml. of xylene. The reaction mixture was refluxed for 18 hr. and filtered hot.

The xylene solution was distilled under reduced pressure, leaving an oily residue, from which 3.4 g. of white solid, m.p. 137–139°, separated on the addition of a few milliliters of ethanol. The white solid did not depress the melting point of an authentic sample of tetrakis(*m*-trifluoromethylphenyl)tin. The ethanol solution of the oil was then distilled at atmospheric pressure and then finally at reduced pressure after all the ethanol had distilled. A straw yellow liquid, b.p. 154–157° (0.2 mm.), n^{26}D 1.5372, was obtained, weighing 20.0 g. (0.032 mole, 64%). An analytical sample with no change in physical constants was obtained by redistilling a small sample.

Anal. $C_{21}H_{12}BrF_9Sn$: C, 39.79; H, 1.91; Sn, 18.72. Found: C, 30.59; H, 2.01; Sn, 18.82.

Attempted Synthesis of Tris(*m*-trifluoromethylphenyl)tin Hydride. Procedure A.—A solution of 6.3 g. (0.010 mole) of tris(*m*-trifluoromethylphenyl)tin bromide in 75 ml. of ether was added dropwise to 2.0 g. (0.053 mole) of lithium aluminum hydride suspended in 25 ml. of ether; then, after addition was complete (0.5 hr.), the reaction mixture was stirred for 45 min. and then carefully hydrolyzed with water. During hydrolysis, the reaction mixture successively became green, orange-yellow, and finally turned colorless on swirling in the separatory funnel. The ether solution was washed several times with water, separated and dried over anhydrous sodium sulfate. If air was excluded, the solution remained green.

Distillation of the solvent gave a white solid, m.p. 88–96°. Recrystallization from hexane raised the melting point to 96.7–100.2°. An infrared spectrum of the material showed no characteristic Sn–H absorption in the range 1800–1900 cm.$^{-1}$.

Procedure B.—A solution of 2.0 g. (3.2 mmoles) of tris(*m*-trifluoromethylphenyl)tin bromide in 75 ml. of ether was added dropwise (over a period 9.5 min.) to 1.5 g. (0.040 mole) of lithium aluminum hydride in 25 ml. of ether kept at −20 to −25°. After completion of addition, the reaction mixture was stirred at −20 to −25° for 2 hr.

During this interval, ten 4-ml. aliquots were withdrawn and worked up in the usual fashion (see procedure A). The aqueous portions of the worked up aliquots were set aside and tested for bromide and free fluoride ion using standard analytical procedures.[8] The isolated products were examined in the infrared for a Sn–H band in the 1800–1900-cm.$^{-1}$ frequency region. The results indicated free bromide ion in all the worked-up aliquots, but no fluoride ion. No characteristic absorption for Sn–H in the infrared was found for the isolated products.

Procedure C.—A solution of 5.0 g. (7.9 mmoles) of tris(*m*-trifluoromethylphenyl)tin bromide in 175 ml. of ether was added dropwise to 3.0 g. (0.079 mole) of lithium aluminum hydride suspended in 25 ml. of ether kept at −78° for 1.0 hr., then carefully hydrolyzed with degassed (boiled) water, and then allowed to come to room temperature. During hydrolysis, the reaction mixture again took on a green color, which turned orange-yellow on transferal of the supernatant ether solution to the separatory funnel and finally turned colorless on swirling in the separatory water, was separated, and dried over anhydrous sodium sulfate.

The ether solution was distilled, leaving a white solid, m.p. 88–95°. Two recrystallizations form methanol–water, followed by one recrystallization from hexane, yielded 1.4 g. (0.13 mmole, 32%) of hexakis(*m*-trifluoromethylphenyl)ditin, m.p. 100.6–102.0°. An analytical sample, m.p. 100.6–101.9°, was prepared by recrystallizing the white solid once more from hexane, followed by a final recrystallization from isopropyl alcohol.

Anal. $C_{42}H_{24}F_{18}Sn_2$: C, 45.53; H, 2.18; Sn, 21.43. Found: C, 45.71; H, 2.04; Sn, 20.77.

Preparation of Tetrakis(*p*-chlorophenyl)tin (XX).—A solution of 95.7 g. (0.50 mole) of *p*-bromochlorobenzene in 500 ml. of ether was added slowly to 13.0 g. (0.51 g.-atom) of magnesium suspended in 100 ml. of ether in a three-necked flask equipped with stirrer, reflux condenser, a nitrogen source, and dropping funnel. After addition was complete, the reaction mixture was stirred at room temperature for 1 hr. A solution of 53.6 g. (0.12 mole) of stannic bromide in 100 ml. of benzene was then added during 1.5 hr. The reaction mixture was refluxed for 1 hr., stirred overnight without heating, and slowly hydrolyzed with water. Separation of the ether layer, washing it with water, and drying it over anhydrous sodium sulfate was followed by distillation of the solvent at reduced pressure. The solid which remained was recrystallized from cyclohexane to yield 34.8 g. (51.3%) of product melting at 197–199°.[26]

Tris(*p*-chlorophenyl)tin Chloride (XIX).—Tetrakis(*p*-chlorophenyl)tin (30.7 g., 0.054 mole) was mixed with 4.69 g. (0.018 mole) of stannic chloride in a round-bottomed flask equipped with magnetic stirrer and reflux condenser with a calcium chloride drying tube. The reaction mixture was heated at 200–210° for 2.5 hr., and crystallized on cooling. Recrystallization from cyclohexane gave 20.0 g. (72%) of product, m.p. 109.0–110.5°.

Attempted Synthesis of Tris(*p*-chlorophenyl)tin Hydride.—A solution of 20.0 g. of tris(*p*-chlorophenyl)tin chloride in 200 ml. of ether was added slowly to 5.0 g. of lithium aluminum hydride suspended in 200 ml. of ether. After addition was complete, the reaction mixture was stirred for 2.5 hr. without heating. The reaction mixture was cooled in an ice bath, and water was added cautiously until there was no gas evolution. A solution of 40.0 g. of sodium potassium tartrate in 160 ml. of water was added. The

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[26] E. Krause and K. Weinberg, *Ber.*, **62**, 2235 (1929).

yellow ether layer separated, and the aqueous layer was washed with additional ether. The combined ether fractions were washed with water and dried over anhydrous sodium sulfate.

The colorless ether solution was filtered from the yellow sodium sulfate and distilled at reduced pressure, leaving a yellowish liquid. Addition of hexane precipitated a white solid, m.p. 224–226° (lit.[26] m.p. 224–226°).

Distillation of the hexane solution at reduced pressure gave a liquid whose infrared spectrum was identical with that of chlorobenzene.

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The Preparation and Stabilization of Acetylenic Boranes[1a]

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An investigation of the preparation of acetylenic boranes has led to a study of the reactions of sodium acetylide, sodium alkylacetylides, and sodium arylacetylides with boron trifluoride, boron trichloride, and methyl borate. Evidence was obtained for the existence of acetylenic boranes at low temperatures (−60°); however, the products proved to be unstable above −30°. A satisfactory method for the stabilization of acetylenic boranes was developed which consists in their isolation as amine complexes. The method involves the reaction between sodium acetylide or a substituted sodium acetylide and a boron halide–amine complex. $3NaC{\equiv}CH + BF_3{\cdot}pyridine \longrightarrow (HC{\equiv}C)_3B{\cdot}pyridine + 3NaF$. Triethynylborane–pyridine, tri(phenylethynyl)borane–pyridine, triethynylborane–diethylamine, and triethynylborane–trimethylamine were prepared by this method. These compounds are crystalline solids, stable to the atmosphere and to shock. Acetylenic borane–amine complexes undergo transamination. Several amine complexes of triethynylborane have been prepared by reacting triethynylborane–pyridine with the desired amine: $(HC{\equiv}C)_3B{\cdot}pyridine + (C_2H_5)_2NH \longrightarrow (HC{\equiv}C)_3B{\cdot}N(C_2H_5)_2H + pyridine$.

The acetylides of many metals, Li, Na, K, Rb, Co, Sn, Si, Ag, Hg, Cu, Mg, and Zn, have been reported in the literature.[2–7] Conspicuous by their absence from the list of reported acetylides are those of the group IIIA elements. Preparations of sodium tetra(phenylethynyl)borate, $NaB(C{\equiv}CC_6H_5)_4$, and ammonium tetra(phenylethynyl)borate, $NH_4B(C{\equiv}CC_6H_5)_4$, have been reported by two different routes.[8,9] Kruerke[8] reported the reaction of phenylethynylsodium with boron tribromide in benzene at −60°, to produce sodium tetra(phenylethynyl)borate, $NaB(C{\equiv}CC_6H_5)$. The Russian workers[9] treated phenylethynylmagnesium bromide with potassium fluoborate to form potassium tetra(phenylethynyl)borate. This compound was converted to the stable ammonium salt by the addition of ammonium chloride.

Preparations of boranes containing one acetylenic group have been reported. Soulie, *et al.*,[10,11] reported the preparation of pyridine complexes of diphenyl alkynylboranes, $(C_6H_5)_2BC{\equiv}CR{\cdot}pyridine$. Hartman and Birr[12] reported the preparation of monoacetylenic boranes of the type, $R_2B{-}C{\equiv}C{-}R$, while Matteson and Peacock[13] have reported the preparation of dibutyl ethynylboronate, $HC{\equiv}CB(OC_4H_9)_2$, and dibutyl hexynylboronate, $C_4H_9C{\equiv}C{-}B{-}(OC_4H_9)_2$. In our studies of organoboron compounds, we found it of interest to investigate the preparation of triacetylenic boranes in the uncomplexed form. The simplest compound, triethynylborane, $B(C{\equiv}CH)_3$, received the most attention. It was speculated that this compound should have a boiling point in the range 0–20°, in comparison with 95° for triethylborane and 55° for trivinylborane. Also triethynylborane should be soluble in ethers and hydrocarbons, as are triethyl- and trivinylborane. For these reasons the proposed methods of preparation were designed to isolate the desired product as a gas, or to isolate it in solution from which it could be easily removed by distillation or detected by infrared analysis. Unfortunately triethynylborane does not appear to be stable above −30°. The nature of the acetylenic group and the reacting boron species were varied in an effort to isolate any stable acetylenic borane. It appeared that a polymer-like substance was formed in all cases. Attempts to identify accurately the nature of the products when these polymer like substances were formed were plagued by inconsistent carbon–hydrogen analyses (presumably due to the formation of boron carbide on combustion). In spite of our inability to determine accurately the exact nature of the polymeric products, we were able to evaluate the possibility of preparing acetylenic boranes from acetylenic sodium compounds and boron halides or boron esters. Acetylenic boranes were finally prepared, but only when stabilized as amine complexes.

Experimental

All reactions were run in a dry, oxygen-free system. This was accomplished by flash flaming under a stream of nitrogen all assembled apparatus prior to use.

Preparation of Sodium Acetylide.—A round-bottomed, creased flask, with a stopcock at the base, was equipped with a gas addition tube extending to the bottom, a high speed stirrer, and a two-necked connecting tube. To the two-necked connecting tube was attached a 0–250° thermometer and a water-cooled condenser. A T-tube was attached to the top of the condenser, with one end connected to a nitrogen source and the other end to a bubbler. To the gas addition tube was connected an acetylene

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