the residue thus obtained was crystallized from benzene as colorless crystals, m.p. 199–200°.

Anal. Calcd. for $C_{25}H_{24}O_2N_2$: C, 78.12; H, 6.25; N, 7.29. Found: C, 77.86; H, 6.18; N, 7.37.

The ring-opened piperidide was soluble in hot benzene, but sparingly soluble in petroleum ether.

The infrared spectrum of the piperidide showed absorption at 1600 cm.$^{-1}$, 3332 cm.$^{-1}$ (—NH stretching), and 1640 cm.$^{-1}$ and 1525 cm.$^{-1}$ (amide I and II bands).

Preparation of Ig.—A 1.0-g. sample of pyridine-4-carboxaldehyde, 1.8 g. of hippuric acid, 2.7 g. of acetic anhydride, and 0.6 g. of freshly fused sodium acetate were heated on a boiling water bath for 0.5 hr. The reaction mixture was poured onto about 10 ml. water. After cooling, the product that was precipitated was filtered off, washed with a little ethyl alcohol, and crystallized from benzene as dirty green crystals, m.p. 167°.

Anal. Calcd for $C_{15}H_{10}O_2N_2$: C, 72.00; H, 4.00; N, 11.20. Found: C, 71.58; H, 4.14; N, 11.22.

Ig was soluble in hot benzene and hot acetic acid, but was sparingly soluble in ethyl alcohol and petroleum ether and gave no color with concentrated sulfuric acid.

The infrared spectrum of Ig showed a strong absorption at 1810 cm.$^{-1}$ which might be attributed to a conjugated carbonyl group, and a medium intensity band at 1660 cm.$^{-1}$ (>C═H stretching).[4]

Direct Synthesis of Organotin Compounds. III. Reaction of α-Substituted Benzyl Halides with Metallic Tin

KEIITI SISIDO, YOSIYUKI TAKEDA, AND HITOSI NOZAKI

Department of Industrial Chemistry, Faculty of Engineering, Kyôto University, Kyôto, Japan

Received November 20, 1961

Wurtz condensation products, instead of organotin compounds, were obtained in the reaction of metallic tin powder with diphenylmethyl chloride, α-phenylethyl chloride, anethole hydrobromide, and benzal chloride, respectively, in boiling toluene as a solvent. When the reaction was carried out in water suspension, hydrolysis occurred along with the condensation. Bis(diphenylmethyl)tin dichloride was prepared from diphenylbis(diphenylmethyl)tin by the preferential cleavage of phenyl groups, and the reaction of diphenylmethylpotassium or -magnesium bromide with stannic chloride was examined.

A previous paper[1] from this laboratory recorded the reaction of metallic tin powder with benzyl chloride and its ring-substituted derivatives. Whereas dibenzyltin dihalides were obtained in toluene solution, tribenzyltin halides were the products in water-suspension reaction. The present paper comprises an examination of the reaction of metallic tin with α-substituted benzyl halides in these media. No detectable amounts of organotin compounds were formed, but the Wurtz type products have been obtained in fair to excellent yields.

Upon treatment with metallic tin powder suspended in boiling toluene, diphenylmethyl chloride afforded *sym*-tetraphenylethane in an 85% yield. Similar reaction of α-phenylethyl chloride gave a mixture of *meso*- and *dl*-2,3-diphenylbutane in an 82% yield. Remarkably high yields of these hydrocarbons prompted the authors to examine the reaction of anethole hydrobromide under similar conditions in view of the interests in the preparation of hexestrol derivatives.[2] The reaction, however, afforded less satisfactory yields (12–15%) of *meso*-3,4-bis(*p*-methoxyphenyl)hexane, which can satisfactorily be explained by the thermal instability of anethole hydrobromide at the boiling point of toluene.

When benzal chloride was heated with metallic tin suspended in toluene under refluxing for three hours, α-stilbene dichloride and *trans*-stilbene were obtained in 12% and 67% yields, respectively. A shorter period of refluxing (30 min.) changed the product ratio in favor of α-stilbene dichloride (50%) over *trans*-stilbene (27%).[3]

Attempted condensation of α-methoxybenzyl chloride by means of tin powder under similar conditions afforded a resinous mixture, from which nothing identifiable could be isolated.

Replacement of toluene with water in these reactions resulted in lowering of the yields of Wurtz type condensates, concurrent hydrolysis of the halides being observed. With water as a reaction medium, diphenylmethyl chloride gave a 74% yield of *sym*-tetraphenylethane besides benzhydrol and bisbenzhydryl ether, while α-phenylethyl chloride afforded a 33% yield of *meso*-2,3-diphenylbutane along with α-phenylethyl alcohol, bis-α-phenylethyl ether, and styrene.[4] The reaction of benzal chloride with tin powder suspended in water afforded *trans*-stilbene and benzaldehyde in 23% and 43% yields, respectively, no stilbene dichloride being isolated. Similar treatment of α-methoxybenzyl chloride gave mainly benzaldehyde besides a small amount of tar.

(1) K. Sisido, Y. Takeda, and Z. Kinugawa, *J. Am. Chem. Soc.*, **83**, 538 (1961). *Cf.* K. Sisido and Y. Takeda, *J. Org. Chem.*, **26**, 2301 (1961).

(2) (a) K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **70**, 778 (1948). (b) K. Sisido, H. Nozaki, and H. Kuyama, *J. Org. Chem.*, **14**, 1124 (1949). (c) K. Sisido, Y. Udô, and H. Nozaki, *J. Org. Chem.*, **26**, 1227 (1961).

(3) Ogata and Nakamura have previously recorded a similar stepwise dechlorination condensation of benzal chloride by the action of reduced iron suspended in water. See Y. Ogata and H. Nakamura, *J. Org. Chem.*, **21**, 1170 (1956).

(4) The hydrolysis of diphenylmethyl chloride and α-phenylethyl chloride in water was recorded by A. M. Ward, *J. Chem. Soc.*, 445, 2285 (1927).

The most plausible path of the present Wurtz condensation was the thermal decomposition of substituted benzyltin compounds or of similar reaction intermediates. When bis(diphenylmethyl)tin dichloride was treated in boiling xylene for two hours, it decomposed to afford stannous chloride and *sym*-tetraphenylethane in yields of 83% and 75%, respectively. In boiling toluene, however, it remained essentially unchanged and gave as the decomposition product stannous chloride only in a 6% yield. This fact correlates with the actual decomposition temperature of this compound, 115–117°, as determined by the melting point method.

Similarly, when dibenzyltin dichloride, m.p. 161–163°[1] and decomposition point 189–190°, was treated in boiling isoamylbenzene—*i.e.*, at 200°—it gave stannous chloride and bibenzyl in good yields but in boiling *n*-butylbenzene—*i.e.*, at 180°—it remained unchanged. It was conceivable that the thermal decomposition of the organotin compounds was greatly facilitated by the substituent on the α-position of benzyl group. On the other hand, it would be unreasonable to assume that carbon-tin bonding, which was formed by the reaction of metallic tin with benzyl chloride or even with methylvinylcarbinyl bromide, had not been produced between α-substituted benzyl group and tin atom. Steric bulkiness was considered not to be obstructive in view of the facile accessibility of bis(diphenylmethyl)tin dichloride and other organotin compounds containing such bulky groups as triphenylmethyl,[5a] 9-fluorenyl,[5b c] 9-phenanthryl,[5d] or 2-biphenylyl.[5d] In addition, the electronic effect of the α-substituent appeared to be irrelevant to the failure, because substitution with an electron-donating methyl group and an electron-withdrawing chlorine atom on the α-carbon both impeded the formation of organotin compound.

Bis(diphenylmethyl)tin dichloride was synthesized from diphenylbis(diphenylmethyl)tin taking advantage of the preferential cleavage of phenyl groups by ethanolic hydrochloric acid. A similar cleavage reaction was utilized for the preparation of dibenzyltin dichloride from diphenyldibenzyltin[6] as well as of diphenyl(triphenylmethyl)tin chloride from triphenyl(triphenylmethyl)tin.[5a] The required intermediate diphenylbis(diphenylmethyl)tin was obtained in a 58% yield by the reaction of diphenyltin dichloride with excess potassium diphenylmethide in ether.

During the course of this synthesis, it was found that tetrakis(diphenylmethyl)tin could not be synthesized by the reaction of tin tetrachloride with diphenylmethylpotassium or -magnesium bromide in ether. Both of these reactions gave, on hydrolysis, stannous chloride and *sym*-tetraphenylethane in about 1:1 molar ratio, the yields based on the tin tetrachloride being 89% and 85%, respectively, with recovery of the remainder of diphenylmethane. Extraction of the reaction mixture prior to hydrolysis afforded a small amount of unstable organotin compound, presumably bis(diphenylmethyl)tin [Sn(II)], which decomposed rapidly in air giving benzophenone and benzhydrol besides reddish tar. The reaction, therefore, may be written as follows:

$$SnCl_4 + 4(C_6H_5)_2CHK \longrightarrow$$

$$[(C_6H_5)_2CH]_2Sn + (C_6H_5)_2CHCH(C_6H_5)_2 + 4KCl$$

$$[(C_6H_5)_2CH]_2Sn + 2HCl \longrightarrow 2C_6H_5CH_2C_6H_5 + SnCl_2$$

Krause *et al.*[7] have reported similar anomalous reactions of *tert*-butylmagnesium[7a] or cyclohexylmagnesium[7b] chloride with tin tetrachloride giving isobutylene and di-*tert*-butyltin [Sn(II)] or bicyclohexyl- and hexacyclohexylditin, respectively.

Experimental[8]

Reaction of Diphenylmethyl Chloride with Tin Powder Suspended in Toluene.—To a stirred suspension of 17.8 g. (0.15 g.-atom) of tin powder[9] in 150 ml. of boiling toluene was added 30.3 g. (0.15 mole) of diphenylmethyl chloride[10] within 3 min., efficient stirring and refluxing being continued for an additional 3 hr. The solvent was evaporated in vacuum and the solid residue was extracted with 100 ml. of acetone in a Soxhlet apparatus. Recovery of unchanged tin (9.2 g. or 0.077 g.-atom) was nearly quantitative.

The acetone solution was poured into 300 ml. of 3 *N* hydrochloric acid in order to remove stannous chloride, and the precipitated solids were collected by suction filtration, washed with water, and dried. Recrystallization of this solid (24.8 g.) from ethanol gave 20.5 g. (85%) of *sym*-tetraphenylethane, m.p. and mixed m.p. with an authentic sample[11] 209–210° (lit.[11] m.p. 209°), whose analyses for carbon and hydrogen agreed with calculated values.

Detection of organotin compounds was carried out on both the crude precipitate and the recrystallization mother liquor with negative results.

Reaction of α-Phenylethyl Chloride with Tin Powder in Toluene.—The reaction was run as above using 17.8 g. (0.15 g.-atom) of tin powder suspended in 150 ml. of boiling toluene and 21.5 g. (0.15 mole) of α-phenylethyl chloride.[12] After removal of 9.3 g. (0.078 g.-atom) of unchanged tin, the toluene solution was shaken with 300 ml. of 3 *N* hydrochloric acid solution to remove stannous chloride. Evaporation of toluene afforded a yellowish oil, which on storing in a refrigerator for 3 days gave 11.4 g. of solid. Recrystallization of this solid from methanol gave 10.4 g. (68%) of *meso*-2,3-diphenylbutane, m.p. and mixed m.p. with an

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(5) (a) J. C. Bailie, *Iowa State Coll. J. Sci.*, **14**, 8 (1939); *Chem. Abstr.*, **34**, 6241 (1940); (b) H. Zimmer and H. W. Sparmann, *Naturwissenschaften*, **40**, 220 (1953); (c) H. Zimmer and H. W. Sparmann, *Ber.*, **87**, 645 (1954); (d) G. Bähr and R. Gelius, *Ber.*, **91**, 812, 818, 825, 829 (1958).

(6) G. A. Razuvaev and V. Fetyukova, *Zh. Obshch. Khim.* (*J. Gen. Chem. USSR*), **21**, 1010 (1951); *Chem. Abstr.*, **46**, 1479 (1952).

(7) (a) R. Krause and K. Weinberg, *Ber.*, **63**, 381 (1930). (b) E. Krause and R. Pohland, *Ber.*, **57**, 532 (1924).

(8) All temperatures are uncorrected. Microanalyses for carbon and hydrogen were performed by Miss Kenko Ogawa. Detection and determination of tin in a sample was carried out by the method described in ref. 1.

(9) Tin powder of the same grade as described in ref. 1 was used in the present reactions.

(10) Prepared from benzhydrol and dry hydrogen chloride in cold benzene [W. T. Nauta and D. Mulder, *Rec. trav. chim.*, **58**, 1070 (1939)].

(11) W. H. Zartmann and H. Adkins, *J. Am. Chem. Soc.*, **54**, 1668 (1932).

(12) Prepared by the addition of hydrogen chloride to styrene [G. L. Goerner and W. H. Hines, *J. Am. Chem. Soc.*, **70**, 3511 (1948)].

authentic specimen[2a] 122–123° (lit.[2a] m.p. 122.5°). Analyses for carbon and hydrogen agreed with calculated values.

Distillation of the oily part *in vacuo* gave 2.0 g. (13%) of *dl*-2,3-diphenylbutane, b.p. 117–121°/5 mm. (lit.[13] b.p. 153–156°/14 mm.), which showed correct analytical values for carbon and hydrogen.

Reaction of Anethole Hydrobromide with Tin Powder in Toluene.[14]—To a suspension of 17.8 g. (0.15 g.-atom) of tin powder in 80 ml. of boiling toluene a solution of anethole hydrobromide prepared from 14.8 g. (0.1 mole) of anethole and 35 ml. of toluene was added all at once and the whole mixture was refluxed for 8 hr. and then subjected to steam distillation. The residue was extracted with benzene and this benzene solution was washed, dried, and concentrated. Treatment of the residual sirup with methanol gave 1.8–2.2 g. (12–15%) of *meso*-3,4-bis(*p*-methoxyphenyl)hexane, m.p. and mixed m.p. 144° (lit.[2a] m.p. 144°).

Reaction of Benzal Chloride with Tin Powder in Toluene.—When a mixture of 24.2 g. (0.15 mole) of benzal chloride and 17.8 g. (0.15 g.-atom) of tin powder was refluxed in 150 ml. of toluene for 3 hr. under stirring, recovery of unchanged tin was 8.0 g. (0.067 g.-atom). The acetone extract did not contain any organotin compound, and this was poured into 3 *N* hydrochloric acid solution to separate 14.2 g. of yellow oil, which was distilled *in vacuo* to give 10.2 g. of solid, b.p. 134–139°/6 mm., and 3.4 g. of high boiling residue. Recrystallization of the distillate from 80% aqueous ethanol afforded 9.0 g. (67%) of *trans*-stilbene, m.p. and mixed m.p. with an authentic sample[15] 124–125° (lit.[15] m.p. 124°). Dibromide, m.p. 237–238° (lit.[15] m.p. 238°), was prepared. Both gave correct analyses for carbon and hydrogen.

Recrystallization of the residual solid from hexane led to the isolation of 2.3 g. (12%) of α-stilbene dichloride, m.p. and mixed m.p. with an authentic sample[3] 191–193° (lit.[3] m.p. 191–193°), whose analyses agreed with calculated values.

When the same mixture was refluxed for 30 min., 3.4 g. (27%) of *trans*-stilbene and 9.4 g. (50%) of α-stilbene dichloride were obtained with recovery of about 1 g. of benzal chloride.

Reaction of Diphenylmethyl Chloride with Tin Powder Suspended in Water.—To a stirred suspension of 17.8 g. (0.15 g.-atom) of tin powder in 150 ml. of boiling water 30.3 g. (0.15 mole) of diphenylmethyl chloride was added dropwise in 3 min., vigorous stirring and refluxing being continued for 2 hr. After cooling the whole reaction mixture was filtered with suction and the residual solids were washed with water, dried, and extracted with 100 ml. of acetone, 9.0 g. (0.076 g.-atom) of tin being recovered. Detection of organotin compounds from the acetone solution was negative. Evaporation of the solvent left 24.8 g. of solid, which was recrystallized from ethanol giving 18.4 g. (74%) of *sym*-tetraphenylethane, m.p. and mixed m.p. 210–210.5°.

Evaporation of the combined mother liquors afforded a yellow solid, which was distilled in vacuum to give 2.8 g. of solid distillate, b.p. 174–176°/15 mm., m.p. 64–66°, and 2.8 g. of a residue. Recrystallization of the distillate from petroleum ether (b.p. 30–50°) gave 2.5 g. (10%) of benzhydrol, m.p. 67–68° (lit.[16] m.p. 66–69°), phenylurethane, m.p. 136–138.5° (lit.[16] m.p. 138–140°), both with correct analyses for carbon and hydrogen.

Upon recrystallization of the distillation residue from petroleum ether (b.p. 30–50°), 1.3 g. (5%) of bisbenzhydryl ether, m.p. 108–110° (lit.[17] m.p. 109–110°), was obtained. Analyses for carbon and hydrogen showed correct values.

Reaction of α-Phenylethyl Chloride with Tin Powder Suspended in Water.—The reaction was carried out as above using 17.8 g. (0.15 g.-atom) of tin powder and 21.6 g. (0.15 mole) of α-phenylethyl chloride in 150 ml. of boiling water for 2 hr. After cooling the oily products were extracted with three 50-ml. portions of ether, and the combined ethereal solutions were washed, dried over calcium chloride, and concentrated to leave 18.0 g. of yellow oil, which on distillation *in vacuo* gave 1.0 g. (6%) of styrene, b.p. 31–34°/20 mm., n^{20}_{D} 1.5478, and 7.1 g. (39%) of α-phenylethyl alcohol, b.p. 98–102°/20 mm., n^{20}_{D} 1.5246.

For identification, styrene was converted into styrene dibromide, m.p. and mixed m.p. with an authentic specimen[18] 74–76°, and α-phenylethyl alcohol into phenylurethane, m.p. 93–94.5° (lit.[16] 93–94°). Both gave correct analyses for carbon and hydrogen. Recrystallization of the distillation residue from methanol afforded 5.1 g. (33%) of *meso*-2,3-diphenylbutane, m.p. and mixed m.p. 122–123°.[2a]

Reaction of Benzal Chloride with Tin Powder Suspended in Water.—Upon running the reaction as above using 11.9 g. (0.10 g.-atom) of tin powder and 16.2 g. (0.10 mole) of benzal chloride in 100 ml. of water for 1.5 hr., 4.6 g. (43%) of benzaldehyde, b.p. 62–64°/14 mm., n^{20}_{D} 1.5455, was isolated from the products by distillation. The 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 234–235° (lit.[19] m.p. 234–235°), gave correct analyses for carbon and hydrogen. Recrystallization of the distillation residue from 80% aqueous ethanol afforded 2.1 g. (23%) of *trans*-stilbene, m.p. and mixed m.p. 124–125° (lit.[15] m.p. 124°). Negative test for halogen on the ethanolic mother liquor indicated the absence of α-stilbene dichloride.

Thermal Decomposition of Bis(diphenylmethyl)tin Dichloride.—A solution of 13.1 g. (0.025 mole) of bis(diphenylmethyl)tin dichloride in 50 ml. of toluene was refluxed vigorously for 3 hr. At the end of this period, a very small amount of white solid was formed. After filtration, the solvent was evaporated under diminished pressure to give 12.7 g. of solid, which on recrystallization from cyclohexane-benzene (3:2) afforded 11.8 g. (90%) of the starting organotin compound, fine needles decomposing at 115–117°.

The insoluble solid was washed with hot benzene to leave 0.3 g. (6%) of anhydrous stannous chloride, which was identified by positive tests for stannous cation and chloride anion.

When 13.1 g. (0.025 mole) of bis(diphenylmethyl)tin dichloride was refluxed in xylene for 2 hr., 3.8 g. (83%) of anhydrous stannous chloride and 3.0 g. (75%) of *sym*-tetraphenylethane, m.p. 210–211° (lit.[11] m.p. 209°) were obtained.

Thermal Decomposition of Dibenzyltin Dichloride.—On refluxing a solution of 9.3 g. (0.025 mole) of dibenzyltin dichloride in 50 ml. of isoamylbenzene at 201–202° for 3 hr., an abundant formation of white solid was observed. It was separated by filtration of hot solution, washed with hot toluene to leave 4.1 g. (84%) of anhydrous stannous chloride. Distillation of the organic part under diminished pressure gave, after removal of the solvents, 3.4 g. (75%) of bibenzyl, b.p. 155–157°/9 mm., m.p. 51° (lit.[11] m.p. 52–53°).

Another run using 9.3 g. (0.025 mole) of dibenzyltin dichloride in 50 ml. of boiling *n*-butylbenzene at 183–184° for 3 hr. resulted in formation of only 0.25 g. (5%) of anhydrous stannous chloride along with the recovery of 8.7 g. (93%) of dibenzyltin dichloride.

Diphenylbis(diphenylmethyl)tin.—After a solution of potassium diphenylmethide in liquid ammonia was prepared

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(13) H. J. Barber, R. Slack, and A. M. Woolman, *J. Chem. Soc.*, 99 (1943).

(14) The authors are indebted to N. Sugimoto for technical assistance in this part of experiments. The toluene solution of anethole hydrobromide was prepared according to the method of Kharasch and Kleiman (M. S. Kharasch and M. Kleiman, *J. Am. Chem. Soc.*, **65**, 491 (1943)).

(15) I. A. Pearl and W. M. Denn, *J. Am. Chem. Soc.*, **60**, 57 (1938).

(16) H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

(17) A. N. Lange, "Handbook of Chemistry," 9th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1956, p. 422.

(18) T. W. Abott and J. R. Johnson, *Org. Syn.*, Coll. Vol. I, 440, 1941.

(19) H. B. Haas and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949).

by the method of Yost and Hauser[20] from 9.8 g. (0.25 g.-atom) of potassium metal and 42.1 g. (0.20 mole) of diphenylmethane in 250 ml. of anhydrous liquid ammonia, the solvent was replaced by an equal volume of anhydrous ether. The resulting red suspension was then refluxed with vigorous stirring for 4 hr. in order to remove the last trace of ammonia.[21]

To this suspension, cooled to 10°, was added dropwise a solution of 17.2 g. (0.05 mole) of diphenyltin dichloride in 100 ml. of anhydrous ether during 10 min. under vigorous stirring. After 1 hr. of stirring at room temperature, the mixture was heated gradually to reflux and kept boiling for an additional 2 hr.

On cooling, the mixture was treated with aqueous 10% ammonium chloride solution and the whole mixture was filtered with mild suction. The solid residue (16.3 g.) was washed with water followed by ether and dried. The filtrate was evaporated to leave 27.7 g. of yellow oil and 3.7 g. of solid. The combined solid materials (20.0 g.) were recrystallized from benzene to give 17.7 g. (58%) of diphenylbis(diphenylmethyl)tin, fine crystals melting at 175–177° with slight decomposition. Infrared spectra (KBr disk): 1450 (s), 1430 (m), 1073 (s), 1035 (s), 850 (m), 810 (s), 757 (s), 747 (s), 735 (m), 705–700 (vs), and 680 cm.$^{-1}$.

Anal. Calcd. for $C_{38}H_{32}Sn$: C, 75.15; H, 5.31; Sn, 19.54. Found: C, 75.38; H, 5.03; Sn, 19.53.

Bis(diphenylmethyl)tin Dichloride.—Into an ethanolic 5 *N* hydrochloric acid solution was added in portions with occasional shaking 15.2 g. (0.025 mole) of diphenylbis(diphenylmethyl)tin, and the resulting mixture was heated at 50° for 3 hr. After the mixture was allowed to stand overnight at room temperature, the solid materials were separated, washed with ethanol followed by petroleum ether (b.p. 30–50°), and recrystallized from cyclohexane-benzene (3:2) to give 10.5 g. (80%) of bis(diphenylmethyl)tin dichloride, fine needles decomposing at 115–117° into a reddish mass. Infrared spectra (KBr disk): 1450 (s), 1035 (m), 850 (w), 820 (m), 757 (s), 747 (s), and 700 (vs) cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{22}Cl_2Sn$: C, 59.59; H, 4.23; Sn, 22.65. Found: C, 59.34; H, 4.27; Sn, 22.35.

Attempted Preparation of Tetrakis(diphenylmethyl)tin. (a) Using Potassium Diphenylmethide in Ether.—A suspension of 30.9 g. (0.15 mole) of potassium diphenylmethide in 150 ml. of anhydrous ether was obtained similarly[20,21] and to this was added, on cooling below 10°, a solution of 7.8 g. (0.03 mole) of tin tetrachloride in 150 ml. of dry benzene in 20 min. under vigorous stirring. The resulting thick paste was stirred at room temperature for 1 hr. and under refluxing for an additional 2 hr. After treatment with aqueous 2 *N* hydrochloric acid solution, the organic layer was separated, washed with water, and dried over calcium chloride. Evaporation of the solvent gave 25.2 g. of oil, which gave negative tests for tin and halogen. A pasty mass obtained on storing the oil in a refrigerator for 2 days was freed from oil by suction filtration to afford 7.7 g. of white solid, and the liquid part was distilled with steam to leave an additional 2.3 g. of solid along with the recovery of 14.7 g. (0.086 mole) of diphenylmethane. Combined solids (10.0 g.) were recrystallized from toluene to give 8.5 g. (0.025 mole or 85%) of *sym*-tetraphenylethane, m.p. and mixed m.p.[11] 209–211°, which gave correct analyses for carbon and hydrogen.

A by-product of stannous chloride was determined by volumetric titration with 0.2 *N* potassium iodate solution using potassium iodide–starch as an indicator: 5.1 g. (0.027 mole or 89%).

When the unhydrolysed reaction mixture was extracted with cold ether, 7.8 g. of orange-colored oil was obtained. This was treated with petroleum ether (b.p. 30–50°) to leave 1.1 g. of yellow solid containing tin, decomposing at 80–87°. The solid in air turned readily into reddish tar, and attempted recrystallization of the solid from benzene or light petroleum (b.p. 70–80°) was unsuccessful. From the decomposition product was isolated 0.2 g. of benzophenone, m.p. 46–47°, the oxime, m.p. 140–141° (lit.[22] m.p. 141–142°), which gave correct analyses for carbon and hydrogen, and 0.15 g. of benzhydrol, m.p. 66–67° (lit.[16] m.p. 67–68°), whose analyses agreed with calculated values.

(b) Using Diphenylmethylmagnesium Bromide in Ether.—A solution of 40.7 g. (0.15 mole) of diphenylmethylmagnesium bromide in 150 ml. of anhydrous ether was prepared by the method of Hauser *et al.*,[23] and this was worked up as above with 7.8 g. (0.03 mole) of tin tetrachloride in 150 ml. of dry benzene. Isolation of the product was performed by the same procedure to afford 8.7 g. (0.026 mole or 87%) of *sym*- tetraphenylethane, m.p. 209–210°, and 5.0 g. (0.026 mole or 87%) of stannous chloride. No organotin compound was detected among the reaction products.

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[20] R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).

[21] A trace amount of ammonia remaining in the reaction mixture formed an insoluble adduct with tin compound causing a serious loss of the material. Vigorous stirring and refluxing of the suspension for more than 3 hr. were required in order to secure a good result.

[22] A. Lachman, *Org. Syn.*, Coll. Vol. II, 70 (1944).

[23] C. R. Hauser and D. S. Hoffenberg, *J. Am. Chem. Soc.*, **77**, 5742 (1955).