Thermal decomposition of 9,10-bisformamido-9,10-ethanoanthracene. A small sample of the ethano compound (m.p. 330°C.) was heated for 10 min. under nitrogen in a 334° vapor bath. The material melted, then changed with effervescence to a dark green powder. This did not melt below 400° (hot bar). Ultraviolet spectra of the untreated and heat-treated compound was determined. Characteristic bands of anthracene were observed in the spectrum of the heat-treated sample, while none appeared in that of the untreated one.

Thermal decomposition of 9,10-diamino-9,10-ethanoanthracene. Samples (1.0 g.) of the diamine were heated under nitrogen in a 140°, 155°, and 194° vapor bath. No visible changes were observed in the first two cases, while at 194° the originally clear, colorless melt effervesced and turned to a brilliant red, and on cooling deposited red crystals. These showed a characteristic anthracene spectrum in the ultraviolet.

A solution of the ethanoanthracene diamine in *o*-dichlorobenzene (b.p. 180°) was heated at reflux for 4 hr. under nitrogen. Strong anthracene bands developed in the ultraviolet spectrum of this solution.

Polymer from 9,10-dihydro-9,10-ethanoanthracene-9,10-diisocyanate. A solution containing 2.88 g. (0.01 mole) diisocyanate in 15 ml. of dimethyl sulfoxide was prepared. To it was added a solution of 1.16 g. (0.01 mole) of hexamethylenediamine in 10 ml. of dimethyl sulfoxide. After stirring at 40–50° under nitrogen for 1 hr., a clear viscous solution resulted. A film was cast, and the remaining portion was poured into water. The polymer was washed with water, and dried in a vacuum oven at 90°. It had a polymer melt temperature (PMT) of 294°[18] with gas evolution and foaming. The films were drawable about 1.5X at 150°. Drawn strips were boiled off, but showed no crystallinity by X-ray.

The polymer when heated at 250–275° turned yellow and showed anthracene bands in the ultraviolet. Small samples of the polymers were placed in a tube which was connected to an infrared gas cell and to a vacuum pump. The tube and cell were evacuated to *ca.* 1 mm. pressure, the tube was immersed into a 275° vapor bath for 2 min. The polymer discolored strongly. The cell was now closed, and the infrared spectrum of the contents was recorded. The characteristic band of ethylene was detected, indicating that this polymer converted quite readily to the corresponding anthracene polyurea.

Polymerization of the diisocyanate with 2,2-bis(4-aminophenylpropane). To a solution of 2.88 g. (0.01 mole) of diisocyanate in 25 ml. of dimethyl sulfoxide was added with stirring under nitrogen a solution of 2.26 g. of (0.01 mole) of 2,2-bis(4,4′-diaminodiphenyl)propane in 20 ml. of the same solvent. After 10 min., 4 drops of triethylamine was added as catalyst for the reaction. The solution was stirred 3 hr. and was then poured into water to precipitate the polymer. The polymer was collected, washed with water, and dried in a vacuum oven at 90°. It weighed 4.8 g. and melted at 298° with yellowing and effervescence.

Polymerization of the diisocyanate and tetramethyleneglycol. In a small polymer tube were placed 6.33 g. of the diisocyanate and 1.978 g. of tetramethyleneglycol. The mixture was heated in a 205° vapor bath; the initially thin melt became very viscous after *ca.* 15 min. and solidified to a mass after 1 hr. Heating was continued for an additional hour. The polymer had a melt temperature of 220–230°.

When heated to 245°, the pale yellow product of the above reaction foamed to about four times its original volume, and became brilliant yellow. The ultraviolet spectra of these two polymers were determined in dimethyl sulfoxide. The spectrum obtained from the "degraded" polymer showed two bands at 263 mμ and 269 mμ, respectively, while the original polymer did not show these bands.

Polymerization of the diamine (II) *with sebacoyl chloride.*[2] A solution of 1.83 g. freshly recrystallized diamine in 30 ml. of chloroform was placed in a high speed mixer. To this was added simultaneously with stirring 1.85 g. of sebacoyl chloride in 10 ml. of chloroform and 1.65 g. of sodium carbonate in 60 ml. of water. The mixture was stirred for 10 min. and the chloroform evaporated. The polymer was collected, washed with water and dried in a vacuum oven at 70°. The yield of polymer was 2.2 g., with a PMT[18] of 350°.

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(18) R. G. Beaman and F. B. Cramer, *J. Polymer Sci.*, **21**, 223 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Preparation of Some New Modifications of Diphenyltin[1]

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Preparations of diphenyltin described earlier[2,3] lead to yellow products of very high or very low solubility in benzene. The preparation of yellow modifications of intermediate solubility, and of two colorless modifications are described in this paper. Diphenyltin dihydride, whose preparation and characterization are described, decomposes in the presence of amines to produce yellow modifications of diphenyltin. Decomposition in methanolic solutions leads to a colorless modification of degree of polymerization of five or six. This modification in turn can be converted into a less soluble crystalline modification by dissolving in solvents such as dimethylformamide, dimethyl sulfoxide, and morpholine. It also undergoes thermal and photochemical transformations into yellow diphenyltin.

Diphenyltin has been prepared in two ways which are fundamentally different. Krause and Becker[2] prepared it by reaction of phenylmagnesium bromide with stannous chloride;

$$2\ C_6H_5MgBr + SnCl_2 \longrightarrow (C_6H_5)_2Sn + 2MgBrCl$$

The product was described as a bright yellow solid which softened at 126° and melted to a deep red liquid at 130°. It was monomeric, but its molecular weight increased over three days by a factor of three and over five months by a factor of about five. The elemental analyses agreed with the theoretical values. When Jensen and Clauson-Kaas attempted

(1)(a) Support of this work by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged. (b) Taken in part from the M.S. thesis of A. G. Armour, September 1956.

(2) E. Krause and R. Becker, *Ber.*, **53**, 173 (1920).

(3) E. Krause and R. Pohland, *Ber.*, **57**, 532 (1924).

to prepare the compound by the same procedure, they were unable to obtain material with the correct tin analysis and they found that the melting points of various preparations differed considerably.[4]

A second method of preparation of diphenyltin was described by Chambers and Scherer:

$$(C_6H_5)_2SnCl_2 + 4Na \longrightarrow (C_6H_5)_2SnNa + 2NaCl$$

$$(C_6H_5)_2SnNa_2 + 2NH_4Br \longrightarrow 2NH_3 + 2NaBr + (C_6H_5)_2SnH_2$$

$$(C_6H_5)_2SnH_2 \longrightarrow H_2 + (C_6H_5)_2Sn$$

The reaction was carried out in liquid ammonia, and the diphenyltin hydride was described as a dark solid which decomposed to a polymeric form of diphenyltin[5] on evaporation of the ammonia and warming to room temperature. If ether was added before evaporation of the ammonia a monomeric product was obtained. This product did not melt below its decomposition temperature of 205°. Jensen and Clauson-Kaas were able to repeat this work satisfactorily, with the exception that they had difficulty in obtaining an analytically pure product.

These products were always yellow and the low molecular weight samples were quite soluble in benzene, chloroform, and ethylene chloride. They were insoluble in ethanol. Solutions exposed to the air deposited a white solid presumed to be diphenyltin oxide.

Two striking characteristics may be noted from the above summary: first, diphenyltin is yellow (as is dicyclohexyltin[3]), whereas salts of divalent tin are colorless; second, the molecular weight is variable. More recently it has been found that dicyclopentadienyltin is colorless. Magnetic susceptibility measurements have shown that diphenyltin[3] and dicyclopentadienyltin[6] are not radicals, and the low dipole moments[4] of monomeric and polymeric diphenyltin indicate that they are not dipolar.

This paper describes the first results of an investigation of the organic derivatives of divalent tin whose objectives include a study of methods of preparation and chemical behavior toward reducible compounds, free radicals, unsaturated compounds, and various electrophilic and nucleophilic reagents.

We have prepared pure diphenyltin by two methods. The first involves the reaction between stannous chloride and phenyllithium, which has already been reported[7] without indication of purity of the product. Purification of the product was effected by repeated precipitation from benzene and from chloroform by the addition of methanol. The molecular weight of this material was determined by the isopiestic method in methylene chloride. Twenty-four hours after preparation the molecular weight indicated an average degree of polymerization of six. (When the cryoscopic method was used with benzene as solvent, no meaningful value could be obtained because the cooling curves indicated that a solid solution was formed.)

The second method used involved the reduction of diphenyltin dichloride with lithium aluminum hydride. At first it was observed that some heat was evolved when the two reactants were mixed in ether, and a very small amount of white precipitate appeared. When an amine or sodium hydroxide pellets were added, gas evolution soon began and a yellow precipitate began to appear. The reaction was complete in fifteen hours. When diethylamine was used, 74% of crude diphenyltin was obtained. After purification the yield was 32% of product with an average degree of polymerization (cryoscopic) of 8.6 ± 1.1. When tri-*n*-butylamine was used as the base, the product was much less soluble in benzene, but could be purified by solution in benzene and precipitation by methanol.

Later it was found that diphenyltin dihydride is more stable than would be indicated by the published literature.[5] Diphenyltin dichloride reacts readily with lithium aluminum hydride in ether. Hydrolysis of the reaction mixture near 0° provides a solution containing an essentially quantitative yield of diphenyltin dihydride as indicated by the yields of hydrogen and diphenyltin obtained upon decomposition of the dihydride as described below. The dihydride has been isolated in the pure state by recrystallization from petroleum ether–methylene chloride and melts at −21° to −20°. It is moderately stable in benzene at room temperature, but decomposes readily upon heating to give tin, tetraphenyltin, and hydrogen.[8]

If diethylamine is added to an ether solution of diphenyltin dihydride, hydrogen is evolved, and bright yellow diphenyltin, form A, precipitates. This material is more intense in color than that described above and is essentially insoluble in solvents such as benzene and chloroform. Because of this its molecular weight could not be determined.

If the ether solution is diluted with about four volumes of methanol, relatively slow gas evolution ensues and a precipitate begins to appear one to three hours later. In twelve to twenty-four hours the precipitation is complete, and a total yield of over 90% of *colorless* diphenyltin, form B, is ob-

(4) K. A. Jensen and N. Clauson-Kaas, *Z. anorg. u. allgem. Chem.*, **250**, 277 (1943).

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

(6) E. O. Fischer and H. Grubert, *Z. Naturforsch.*, **11b**, 423 (1956).

(7) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

(8) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Applied Chem.*, **7**, 366 (1957). These investigators prepared the hydride under slightly different conditions from ours, and they showed that it could not be distilled.

tained. It is analytically pure after drying *in vacuo*. Its identity as diphenyltin was established by elemental analysis and by its reactions. Since various samples have melted in the range 88–115°, albeit sharply, when placed in a preheated bath, the material is not homogeneous. If the bath is not preheated, melting (probably preceded by decomposition) does not occur until the temperature is near 250°. Molecular weight determinations have indicated degrees of polymerization between five and six in benzene and methylene chloride. The transition implied by the melting behavior can be effected on a synthetic scale by heating the colorless material at 70–80° for three hours providing a product similar to that obtained from the amine-catalyzed decomposition of the hydride.

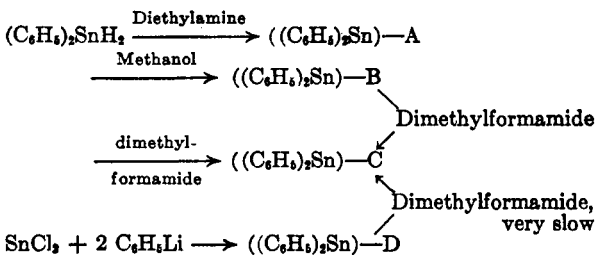
A photochemical transition of form B to a yellow modification can be observed upon exposure to light.

If form B is dissolved in dimethylformamide at room temperature, the clear, light yellow solution which results soon deposits colorless crystals of yet another variety, form C, which melts around 250°. Similar behavior occurs in dimethylsulfoxide, morpholine, pyridine, methyl ethyl ketone, and acetonitrile-benzene. This does not occur with benzene, toluene, ether, or dioxane. Toluene, dioxane, pyridine, ethylene glycol, diethyl ether, and styrene can be used as solvents for recrystallization of C. Decomposition of the hydride in dimethylformamide, dimethylsulfoxide, or morpholine also yields a crystalline product, the rate of decomposition increasing with solvent in the order named.

When the yellow modification obtained from the reaction of phenyllithium with stannous chloride, form D, is dissolved in dimethylformamide, complete solution occurs. Crystalline material appears, but so slowly that even after a year at room temperature the solution still has a rather deep yellow color due to unconverted D.

These reactions involving the formation and interconversions of the forms of diphenyltin are summarized in Chart 1. It is clear that modification B is the most labile, and it may be that modification C is the most stable thermodynamically. Its formation from A has not been clearly demonstrated, however. The x-ray powder patterns[9] show that the structures of these forms are different. Furthermore, the differences, which persist in solutions, are molecular in nature, and not merely crystallographic. This is borne out, for example, by the differences in color of the solutions.

CHART I



EXPERIMENTAL

All melting points are uncorrected.

In all cases where diphenyltin or diphenyltin dihydride was used a nitrogen atmosphere was maintained, although no special equipment was used.

Analysis for tin was carried out by the method described by Gilman and Rosenberg.[10] Other analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Preparation of diphenyltin from stannous chloride and phenyllithium (Form D). Phenyllithium was prepared in a three-neck flask fitted with a stopcock on the bottom. A second three-neck round-bottom flask was cooled in a Dry Ice–acetone bath at −20°. It was flushed out with nitrogen and then 84 g. (0.144 mole) of anhydrous stannous chloride,[11] 150 ml. anhydrous ether and 500 ml. of benzene were added. The ether was used in order to prevent freezing of the benzene, which in turn was necessary to keep the diphenyltin from precipitating. Then about 2*M* phenyllithium solution (whose concentration had been determined accurately), containing 0.288 mole was added with vigorous stirring, under nitrogen, over a 3-hr. period. The reaction mixture was allowed to warm up to room temperature and the lithium salts settled out, revealing a deep red solution. It was filtered into a 1-l. Claisen flask and concentrated under reduced pressure, nitrogen being passed into the solution through the capillary used to prevent bumping, with warming to no higher than 40°. When only a viscous oil was left, 50 ml. of benzene was added and the resulting solution filtered into 300 ml. of methanol. The Claisen flask was washed with two 25-ml. portions of benzene which were also passed through the filter into the methanol. At this stage the diphenyltin was in a viscous second layer. The methanol-benzene was decanted and 200 ml. of fresh methanol was added. Upon stirring, the viscous mass gradually became solid and was then filtered and dried overnight in a vacuum disiccator. This material amounted to 80 g. (72% yield of impure diphenyltin containing 42.0% tin).

This product was dissolved in 100 ml. of benzene under nitrogen and filtered. Then 300 ml. of methanol was added slowly with stirring whence the diphenyltin precipitated as an oil again. The supernatant was poured off and 300 ml. of fresh methanol was added. The oil solidified gradually when stirred and was filtered off. Drying as before left 70 g. with 42.5% Sn.

The reprecipitation was repeated from benzene but with Norit treatment yielding 62 g. with 42.7% Sn. Successive reprecipitations from 70 ml. of chloroform twice and then from benzene yielded products containing 43.1%, 43.25%, and 43.30% Sn respectively, 41 g. (37%) being the final yield.

Anal. Calcd. for $C_{12}H_{10}Sn$: C, 52.82; H, 3.69; Sn, 43.50. Found: C, 52.91; H, 3.62; Sn, 43.30. Mol. wt. 1630 (isopiestic, methylene chloride).

Preparation of diphenyltin by the reaction of lithium aluminum hydride with diphenyltin dichloride in the presence of amines. To a solution of 27.7 g. (0.0813 mole) of diphenyltin

(9) For the determination of which we thank Dr. H. M. Haendler.

(10) H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, 75, 3592 (1953).

(11) H. Stephen, *J. Chem. Soc.*, 2786 (1930).

dichloride in 50 ml. absolute ether was added 8.4 ml. (0.0813 mole) of diethylamine. Immediately the white diethylamine–diphenyltin dichloride complex appeared as a precipitate. Then 225 ml. of an ether solution containing 0.122 mole of lithium aluminum hydride was added, with cooling of the reaction mixture in an ice bath. An orange precipitate appeared, which turned brown after about an hour. Gas evolution occurred for at least 6 hr.; after about 15 hr. the reaction mixture was filtered providing 16.5 g. of crude diphenyltin. It was purified by dissolution in hot benzene or chloroform followed by addition of methanol. Precipitations using benzene, chloroform, and benzene successively yielded 7.0 g. of pure yellow diphenyltin.

Anal. Calcd. for $C_{12}H_{10}Sn$: C, 52.82; H, 3.69; Sn, 43.50. Found: C, 51.93; H, 3.80; Sn, 43.60; mol. wt. 2350 ± 300 (cryoscopic in benzene).

When tri-*n*-butylamine was used in place of diethylamine, the diphenyltin obtained was bright golden in color and much less soluble in benzene or chloroform. In spite of its low solubility it was possible to purify a sample, whose tin analysis (43.2%) indicated a high degree of purity.

Preparation of diphenyltin dihydride. To a slurrry containing 1.90 g. (0.050 mole) of lithium aluminum hydride and 35 ml. of dry ether at 0° was added dropwise over 30 min. a solution of 17.2 g. (0.05 mole) of diphenyltin dichloride in 50 ml. of ether. The mixture was stirred with continued cooling for another 30 min. and excess lithium aluminum hydride was destroyed by dropwise addition of 100 ml. of water. After essentially all of the solids were dissolved, the ether layer was separated and washed thrice with 100-ml. portions of ice water. The ether solution was dried over calcium chloride and concentrated under reduced pressure, the last traces of ether being removed by pumping at less than 1 mm. for several hours, leaving 12.2 g. (89%) of a colorless to pale yellow liquid. Recrystallization from petroleum ether (b.p. 30–60°)–methylene chloride (1:1) with cooling to −70° yielded clusters of white needles, m.p. −21 to −20°; n_D^{25} 1.6128.

Anal. Calcd. for $C_{12}H_{12}Sn$: Sn, 43.28. Found: Sn, 42.96, 43.06.

Decomposition of diphenyltin dihydride in methanol. Colorless diphenyltin (Form B). Quantities used were 3.94 g. (0.100 mole) of lithium aluminum hydride in 35 ml. of ether and 34.4 g. (0.100 mole) of diphenyltin dichloride in 50 ml. of ether. The procedure described above was followed through the washing of the ether solution of diphenyltin dihydride. It was then poured into 400 ml. of methanol, and the resulting solution allowed to stand after fitting the containing flask with a Bunsen valve. After 1 to 3 hr., evolution of gas began, and a precipitate appeared shortly afterwards. After a few tenths of a gram had appeared the mixture was filtered and allowed to stand for about 15 hr. and filtered again. The diphenyltin was washed with methanol and dried in a vacuum desiccator at room temperature for at least 12 hr.; yield 26.7 g. (97.8%).

When a conventional melting point determination was carried out, no melting occurred. Instead, the sample changed from white to yellow at about 70–80° and underwent decomposition gradually after the temperature had passed 225°. However, when the sample was placed in a preheated bath, the analytical sample melted at 86–88°.

Anal. Calcd. for $C_{12}H_{10}Sn$: C, 52.80; H, 3.69; Sn, 43.50. Found: C, 52.64; H, 3.80; Sn, 43.03; mol. wt., 1290 (isopiestic in ether), 1310 (cryoscopic in benzene).

Samples from other similar preparations had variable melting points. The highest observed was 110–116°; two molecular weight determinations on this sample gave 1680 and 1780 (cryoscopic in benzene).

Decomposition of the hydride in other solvents. A solution of hydride (0.025 mole in 75 ml. ether) was decomposed as follows:

(1) To 25 ml. was added 2 ml. of diethylamine. Within 2 hr. 2.12 g. (93.7%) of a deep yellow modification of diphenyltin, form A, appeared, and a quantitative yield of hydrogen was evolved.

Anal. Calcd. for $C_{12}H_{10}Sn$: Sn, 43.50. Found: Sn, 43.65, 43.73.

(2) To another 25 ml. was added 3 ml. of concd. hydrochloric acid whereupon a quantitative yield of hydrogen according to the following equation was evolved: $(C_6H_5)_2SnH_2 + 2\ HCl \rightarrow (C_6H_5)_2SnCl_2 + 2\ H_2$. Evaporation of the solution to a small volume yielded 2.44 g. (85%) of diphenyltin dichloride, m.p. 41–42°, undepressed upon admixture with an authentic sample of m.p. 42–43°.

Another sample containing 0.100 mole of hydride in 105 ml. of ether was decomposed partially as follows:

(1) To 15 ml. was added 20 ml. of morpholine. Very rapid gas evolution occurred and a yellow-orange precipitate (3.50 g., 85%) was filtered off after 8 hr.

(2) To 15 ml. was added 20 ml. of dimethylsulfoxide. Gas evolution was considerably slower so the solution was not filtered for 20 hr.; yield 3.41 g., 83% of light yellow crystals.

(3) To 15 ml. was added 20 ml. of dimethylformamide. In this case gas evolution was still slower, but after 20 hr., 3.58 g., 87% of colorless crystalline product was obtained.

Transformations of colorless diphenyltin. (1) To 12 ml. of dimethylformamide was added 0.70 g. of colorless diphenyltin. Complete solution occurred in less than a minute. After 2 hr. crystals were present in the flask. These were filtered off, washed with ether, and dried *in vacuo;* yield 0.50 g., 71%.

Anal. Calcd. for $C_{12}H_{10}Sn$: Sn, 43.40. Found: Sn, 43.91, 43.51.

This crystalline product, form *C*, decomposes in hot dimethylformamide, and so cannot be recrystallized from this solvent. Toluene is very effective for recrystallization, providing crystals containing entrapped toluene which can be removed at 100° at reduced pressure. Other effective solvents include pyridine, dioxane, ethylene glycol diethyl ether, morpholine, and styrene. In the latter case the styrene solution was heated until it was fairly viscous from polymerization, and yet a high recovery of diphenyltin was made. This indicates that the diphenyltin does not react with growing polystyrene radicals. Dimethylsulfoxide is not a good recrystallizing solvent because of decomposition of the tin compound.

(2) A sample was placed in an Erlenmeyer flask and spread out so that the depth was no more than about a millimeter. It was then heated for 0.5 hr. at 50–70°, 1.5 hr. at 70°, and 1.5 hr. at 80°. During this time the sample turned yellow.

Anal. Calcd. for $C_{12}H_{10}Sn$: C, 52.84; H, 3.69; Sn, 43.50. Found: C, 52.44; H, 3.95; Sn, 43.49.

The product did not melt up to about 270° whether the bath was preheated or not. It was much less soluble in organic solvents such as benzene, ether, and methylene chloride than the colorless modification. Both the colorless and yellow modifications, as well as that obtained from the phenyllithium–stannous chloride reaction, have identical infrared spectra.

When samples of the colorless diphenyltin were dissolved in pyridine, methyl ethyl ketone, morpholine, and benzene–acetonitrile, precipitation of crystalline material occurred in each case within 5 hr. With dioxane, on the other hand, no crystallization occurred.

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