Experimental

Reduction of 3,6-diphenyl-*s*-tetrazine (II). (A) Lithium Aluminum Hydride Reduction.—A 1-l. three-necked flask was fitted with a nitrogen inlet tube, stirrer, and a condenser topped with a calcium chloride drying tube which in turn was connected to a water trap. The flask was charged with 3.0 g. of lithium aluminum hydride and 250 ml. of ether. A steady stream of nitrogen was passed through the flask and a solution of 10 g. (0.043 mole) of 3,6-diphenyl-*s*-tetrazine[5] in 100 ml. of anhydrous ether was added as rapidly as possible through the condenser. There was an immediate loss of purple color. The mixture was refluxed on a steam bath for 1 hr.

The mixture was cooled and 15 ml. of water was added dropwise. This was followed by the addition of 250 ml. of 10% sulfuric acid. The yellow ether layer was separated, dried over sodium sulfate, and the ether evaporated. A yellow solid (6.8 g.) was collected, m.p. 92–93°. This was identified as benzalazine.

Treatment of II with nitric acid did not produce the characteristic purple color of tetrazines. The material did not depress the melting point of an authentic sample of benzalazine[6] and infrared spectrum was identical with that of benzalazine.

Anal. Calcd. for $C_{14}H_{12}N_2$: N, 13.45. Found: N, 13.62.

A 10-ml. sample of the aqueous hydrolyzate from above was heated on a steam bath with 0.1 ml. of benzaldehyde. A yellow solid soon separated and was identified as benzalazine, m.p. 92–93°. The infrared spectrum was also identical with that of benzalazine.

(B) Sodium Borohydride Reduction.—This reduction was carried out in the same manner as A except that methanol was used as a solvent. Five grams of II gave 2.2 g. of benzalazine, m.p. 91–93°.

(C) Sodium Dithionite Reduction.—A solution of 3 g. (0.013 mole) of II, 20 ml. of water, and 15.6 ml. of 4.6 *N* sodium hydroxide was warmed on a steam bath and 6 g. of sodium hydrosulfite added over a period of 15 min. The mixture was stirred and heated until all of the purple color disappeared. The mixture was cooled, filtered, and the precipitate was washed with benzene. The product, m.p. 183–184° (closed tube) and 190–192° (open tube), was identical with 1,2-dihydro-3,6-diphenyl-*s*-tetrazine[3] which had been previously prepared by the reduction of 3,6-diphenyl-*s*-tetrazine with hydrogen sulfide.[7]

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(5) J. Allegretti, J. Hancock, and R. S. Knutson, *J. Org. Chem.*, **27**, 1463 (1962).

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Some Reactions of Hexaphenyldilead

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At elevated temperatures, hexaphenyldilead is decomposed into tetraphenyllead and elemental lead, two moles of starting material yielding three moles of tetraphenyllead.[2] In the presence of acids, however, decomposition of hexaphenyldilead takes place at room temperatures.[3,4]

Halogen acids cleave, in a stepwise sequence, two of the phenyllead bonds in tetraphenyllead to yield, in the first step, benzene and triphenyllead halide. Triphenyllead halide in turn further reacts to form additional benzene and diphenyllead dihalide (reactions 2 and 3). Hexaphenyldilead, in comparison, when treated with halogen acids yields lead halide as well as triphenyllead halide, diphenyllead dihalide, and benzene.

We were interested in two aspects of these reactions: (a) if hexaphenyldilead decomposes to tetraphenyllead in the molar ratio of 2:3, why the combined yield of the products, triphenyllead halide and diphenyllead dihalide, has never been reported to surpass 50%[3,4] and (b) how it is possible to form lead halide in view of the fact that it is not formed under similar conditions in the reaction of either tetraphenyllead, triphenyllead chloride, or diphenylleaddi halide with halogen acids.

We have found that hexaphenyldilead, in the presence of two molar equivalents of acetic acid, did not react at room temperature when *n*-heptane or benzene were used as solvents. At reflux temperatures, however, the reaction proceeded smoothly. The products obtained were benzene (90% based on acetic acid), lead acetate (41%), tetraphenyllead (25%), triphenyllead acetate (18%), and some unchanged hexaphenyldilead (3%). When hexaphenyldilead was refluxed in acetic acid, however, lead acetate and diphenyllead diacetate were the only products isolated. In a similar manner, excess thiolacetic acid reacted with hexaphenyldilead yielding similar amounts of analogous compounds.

In accounting for the products formed, we have considered the following reaction scheme.

$$\mathrm{Ph_6Pb_2} \rightleftharpoons [\mathrm{2Ph_3Ph}] \longrightarrow \mathrm{Ph_4Pb} + [\mathrm{Ph_2Pb}] \tag{1}$$

$$\mathrm{Ph_4Pb} + \mathrm{HOAc} \longrightarrow \mathrm{Ph_3PbOAc} + \mathrm{PhH} \tag{2}$$

$$\mathrm{Ph_3PbOAc} + \mathrm{HOAc} \longrightarrow \mathrm{Ph_2Pb(OAc)_2} + \mathrm{PhH} \tag{3}$$

$$[\mathrm{Ph_2Pb}] + \mathrm{2HOAc} \longrightarrow \mathrm{Pb(OAc)_2} + \mathrm{2PhH} \tag{4}$$

The initial assumption is that hexaphenyldilead is thermally decomposed in the presence of acetic acid to tetraphenyllead and the relatively unstable diphenyllead. In the presence of less than an excess of acetic acid, reactions 2 and 4 are competitive, thus accounting for the formation of lead acetate, tetraphenyllead, and triphenyllead acetate. In the presence of excess acetic acid, reactions 2 and 3 go to completion and the final products are diphenyllead diacetate and lead acetate (*via* reaction 4).

Since triphenyllead acetate and diphenyllead diacetate are thermally stable under the conditions used, the accounting for the formation of lead acetate by an alternate reaction to reaction 4, such as a disproportionation of the triphenyllead acetate and diphenyllead diacetate, was ruled out. As no hydrogen evolution was observed during the reaction, it appeared equally unlikely that the formation of lead acetate occurred from reactions of elemental lead and acetic acid or between a triphenyllead hydride intermediate and acetic acid.

Hexaphenyldilead has been reported to react with oxygen to yield triphenyllead oxide.[5,6] In an analogous reaction with sulfur, we obtained triphenyllead sulfide in 59% yield; however, it was interesting to note that detectable amounts of tetraphenyllead and diphenyllead sulfide could be identified as by-products. This lends support to the reaction sequence given, particu-

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(2) For a review, see R. W. Leeper, L. Summers, and H. Gilman, *Chem. Rev.*, **54**, 101 (1954).

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larly as it applies to the decomposition of hexaphenyldilead (reaction 1).

As final evidence for decomposition of hexaphenyldilead into tetraphenyllead and diphenyllead, we studied the reaction of hexaphenyldilead with 1,2-dibromoethane. Recent studies have shown that hexaethyldistannane when treated with 1,2-dibromoethane yields as the main products triethyltin bromide and ethylene.[7] When hexaphenyldilead reacted with 1,2-dibromoethane, the only nonvolatile products were tetraphenyllead (81%) and lead bromide (98%) based upon the assumed disproportionation of diphenyllead to tetraphenyllead and elemental lead followed by the reaction sequence shown.

$$2\mathrm{Ph_6Pb_2} \longrightarrow 2\mathrm{Ph_4Pb} + [2\mathrm{Ph_2Pb}]$$

$$[2\mathrm{Ph_2Pb}] \longrightarrow \mathrm{Ph_4Pb} + \mathrm{Pb}$$

$$2\mathrm{Ph_6Pb_2} \longrightarrow 3\mathrm{Ph_4Pb} + \mathrm{Pb} \tag{5}$$

$$\mathrm{Pb} + \mathrm{BrCH_2CH_2Br} \longrightarrow \mathrm{CH_2{=}CH_2} + \mathrm{PbBr_2}\text{[8]} \tag{6}$$

It seems consistent with the experimental data now available that hexaphenyldilead undergoes an initial decomposition to tetraphenyllead and elemental lead *via* the unstable intermediate diphenyllead. In the presence of acids this initially formed diphenyllead reacts to form lead acetate and benzene (reaction 4).

This reaction scheme would also explain why, in the presence of acids, the combined yields of triphenyllead halide and diphenyllead dihalides are stoichiometrically limited to 50%.

Experimental

All reactions were followed and products identified by thin layer chromatographic techniques using silica gel G as a solid phase and either carbon tetrachloride or benzene–hexane mixtures as solvents. A dithizone spray (6 mg./100 ml. of chloroform) was used. Triphenyllead compounds gave yellow spots, diphenyllead compounds gave red spots, and tetraphenyllead gave no color reaction with dithizone. Tetraphenyllead gave a yellow spot using a permanganate spray.

Melting points were determined with a Thomas–Hoover melting point apparatus. Where possible, mixture melting points with authentic samples and comparison of infrared spectra with those of authentic samples were used as confirmatory identification of the products.

Hexaphenyldilead was prepared by the established Grignard method. Careful purification by successive recrystallizations resulted in thin layer chromatograms in which the complete absence of tetraphenyllead was demonstrated.

Hexaphenyldilead–Acetic Acid (Ratio 1:2).—Hexaphenyldilead, 4.38 g. (5.0 mmoles), and glacial acetic acid, 0.60 g. (10 mmoles), dissolved in 50 ml. of *n*-heptane was refluxed for 3 hr. No visible evolution of hydrogen was noted during the reaction. During the 3-hr. period, the reaction was followed by thin layer chromatographic techniques as described. Periodic sampling showed the disappearance of hexaphenyldilead and the formation of tetraphenyllead, lead(II) acetate, and triphenyllead acetate. After completion of the reaction, the liquid phase was distilled and investigated using v.p.c. techniques. Vapor phase chromatography indicated the liquid phase to contain only *n*-heptane and benzene and by comparison of peak sizes, the amount of benzene obtained in the reaction was calculated to be 0.7 g. (90%). The solid residue remaining after the removal of the solvent (4.11 g.) was extracted with boiling chloroform. The insoluble residue (1.31 g.) consisted of lead acetate, identified by its solubility in water and black precipitate with hydrogen sulfide. From the chloroform extract, 1.27 g. of tetraphenyllead was precipitated by adding alcohol and identified by mixture melting point. The mother liquor contained 0.87 g. of triphenyllead acetate and 0.13 g. of unchanged hexaphenyldilead, identified by mixture melting point and infrared spectra.

Hexaphenyldilead–Acetic Acid (Excess).—A solution of hexaphenyldilead, 2.20 g. (2.5 mmoles), was refluxed in 20 ml. of glacial acetic acid for 5 min. During the reaction period, a white precipitate formed which, after the reaction was complete, was filtered and extracted with chloroform. The residue (0.81 g.) was shown to be lead(II) acetate (99%), identified as before; the filtrate was evaporated under vacuum; the residue, m.p. 203–206°, recrystallized from benzene–acetic acid to yield 1.41 g. (94%) of diphenyllead diacetate, m.p. 208–209°. Mixture melting point with an authentic sample gave no depression.

Hexaphenyldilead with Excess Thiolacetic Acid.—A solution of 2.20 g. (2.5 mmoles) of hexaphenyldilead was dissolved in 20 ml. of thiolacetic acid and refluxed for 5 min. During the reaction 0.50 g. of a black precipitate of lead sulfide formed, apparently from decomposition of lead (II) thiolacetate. This corresponds to an 89% yield of the latter compound. From the filtrate, after removal of the excess thiolacetic acid, there was obtained 1.58 g. of residue which was recrystallized from ethanol to yield 0.90 g. (70%) of diphenyllead dithiolacetate, m.p. 94–95°. Thin layer chromatography of the mother liquor showed some triphenyllead thiolacetate and possibly diphenyllead sulfide $[(\mathrm{C_6H_5})_2\mathrm{PbS}]_n$.

Hexaphenyldilead with Sulfur.—A benzene solution of 64 mg. (2 mmoles) of sulfur was added to a benzene solution containing 1.75 g. (2 mmoles) of hexaphenyldilead and left to stand for 10 days at room temperature. After 1 hr., the clear solution had become turbid. After 10 days, 20 mg. of precipitate was filtered and the solvent evaporated under vacuum to leave a residue of 1.68 g. The residue was dissolved in chloroform, alcohol added, and, after a few minutes, a colorless precipitate, 0.43 g. (24%) of hexaphenyldilead, settled out of solution (identified by infrared spectra). Some tetraphenyllead could be detected in this precipitate using thin layer chromatography techniques. The solvent was partially removed from the mother liquor; the precipitate that formed was filtered and recrystallized from ethanol. The yield was 1.02 g. (59%) of bis(triphenyllead) sulfide, m.p. 139–140°, identified by mixture melting point with an authentic sample. The remaining mother liquor contained some diphenyllead sulfide and bis(triphenyllead) sulfide according to thin layer chromatography experiments.

Hexaphenyldilead with 1,2-Dibromoethane.—Hexaphenyldilead, 4.39 g. (5 mmoles), dissolved in 30 ml. of warm 1,2-dibromoethane was refluxed for 15 min. The solution turned yellow followed by the formation of a white precipitate. The precipitate was filtered (3.83 g.), washed with solvent, and ether extracted with hot chloroform and the insoluble portion filtered. The insoluble residue (0.9 g., 98%) was identified as lead bromide by classical techniques. The chloroform and original 1,2-dibromoethane filtrates were combined, the solvents removed under vacuum, and the residue recrystallized from chloroform to yield 3.14 g. (81% yield) of tetraphenyllead, m.p. 226–228°. The filtrate contained some unchanged hexaphenyldilead as shown by thin layer chromatography experiments.

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[8] Razuvaev[7] has carried out the analogous reaction with hexaethyldilead and obtained similar results. Their explanation of the formation of tetraethyllead as a consequence of the disproportionation of triethyllead bromide appeared to be inconsistent with their prior description of the thermal stability of triethyllead bromide.

Friedel–Crafts Isomerization. VI. Aluminum Chloride-Catalyzed Isomerization of Fluorobiphenyls

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Examples of phenyl group migration in substituted aromatics under Friedel–Crafts isomerization conditions are not numerous. Weingarten[1] reported re-

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[1] H. Weingarten, *J. Org. Chem.*, **27**, 2024 (1962).