[CONTRIBUTION FROM THE ETHYL CORPORATION, BATON ROUGE RESEARCH LABORATORY]

Preparation of Tetravinyllead and Some Phenylvinyllead Compounds. Some Reactions of Tetravinyllead[1]

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Tetravinyllead, triphenylvinyllead and diphenyldivinyllead were prepared by the reaction of vinylmagnesium bromide with lead chloride (or lead acetate), triphenyllead chloride and diphenyllead dichloride, respectively, in tetrahydrofuran. Tetravinyllead was also prepared by the reaction of vinylmagnesium chloride with lead chloride in tetrahydrofuran. The reactions of tetravinyllead with chlorine, hydrogen chloride and carboxylic acids were studied.

Preparations of the vinyl compounds of the Group IV elements, silicon,[2] germanium[3] and tin[4] by the reaction of the tetrachlorides of these elements with vinylmagnesium bromide in tetrahydrofuran have been reported previously. This paper describes the preparation of some vinyllead compounds.

In the first synthesis of tetravinyllead, it was prepared from lead chloride or lead diacetate and

$$4CH_2{=}CHMgX + 2PbY_2 \longrightarrow Pb(CH{=}CH_2)_4 + 2Pb + 4MgXY$$

vinylmagnesium bromide in tetrahydrofuran in a reaction similar to that used in the preparation of tetraethyllead[5] by the Grignard reaction. Tetravinyllead also was prepared from lead dichloride and vinylmagnesium chloride. As the lead salt was added to the Grignard solution, a vigorous exothermic reaction occurred with deposition of lead metal.

Triphenylvinyllead and diphenyldivinyllead were also prepared by the Grignard reaction.

To discover whether saturated aqueous ammonium chloride was a suitable reagent for destroying excess Grignard and washing out salts (*i.e.*, one which would not cause cleavage of the vinyl-to-lead bond) aliquots of the tetrahydrofuran solutions of the reaction mixtures were treated with aqueous ammonium chloride. Decomposition from hydrolysis by the ammonium chloride was compared with normal decomposition occurring over a period of time. Triphenylvinyllead and diphenyldivinyllead showed no decomposition on standing or on hydrolysis after one day. On the other hand, tetravinyllead showed considerable decomposition on hydrolysis with ammonium chloride after standing one day, much more than was observed after standing three days without ammonium chloride addition; consequently, since ammonium chloride caused cleavage of tetravinyllead, its use was avoided. The hydrolysis step for tetravinyllead was omitted. The triphenylvinyllead and diphenyldivinyllead reaction mixtures were hydrolyzed with saturated ammonium chloride.

The yields of the unisolated products, given in the Experimental Section, were determined directly in the reaction mixture. The method used was based on that of Griffing, *et al.*,[6] for the determination of organic lead compounds in gasoline. Carbon and hydrogen analyses of the liquid vinyllead compounds were difficult to obtain because of a tendency of these materials to decompose explosively during combustion. Good carbon and hydrogen analyses were obtained in those attempts in which explosions did not occur.

Infrared spectra of these compounds were consistent with those expected for these structures. The presence of the vinyl group was confirmed by an absorption peak in the infrared at 6.3 μ. However, the infrared spectrum of tetravinyllead prepared from vinylmagnesium bromide showed a band at 8.6 μ, indicating the presence of ethyl-to-lead bonds originating from ethyl bromide contaminant in the vinyl bromide used to make the Grignard reagent. It was for this reason that the preparation of tetravinyllead was repeated using vinylmagnesium chloride. Infrared analysis of this sample of tetravinyllead showed no evidence of ethyl-to-lead bonds.

The vapor phase chromatogram of the tetravinyllead prepared from vinylmagnesium bromide had a large peak for tetravinyllead at a retention time of 29 minutes. The only other peaks were two smaller ones at higher retention times, probably from ethylvinyllead compounds. Absence of any peak at a retention time of 41 minutes indicated there was no tetraethyllead in the product. The area under the large peak indicated at least 90% purity.

The tetravinyllead prepared from vinylmagnesium bromide showed the tetravinyllead peak at the same retention time and a complete absence of the smaller peaks for ethylvinyllead compounds. This is in good agreement with the infrared data.

The cleavage of tetravinyllead with chlorine, hydrogen chloride and carboxylic acids was investigated. Some vinyllead compounds were prepared by these reactions. The reaction of tetravinyllead with chlorine in acetic acid resulted in the formation of divinyllead dichloride. Tetraethyllead reacts similarly with chlorine,[7] yielding diethyllead dichloride. Treatment of tetravinyllead in hexane with hydrogen chloride resulted in the formation of trivinyllead chloride.

Tetravinyllead seems to be more reactive to cleavage than tetraethyllead. A liquid mixture of equivalent amounts of tetravinyllead and acetic acid with silica gel catalyst underwent a reaction in 20 minutes at room temperature with the evolution of gas to yield a white solid, trivinyllead acetate. A similar mixture of tetraethyllead and acetic acid

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[1] Presented at the Boston Meeting of the American Chemical Society, April, 1959.

[2] S. D. Rosenberg, J. J. Walburn, T. D. Stankovich, A. E. Balint and H. E. Ramsden, *J. Org. Chem.*, **22**, 1200 (1957).

[3] D. Seyferth, THIS JOURNAL, **79**, 2738 (1957).

[4] D. Seyferth and F. G. A. Stone, *ibid.*, **79**, 515 (1957).

[5] P. Pfeiffer and P. Truskier, *Ber.*, **37**, 1127 (1904).

[6] M. E. Griffing, A. Rozek, L. J. Snyder and S. R. Henderson, *Anal. Chem.*, **29**, 190 (1957).

[7] G. Grüttner and E. Kraus, *Ber.*, **49**, 1415 (1916).

showed no signs of reaction or formation of solids even after 24 hours.

The reaction between tetravinyllead and trichloroacetic acid was violently exothermic. When equivalent amounts were used, the product was trivinyllead trichloroacetate.

Table I gives a comparison of melting points of some solid vinyllead compounds with the corresponding ethyllead compounds. The melting points of the trivinyllead salts given here were obtained after purification by sublimation.

TABLE I

COMPARISON OF VINYLLEAD COMPOUNDS WITH ETHYLLEAD COMPOUNDS

Compound	Melting points, °C. R = (CH_2=CH–)	 R = (CH_3CH_2–)
$(C_6H_5)_3PbR$	32–33	49–50
R_3PbCl	119–121	172
R_2PbCl_2	>300	Dec. at room temp.
$R_3PbOCOCH_3$	168–170	160
$R_3PbOCOCCl_3$	>300	141

Experimental[8]

Starting Materials.—Triphenyllead chloride[9] and tetraphenyllead[10] were synthesized by established procedures.

Diphenyllead dichloride was prepared using a slight modification of the procedure of Gilman and Robinson.[9] Tetraphenyllead (89.9 g.) was dissolved in chloroform. Dry hydrogen chloride was added at a fast rate with mechanical stirring. After 5–15 minutes, a thick precipitate suddenly formed. The addition of hydrogen chloride was continued for 5–10 minutes after the precipitation began. The product was washed with chloroform, dried in air, and weighed 73 g. (97% yield).

Anal. Calcd. for $C_{12}H_{10}PbCl_2$: Cl, 16.40. Found: Cl, 16.28.

Tetravinyllead from Lead Chloride and Vinylmagnesium Bromide.—To a dry flask fitted with a Dry Ice condenser, a stirrer and an addition funnel, 24.3 g. of clean (shiny) magnesium turnings (1 mole) and 600 ml. of tetrahydrofuran (refluxed two hours with and distilled from lithium aluminum hydride) were added. A portion (200–250 ml.) of a solution consisting of 107 g. of vinyl bromide (1 mole) in 400 ml. of dry tetrahydrofuran was added. The mixture was stirred and heated to reflux temperature to start the reaction. The reaction usually started within a half-hour and needed to be moderated by cooling with an ice-bath just after starting. The remaining tetrahydrofuran solution of vinyl bromide then was added dropwise so as to maintain a gentle reflux. After the reaction subsided, the mixture was refluxed for one hour more. The Dry Ice condenser was replaced by a water condenser, and the Grignard reagent was again brought to reflux. The source of heat was removed, and 139 g. of lead chloride (0.5 mole) was added in very small portions. A vigorous exothermic reaction occurred, and the lead chloride addition was controlled to maintain an active reflux. Transient yellow, brown and dark green colors gave way to a jet black color near the end of the reaction. The reaction mixture was refluxed one hour further after the addition of the lead chloride. The reaction mixture was filtered through a fine sintered glass funnel, and the lead powder was washed several times with small portions of tetrahydrofuran. The tetrahydrofuran was removed by distillation through a one-foot Vigreux column with a pot temperature of 90°.[11] A slight vacuum was used during the distillation. After the tetrahydrofuran was removed, a damp solid remained. The flask was then immersed up to its neck in an oil-bath at 70–85° and fitted with a Claisen head and a receiver which was immersed in a Dry Ice-bath. Under a vacuum of 0.5–1 mm., tetravinyllead gradually collected in the receiver over a 24-hour period. The product was redistilled through a two-foot fractionating column filled with fine helices, at 30–40° (1–2 mm.), giving 32.3 g. (41% yield) of colorless liquid. An oil-bath at 85–95° (but not over 95°) was used as a source of heat. A middle fraction was taken as the analytical sample, $n^{27.5}D$ 1.5408.

Anal. Calcd. for $C_8H_{12}Pb$: C, 30.46; H, 3.84; Pb, 65.69. Found: C, 30.31; H, 4.12; Pb, 65.34.

In another run on a smaller scale, dithizone analysis of the reaction mixture indicated a 61.7% yield of tetravinyllead. Some of the samples of tetravinyllead decomposed explosively on combustion during carbon and hydrogen analysis.

Although tetravinyllead decomposes at room temperature with the deposition of a yellow solid, it can be stored for at least two months in the dark at −26° without appreciable decomposition.

Tetravinyllead from Lead Acetate and Vinylmagnesium Bromide.—The procedure was the same as that in the preparation above except that 162.7 g. of anhydrous lead acetate (0.5 mole) was used instead of lead chloride. The product weighed 22.48 g. (28.5% yield). The product was fractionated at 30–40° (1–2 mm.). With the pot temperature at 90° under 1 mm., the distillation stopped midway. A sample of the fractionated product was analyzed. The residue then was vacuum distilled with a Claisen head and the distillate was fractionated at a pot temperature of 90° and 1 mm. Some losses were incurred here so that the redistilled product weighed 13.4 g.

Anal. Calcd. for $C_8H_{12}Pb$: Pb, 65.69. Found: Pb, 65.35.

In another run on a smaller scale, dithizone analysis[7] of the reaction mixture indicated a 48.1% yield of tetravinyllead.

Tetravinyllead from Lead Chloride and Vinylmagnesium Chloride.—The vinylmagnesium chloride was prepared according to the procedure of Rosenberg, *et al.*,[12] from 35.9 g. of magnesium turnings (1.47 mole), 0.28 ml. of ethyl bromide catalyst, 110.3 g. of vinyl chloride (1.75 mole) and 314 g. of tetrahydrofuran. The procedure followed was then the same as that in the preparation of tetravinyllead from vinylmagnesium bromide and lead chloride except that 300 ml. more of tetrahydrofuran was added and 205 g. of lead chloride (0.737 mole) was used. Dithizone analysis of the filtered reaction mixture showed a 45.3% yield of tetravinyllead. The product distilled at about 34° (0.6 mm.) giving 39.8 g. (34.3% yield) of tetravinyllead. A middle fraction was taken as the analytical sample, $n^{26}D$ 1.5430.

Anal. Calcd. for $C_8H_{12}Pb$: Pb, 65.69. Found: Pb, 65.47.

Triphenylvinyllead.—To a Grignard solution prepared from 1.06 g. of magnesium (0.0436 mole) and 4.66 g. of vinyl bromide (0.0436 mole) in 40 ml. of tetrahydrofuran, was added 100 ml. of tetrahydrofuran and 20.64 g. of triphenyllead chloride (0.0436 mole). This mixture was refluxed with mechanical stirring for 24 hours. The solids went into solution on refluxing. The reaction mixture was hydrolyzed by shaking twice with saturated aqueous ammonium chloride. The tetrahydrofuran layer was separated and dried over anhydrous sodium sulfate. The tetrahydrofuran was removed through a one-foot Vigreux column under slight vacuum, leaving a liquid plus a small amount of solid. This residue was extracted twice with 100 ml. of boiling hexane and the extract was filtered to remove triphenyllead chloride. The hexane was removed, leaving a yellow oil. Attempts to distil the oil under vacuum in a Claisen flask resulted in extensive decomposition with deposition of lead metal. Therefore the oil was placed in a Hickman molecular still and very slowly distilled at 0.05–0.06 mm. with a pot temperature of 160–170°. A colorless liquid distilled which solidified to a somewhat yellow solid in the receiver immersed in a Dry Ice-bath. The product melted when it was warmed slightly. A black streak was found at the bottom of the still at the end of the distillation, indicating the beginning of thermal decomposition to form lead metal. When the product was allowed to stand overnight, it solidified to 4.77 g. (23.6% yield) of pure white

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[8] All reactions were carried out under a nitrogen atmosphere.

[9] H. Gilman and J. R. Robinson, THIS JOURNAL, **51**, 3112 (1929).

[10] H. Gilman, L. Summers and R. W. Leeper, *J. Org. Chem.*, **17**, 630 (1952).

[11] A higher pot temperature should be avoided because of the hazardous nature of the thermally unstable tetravinyllead.

[12] S. D. Rosenberg, A. J. Gibbons, Jr., and H. E. Ramsden, THIS JOURNAL, **79**, 2137 (1957).

crystals. These crystals were spread out on a towel and, after a day, were pressed down and spread again on a new dry towel. After two more days of such treatment these crystals, m.p. 33–34°, were analyzed.

Anal. Calcd. for $C_{20}H_{18}Pb$: C, 51.59; H, 3.90. Found: C, 51.58; H, 4.07.

Diphenyldivinyllead.—The procedure was, in general, the same as that in the preparation of triphenylvinyllead except that diphenyllead dichloride was used instead of triphenyllead chloride. The Grignard reagent was prepared from 3.17 g. of magnesium (0.130 mole) and 14.0 g. of vinyl bromide (0.130 mole) in 120 ml. of tetrahydrofuran. To the Grignard solution, 28.18 g. of diphenyllead dichloride and 120 ml. of tetrahydrofuran were added. The procedure for isolation was the same, except that petroleum ether, b.p. 30–60°, was used instead of hexane for the extraction, and the pot temperature during the molecular distillation was 120–155°. The yield was 13.69 g. (50.1%) of pale yellow liquid. This was redistilled in a molecular still, and a middle fraction analyzed.

Anal. Calcd. for $C_{16}H_{16}Pb$: C, 46.25; H, 3.88; Pb, 49.87. Found: C, 46.10; H, 3.89; Pb, 49.48.

Trivinyllead Acetate.—Tetravinyllead (1.000 g. or 0.00318 mole) prepared from vinylmagnesium bromide, 0.1962 g. glacial acetic acid (0.00318 mole + 3% excess) and a piece of silica gel as catalyst were mixed. A gas was evolved, and after 20 minutes the mixture solidified to a white crystalline mass. This solid was heated on a steam-bath for 1/2 hour to complete the reaction. The precipitate was washed several times with petroleum ether, leaving 0.89 g. (81% yield) of product, m.p. 168–170°. The product was sublimed at 100° (1 mm.) to obtain the analytical sample, m.p. 168–170°. (The solid can be crystallized from benzene.)

Anal. Calcd. for $C_8H_{12}O_2Pb$: C, 27.66; H, 3.48. Found: C, 27.50; H, 3.70.

A sample of trivinyllead acetate prepared in 84% yield from tetravinyllead from vinylmagnesium chloride melted at 169–170°. The mixture melting point of this sample with some of the analytical sample above was 168–170°.

Trivinyllead Chloride.—Tetravinyllead (1.00 g. or 0.00318 mole) prepared from vinylmagnesium bromide was dissolved in 10 ml. of hexane. Dry hydrogen chloride was passed through the solution. The precipitate was filtered and washed with hexane, and the filtrate was treated with more hydrogen chloride. The process was repeated until a precipitate was obtained which did not melt when heated up to 200°. Four fractions were obtained, melting at 114–118°, 117–120°, 120–122° and 120–122°. Later fractions, which did not melt below 200°, were discarded. The combined solids weighed 0.31 g. (30.3% yield). A portion was sublimed at 90° (1 mm.) to give a white solid, m.p. 119–121°, which was analyzed.

Anal. Calcd. for C_6H_9ClPb: C, 22.25; H, 2.80. Found: C, 22.35; H, 2.90.

A sample of trivinyllead chloride was prepared from the tetravinyllead from vinylmagnesium chloride. This sample was sublimed at 90° (1 mm.) to give a product melting at 120–122°. The mixture melting point of this sample with some of the analytical sample above was 120–122°.

Trivinyllead Trichloroacetate.—Tetravinyllead (1.000 g. or 0.00318 mole) prepared from vinylmagnesium bromide was mixed slowly (caution) with 0.536 g. trichloroacetic acid (0.00318 mole + 3% excess) and a piece of silica gel as catalyst. A violent exothermic reaction occurred, leaving a solid product with a brown tint. The product was washed several times with petroleum ether to remove unreacted starting materials. The product was sublimed at 180–195° (1 mm.) to obtain the analytical sample which did not melt below 300°. The crude product weighed 1.06 g. (74% yield).

Anal. Calcd. for $C_8H_9Cl_3O_2Pb$: C, 21.32; H, 2.01. Found: C, 21.01; H, 1.76.

Divinyllead Dichloride.—A saturated solution of chlorine in acetic acid was added to 1.00 g. of tetravinyllead until the yellow color persisted. The white precipitate which formed was filtered, and more chlorine in acetic acid was added to the filtrate, which was allowed to stand overnight. The additional solids which deposited from the filtrate were collected and combined with the original white solid. The combined dry product weighed 0.7664 g. (72% yield). Dithizone analysis showed the product to contain 92% divinyllead salt, a slight amount of trivinyllead salt and no inorganic lead salts. The product was recrystallized from methanol and water to give white crystals which were dried at 100° (20 mm.) for 2 hours for analysis.

Anal. Calcd. for $C_4H_6Cl_2Pb$: C, 14.46; H, 1.82. Found: C, 14.31; H, 1.80.

This sample showed the presence of trace amounts of ethyllead compounds by infrared analysis. Another sample of divinyllead dichloride prepared from the tetravinyllead from vinylmagnesium chloride possessed the same spectrum, except that there was no evidence for ethyllead contaminants.

Infrared spectra were obtained on all of the above vinyllead salts. The presence of the vinyl group was confirmed by an absorption peak at 6.3 μ. Infrared spectra of the trivinyllead salts indicate no ethyl-to-lead bonds (8.6 μ).

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL COMPANY]

The Reaction of Sulfur Dichloride with Methylamine[1]

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The reaction of sulfur dichloride with methylamine in hexane solution has been investigated and found to produce an amorphous polymer of approximate composition $(CH_3NS)x$, *crystalline* $(CH_3NS)_4$ *and two crystalline isomers of molecular formula* $(CH_3N)_3S_5$. *Possible structures and a reaction mechanism are proposed.*

Formation of cyclic S_4N_4 by the action of NH_3 on SCl_2 or S_2Cl_2 has long been known.[2,3] Goehring and Weis[4] have reported that SCl_4 and n-$C_4H_9NH_2$ at −60° gave (A), a yellow oil stable only below 50°. Levi[5] obtained a crystalline compound (B) by action of S_2Cl_2 on $C_2H_5NH_2$. Becke-Goehring and Jenne[6] have repeated Levi's work recently and extended it to other amines. Lengfeld and Stieglitz,[7] on treatment of SCl_2 with $C_2H_5NH_2$ in hexane,

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(1) Presented at the 134th meeting of the American Chemical Society, Chicago, Illinois, September 7–12, 1958.

(2) R. Schenck, *Ann. Chem. Liebigs*, **290**, 171 (1896).

(3) M. Goehring, "Ergebnisse und Probleme der Chemie die Schwefelstickstoffverbindungen," Akademie-Verlag, Berlin, 1957, pp. 1–26.

(4) M. Goehring and G. Weis, *Angew. Chem.*, **68**, 678 (1956).

(5) T. G. Levi, *Gazz. chim. ital.*, **61**, 294 (1931).

(6) M. Becke-Goehring and H. Jenne, *Angew. Chem.*, **70**, 399 (1958).

(7) F. Lengfeld and J. Stieglitz, *Ber.*, **28**, 2742 (1895).