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SYNTHESIS OF ORGANOLEAD COMPOUNDS
IV. PREPARATION AND REACTIONS OF TRIS[(TRIMETHYLSILYL)METHYL]PLUMBYLMAGNESIUM CHLORIDE

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SUMMARY

The preparation, properties, and reactions of tris[(trimethylsilyl)methyl]plumbylmagnesium chloride are described. Tetrakis[(trimethylsilyl)methyl]lead and several related new silicon-substituted organolead compounds and their proton magnetic resonance spectra are reported.

INTRODUCTION

A recent report from this laboratory has described the preparation and reactions of trimethylplumbylmagnesium chloride and triethylplumbylmagnesium chloride[1]. These complexes were found to be fairly stable in tetrahydrofuran solution and highly reactive toward alkyl halides. The complexes were prepared from reaction of alkylmagnesium chlorides with lead chloride at 5° in tetrahydrofuran.

$$3\,RMgCl + PbCl_2 \xrightarrow{THF} R_3PbMgCl + 2\,MgCl_2 \tag{1}$$

Derivatives were prepared according to:

$$R_3PbMgCl + R'Cl \xrightarrow{THF} R_3R'Pb + MgCl_2 \tag{2}$$

Seyferth and Freyer[2] have described the preparation of tetrakis[(trimethylsilyl)methyl]lead (37% yield) from reaction of (trimethylsilyl)methylmagnesium chloride with lead chloride in tetrahydrofuran.

$$4\,(CH_3)_3SiCH_2MgCl + 2\,PbCl_2 \xrightarrow{THF} [(CH_3)_3SiCH_2]_4Pb + Pb + 4\,MgCl_2 \tag{3}$$

They added lead chloride to the Grignard reagent in tetrahydrofuran at $-10°$ and described the solution as becoming deep red-brown in color. In our studies on the preparation of trialkylplumbylmagnesium chloride complexes it was found that the characteristic color in tetrahydrofuran solution was dark greenish-brown; therefore, we believed the color noted by Seyferth and Freyer was due to formation of tris[(trimethylsilyl)methyl]plumbylmagnesium chloride. A study was initiated to investigate this postulate.

This paper describes the preparation and some reactions of tris[(trimethylsilyl)methyl]plumbylmagnesium chloride. These reactions have resulted in the preparation of some new silicon-substituted organolead compounds.

DISCUSSION

Reaction of three moles of (trimethylsilyl)methylmagnesium chloride with one mole of lead chloride in tetrahydrofuran gives dark reddish-brown, homogeneous solutions which contain tris[(trimethylsilyl)methyl]plumbylmagnesium chloride. The reactions which probably occur in the preparation of the organometallic compound are as follows:

$$2\,(CH_3)_3SiCH_2MgCl + PbCl_2 \xrightarrow{THF} [(CH_3)_3SiCH_2]_2Pb + 2\,MgCl_2 \qquad (4)$$

$$[(CH_3)_3SiCH_2]_2Pb + (CH_3)_3SiCH_2MgCl \xrightarrow{THF} [(CH_3)_3SiCH_2]_3PbMgCl \qquad (5)$$

Qualitatively, tetrahydrofuran solutions of the complex seem to be more stable than solutions of trimethylplumbylmagnesium chloride and triethylplumbylmagnesium chloride[1]; however, decomposition occurs within a few hours in refluxing tetrahydrofuran with formation of tetrakis[(trimethylsilyl)methyl]lead and metallic lead[2]. The most probable route of the decomposition is given by the following equations.

$$[(CH_3)_3SiCH_2]_3PbMgCl \xrightarrow{\Delta} [(CH_3)_3SiCH_2]_2Pb + (CH_3)_3SiCH_2MgCl \qquad (6)$$

$$2[(CH_3)_3SiCH_2]_2Pb \xrightarrow{\Delta} [(CH_3)_3SiCH_2]_4Pb + Pb \qquad (7)$$

These equations are similar to those proposed earlier by Gilman and Bailie[3]. An equilibrium reaction for eqn. (6) was ruled out for reasons outlined in the previous paper[1].

Tris[(trimethylsilyl)methyl]plumbylmagnesium chloride was characterized by preparation of several derivatives according to eqn. (2). Table 1 lists the yields of the derivatives, along with molecular weights of the new organolead compounds, indicating them to be monomeric as expected. The yields in Table 1 are based on the amount

TABLE 1

REACTIONS OF TRIS[(TRIMETHYLSILYL)METHYL]PLUMBYLMAGNESIUM CHLORIDE

Reactant	Product	Yield (%)	Mol. wt.	
			Calcd.	Found
CH_3Cl	$[(CH_3)_3SiCH_2]_3CH_3Pb$	93	484	496
C_2H_5Cl	$[(CH_3)_3SiCH_2]_3C_2H_5Pb$	82	498	507
$(CH_3)_3SiCH_2Cl$	$[(CH_3)_3SiCH_2]_4Pb$	81	556	585
CH_2Cl_2	$\{[(CH_3)_3SiCH_2]_3Pb\}_2CH_2$	90	951	962
$HCCl_3$	$[(CH_3)_3SiCH_2]_3PbCl$		504	550
CCl_4	$[(CH_3)_3SiCH_2]_3PbCl$		504	500

of lead chloride used in preparation of the complex. The high yields indicate almost quantitative formation and reaction with little decomposition under the conditions used. In the reaction of tris[(trimethylsilyl)methyl]plumbylmagnesium chloride with chloroform and carbon tetrachloride the only observable reaction was decomposition (formation of lead metal); however, in both reactions a small amount of tris[(trimethylsilyl)methyl]lead chloride was recovered.

Table 2 contains a tabulation of the observed chemical shifts and spin–spin coupling constants of the silicon-substituted organolead compounds prepared in this investigation. The spectra were obtained in carbon tetrachloride solution with TMS as internal standard. Long-range coupling was not observed between the methyl protons attached to the silicon with the lead over four σ bonds (H–C–Si–C–^{207}Pb); whereas long-range coupling is readily observable in some neopentyllead compounds (H–C–C–C–^{207}Pb)[4]. The coupling constant in this case is probably small and not resolved, which is consistent with the small long-range coupling constant (H–C–Si–C–^{207}Pb) which has been reported for (trimethylplumbyl) (trimethylsilyl)methane (2.20 Hz)[5].

TABLE 2

PROTON MAGNETIC RESONANCE DATA

Compound	τ (ppm)				$J(^{207}\text{Pb})^a$ (Hz)		
	CH_3Si	$SiCH_2Pb$	Other		$SiCH_2Pb$	Other	
$[(CH_3)_3SiCH_2]_4Pb$	9.95	9.50			80.0		
$[(CH_3)_3SiCH_2]_3CH_3Pb$	9.95	9.55	CH_3Pb	9.17	82.5	$PbCH_3$	54.5
$[(CH_3)_3SiCH_2]_3C_2H_5Pb$	9.96	9.58	C_2H_5Pb	8.48^b	77.0	$PbCH_2C$	53.0
						$PbCCH_3$	150.0
$[(CH_3)_3SiCH_2)_3Pb]_2CH_2$	9.95	9.48	$PbCH_2Pb$	8.45	80.0	$PbCH_2Pb$	51.0
$[(CH_3)_3SiCH_2]_3PbCl$	9.85	8.75			13.5		

[a] Lead has 21.11% natural abundance of its isotope ^{207}Pb of $\frac{1}{2}$ spin. [b] Multiplet.

All of the compounds in Table 1 are new organolead compounds except tetrakis[(trimethylsilyl)methyl]lead and tris[(trimethylsilyl)methyl]lead chloride, which were reported by Seyferth and Freyer[2]. The usefulness of the reactions described in this investigation is demonstrated in the high yield of tetrakis[(trimethylsilyl)methyl] lead as compared to the previous preparation while both methods require approximately the same amount of work and time.

In view of the ease of formation of tetrakis[(trimethylsilyl)methyl]lead it is surprising that such difficulty was encountered in the attempted preparation of tetraneopentyllead[4,6,7]. The successful synthesis of tetraneopentyllead has only recently been reported from reaction of trineopentyllead bromide and neopentylmagnesium chloride[8]. This phenomenon is currently being investigated in our laboratory and will be reported on in a subsequent publication.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride before use. Lead chloride was obtained from Fisher Scientific Company and used without purification. The proton magnetic resonance spectra were recorded using a Varian Associates A-60 spectrometer. Molecular weights were determined by the differential vapor pressure technique in benzene solution at 37° using a Mechrolab Model 302 vapor pressure osmometer. Because of insolubility in benzene, the molecular weight of tris[(trimethylsilyl)methyl]lead chloride was measured in THF.

The reactions were performed in a 1000-ml three-necked round-bottom flask equipped with condenser (Dewar filled with Dry Ice–acetone) and magnetic or paddle stirrer. The lead salt was added from a 50-ml round-bottom flask connected to the reaction vessel by a short piece of Gooch tubing. The Grignard reagents were prepared from magnesium turnings and a slight excess of the alkyl halide. The excess alkyl halide was then removed by heating at reflux for a few minutes under a nitrogen flush.

Lead contents of the new organolead derivatives were determined by reaction with bromine in carbon tetrachloride, destruction with nitric and perchloric acid and titration with ethylenediaminetetraacetic acid (EDTA) to the endpoint using xylenol orange as indicator. During the hydrolysis of the reaction mixtures enough dilute HCl was added to solubilize the precipitated magnesium salts.

1. *Tris[(trimethylsilyl)methyl]plumbylmagnesium chloride*

The Grignard reagent, prepared from 8.0 g (0.33 g-atom) of magnesium and 41 g (0.33 mole) of (chloromethyl)trimethylsilane in 450 ml of tetrahydrofuran, was cooled to 5°, and 27.8 g (0.1 mole) of lead chloride was added slowly over a 15-minute period. A dark reddish-brown and homogeneous solution was obtained. The complex was characterized by several derivatives as described below.

2. *Tetrakis[(trimethylsilyl)methyl]lead*

Tris[(trimethylsilyl)methyl]plumbylmagnesium chloride was prepared as described above from 27.8 g (0.1 mole) of lead chloride and (trimethylsilyl)methylmagnesium chloride in 450 ml of THF. To this solution was added 12.4 g (0.1 mole) of (chloromethyl)trimethylsilane at 5°. The ice-bath was removed and the solution was allowed to warm to ambient temperature. After stirring for 1 h the reddish-brown color disappeared and a gelatinous precipitate was formed. No lead metal was observed. The mixture was hydrolyzed with 300 ml of water and the THF was removed by distillation at atmospheric pressure. After removal of the THF the product separated as a colorless layer below the aqueous layer. The product was separated and washed several times with water to remove all traces of THF. All the volatile impurities were steam-distilled from the product. It was then dried by filtering through a bed of calcium chloride. After drying 45.6 g (81.0%) of the colorless product was obtained. When completely dry the material crystallized and melted at 24–25°. (Found: Pb, 37.40. $C_{16}H_{44}PbSi_4$ calcd.: Pb, 37.26%.)

3. *Bis{tris[(trimethylsilyl)methyl]plumbyl}methane*

Tris[(trimethylsilyl)methyl]plumbylmagnesium chloride was prepared from 27.8 g (0.1 mole) of lead chloride in 500 ml of THF at 5°. To the solution was added 8.0 ml of methylene dichloride. The mixture was warmed to ambient temperature and stirred for 30 minutes and heated to 50° for 20 min. The reddish-brown color disappeared and a gelatinous precipitate was formed. The reaction mixture was hydrolyzed with 400 ml of water and the THF was removed by distillation. The heavy oily product was separated from the aqueous phase and washed several times with water. The volatile impurities were removed by steam distillation. The light yellow oil was then crystallized from a mixture of acetone and chloroform (50 %) at −10°; 42.5 g (80 %) of white crystalline solid melting at 39–42° was obtained. (Found: Pb, 43.44. $C_{25}H_{68}Pb_2Si_6$ calcd.: Pb, 43.59 %.)

4. *Tris[(trimethylsilyl)methyl]methyllead*

Tris[(trimethylsilyl)methyl]plumbylmagnesium chloride was prepared from 27.8 g (0.1 mole) of lead chloride and 0.30 mole of (trimethylsilyl)methylmagnesium chloride in 500 ml of THF at 5°. Into the solution was condensed 25 ml of methyl chloride. The reddish-brown color disappeared immediately. The solution was warmed to ambient temperature and hydrolyzed with 400 ml of water. The THF was removed by distillation at atmospheric pressure. The heavy product was separated from the aqueous layer and washed several times with water. The cloudy liquid was then vacuum-distilled, and the fraction boiling at 87–88° (0.3 mm) was collected and weighed; 45.0 g (93 %) of product was obtained. (Found: Pb, 42.79. $C_{13}H_{36}PbSi_3$ calcd.: Pb, 42.82 %.)

5. *Tris[(trimethylsilyl)methyl]ethyllead.*

Tris[(trimethylsilyl)methyl]plumbylmagnesium chloride was prepared from 27.8 g (0.1 mole) of lead chloride in 500 ml of THF at 5°. Into the solution was condensed 35 ml of ethyl chloride. The solution was then warmed to ambient temperature for 10 min and to 55° for 15 min. The characteristic color of the complex disappeared and a gelatinous precipitate was formed. The mixture was hydrolyzed with 400 ml of water and the THF was removed by distillation at atmospheric pressure. The heavy organic phase was then extracted into petroleum ether (b.p. 37–54°) for easier handling. The petroleum ether was evaporated and the oily product was vacuum-distilled. The colorless liquid boiling at 97–99° (0.7 mm) was collected. (Found: Pb, 41.42. $C_{14}H_{38}PbSi_3$ calcd.: Pb, 41.61 %.)

6. *Reaction of tris[(trimethylsilyl)methyl]plumbylmagnesium chloride with chloroform and carbon tetrachloride*

Tris[(trimethylsilyl)methyl]plumbylmagnesium chloride (0.1 mole) was prepared as described above in 500 ml of THF. In separate experiments 4.0 g (0.026 mole) of carbon tetrachloride and 6.0 ml (~0.075 mole) of chloroform were added over a 15-min period respectively. The reaction mixture was warmed to room temperature and stirred for 15 min and then to 50° and stirred for 1 h. The mixture was hydroylzed with water, and the THF was removed by distillation. After cooling, the aqueous solution was extracted with petroleum ether. A white precipitate which collected in the ether layer was produced in both experiments. The petroleum ether was filtered and the white gelatinous precipitate recovered. Recrystallization of the white solid from toluene gave crystals which melted at 213–215° (reported[2] 214–216°). Approximately 4–6 g of the white solid was obtained in the CCl_4 and $HCCl_3$ reactions. It was identified as $[(CH_3)_3SiCH_2]_3PbCl$. (Found: Pb, 39.89, Cl, 6.88. $C_{12}H_{33}ClPbSi_3$ calcd.: Pb, 41.08, Cl, 7.03 %.)

Evaporation of the petroleum ether gave several grams of tetrakis[(trimethylsilyl)methyl]lead (≈50% yield) in both experiments.

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