

## TRIPHENYLPLUMBYL-CONTAINING *p,p'*-DISUBSTITUTED 1,3-DIPHENYLTETRAMETHYLDISILOXANES

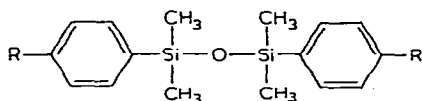
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### SUMMARY

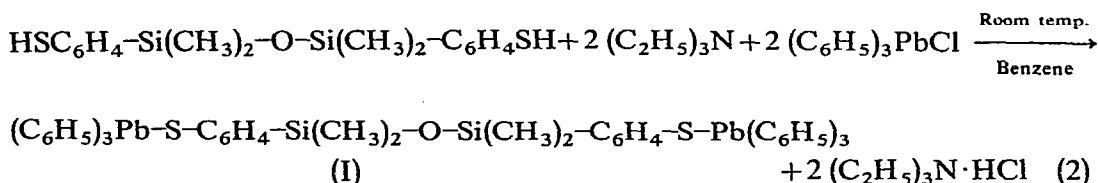
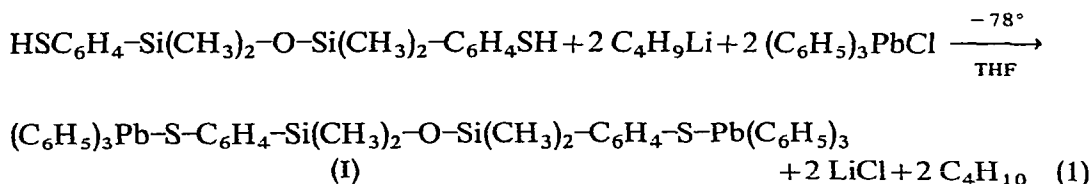
#### Compounds of the type

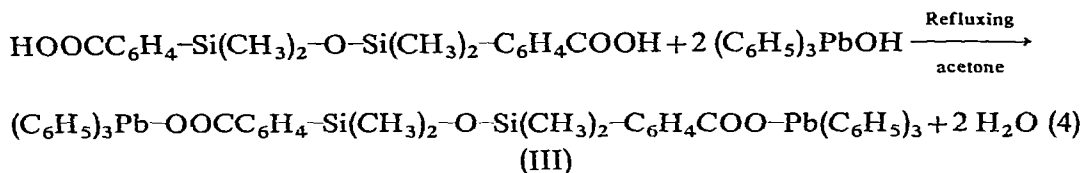
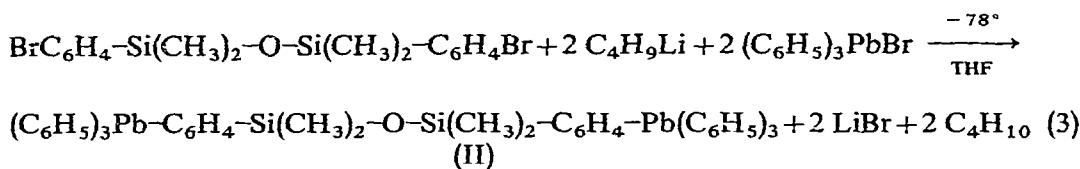


where R = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbS; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbOOC were synthesized. Physical properties and analytical data of the new compounds are reported. Infrared, nuclear magnetic resonance and thermal data are discussed.

### INTRODUCTION AND DISCUSSION

The synthesis and reactions of difunctional analogs of 1,3-dichlorotetramethyldisiloxane have not been studied in great detail<sup>1-3</sup>. However, recently a number of new symmetrical difunctional disiloxanes have been synthesized by the reaction of 1,3-dichlorotetramethyldisiloxane with the appropriate lithium reagents<sup>4</sup>. The present work deals with the synthesis of triphenylplumbyl-substituted compounds of the various difunctional analogs of 1,3-dichlorotetramethyldisiloxane. Reactions and products obtained thereby are represented in the following equations:





All the products obtained are crystalline solids soluble in common organic solvents. Compound (I) was obtained in better yield by reaction (2). Yields of compounds (I) and (III) were quantitative. In reaction (3) poor yields of compound (II) were obtained when triphenyllead chloride was used instead of the bromide. Attempts to synthesize corresponding triphenylplumbyl derivatives of 1,3-bis(*p*-hydroxyphenyl)-tetramethyldisiloxane failed. Routes (1), (2) and (4) gave unreacted starting materials whereas route (3) gave an insoluble polymeric material and unreacted lead halide.

#### Thermal characteristics

The melting points for compounds (I), (II) and (III) as determined by capillary tube method and by Differential Scanning Calorimetry (DSC), are recorded in Table I.

TABLE I  
DATA AND ANALYSES OF ORGANOMETALLIC DERIVATIVES

Compound	Yield (%)	M.p. (°C)	Analytical data (%)	
			Found	Calcd.
$[p\text{-(C}_6\text{H}_5)_3\text{PbSC}_6\text{H}_4\text{Si}(\text{CH}_3)_2]_2\text{O}$ (I)	98	127.5	C 51.24 H 3.96 S 4.99	50.98 4.11 5.21
$[p\text{-(C}_6\text{H}_5)_3\text{PbC}_6\text{H}_4\text{Si}(\text{CH}_3)_2]_2\text{O}$ (II)	60	162	C 53.45 H 4.35	53.79 4.34
$[p\text{-(C}_6\text{H}_5)_3\text{PbOOCC}_6\text{H}_4\text{Si}(\text{CH}_3)_2]_2\text{O}$ (III)	95	63	C 51.89 H 4.09	51.93 4.04

Compound (I) has a sharp melting point whereas (II) and (III) appear to soften and turn waxy at their melting point. All three compounds exhibit an exothermic transition around 330° similar to that found for the decomposition of tetraphenyllead. Compound (III) also shows an exotherm at 239° which is close to the melting point of the parent acid and may thus be indicative of the rupture of the lead-oxygen bond.

*Spectral correlation*

The characteristic silicon-carbon and siloxane vibrational modes are listed in Table 2. For the purpose of identification these absorptions along with those asso-

TABLE 2

SPECTRAL DATA FOR ORGANOMETALLIC DERIVATIVES

Compound	IR (cm <sup>-1</sup> ) <sup>a</sup>				PMR (Hz) <sup>b</sup>	
	SiCH <sub>3</sub> sym. def.	SiC <sub>6</sub> H <sub>5</sub> str.	SiOSi str.	SiCH <sub>3</sub> str., rock	Phenyl	Methyl
(I)	1260	1125	1075	838, 795	448.2	6.5
(II)	1260	1120	1075	835, 793	449.5	20.5
(III)	1260	1109	1060	832, 799	434.5	10.5

<sup>a</sup> As KBr disc. <sup>b</sup> Acetone-*d*<sub>6</sub>, carbon tetrachloride or dimethylsulfoxide as solvent and TMS as internal standard.

ciated with the triphenyllead group were found to be most useful<sup>4,5</sup>. Of particular interest for compound (III) is the spectral region between 1300–1600 cm<sup>-1</sup> associated with lead-carboxylate modes. These broad intense absorption bands are found at 1545 cm<sup>-1</sup>, 1535 cm<sup>-1</sup> and 1345 cm<sup>-1</sup>. Exact agreement was found for the observed and calculated number of protons via integration of the PMR spectra thus confirming the expected structure.

## EXPERIMENTAL

Difunctional 1,3-dichlorotetramethyldisiloxanes were synthesized by known methods<sup>1</sup>. *n*-Butyllithium (1.5 *M* in *n*-hexane) was obtained from Foote Mineral Company. Reactions involving *n*-butyllithium were carried out under an argon atmosphere. Tetrahydrofuran was dried over lithium aluminum hydride and distilled under argon prior to use. Melting points were determined using a Thomas Hoover Capillary Melting Point Apparatus and Du Pont Model-900 Thermal Analyzer. Infrared spectra were recorded on a Beckman Model IR-12 Spectrophotometer and Proton Magnetic Resonance spectra with a Varian Model A-60.

*1,3-Bis[(p-triphenylplumbyl)phenylthio]tetramethyldisiloxane*

Triphenyllead chloride (9.47 g, 0.02 mole) was added to a solution of 1,3-bis-(*p*-mercaptophenyl)tetramethyldisiloxane (3.5 g, 0.01 mole) and triethylamine (2.22 g, 10% excess over 0.02 mole) in benzene (200 ml). The reaction mixture was stirred at room temperature for 5 h. Precipitated triethylamine hydrochloride was filtered. Evaporation of benzene from the filtrate under reduced pressure gave crude product which was recrystallized from a benzene/hexane mixture giving pure compound (11.9 g, 98% yield).

*1,3-Bis[(p-triphenylplumbyl)phenyl]tetramethyldisiloxane*

A solution of *n*-butyllithium (13.3 ml, 0.02 mole) in *n*-hexane was added dropwise to a well stirred solution of 1,3-bis(*p*-bromophenyl)tetramethyldisiloxane

(4.44 g, 0.02 mole) in tetrahydrofuran (500 ml) at  $-78^{\circ}$ . The mixture was stirred at  $-78^{\circ}$  for 2 h and then allowed to warm up to  $0^{\circ}$ . A thick white gel was formed. The mixture was cooled to  $-10^{\circ}$  and a solution of triphenyllead bromide (10.36 g, 0.02 mole) in tetrahydrofuran (100 ml) was added dropwise to the reaction mixture. The contents were stirred for another hour and the solution was then allowed to warm up to room temperature. Evaporation of tetrahydrofuran and subsequent recrystallization of the crude product from acetone gave pure compound (6.7 g, 60% yield).

*1,3-Bis[(p-triphenylplumbyloxycarbonyl)phenyl]tetramethyldisiloxane*

A well stirred mixture of triphenyllead hydroxide (9.11 g, 0.02 mole) and 1,3-bis-(*p*-carboxyphenyl)tetramethyldisiloxane (3.74 g, 0.01 mole) in acetone (250 ml) was refluxed for 6 h. The clear solution thus obtained was evaporated under reduced pressure to give the crude product. Recrystallization from acetone gave pure compound (11.7 g, 95% yield).

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