THE SYMMETRIZATION OF A SILAORGANOMERCURIAL*

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SUMMARY

The question of possible solvolysis of [(phenyldimethylsilyl)methyl]mercuric salts as a means of producing intermediate siliconium ions is examined. A competitive symmetrization reaction is reported and provides a contrast between the chemistry of these compounds and their carbon analogs.
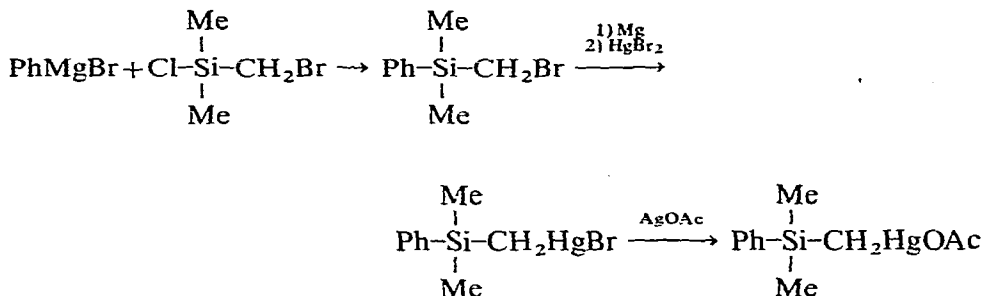
INTRODUCTION

Organosilicomercurials of the type $R_3SiHgOAc$ have not been prepared. Our results in the oxidation of silanes by mercuric acetate suggest that such species must be very unstable[1]. While we have attempted general approaches to these compounds in order to provide intermediates for the generation of siliconium ions, our efforts have been without success. An alternate approach to siliconium ions involves substrates in which a carbonium ion is formed with some degree of concomitant participation of a neighboring group attached to a silicon atom. [(Phenyldimethylsilyl)methyl]-mercuric acetate was chosen, as the corresponding neophylmercuric acetate should allow a ready comparison and serve as a reference point. It was hoped that the formation of a primary carbonium ion adjacent to a quaternary silicon atom would allow the participation of an aryl group with formation of a positive silicon species. Unfortunately this aim was not realized and a limit may be set on the stability of such species. However, the real limitation of the system lies not in the slow rate of solvolysis but in a symmetrization reaction which is competitive. This report will compare the behavior of a neophylmercuric salt and the analogous [(phenyldimethyl-silyl)methyl]mercuric salt.

RESULTS AND DISCUSSION

[(Phenyldimethylsilyl)methyl]mercuric acetate was prepared by the following synthetic scheme.

$$\underset{\underset{\overset{|}{Me}}{|}}{PhMgBr+Cl-\overset{\overset{\displaystyle Me}{|}}{Si}-CH_2Br} \rightarrow \underset{\underset{\overset{|}{Me}}{|}}{Ph-\overset{\overset{\displaystyle Me}{|}}{Si}-CH_2Br} \xrightarrow[\text{2) HgBr}_2]{\text{1) Mg}}$$

$$\underset{\underset{\overset{|}{Me}}{|}}{Ph-\overset{\overset{\displaystyle Me}{|}}{Si}-CH_2HgBr} \xrightarrow{\text{AgOAc}} \underset{\underset{\overset{|}{Me}}{|}}{Ph-\overset{\overset{\displaystyle Me}{|}}{Si}-CH_2HgOAc}$$

The acetate is a white crystalline material which is stable to normal light conditions.

A 0.02 M solution of the corresponding perchlorate in 90% aqueous dioxane was prepared by dissolving the acetate in an appropriate quantity of an acidic aqueous dioxane solution (0.02 M $HClO_4$). The anticipated reaction can be monitored by observing the thiocyanate equivalence of the solution. It should decrease from one to zero equivalents by a first-order process if a solvolysis reaction occurs[2] (eqn. 1).

$$R-HgClO_4 \rightarrow \text{Solvolysis products} + Hg \tag{1}$$
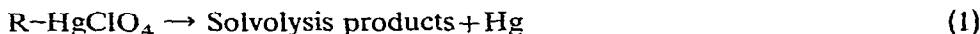
However, at 100° excellent second order kinetics are observed with $k_2 = 1.1 \times 10^{-2}$ $l \cdot mole^{-1} \cdot sec^{-1}$. The ultimate yield of free mercury is 50% based on the above reaction and is produced at one half the rate of disappearance of titratable mercury. At 65% decrease in mercury titer, the yield of mercury is 33%. The organic product is the symmetrized bis[(phenyldimethylsilyl)methyl]mercury whose structure was confirmed by independent synthesis. The apparent net stoichiometry of the reaction is given by the incomplete eqn. (2).

$$2 R-HgX \rightarrow R_2Hg + Hg + ? \tag{2}$$

If the reaction involves a symmetrization, mercuric salts should be formed according to eqn. (3).

$$2 R-HgX \rightarrow R_2Hg + HgX_2 \tag{3}$$

The deposition of free mercury results from a reduction of the mercuric salt by solvent. Mercuric acetate reacts rapidly with the solvent under the reaction conditons. The rate-determining step must involve symmetrization. An equilibrium is not established because of the loss of the mercuric salts by reduction by solvent.
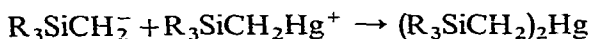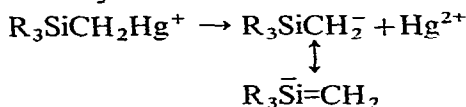
[(Phenyldimethylsilyl)methyl]mercuric acetate is recovered unchanged after 5 hours at 100°, indicating that the perchlorate salt in the experiments containing perchloric acid is the reactive species.

The observed reaction is essentially the reverse of the expected process in the carbon analog. Diphenylmercury is cleaved[3] by mercuric iodide in 90% aqueous dioxane at 25° with $k_2 = 6.80$ $l \cdot mole^{-1} \cdot sec^{-1}$. Dineophylmercury reacts[4] rapidly with mercuric chloride at 25°. Therefore, the reverse of the observed silicon reaction occurs for the carbon compounds at a faster rate and at a lower temperature. Of course the rate of cleavage of the bis[(phenyldimethylsilyl)methyl]mercury could be relatively rapid, but it cannot occur if the mercuric salt is reduced and removed from the system.

In sharp contrast to the behavior of the silicon compounds, the carbon analog,

neophylmercuric perchlorate, does not symmetrize. Excellent first order kinetics for a solvolysis reaction are observed and the yield of free mercury is quantitative. The first order rate constant is 2.5×10^{-4} sec^{-1}. Therefore, the symmetrization reaction is *not* competitive with the solvolysis reaction.

The behavior of the silicon compound may be linked to both the inductive effect of silicon and the available d orbitals. While the lower electronegativity of silicon is expected to enhance the stability of a carbonium ion formed in a solvolysis reaction, these inductive effects also should enhance the electrophilic attack of sila-alkylmercuric ion on a mercury-bound carbon atom, leading to symmetrization. In addition, the transition state for the symmetrization reaction may be stabilized by the availability of d orbitals on silicon.

$$R_3SiCH_2Hg^+ \rightarrow R_3SiCH_2^- + Hg^{2+}$$
$$\updownarrow$$
$$R_3\bar{S}i=CH_2$$

$$R_3SiCH_2^- + R_3SiCH_2Hg^+ \rightarrow (R_3SiCH_2)_2Hg$$

The above two step sequence serves to emphasize the effect of d orbital stabilization of a negative charge. The two-step mechanism would undoubtedly be a first-order process because the second step would be expected to be rapid with respect to the first step. The transition state for the bimolecular process can be pictured as similar to the four-centered intermediates proposed for the cleavage of dialkylmercurials by mercuric halides[5].

The absence of a solvolysis reaction for [(phenyldimethylsilyl)methyl]mercuric perchlorate may be due to the inability of silicon to bear the positive charge required for aryl migration to occur. The solvolysis then would involve an unstabilized primary carbonium ion which should be reflected by a small rate constant. The solvolysis of methylmercuric perchlorate is extremely slow ($k_{estimated}$ *e.g.* $3 \cdot 10^{-7}$ sec^{-1} at 100°)[3]. Even if silicon inductively stabilizes a primary carbonium ion, the rate enhancement would have to be a factor of approximately 10^3 in order to allow competition with the symmetrization reaction

EXPERIMENTAL

Preparation of phenyl(bromomethyl)dimethylsilane

Phenylmagnesium bromide was prepared from 11.80 g (0.075 mole) of bromobenzene and 1.9 g (0.075 mole) of magnesium turnings in 100 ml of ether. The Grignard solution was filtered through glass wool under nitrogen and added dropwise to a stirred solution of 14.06 g (0.075 mole) (bromomethyl)dimethylchlorosilane (Columbia Organic Chemicals Company, Inc.) in 100 ml of ether. Upon completion of addition, the reaction mixture was stirred under reflux for 48 h. The reaction mixture was poured over cracked ice and worked up in a conventional manner. The crude liquid thus obtained was distilled under reduced pressure giving 9.04 g (54% yield) of a colorless liquid b.p. 78° (0.6 mm). (Found: C, 47.02; H, 5.70; Si, 11.97. $C_9H_{13}BrSi$: calcd.: C, 47.16; H, 5.72; Si, 12.24%.)

Preparation of [(phenyldimethylsilyl)methyl]mercuric bromide

The Grignard reagent [(phenyldimethylsilyl)methyl]magnesium bromide was

prepared from 6 g (0.026 mole) of (bromomethyl)dimethylphenylsilane and 0.64 g (0.0262 mole) of magnesium turnings in 100 ml of anhydrous ether. The Grignard solution was filtered under nitrogen through glass wool to remove remaining magnesium and then added dropwise to a stirred slurry of 9.15 g (0.0254 mole) of mercuric bromide in 100 ml of ether. Aluminum foil was wrapped about the reaction vessel to prevent entrance of light. After the reaction mixture had been stirred for 6 h, it was hydrolyzed with 30 ml of 10% aqueous acetic acid solution. The organic portion was isolated from the reaction mixture, washed 6 times with water and once with saturated sodium chloride solution, dried over anhydrous magnesium sulfate and stripped of low-boiling solvents by means of a rotary evaporator. The remaining residue was a colorless oil weighing 6.72 g (62% yield). Cooling of an ethanolic solution of this oil produced colorless crystals which were recrystallized from absolute ethanol, m.p. 35–36°. (Found: C, 25.20; H, 3.02. $C_9H_{13}BrHgSi$ calcd.: C, 25.15; H, 3.05%.)

Preparation of [(phenyldimethylsilyl)methyl]mercuric acetate

A solution of 0.7322 g (0.00171 mole) of [(phenyldimethylsilyl)methyl]mercuric bromide in 25 ml of absolute methanol was stirred with 0.284 g (0.00171 mole) of silver acetate. The reaction vessel was wrapped with aluminum foil to shield the reaction mixture from light. After 20 h, the reaction mixture was filtered to remove silver bromide and the filtrate was stripped of low boiling materials on a rotary evaporator, yielding a colorless oil. This was dissolved in petroleum ether and placed in a freezer. After several hours, a crop of colorless crystals was obtained. Recrystallization from the same solvent gave 0.563 g (81%) of colorless crystals, m.p. 45.7–47°. (Found: C, 32.54; H, 3.96; Hg, 48.94; Si, 6.36. $C_{11}H_{16}HgO_2Si$ calcd.: C, 32.31; H, 3.95; Hg, 49.06; Si, 6.87%.)

Preparation of neophylmercuric bromide

The reaction between neophyl chloride and magnesium was considerably slower than for the silicon analog and prolonged stirring of the reactants (10–20 h) was required to obtain a good yield (70–80%) of neophylmagnesium chloride. The reaction of Grignard reagent with mercuric chloride and subsequent work-up was identical to the procedure described for the silicon analog. An oil was obtained upon work-up which was stirred for 4 h with an excess of sodium bromide in absolute ethanol to insure that no neophylmercuric chloride was present. Upon removal of inorganic salts and ethanol, a 49% yield of colorless crystalline material was obtained. When recrystallized from absolute methanol this material melted at 44–45°.

Preparation of neophylmercuric acetate

The mercuric acetate derivative was obtained by the silver acetate methanol method described for the preparation of [(phenyldimethylsilyl)methyl]mercuric acetate. (Found: C, 36.55; H, 4.05; Hg, 50.77. $C_{12}H_{15}HgO_2$ calcd.: C, 36.58; H, 4.10; Hg, 51.05%.)

Procedure for solvolysis of organomercuric perchlorates

The kinetic procedure followed for the solvolysis of both neophylmercuric perchlorate and the silicon analog is described for the solvolysis of neophylmercuric

perchlorate. A solution of 25.00 ml of distilled water and 0.1453 g of 70% perchloric acid (1.013×10^{-3} mole) contained in a 250-ml volumetric flask was diluted to 250 ml with freshly distilled dioxane producing a 4.05×10^{-3} M solution of perchloric acid. Exactly 50.00 ml of this solution was transferred to a flask containing 0.3927 g (1.00×10^{-3} mole) of neophylmercuric acetate which dissolved immediately in the solvent giving a 2.00×10^{-2} M solution of neophylmercuric acetate. A total of 8 aliquots of 5.00 ml each of this solution were sealed in 15 by 125 mm pyrex test tubes and placed in a constant temperature bath at 100.00°. After a 3 min temperature equilibration period, one of the aliquots was removed from the bath and placed immediately in a dry ice/isopropyl alcohol bath to freeze the solution and stop the solvolysis reaction. As this was done a minute timer was started. Thus this first aliquot was used to determine initial concentration of neophylmercuric species in solution. The test tubes were then removed at 24 min intervals following the same procedure for halting the reaction as for the initial aliquot. Determination of neophylmercuric species concentration was carried out by adding the contents of each test tube to a 50 ml Erlenmeyer flask containing 5.00 ml of 0.02796 N sodium thiocyanate solution and back-titrating the excess sodium thiocyanate with 0.02685 N silver nitrate solution using saturated ferrous ammonium sulfate in acidic media as indicator. The end-point of the titration was taken to be when the solution turned milk-white. It is most important that the temperature of the titrated liquid be maintained below 5°. If not, poor end-points result.

The preparation of bis[(phenyldimethylsilyl)methyl]mercury

A filtered solution of [(phenyldimethylsilyl)methyl]magnesium bromide in ether, prepared from 1.52 g (0.006 mole) of (bromomethyl)dimethylphenylsilane and 0.5 g (0.02 mole) of magnesium, was added under nitrogen to a stirred ethereal solution (75 ml) of 2.44 g (0.006 mole) of [(phenyldimethylsilyl)methyl]mercuric bromide. After being stirred for 18 h, the reaction mixture was hydrolyzed with 10 ml of 10% aqueous acetic acid, the organic phase was separated, washed twice each with water, saturated sodium bicarbonate, saturated sodium thiosulfate and saturated sodium chloride solution, it was dried over anhydrous magnesium sulfate and stripped of low-boiling solvents by means of a rotary evaporator. The oily residue was crystallized from methanol at $-78°$. The material thus obtained was a semisolid which was placed under low pressure for 2 days to remove volatile materials. VPC analysis indicated that only one species was present. In addition to the complex aromatic proton resonance, the NMR spectrum of this compound in carbon tetrachloride exhibited singlet resonances at τ 9.80 and 9.68 ppm in the ratio of 3 to 1. (Found: C, 33.62; H, 6.18; Hg, 47.10; Si, 13.00. $C_{18}H_{26}Si_2Hg$ calcd.: C, 33.75; H, 6.14; Hg, 46.96; Si, 13.15%.)

Isolation of the symmetrized product

A solution prepared from 1.25 g (0.003 moles) of [(phenyldiphenylsilyl)methyl]-mercuric acetate and 150 ml of 10% aqueous dioxane which was 0.02 M in perchloric acid was allowed to react for 10 hours at 90°. Analysis of a 2 ml aliquot of this solution indicated that the reaction had proceeded to the extent of 65% of the theoretical at this time. The solution was cooled immediately to room temperature. The organic material was decanted in order to obtain the free mercury. After washing with ether

and drying, the mercury obtained weighed 0.197 g (0.00099 mole) which corresponds to a 66% yield of the theoretical. The decantate was diluted with 650 ml of water and then extracted four times with ether. The combined extracts were washed five times with water, three times with saturated sodium thiosulfate, two times with saturated sodium chloride and then dried over magnesium sulfate. After removal of the solvent, 0.426 g (0.00083 mole) of the symmetrized product was obtained. The calculated yield is 62%. The identity of this product was confirmed by its NMR spectrum.

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