Journal of Organometallic Chemistry, 96 (1975) 169—173

REACTIONS OF SILYLMERCURY COMPOUNDS WITH SODIUM AND POTASSIUM IN THE AROMATIC SOLVENTS

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(Received March 2nd, 1975)

Summary

Bis(triethylsilyl)mercury (I) and triethylsilyl(pentaethyldisilanyl)mercury (II) react with metallic sodium or potassium in benzene solution to give phenyltriethylsilane (III) and a mixture of III and 1-phenyl-2,2,3,3,3-pentaethyldisilane, respectively, instead of the expected silylmetallic compounds (e.g. Et_3SiM and Et_5Si_2M, where M = Na or K). These results may be explained by the intermediate formation of silylmetallic compounds which reacted with the solvent. The reaction of I with potassium in toluene proceeds analogously.

Introduction

Earlier we showed that trialkylgermylmetallic compounds, R_3GeM (R = Me, Et, i-Pr; M = Li, Na, K, Rb or Cs) may be obtained by action of an alkaline metal on germylmercurials $(R_3Ge)_2Hg$. These reactions occur in nonpolar solvents (hexane, benzene) [1-4] and in diethyl ether or THF [2,5-7]. The yields of R_3GeM are high. Thus the by-processes (e.g. reaction of R_3GeM with solvent) are absent or proceed slowly.

In a similar manner trimethylsilyllithium [8-10] and triethylsilyllithium [2, 11] were prepared in THF or benzene (eqn. 1).

$$(R_3Si)_2Hg + 2\,Li \xrightarrow[\text{or THF}]{C_6H_6} 2\,R_3SiLi + Hg \qquad (R = Me, Et) \qquad (1)$$

Moreover, trimethylsilyllithium prepared in benzene solution may be sublimed in high vacuum at 60°C [10].

Recently it was found that trialkylgermylmetallic compounds can be prepared by treating hexaalkyldigermanes with alkali metals in hexamethylphosphotriamide (HMPA) [12]. However, attempts to using this convenient method for the preparation of trialkylsilyl alkali metal compounds were unsuccessful.

In particular it has been found that in reactions of metallic lithium with hexamethyldisilane in THF [13] or with hexabutyldisilane in HMPA [12] the rate of formation of silyllithium compounds is comparable to the rate of reaction with the solvent.

It seemed interesting to attempt to extend reaction 1 to the synthesis of triethylsilyl-sodium and -potassium in aromatic solvents.

Results and discussion

The reaction of bis(triethylgermyl)mercury with sodium or potassium in benzene proceeds at room temperature for about 4 h to give Et_3GeM (M = Na or K) (82-87%) [1]. Under comparable conditions the reaction of bis(triethylsilyl)mercury (I) with sodium is slower (6-8 days) and more complex. It affords mercury (89%), phenyltriethylsilane (III) (39%), triethylsilane (9%), phenylsodium and sodium hydride (eqn. 2). Moreover the reaction mixture contains triethylsilylsodium, proved by the formation of $Et_3SiGeEt_3$ (26%) and NaBr (27%) on addition of triethylbromogermane (eqn. 3).

$$\underset{(I)}{(Et_3Si)_2Hg} + 2\,Na \xrightarrow{C_6H_6} Hg + \underset{(III)}{Et_3SiPh} + PhNa + Et_3SiH + NaH + Et_3SiNa \qquad (2)$$

$$Et_3SiNa + Et_3GeBr \rightarrow Et_3SiGeEt_3 + NaBr \qquad (3)$$

A reaction carried out in similar fashion with silylmercurial I and potassium in benzene resulted in formation of III, potassium hydride and mercury (eqn. 4). The yields of the first two products were 97% and 90%. Analogously, treatment of triethylsilyl(pentaethyldisilanyl)mercury (II) with potassium in benzene at room temperature results in almost quantitative formation of III and 1-phenyl-2,2,3,3,3-pentaethyldisilane (IV).

$$(Et_3Si)_2Hg + 2\,K \xrightarrow{C_6H_6} Hg + 2\,Et_3SiPh + 2\,KH \qquad (4)$$

A reasonable mechanism for the formation of the main products observed is given in eqns. 5-7. Reaction 5 involves the transfer of organosilyl fragments from mercury to the sodium (or potassium) atom (cf. eqn. 1). The initial silylmetallic product, Et_3SiM, is able to react with benzene as shown in eqn. 6. The reactivity of metallated compounds increases in the order $Et_3SiLi \leqslant Et_3SiNa < Et_3SiK \leqslant Et_5Si_2K$. Further reaction (eqn. 7) of phenylsodium or -potassium with triethylsilane or pentaethyldisilane gives silane (III) or disilane (IV).

$$(Et_3Si)_2Hg + 2\,M \xrightarrow{C_6H_6} 2\,Et_3SiM + Hg \qquad (5)$$

$$Et_3SiM + C_6H_6 \rightarrow Et_3SiH + PhM \qquad (6)$$

$$PhM + Et_3SiH \rightarrow PhSiEt_3 + MH \qquad (7)$$

(M = Na, K)

The following observations are consistent with the scheme proposed. Benzene is not metallated by metallic potassium or sodium—potassium alloy [14] but it is metallated by alkylsodium compounds [15] and ethylpotassium [16,17].

n-Butylpotassium is a more efficient metallating agent of benzene than is n-butyllithium [18,19]. Silyl- and germyl-metallic compounds (e.g. triphenylsilyllithium [20,21] and triethylgermylpotassium [12]) metallate hydrocarbons such as triphenylmethane (pK_a = 33 [22]) and diphenylmethane (pK_a = 35) but afford no metallated toluene (pK_a = 37)*. It is also known that organolithium compounds alkylate triethylsilane in diethyl ether by a reaction similar to that shown in eqn. 7 [24,25] and ethylpotassium reacts with triethylgermane in hexane to produce tetraethylgermane [26]. n-Butylsodium, however, was found not to react with triethylsilane in petroleum ether [15].

These observations led us to examine the corresponding reaction of phenylpotassium with triethylsilane. When phenylpotassium obtained from diphenylmercury and metallic potassium was allowed to react with Et_3SiH, phenyltriethylsilane (III) was formed in high yield.

As is well known, toluene is more reactive toward metallation than is benzene, and it is metallated in the methyl group to yield benzylmetallic compounds. This is in accord with the reaction of metallic potassium with silylmercurial I in toluene solution, in the course of which mercury (ca. 100% yield), benzyltriethylsilane (37%), triethylsilane (54%) and benzylpotassium (60%) are formed. Thus, in this case also reaction between the triethylsilylpotassium generated and the solvent proceeds in two steps, the first being a metallation of the toluene, and the second a hydride displacement by the benzyl anion (eqns. 5-7).

However, the preliminary results obtained indicate that Et_3SiK could be prepared free from by-products by the reaction of silylmercurial I with metallic potassium at room temperature in triethylsilane as solvent. This solvent may be advantageous because of its reasonable resistance to cleavage by alkali metals (e.g. lithium and sodium—potassium alloy [27,28]) and triethylsilylmetallic and related compounds. For example, triethylsilyltriethylgermane, $Et_3SiGeEt_3$, was prepared from Et_3GeLi and Et_3SiH only by prolonged heating at 80-90°C [2].

The reaction of triethylsilylpotassium with chlorotrimethylsilane in triethylsilane solution proceeds smoothly to give coupling product, $Et_3SiSiMe_3$, and the symmetrical disilanes Et_6Si_2 and Me_6Si_2.

Experimental

All reactions were carried out in evacuated sealed ampoules under careful exclusion of oxygen and moisture following the technique described in ref. 29. GLC analysis of the reaction products was performed on a Tsvet-4 chromatograph with a thermal conductivity detector. A 1m column with Apiezon L (15%) on Chromaton H-AB or a 2m column with Reoplex-400 (15%) on Airosil was used. The reaction mixture was separated by preparative chromatography on the same device.

Reaction of bis(triethylsilyl)mercury (I) with sodium in benzene. Into a 40 ml ampoule, previously swept out with dry argon, were placed 20 ml of benzene, 1.65 g (71.7 mmol) of sodium in the form of small pieces of thin foil and 2.27 g (5.27 mmol) of I. After degassing, the ampoule was sealed off and the mixture shaken at room temperature for 6 days. The organic layer was

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[*] The reaction of Ph_3SiLi with toluene and subsequent carbonization gave only the traces of phenylacetic acid [23].

decanted from the metallic mercury (0.94 g, 89%) and fine crystalline solid (PhNa and NaH). To the organic layer was added excess of bromotriethylgermane (3 ml) and the mixture allowed to stand at 20°C for 12 h. Sodium bromide (0.26 g, 27%) was precipitated. The solvent was removed under reduced pressure. GLC analysis of the residue revealed triethylsilane (0.10 g, 9%), phenyltriethylsilane (0.70 g, 39%) and $Et_3SiGeEt_3$ (0.68 g, 26%).

Reaction of I with potassium in benzene. A mixture of I (2.45 g, 5.68 mmol) and metallic potassium (1.43 g, 36.8 mmol) in benzene (20 ml) was shaken at 20°C for 6 days. Treatment of the reaction mixture as described above gave mercury (1.08 g, 95%), potassium hydride (0.39 g, 90%) and phenyltriethylsilane (2.00 g, 97%).

Reaction of I with potassium in toluene. A mixture of I (2.80 g, 6.49 mmol), potassium (1.53 g, 39.1 mmol) and toluene (25 ml) was shaken at room temperature for 6 days. Metallic mercury (1.30 g, ≈100%) and crystalline solid ($PhCH_2K$ and KH) were precipitated. The solid was separated from the organic layer, washed with hexane, dried under reduced pressure and treated with isopropanol and hexane. Toluene (0.71 g, 60%) was detected by GLC of the hexane solution. The organic layer was treated in the same manner as described above to give triethylsilane (0.81 g, 54%) and benzyltriethylsilane (0.99 g, 37%).

Reaction of triethylsilyl(pentaethyldisilanyl)mercury (II) with potassium in benzene. To a preliminarily degassed mixture of potassium (1.30 g, 33.2 mmol) and benzene (35 ml) in an evacuated ampoule II (2.76 g, 5.33 mmol) was added. The mixture was shaken at room temperature for 6 days. Treatment of the reaction mixture in the same manner as described above gave mercury (0.80 g, 75%), potassium hydride (0.25 g, 78%), phenyltriethylsilane (0.76 g, 99%) and 1-phenyl-2,2,3,3,3-pentaethyldisilane (1.06 g, 95%). The latter product was separated by GLC. B.p. 123-125°C/1.5 Torr; n_D^{20} 1.4860. (Found: C, 69.03; H, 10.68; Si, 19.75. $C_{16}H_{30}Si_2$ calcd.: C, 68.98; H, 10.86; Si, 20.16%.)

Reaction of phenylpotassium with triethylsilane. A mixture of diphenylmercury (0.90 g, 2.54 mmol), potassium (1.20 g, 30.7 mmol) and triethylsilane (20 ml; large excess) was shaken at room temperature for 2 days. The organic layer was decanted from the metallic mercury (0.38 g, 74%). Phenyltriethylsilane formed was detected by GLC. The yield was 0.54 g (74%).

Reaction of I with potassium in triethylsilane. A mixture of I (2.79 g, 6.47 mmol), metallic potassium (2.10 g, 53.7 mmol) and triethylsilane (20 ml, large excess) was shaken at 20°C for 5 days. The organic layer was decanted from the mercury (1.15 g, 89%) and added to a solution of chlorotrimethylsilane (5 ml) in triethylsilane (20 ml). The mixture was kept at room temperature for 12 h, after which the characteristic reddish-brown colour of the silylpotassium compound had disappeared. Potassium chloride (0.75 g, 87%) was precipitated. After the triethylsilane had been distilled off in vacuo, the residue was analyzed by GLC; 1,1,1-trimethyl-2,2,2-triethyldisilane (0.55 g, 25%), hexaethyldisilane (0.78 g, 29%) and hexamethyldisilane (0.70 g, 42%) were detected.

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