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REACTIONS OF TRIETHYLSILYLPOTASSIUM AND RELATED COMPOUNDS WITH VINYLTRIMETHYLSILANE IN BENZENE SOLUTION

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Summary

The reaction of triethylsilylpotassium with vinyltrimethylsilane (I) in benzene at room temperature gave as principal products 1-(trimethylsilyl)-2-(triethylgermyl)ethane, phenylpotassium, phenyltrimethylsilane and ethylene. The same reaction was found to occur between triethylgermylpotassium and I. The results suggest that the addition product, $Me_3SiCH(K)CH_2MEt_3$ (M = Si or Ge), formed initially, behave as an active organometallic reagent which could react with benzene to give $Me_3SiCH_2CH_2MEt_3$ and phenylpotassium. The isolation of Me_3SiPh suggests that the silane (I) also reacted with PhK causing vinyl—silicon cleavage. If the triethylgermyllithium reaction is effected then the metalation and C—Si bond cleavage do not occur.

Introduction

It is known that triethylsilyllithium adds to the olefinic linkage of ethylene to give (after hydrolysis) tetraethylsilane [1,2]. We have shown [3] that triethylgermylmetallic compounds, Et_3GeM (M = Li, Na, K), react with ethylene, the yield of the adduct decreasing on going from lithium to sodium to potassium compounds. There is a more striking contrast in reactivity for the alkylmetal compounds, RM. Alkyllithiums have been reported to add to the double bond of ethylene [4]. By contrast, vinylsodium was isolated in high yield from the reaction of ethylene with n-amylsodium [5].

Recently we have shown that triethylsilylpotassium behaves as a very active organometallic reagent [6]. For example, whereas benzene can be split by triethylsilylpotassium at room temperature, the same solvent seems to be truly resistant to cleavage by triethylsilyllithium and triethylgermylmetal compounds. Although treatment of vinyltrimethylsilane (I) with organolithiums is known to result in addition to the olefinic linkage [7-10], the reaction of I with triethylsilylpotassium and related compounds was not investigated. The reaction of alkyllithium reagents, RLi, with I yields the intermediate adducts of the type $Me_3SiCH(Li)CH_2R$ [7-10]. A similar adduct was also formed from the reaction with lithium dimethylphosphide [11].

Results and discussion

Earlier it was reported [6] that triethylsilylpotassium (prepared by the action of metallic potassium on bis(triethylsilyl)mercury in benzene) reacts with benzene to give phenyltriethylsilane and potassium hydride, in almost quantitative yields (eqn. 1). However, if the reaction between potassium and silylmercurial in benzene was carried out in the presence of two equivalents of I, the yield of phenyltriethylsilane was lower (40%). In addition 1-(trimethylsilyl)-2-(triethylsilyl)ethane (49%), phenylpotassium (41%), phenyltrimethylsilane (46%), ethylene (33%) and tetraethylsilane (9%) were detected. The formation of the observed products could be rationalized in terms of the sequence below:

$$\begin{tikzcd}
 & PhK + Et_3SiH \rightarrow Et_3SiPh + KH & (1) \\
Et_3SiK \arrow[ur, "C_6H_6"] \arrow[dr, "Me_3SiCH{=}CH_2", "(a)"'] & & \\
 & Me_3SiCH(K)CH_2SiEt_3 \arrow[d, "C_6H_6", "(b)"'] & (2) \\
 & Me_3SiCH_2CH_2SiEt_3 + PhK &
\end{tikzcd}$$

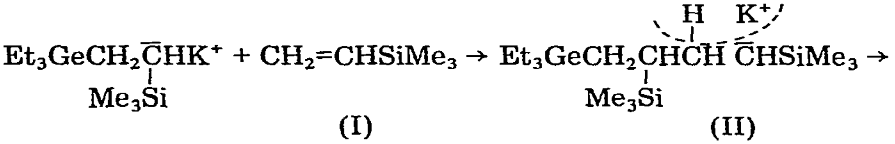
$$\begin{tikzcd}
PhK + Me_3SiCH{=}CH_2 \arrow[r, "(a)"] & Me_3SiPh + CH_2{=}CHK \arrow[d, "C_6H_6", "(b)"'] & (3) \\
 & CH_2{=}CH_2 + PhK &
\end{tikzcd}$$

$$Et_3SiK + CH_2{=}CH_2 \rightarrow Et_3SiCH_2CH_2K \xrightarrow[H_3O^+]{} Et_4Si \qquad (4)$$

The reaction with the silane I was probably initiated by the nucleophilic action of triethylsilylpotassium on the double bond to give $Me_3SiCH(K)CH_2SiEt_3$ as an unstable intermediate. The latter readily captures irreversibly a proton from the solvent (i.e. benzene) to give phenylpotassium and 1-(trimethylsilyl)-2-(triethylsilyl)ethane (eqn. 2b). Phenyltrimethylsilane apparently occurs via displacement reaction of phenylpotassium with I according to eqn. 3a. An analogous transformation has been reported in the reaction of phenyllithium with triphenyl-β-styrylsilane [12]. It is also known that benzene can be metalated by vinylsodium to form ethylene and phenylsodium (cf. eqn. 3b). For comparison purposes, 1-(trimethylsilyl)-2-(triethylsilyl)ethane was synthesized by addition of triethylsilyllithium to ethylene and subsequent treatment with chlorotrimethylsilane (eqn. 5). The identification of phenylpotassium is based on its carbonation.

$$Et_3SiLi + CH_2{=}CH_2 \rightarrow Et_3SiCH_2CH_2Li \xrightarrow{Me_2SiCl} Me_3SiCH_2CH_2SiEt_3 \qquad (5)$$

Finally, the proposed sequence including the eqns. 2 and 3 is well confirmed by reaction of the vinylsilane I with one equivalent of triethylgermylpotassium in benzene. It is known [13] that, unlike triethylsilylpotassium, triethylgermylpotassium does not metalate benzene according to the eqn. 1. However, the products formed included phenylpotassium (19%), 1-(trimethylsilyl)-2-(triethylgermyl)ethane (36%), phenyltrimethylsilane (25%) and ethylene (34%), which may be explained by reactions similar to 2 and 3. In addition, 1,3-bis(trimethylsilyl)-6-(triethylgermyl)hexane (10%) and 1,3-bis(trimethylsilyl)-4-(triethylgermyl)-1-butene (5%) were identified. The formation of the latter involves probably initial attack by anionic species, $Me_3Si\bar{C}HCH_2GeEt_3$, on the silane I to give intermediate II which loses the hydride ion (eqn. 6). Other examples of



$$\underset{Me_3Si}{Et_3GeCH_2\bar{C}HK^+} + CH_2{=}CHSiMe_3 \rightarrow Et_3GeCH_2\underset{Me_3Si}{C}H\overset{H\quad K^+}{CH\,\bar{C}HSiMe_3} \rightarrow$$

(I) (II)

$$Et_3GeCH_2CH(SiMe_3)CH{=}CHSiMe_3 + KH \qquad (6)$$

such reactions which include the formation of a terminal double bond were reported by Nametkin et al. [10].

The reaction of triethylgermyllithium with the vinylsilane I in benzene yields as principal products (after hydrolysis) 1-(trimethylsilyl)-2-(triethylgermyl)ethane (16%) and 1,3-bis(trimethylsilyl)-4-(triethylgermyl)-1-butene (24%). No evidence was found for the presence of phenyllithium. Phenyltrimethylsilane and ethylene were also not formed, a fact indicating that in this case the processes similar to 2b and 3a, b do not proceed. This reaction may also involve the intermediate formation of $Me_3SiCH(Li)CH_2GeEt_3$, which is a much weaker metalating agent than $Me_3SiCH(K)CH_2MEt_3$ (M = Si, Ge).

Experimental

All reactions were carried out in evacuated sealed ampoules with careful exclusion of oxygen and moisture. GLC analyses were made by means of a Tsvet-4 chromatograph with a heat conductivity detector, using helium as the carrier gas and employing a 200 × 0.5 cm column packed with Reoplex-400 (15%) on Airosil. The IR spectra were recorded on a UR-20 spectrophotometer.

Reaction of triethylsilylpotassium with vinyltrimethylsilane in benzene

A mixture of bis(triethylsilyl)mercury (2.98 g, 6.91 mmol), metallic potassium (2.10 g, 53.7 mg atom) and vinyltrimethylsilane (1.79 g, 17.86 mmol) in 25 ml benzene was shaken at room temperature for 6 days; 85 ml (33%) of ethylene was evolved. The crystalline precipitate was separated from the amalgam of potassium (taking advantage of differences in rates of precipitation) and filtered. The crystals were washed with 2 portions of dry benzene. 0.54 g (41%) of phenylpotassium was obtained and converted to the benzoic acid (m.p. 120-121°C) by carbonating with dry carbon dioxide. Mercury (1.14 g, 82%)

was shown to be present in the amalgam. The filtrate was treated with oxygen-free water and dried ($CaCl_2$). After removal of the solvent, tetraethylsilane (0.15 g, 9%), phenyltrimethylsilane (0.78 g, 46%), phenyltriethylsilane (0.88 g, 40%) and 1-(trimethylsilyl)-2-(triethylsilyl)ethane (1.20 g, 49%) were identified in the residue (GLC method). The latter compound was isolated by preparative GLC (see Table 1). IR: 1480w, 1420w, 1380w, 1250vs, 1140s, 1060m, 1020m, 960w, 850vs and 750vs cm^{-1}.

Reaction of triethylgermylpotassium with vinyltrimethylsilane in benzene

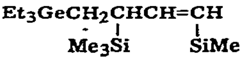
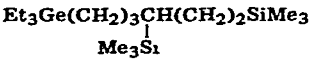
To a solution of triethylgermylpotassium (3.45 g, 17.35 mmol) in 25 ml of benzene was added 1.74 g (17.36 mmol) of vinyltrimethylsilane in 5 ml of benzene. The mixture was allowed to stand overnight at room temperature; 130 ml (33%) of ethylene was evolved and 0.37 g (18%) phenylpotassium was detected. The organic layer was hydrolyzed and worked up in the usual way. GLC analysis of the residue showed the following to be present: 1-(trimethylsilyl)-2-(triethylgermyl)ethane (1.37 g, 36%) IR: 1470m, 1430m, 1380w, 1250vs, 1130s, 1060s, 1025s, 975w, 850vs, 730s, 700s, 630m, and 575s cm^{-1}, 1,3-bis(trimethylsilyl)-6-(triethylgermyl)hexane (0.65 g, 10%) IR: 1470m, 1430m, 1380w, 1250vs, 1080s, 1035m, 980w, 850vs, 740m, 700s, 625m and 575s cm^{-1}, 1,3-bis(trimethylsilyl)-4-(triethylgermyl)-1-butene (0.30 g, 5%), phenyltrimethylsilane (0.65 g, 25%), hexaethyldigermane (0.10 g, 4%) and triethylgermane (1.01 g, 36%). The first three products were isolated by preparative GLC (Table 1).

Reaction of triethylgermyllithium with vinyltrimethylsilane in benzene

A solution of triethylgermyllithium (1.66 g, 9.93 mmol) in 25 ml benzene was added to vinyltrimethylsilane (1.00 g, 9.80 mmol) in 5 ml of benzene. The mixture was allowed to stand overnight at room temperature. The organic layer was worked up in the usual way. GLC analysis of the mixture showed the existence of triethylgermane (0.42 g, 26%), hexaethyldigermane (0.20 g, 13%), 1-(trimethylsilyl)-2-(triethylgermyl)ethane (0.42 g, 16%) and 1,3-bis(trimethylsilyl)-4-(triethylgermyl)-1-butene (0.85 g, 24%), IR: 1605s [ν(C=C)], 1480m,

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE COMPOUNDS PREPARED

Compound	B.p. (°C/Torr)	n_D^{20}	Mol. wt. found (calcd.)	Analysis found (calcd.) (%) C	H	Si	Ge
$Me_3Si(CH_2)_2SiEt_3$	60/2	1.4435	211 (216.5)	61.06 (61.02)	13.07 (13.03)	25.60 (25.95)	
$Me_3Si(CH_2)_2GeEt_3$	69-70/2	1.4577	255 (261.0)	50.92 (50.61)	10.52 (10.81)	10.90 (10.76)	28.17 (27.81)
 $Et_3GeCH_2\underset{Me_3Si}{CH}CH=\underset{SiMe_3}{CH}$	112/2	1.4690	342 (359.2)	53.56 (53.49)	10.86 (10.66)	15.38 (15.63)	19.90 (20.20)
 $Et_3Ge(CH_2)_3\underset{Me_3Si}{CH}(CH_2)_2SiMe_3$	118-120/1	1.4725	350 (389.3)	55.76 (55.53)	11.24 (11.39)	14.41 (14.54)	18.80 (18.64)

1425m, 1385w, 1250vs, 1080s, 1020s, 980w, 850vs, 700s, 630m, and 575s cm^{-1}. The latter compound was isolated by GLC.

1-Trimethylsilyl-2-(triethylsilyl)ethane

A solution of triethylsilyllithium (1.20 g, 9.78 mmol) in 25 ml of benzene was placed in a 100 ml evacuated ampoule. The oxygen-free ethylene (280 ml) was condensed by cooling with liquid nitrogen, into the ampoule before sealing and the ampoule was shaken at room temperature for 24 h. The resulting mixture was added to chlorotrimethylsilane (3 ml) and the solution was allowed to stand overnight at ca. 20°C and then heated for 5 h at 50°C. After the benzene had been distilled off, the residue was vacuum distilled to give 1.59 g (75%) of the desired product.

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