

THE REACTION OF ORGANOSILICON AND ORGANOTIN HYDRIDES WITH ZINC CARBENOIDS GENERATED FROM DIETHYLZINC AND GEMINAL DIIDOALKANES

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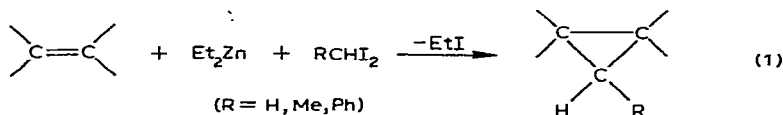
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SUMMARY

The reaction of organosilicon hydrides with diethylzinc and methylene iodide or ethylidene iodide gave methyl- or ethylsilicon compounds in 61–83% yield, respectively. It is concluded that the reaction is an insertion of the methylene or ethylidene group into the silicon–hydrogen bond. The relative reactivities of substituted phenyldimethylsilanes in this homogeneous reaction were investigated. The Hammett ρ -values for the methylene and ethylidene insertions were -1.11 against σ^0 -values and -1.19 against σ -values, respectively. The mechanism of the reaction is discussed and compared with CCl_2 and CH_2 insertion into the silicon–hydrogen bond via halomethylmercury compounds. On the other hand, the reaction of triethyltin hydride with diethylzinc and methylene iodide gave tetraethyltin as the major product and methyltriethyltin as a minor product. In the latter case, the reduction of organic iodide by the organotin hydride predominated over the insertion of the methylene group into the tin–hydrogen bond.

INTRODUCTION

We have reported previously the synthesis of cyclopropane derivatives by the reaction of diethylzinc and *gem*-diiodoalkanes such as methylene iodide, ethylidene iodide and benzal iodide^{1–8}.



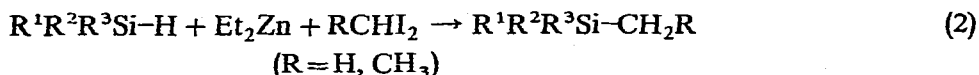
The intermediacy of a zinc carbenoid was confirmed in the reaction⁵. The present paper describes the reaction of the zinc carbenoid with organosilicon and organotin hydrides.

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RESULTS AND DISCUSSION

We have found that the insertion of methylene or ethylidene group into the silicon-hydrogen bond can be accomplished by the reaction of organosilicon hydrides with diethylzinc and methylene or ethylidene iodide.



The reaction of an aryldimethylsilane, diethylzinc and methylene iodide or ethylidene iodide afforded an aryltrimethylsilane or an aryldimethylsilane, respectively, in 61–83% yield. Results are given in Table 1.

TABLE 1

METHYL- AND ETHYLSILICON COMPOUNDS PREPARED BY REACTION (2)

Silane	R in RCHI ₂	Product	Yield (%)
Et ₃ SiH	H	Et ₃ SiMe	61
PhSiMe ₂ H	H	PhSiMe ₃	83
	Me	PhSiMe ₂ Et	64
<i>p</i> -CH ₃ C ₆ H ₄ SiMe ₂ H	H	<i>p</i> -CH ₃ C ₆ H ₄ SiMe ₃	63
	Me	<i>p</i> -CH ₃ C ₆ H ₄ SiMe ₂ Et	70
<i>p</i> -FC ₆ H ₄ SiMe ₂ H	H	<i>p</i> -FC ₆ H ₄ SiMe ₃	74
	Me	<i>p</i> -FC ₆ H ₄ SiMe ₂ Et	82
<i>p</i> -ClC ₆ H ₄ SiMe ₂ H	H	<i>p</i> -ClC ₆ H ₄ SiMe ₃	73
	Me	<i>p</i> -ClC ₆ H ₄ SiMe ₂ Et	63
<i>m</i> -CF ₃ C ₆ H ₄ SiMe ₂ H	H	<i>m</i> -CF ₃ C ₆ H ₄ SiMe ₃	73
	Me	<i>m</i> -CF ₃ C ₆ H ₄ SiMe ₂ Et	58
Et ₃ SnH	H	Et ₃ SnMe	21
		Et ₃ SnEt	53

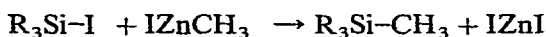
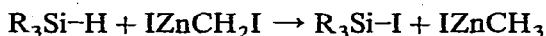
Seyferth *et al.* have already reported the methylenation of organosilicon hydrides by the Simmons–Smith reagent⁹.



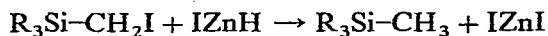
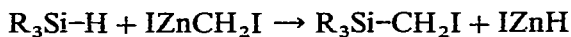
Unlike the Simmons–Smith reaction (3), the reaction with diethylzinc proceeds homogeneously. Consequently, the present procedure would be favorable for kinetic studies of such zinc carbenoid reactions.

Seyferth *et al.*⁹ suggested that reaction (3) proceeds by way of insertion of the methylene group into the silicon-hydrogen bond. However, they also suggested the following two alternate mechanisms.

(a). Reduction of zinc-methylene complex by the silicon hydride, followed by alkylation of the iodasilane formed.



(b). Alkylation of the organosilicon hydride by the iodomethylzinc compound, followed by reduction of the iodomethylsilane by zinc hydride.



Process (a) involves an alkylation of the silicon-iodine bond, while process (b) proceeds via an alkylation of the silicon-hydrogen bond. In the case of the reaction of dialkylzinc (R_2Zn) instead of zinc metal, both processes may result in the formation of silicon-alkyl (Si-R) bond. Our experimental results showed that no silicon compound alkylated by alkyl-zinc group had been formed: No ethyldimethylphenylsilane resulted from dimethylphenylsilane, diethylzinc and methylene iodide, and no n-propyldimethylphenylsilane from dimethylphenylsilane, di-n-propylzinc and ethylidene iodide. These facts lead us to the conclusion that the formation of the alkyl-silicon bond occurs via the insertion of the alkylidene group into the silicon-hydrogen bond.

In contrast, the reaction of triethyltin hydride and the zinc carbenoid generated from diethylzinc and methylene iodide gave tetraethyltin as a major product, together with minor amount of triethylmethyltin.



The reduction of the carbon-iodine bond by organotin hydrides occurs easily under moderate conditions^{10,11}. Therefore, triethyltin hydride may react with iodides formed from diethylzinc and methylene iodide (*e.g.*, CH_2I_2 , EtI , $n-PrI$, $XZnCH_2I$, $XZnI$)^{4,5}, producing triethyltin iodide as an intermediate. Subsequently, triethyltin iodide may react with the ethylzinc compound to form tetraethyltin.



In reaction (4), triethylmethyltin was formed as a minor product and the following two possible mechanisms are conceivable:

(i). Insertion of methylene group into the tin hydrogen bond as in the case of reaction (2).

(ii). Triethyltin hydride may reduce the iodomethylzinc compound formed by the reaction of diethylzinc and methylene iodide⁵ to afford a methylzinc compound. The reaction of this methylzinc compound with triethyltin iodide may result in the formation of triethylmethyltin.



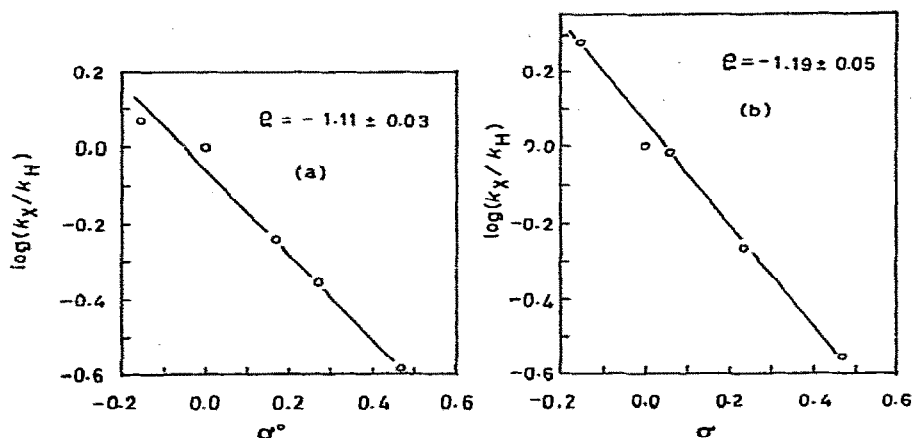
The relative reactivities of various aryldimethylsilanes in reaction (2) are listed in Table 2 and compared with those found for these silanes in mercury compounds, as reported by Seyferth *et al.*^{12,13}. In Fig. 1, $\log k_{rel}$ values for the substituted phenyldimethylsilane in methylene and ethylidene insertion by the zinc carbenoids are plotted against σ^0 - and σ -values, respectively¹⁴. The slopes of the linear plots give ρ -values of -1.11 ± 0.03 and -1.19 ± 0.05 for methylene and ethylidene insertion, respectively.

In comparison, the relative reactivities of aryldimethylsilanes in the methylene insertion reaction via bis(bromomethyl)mercury gave a ρ -value of -1.31 against

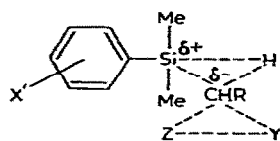
TABLE 2

RELATIVE REACTIVITIES OF SUBSTITUTED PHENYLDIMETHYLSILANES $[X'C_6H_4Si(CH_3)_2H]$ IN REACTION (2)

X'	XZnCH ₂ I ρ -1.11 (σ^0)	XZnCH(CH ₃)I -1.19 (σ)	(BrCH ₂) ₂ Hg ^a -1.31 (σ^0)	PhHgCCl ₂ Br ^b -0.632 (σ)
<i>p</i> -CH ₃	1.20	1.95	1.52	1.25
H	1.00	1.00	1.00	1.00
<i>p</i> -F	0.587	0.955	0.562	0.883
<i>p</i> -Cl	0.443	0.548	0.462	0.733
<i>m</i> -CF ₃	0.267	0.271	0.230	0.482

^a Ref. 4. ^b Ref. 5.Fig. 1. The Hammett correlations of relative reactivities of substituted phenyldimethylsilanes in reaction (2). (a) XZnCH₂I. (b) XZnCH(CH₃)I.

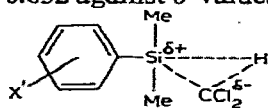
σ^0 -values^{1,2}. These results suggest that the transition states of these reactions are quite similar (I).



Z = XZn, R = H, Y = I
 Z = XZn, R = Me, Y = I
 Z = HgCH₂Br, R = H, Y = Br

(I)

The observed ρ -value for the reaction of organosilicon hydride with the zinc carbenoid is approximately two times as negative as that found for the reaction of these silanes with dichlorocarbene generated from phenyl(bromodichloromethyl)mercury ($\rho = -0.632$ against σ -values) (II)¹³.



(II)

In the cycloadditions to olefins, the zinc carbenoid in reaction (1) thus was found to be more electrophilic than the dichlorocarbene obtained from phenyl(bromodichlo-

romethyl)mercury¹⁵. It would appear that the inductive polar effects exerted by the substituents on the reaction center are more important in these zinc carbenoid reactions.

EXPERIMENTAL

Analyses were performed at the Elemental Analysis Center of Kyoto University. IR spectra were recorded on a JASCO Model IR-E Infrared Spectrophotometer. NMR spectra were taken on a Varian Model T-60 NMR Spectrometer. GLC analyses were carried out using a Shimadzu GC-2C Gas Chromatograph with the combined column of Silicon DC-550 (4.5 m) and Polyethylene Glycol 6000 (0.75 m) at 100°. All boiling points are uncorrected. All reactions were carried out under an atmosphere of nitrogen.

Materials

Diethylzinc, methylene iodide and ethylidene iodide were purified as mentioned in previous papers¹⁻⁸. Dimethylphenylsilane was prepared by the lithium aluminum hydride reduction of chlorodimethylphenylsilane. Other aryl dimethylsilanes were prepared by the reaction of the appropriate aryl Grignard reagent with dichloromethylsilane followed by the reaction with methyl Grignard reagent. GLC analyses showed that the purities of these aryl dimethylsilanes were more than 99% except dimethyl[*m*-(trifluoromethyl)phenyl]silane, whose purity was about 97%. Dimethyl(*p*-tolyl)silane; b.p. 77–78°/22 mm (lit.¹⁶ b.p. 181–182°), n_D^{20} 1.5000 (lit.¹⁶ n_D^{20} 1.5000). Dimethylphenylsilane; b.p. 154–160° (lit.¹⁶ b.p. 158°), n_D^{20} 1.4991 (lit.¹⁶ n_D^{20} 1.4992). Dimethyl(*p*-fluorophenyl)silane; b.p. 51–61°/38 mm (lit.¹⁶ b.p. 160–162°), n_D^{20} 1.4797. (Found: C, 62.53; H, 7.44; F, 12.34. C₈H₁₁FSi calcd.: C, 62.29; H, 7.19; F, 12.32%) IR (liquid film, cm⁻¹): 2959 m, 2141 s, 1588 s, 1499 s, 1248 s, 1228 s, 1161 s, 1106 s, 880 vs, 825 vs, 778 s, and 7.43 s. Dimethyl(*p*-chlorophenyl)silane; b.p. 82°/18 mm (lit.¹⁶ b.p. 199.5°), n_D^{20} 1.5185 (lit.¹⁶ n_D^{20} 1.5188). Dimethyl[*m*-(trifluoromethyl)phenyl]silane; b.p. 72°/35 mm (lit.¹⁷ b.p. 163–164°), n_D^{25} 1.4435 (lit.¹⁷ n_D^{25} 1.4445).

Triethyltin hydride was also prepared by a conventional method¹⁸.

Preparation of alkylsilicon compounds

The preparations of substituted phenyltrimethylsilanes and substituted phenyldimethylethylsilane were carried out as described in the following typical example.

A three necked, round-bottomed flask equipped with a thermometer, a dropping funnel, a reflux condenser topped with a three way cock and a magnetic stirring bar was evacuated and filled with dry nitrogen. Phenyldimethylsilane (0.02 mole, 2.7 g), diethyl ether (20 ml) and diethylzinc (0.04 mole, 4 ml) were introduced via hypodermic syringes. Methylene iodide was added through the dropping funnel over a period of a 1/2 h while stirring at room temperature. An exothermic reaction took place immediately. After the addition was completed, the reaction mixture was allowed to stand at room temperature for 5 h. and then was poured into aq. NH₄Cl and washed with water. The aqueous layer was extracted three times with ether. The combined organic solution was dried over MgSO₄. Ether, ethyl iodide and *n*-propyl iodide were removed by distillation. The residue was fractionally distilled through a

packed column. Phenyltrimethylsilane was obtained 2.5 g (83 %) yield.

Phenyltrimethylsilane* ; b.p. 70–71°/29 mm (lit.¹⁶ b.p. 172°), n_D^{20} 1.4901 (lit.¹⁶ n_D^{20} 1.4901), (*p*-Tolyl)trimethylsilane ; b.p. 91–94°/36 mm (lit.¹⁶ b.p. 193°), n_D^{20} 1.4922 (lit.¹⁶ n_D^{20} 1.4908), (Found : C, 73.27; H, 9.76. C₁₀H₁₆Si calcd. : C, 73.09; H, 9.81 %.) (*p*-Fluorophenyl)trimethylsilane ; b.p. 74–75°/30 mm (lit.¹⁶ b.p. 93°/60 mm), n_D^{25} 1.4712 (lit.¹⁶ n_D^{25} 1.4711). (*p*-Chlorophenyl)trimethylsilane ; b.p. 57–59°/6 mm (lit.¹⁶ b.p. 207°), n_D^{20} 1.5095 (lit.¹⁶ n_D^{20} 1.5067). (Found : C, 58.77; H, 7.30; Cl, 19.36 : C₉H₁₃ClSi, calcd. : C, 58.51; H, 7.09; Cl, 19.19 %.) [*m*-Trifluoromethyl]phenyl trimethylsilane ; b.p. 70–71°/22 mm (lit.¹⁶ b.p. 58°/15 mm Hg), n_D^{25} 1.4419 (lit.¹⁶ n_D^{25} 1.4413).

Dimethylethyl(*p*-tolyl)silane ; b.p. 77–78°/10 mm (lit.¹⁶ b.p. 216°), n_D^{20} 1.4973 (lit.¹⁶ n_D^{20} 1.4962). (Found : C, 73.85; H, 10.41. C₁₁H₁₈Si, calcd. : C, 74.08; H, 10.17 %.) Dimethylethylphenylsilane ; b.p. 67°/20 mm (lit.¹⁶ b.p. 198°), n_D^{20} 1.4937 (lit.¹⁶ n_D^{20} 1.4938). Dimethylethyl(*p*-fluorophenyl)silane ; b.p. 66°/12 mm, n_D^{20} 1.4798. (Found : C, 66.17; H, 8.43; F, 9.84. C₁₀H₁₅FSi calcd. : C, 65.88; H, 8.29; F, 10.42 %.) IR (liquid film, cm⁻¹) : 2955 m, 2906 m, 1593 s, 1502 s, 1247 s, 1230 s, 1164 s, 1105 s, 830 s, 780 s. NMR (CDCl₃, τ)* : 2.18–2.91 m (4H), aryl; 8.57–9.18 m (5H), ethyl; 9.53 s (6H), methyl. (*p*-Chlorophenyl)dimethylethylsilane ; b.p. 71–73°/6 mm (lit.¹⁶ b.p. 134°/26 mm), n_D^{25} 1.5096 (lit.¹⁶ n_D^{25} 1.4941). (Found : C, 60.71; H, 7.55; Cl, 18.10. C₁₀H₁₅ClSi calcd. : C, 60.43; H, 7.61; Cl, 17.84 %.) Dimethylethyl[*m*-trifluoromethyl]phenylsilane ; b.p. 76–78°/16 mm (lit.¹⁶ b.p. 193.5°), n_D^{20} 1.4505 (lit.¹⁶ n_D^{20} 1.4478). (Found : C, 56.68; H, 6.49; F, 24.90. C₁₁H₁₅F₃Si calcd. : C, 56.87; H, 6.51; F, 24.53 %.)

Reaction of Et₂Zn/CH₂I₂ with triethyltin hydride

Diethylzinc (0.02 mole, 2 ml) and methylene iodide (0.02 mole, 1.6 ml) were allowed to react in 50 ml of toluene. After the mixture has been stirred at 0° for 10

TABLE 3

COMPETITIVE REACTIONS WITH VARIED MOLAR RATIO OF REACTANTS^a

A	B	A/B	k _A /k _B	Average
		0.559	1.21	
CH ₃	CH ₃	1.118	1.12	
				1.20
<i>p</i> -CH ₃ C ₆ H ₄ SiH	C ₆ H ₅ SiH	2.085	1.17	
CH ₃	CH ₃	3.341	1.29	

^a Reaction conditions: Organosilicon hydride, 10 mmole; CH₂I₂, 1 mmole; Et₂Zn, 1.5 mmole; Et₂O, 10 ml; 24.4° ± 0.1; 5 h.

min, the ethyl iodide formed in the reaction mixture was removed under reduced pressure. Triethyltin hydride (0.02 mole, 4 g) was added to the reaction mixture in one portion. A white precipitate formed immediately. The reaction mixture was hydrolyzed with aqueous ammonium chloride and dried over magnesium sulfate.

* The IR spectrum coincided with authentic one collected in the Sadler Standard Spectra.

** Other NMR spectra of aryl dimethylethylsilanes were similar to this one.

Distillation gave 0.9 g (21 %) of triethylmethyltin [b.p. 80–86°/44 mm, n_D^{20} 1.4691 (lit.¹⁹ b.p. 162 – 163°/760 mm, n_D^{20} 1.4656)] and 2.4 g (53 %) of tetraethyltin whose IR spectrum was identical with that of an authentic sample.

Competition reactions

In a dry 50 ml three necked flask equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser topped with a nitrogen inlet tube, were charged dimethylphenylsilane (4.81 mmole, 0.6545 g), dimethyl-*p*-tolylsilane (5.37 mmole, 0.8069 g) and 5 ml of a 0.3 M ether solution of diethylzinc. Five ml of a 0.2 M ether solution of methylene iodide was placed in a dropping funnel under nitrogen. The flask was set in a large water bath whose temperature was regulated at $24.4 \pm 0.1^\circ$. Methylene iodide was added dropwise with stirring. After 5 h. the mixture was treated with 20 ml of aqueous ammonium chloride and washed with water. The organic layer was dried over magnesium sulfate and analyzed directly by GLC. The other competition reactions were carried out in a similar manner.

Relative reactivity were calculated by the following equation²⁰:

$$k_{rel} = k_X/k_Y = (P_X/P_Y) \cdot (O_Y/O_X)$$

where *P* is the mole of product, and *O* is that of reactant. The quasi-first order kinetics with respect to reactants was ascertained as shown in Table 3.

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