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Dimethylgermylene Insertion into the Si-H Bond

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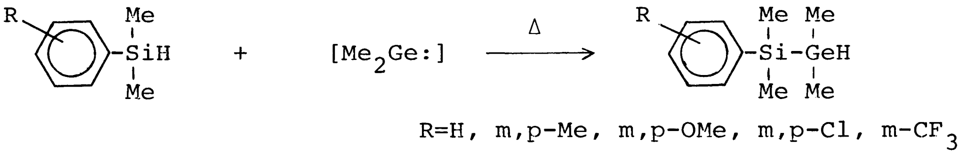
The relative reactivity of seven substituted aryldimethylsilanes to unsubstituted phenyldimethylsilane was examined in the reaction with dimethylgermylene which was generated thermally from 7-germanorbornadiene in benzene at 70 $^{\circ}C$. Electron-withdrawing substituents enhanced the reactivity, and the relative rates could be correlated with the Hammett ρ value of 1.04. Nucleophilic attack by dimethylgermylene at the Si-H bond was postulated via a pentacoordinated intermediate where little charge separation was involved.

The carbene analogues, germylenes (R_2Ge:), have received much attention in organic synthesis as reaction intermediates in recent years.$^{1)}$ In principle, germylenes undergo addition and insertion reaction alike carbenes. But, few detailed mechanistic studies of insertion reactions of germylenes into σ bonds have been performed.$^{2)}$ In this report, we wish to describe the first mechanistic study of germylene insertion into the Si-H bond in terms of the relative reactivity of a series of substituted aryldimethylsilanes toward dimethylgermylene generated from 7,7-dimethyl-7-germanorbornadiene.$^{3)}$

A typical competition reaction is described: A mixture of two aryldimethylsilanes (each 0.5 mmol) and 7,7-dimethyl-7-germanorbornadiene (0.1 mmol) in benzene (2 cm^3) was degassed and heated at 70 $^{\circ}C$ for 2 h. Two kinds of (aryldimethylsilyl)dimethylgermanes were formed as insertion products in 2-4% yields, and identified with GC and GC-MS.$^{4)}$ The relative reactivity can be calculated as the ratio of the yields of insertion products, since the concentrations of two aryldimethylsilanes used in this study are large enough and equal.



R=H, m,p-Me, m,p-OMe, m,p-Cl, m-CF_3

The results are summarized in Table 1.

Table 1 shows clearly that an electron-withdrawing substituent enhances the relative rate constant of insertion. The slope of a plot of log k_{rel} vs. σ gave a ρ value of 1.04 (correlation coefficient=0.922). This correlation based on the Hammett equation indicates clearly that nucleophilic attack by dimethylgermylene

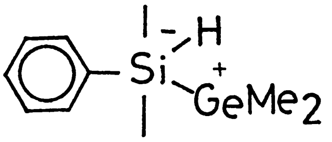
Table 1. Relative Rate Constants for Insertion of 7,7-Dimethyl-7-germanorbornadiene-derived $GeMe_2$ into the Si-H Bonds of $RC_6H_4SiMe_2H$[a)]

R	σ	$\dfrac{k_{RC_6H_4SiMe_2H}}{k_{C_6H_5SiMe_2H}}$
p-OMe	-0.27	0.88 ± 0.19
p-Me	-0.17	1.00 ± 0.09
m-Me	-0.07	1.02 ± 0.04
H	0	1.00
m-OMe	0.12	1.76 ± 0.50
p-Cl	0.23	2.94 ± 0.10
m-Cl	0.37	3.15 ± 0.34
m-CF_3	0.43	4.16 ± 0.11

a) An average of at least 2 or 3 determinations.

at the Si-H bond is involved. The ρ value obtained here is a little higher than that (ρ =0.84) for dimethylsilylene generated photochemically from trisilacycloheptane.[5)] This indicates that the polar effect on the insertion into the Si-H bond by dimethylgermylene is a little larger than by dimethylsilylene.

Finally, we suggest that the mechanism for the germylene at the Si-H bond may be (1) a nucleophilic attack by dimethylgermylene at the Si-H bond of arylsilanes to give a pentacoordinated intermediate or transition state of silicon (I), and (2) a hydride shift from silicon to germanium atoms to form insertion products.



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4) Dimethylgermylene insertion products, (aryldimethylsilyl)dimethylgermanes, and polygermanes from unreacted dimethylgermylene were formed. All new insertion products were identified by comparison with their physicochemical properties with those prepared independently. The relative rates were independent of the initial concentrations of both substrates.

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