Novel Thermal Phenyl Migrations from Carbon to Silicon

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In silicon compounds, vacant $3d$-orbitals are known to act as electron-acceptors towards adjacent π-systems as a result of $(p\text{–}d)\pi$ bonding.[1]

During studies of intramolecular interactions between d_π-orbitals of silicon and non-adjacent π-electron systems, we have found a novel type of rearrangement—the first example of an aryl migration from carbon to silicon.†

When benzyldimethylsilane was heated in an ampoule at 425—450° for 15 hr., or passed slowly through a quartz tube mounted in a thermostatted furnace at 500°, trimethylphenylsilane was obtained in 17·3—87·7% yield, depending on the reaction conditions. The products also contained traces of lower- and higher-boiling materials presumably formed by Si–H/Si–Ph thermal redistribution.[2] The intramolecular nature of the reaction is supported by the fact that benzyltrimethylsilane did not react with any

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† 1,2-Shifts of aryl groups from silicon to carbon by ionic mechanisms are known; see ref. 1, pp. 434—441.

hydrosilanes (*e.g.*, $HSiMeCl_2$) under the same conditions, *i.e.*, phenyl–methylene cleavage did not take place intermolecularly with hydrosilanes. Moreover, dimethyl-(*p*-methylbenzyl)silane and the *m*-isomer gave exclusively trimethyl-*p*-tolylsilane and the *m*-isomer, respectively.

$$X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiHMe_2 \xrightarrow{440^\circ} X{\cdot}C_6H_4SiMe_3$$

(I) a, X = H
b, X = *p*-Me
c, X = *m*-Me

(II) a, X = H
b, X = *p*-Me
c, X = *m*-Me

We have also investigated possible aryl migrations from carbon to silicon in a number of other compounds. For example, 5-aryl-2,4,4-trimethyl-2,4-disilapentanes (III) undergo rearrangement quantitatively, (IIIa) and (IIIb) giving exclusively (IVa) and (IVb), respectively.

$$X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiHMe_2 \xrightarrow{370^\circ} H{\cdot}CH_2{\cdot}SiMe_2{\cdot}CH_2{\cdot}SiMe_2{\cdot}C_6H_4{\cdot}X$$

(III) a, X = H
b, X = *p*-Me
c, X = *m*-Me

(IV) a, X = H
b, X = *p*-Me
c, X = *m*-Me

Results of thermolyses of dimethyl-(ω-phenylalkyl)-silanes are listed in the Table.

Thermal rearrangement of $Ph[CH_2]_n{\cdot}SiMe_2H$ *to* $H[CH_2]_nSiMe_2{\cdot}Ph$ (*sealed tubes at* 370° *for* 15 hr.)

n	2	3	4	5	6
% Yield ..	0	67·5	38·5	8·7	0

The maximum yield at $n=3$ and lack of rearrangement at $n=2$ and 6 may be taken as evidence for the intramolecular nature of the reaction. The transition states of intramolecular migrations should involve ring formation with a silicon atom, methylene(s), and the phenyl carbon atom to which the ω-(dimethylsilyl)alkyl group is attached, and it is well established that in such a ring-forming transition state, five-membered-ring formation is most favourable while four- and eight-membered rings are generally infeasible.[3]

Thermolysis of some twenty variously substituted (ω-phenylalkyl)hydrosilanes were examined and details will be reported later with mechanistic considerations.

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[1] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, ch. 3.
[2] H. Gilman and D. H. Miles, *J. Org. Chem.*, 1958, **23**, 326.
[3] B. Capon, *Quart. Rev.*, 1964, **18**, 45.