

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 ($p-d$) π bonding.¹

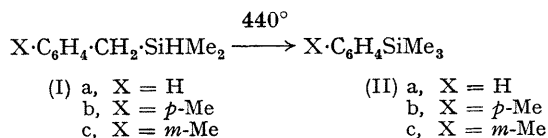
During studies of intramolecular interactions between d_{π} -orbitals of silicon and non-adjacent π -electron systems, we have found a novel type of rearrangement—the first example of an aryl migration from carbon to silicon.†

When benzyldimethylsilane was heated in an ampoule

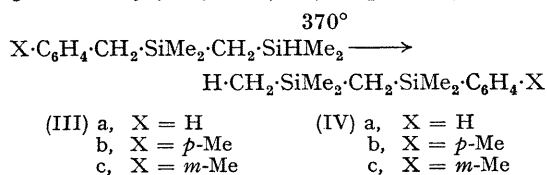
at 425–450° for 15 hr., or passed slowly through a quartz tube mounted in a thermostatted furnace at 500°, trimethylphenylsilane was obtained in 17.3–87.7% yield, depending on the reaction conditions. The products also contained traces of lower- and higher-boiling materials presumably formed by Si–H/Si–Ph thermal redistribution.² The intramolecular nature of the reaction is supported by the fact that benzyltrimethylsilane did not react with any

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

hydrosilanes (*e.g.*, HSiMeCl₂) 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.



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.



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

Thermal rearrangement of Ph[CH₂]_nSiMe₂H to H[CH₂]_nSiMe₂Ph (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.