

ORGANOMETALLIC REARRANGEMENTS.

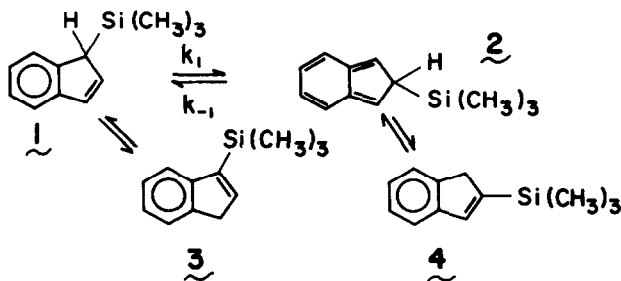
1-TRIMETHYLSILYL- AND 1-TRIMETHYLGGERMYLINDENE¹

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The temperature dependence of the nmr spectrum of 5-trimethylsilylcyclopentadiene is generally attributed to migration of metal from carbon to carbon at a rate in excess of 10^3 sec^{-1} below 100° .² Reported here is chemical verification for the thermally-induced migration of silicon from carbon to carbon, along with observations on a possible mechanism. On heating as a neat liquid at 155° in the absence of air for 118 hours, 1-trimethylsilylindene (1)³ affords a mixture of starting material (ca. 54%), 2-(28%) (3), and 3-trimethylsilylindene (17%) (4). No other products are observed at 300° after sixteen hours, or with 1,1-diphenylethylene as solvent at 150° after seventeen hours. A mechanism for the rearrangement of silicon consistent with these observations is depicted in the Scheme. Migration of silicon from carbon 1



to carbon 2 affords an isoindene (2) or valence-isomeric intermediate; a subsequent proton shift yields product. The observation that buildup of the 2- and 3-isomers is similar allows the inference that an H-shift is rate limiting in each path. That the process k_1, k_{-1} is indeed fast was demonstrated by the nmr spectroscopic technique developed by S. Forsen and R. A. Hoffmann -- double irradiation with chemical exchange.⁴ Saturation of the 1-H resonance at 150° of 1-trimethylsilylindene (2M in tetrachloroethylene) effects a decrease in intensity of the 3-(τ 3.05) but not the 2-proton (τ 3.37) resonance,^{5a} consistent with

exchange of the 1 and 3 protons via the indicated intermediate. Due to the magnitude of the relaxation relative to the exchange rate, the exact rate was not measured; from an estimate of the minimum value of the rate ($> 0.01 \text{ sec}^{-1}$ at 140°) a maximum activation energy of 29 kcal mole⁻¹ can be calculated, taking the pre-exponential factor as 10^{13} sec^{-1} . As the exchange rate is very fast relative to the build up of 3, silicon migrates faster than hydrogen in indene as in cyclopentadiene. ^{2d}

Similarly, 1-trimethylgermylindene⁵ (2M in tetrachroethylene) had an exchange rate for the 1- and 3-protons of $0.06 \pm 0.03 \text{ sec}^{-1}$ at 100° . Temperature dependence of rates estimated⁶ from broadening of the 1-H resonance between 150° and 190° , with the 100° rate, corrected for the assumed statistical factor, gives an activation energy of 22 kcal mole⁻¹ with preexponential of 10^{12} sec^{-1} for migration of germanium from the 1 to 2 position. The slowness of the rates in the indenenes relative to that observed in the cyclopentadienes is consistent with a high energy intermediate such as 2 in the former case.

Such an intermediate is trapped on heating an equimolar mixture of maleic anhydride and 1-trimethylsilylindene at 150° ; sulfuric acid methanolysis⁷ of the adducts (M. W. 286 by mass spectrometry) gives mainly dimethyl 9-trimethylsilyl-1, 2, 3, 4-tetrahydro-1, 4-methanonaphthalene 2, 3-dicarboxylate, characterized by its nmr spectrum: τ 2.97 (4H); 6.43 (m, 2H); 6.65 (s + m, 8H); 8.77 (m, 1H); 10.37 (s, 9H). Thus, it is established that 2-trimethylsilylisoindene is accessible from the energy surface of the silicon migration. Additional support for the proposed mechanism perhaps comes from the observation by A. Davison of the temperature-dependent coalescence of trimethylsilyl resonances in the nmr spectrum of 1, 2-bis-trimethylsilylindene which may be rationalized by an isoindene intermediate or by concerted 1, 2-shifts of both trimethylsilyl groups.⁸ While 2 is not required to be intermediate in the nmr exchange processes, neither can similar intermediates be ruled out in other organometallic rearrangements, such as that of bis-indenyl-mercury.⁹

Carbon-germanium and carbon-silicon bond energies are 58 and 70 kcal mole⁻¹¹⁰ respectively. From the magnitudes of the activation energies for the rearrangements of silicon and germanium in indene relative to the respective bond energies, it can be concluded that new

bonds are formed concurrent to bond breakage; i. e. the reactions are concerted. Tentatively, it may be proposed that the reactions are examples, under the theory of Woodward and Hoffmann,¹¹ of sigmatropic rearrangements of the order [1.5].

Additionally, the temperature dependence of the 100 MHz spectrum of neat 5-trimethylsilylcyclopentadiene (more rapid broadening of the higher field olefinic resonance) indicates that the trimethylsilyl group migrates to the carbon atom bearing the olefinic proton with the higher field resonance, rather than to each carbon randomly.^{12, 13} (see figure)

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A 1,2 rearrangement requires that the higher field olefinic resonance of 5-trimethylsilylcyclopentadiene be assigned to the 1-proton; such an assignment, based on shift alone, is tenuous at best.

13. The authors gratefully acknowledge discussions with R. Hoffmann and M. Saunders.

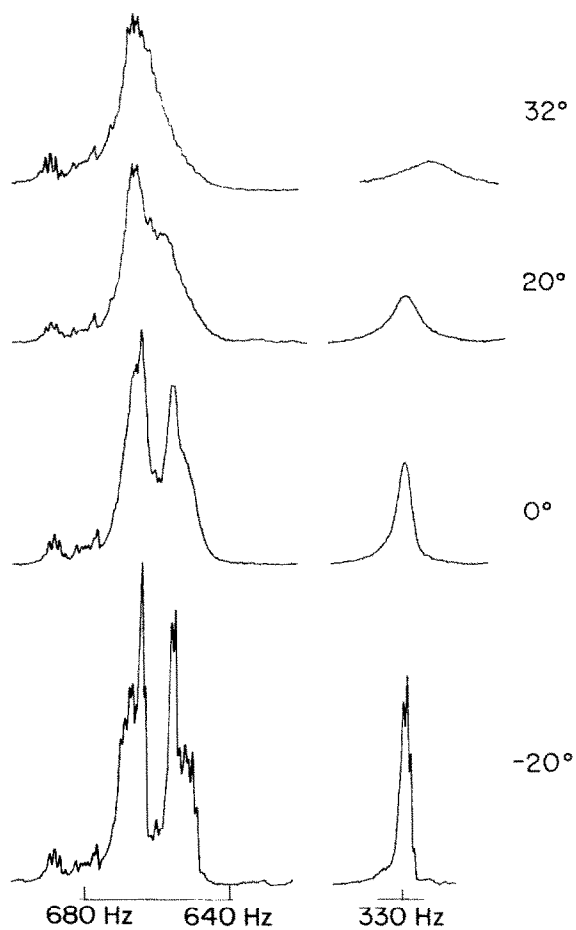


Figure Temperature effect on 100 MHz spectrum of 5-trimethylsilylcyclopentadiene.