

1,5-TRIMETHYLSILYL MIGRATIONS IN 1-TRIMETHYLSILYLINDENE

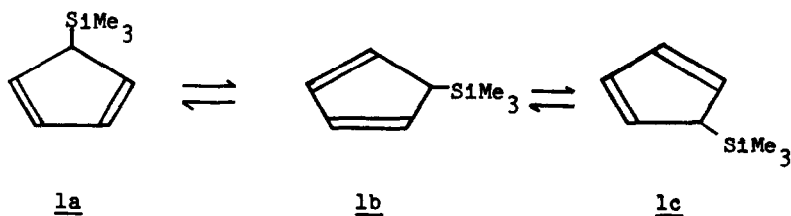
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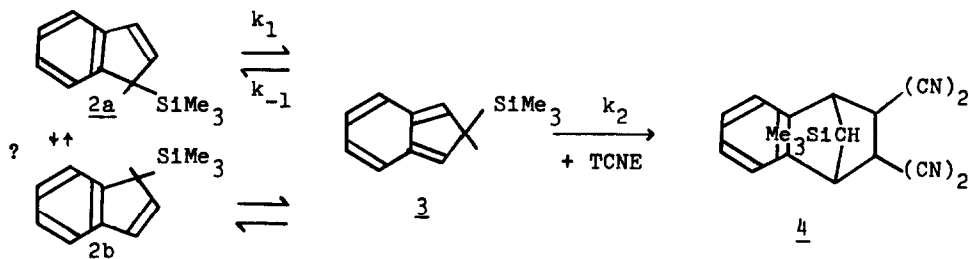
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The temperature dependent nmr-spectrum of 5-trimethylsilylcyclopentadiene, 1, indicates that the magnetic environment of the five ring protons is being averaged at a rate of 10^3 sec^{-1} at 80° .^{1,2,3} While it has been demonstrated that the ring protons are being interconverted by migrations of the trimethylsilyl group,⁴ it is not clear whether these migrations are by 1,5-shifts ($1a \rightleftharpoons 1b \rightleftharpoons 1c \rightleftharpoons \text{etc.}$) or by 1,3-shifts ($1a \rightleftharpoons 1c \rightleftharpoons \text{etc.}$).

The degeneracy of the migrations for 1 makes a choice difficult. The shifts are no longer degenerate in substituted cyclopentadienes, such as 1-trimethylsilylindene, 2. A 1,3-trimethylsilyl shift of 2a would give 2b, while a 1,5-migration would have to give the high energy isoindene, 3. Although 3 would be expected to decay to 2a and 2b giving a formal averaging of the 1- and 3-positions of 2, this averaging is expected to be much slower than a 1,5-trimethylsilyl shift of 1. On the other hand a 1,3-shift of 2a to 2b might not be greatly different in rate than 1,3-shifts of 1. Published nmr-spectra of 2 show no 1,3-averaging below 180° .^{5,6,7} This observation seems inconsistent with direct 1,3-shifts for both 1 and 2.





Dienophiles can be used to trap 3.⁷ For example, when 2 is allowed to stand in ethyl acetate with tetracyanoethylene for one day at room temperature, a 1:1 adduct is formed (mp 209° (d)) (Calc for C₁₈H₁₆N₄Si: C, 68.32; H, 5.10; Found: C, 68.40; H, 5.09). The nmr-spectrum in DMSO-d₆ clearly indicates structure 4. There are a symmetrical four proton aromatic multiplet centered at 2.6 τ, a two proton doublet (J=1.0Hz) due to the bridgehead protons at 5.65τ, a one proton triplet (J=1.0Hz) at 8.1τ due to the bridge proton and a nine proton trimethylsilyl singlet at 10.25τ. Maleic anhydride forms an analogous adduct, albeit only at 80° for 24 hr.

The elegant work of Huisgen on the cyclooctatetraene valence tautomerism has shown how the rate of formation of a reactive valence tautomer can be evaluated by dienophile trapping.⁸ Thus, while the valence tautomerism, 2 ⇌ 3, was too slow to measure precisely by nmr methods, the TCNE-trapping experiment can be used to evaluate the rate of formation of 3. The rate of formation of 4 should be:

$$\frac{d(4)}{dt} = \frac{k_1 k_2 [2] [TCNE]}{k_{-1} + k_2 [TCNE]} = \frac{k_{obs} [2]}{k_2 [TCNE]}$$

$$k_{obs} = k_1 - k_{-1} \cdot k_{obs}$$

For a large excess of TCNE, the rate will be pseudo-first order in 2. Furthermore k_{obs} should be a linear function of k_{obs}/[TCNE] and if k₂ and k₋₁ are of comparable magnitude, k_{obs} will approach k₁ as [TCNE] becomes large.

We have evaluated the rate of formation of 4 using 0.027M ethyl acetate solutions of 2 and excess TCNE. First order rate constants are obtained by the dilatometric technique. A plot of k_{obs} against k_{obs}/[TCNE] is linear and approaches the following values of k₁ as [TCNE] becomes large:

Temperature	40.0°	50.0°	60.0°
k x 10 ⁴ sec ⁻¹	2.6	7.9	21

Thus the rate constant for 1,5-trimethylsilyl migration of 2 is 10¹² exp [-22.5 kcal./RT] sec⁻¹.

Inspection of the rate expression for k_{obs} indicates that the rate should be independent of the dienophile for very reactive dienophiles. We have also examined reaction of 2 with dicyanomaleimide (DCMI).⁹ This dienophile forms

two isomeric adducts, probably exo and endo isomers, which have nmr-spectra very similar to that of 4. At 60.0° a 0.027 M solution of 2 with excess DCMI gave values of k_{obs} , which when plotted against $k_{obs}/[DCMI]$, approached $16 \times 10^{-4} \text{ sec}^{-1}$. While agreement with the TCNE value is quite modest we feel these rate constants are a reasonable measure of k_1 .¹⁰

The relative rates of 1,5-trimethylsilyl migration of 2 and 1 are 1.2:10⁵ at 80°; $\Delta(\Delta F^\ddagger) = 8 \text{ kcal./mole}$. One must associate this energy difference with the reluctance of 2 to form the high energy isoindene intermediate. Fluxional properties have been noted for a number of other cyclopentadienyl and indenyl organometallic pairs: Among them $C_5H_5GeMe_3$ ³ and $C_9H_7GeMe_3$,^{6,7} $C_5H_5SnMe_3$ ³ and $C_9H_7SnMe_3$,^{5,6} and $(C_5H_5)_2Hg$ ¹¹ and $(C_9H_7)_2Hg$.¹² While accurate rates of all these processes are unavailable, examination of the nmr-coalescence temperatures suggests that the $\Delta(\Delta F^\ddagger)$'s are of similar magnitude to $\Delta(\Delta F^\ddagger)$ between 1 and 2. Perhaps all the above compounds undergo 1,5-metal shifts.

These trapping experiments of course provide no information about possible 1,3-shifts of the trimethylsilyl group in 2. One can only say that at 180° such shifts formal through 3 or actual are slow on the nmr time scale. The possible occurrence of slower 1,3-trimethylsilyl shifts must remain an open question.

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