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The Fluxional Behavior of Trimethylsilyl Enol Ether of Triacetylmethane

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In several recent publications we have reported on the exceptionally fast isomerization rates (nmr time scale) of various substituted olefins.[1] In an attempt to investigate further the structure-reactivity relationship in similar systems we examined, inter alia, the trimethylsilyl enol ether of triacetylmethane (I). Reaction of trimethylsilyl chloride with tricetylmethane in the presence of pyridine yielded I: bp 84.5-85°(0.1 mm); uv max (isooctane)280.4 nm (ϵ 8,900), 236.9 nm (ϵ 6,700); ir (CCl_4) 1692 cm^{-1} (C=O), 1600 cm^{-1} (C=C); nmr(CCl_4) δ 0.29 (s,9), 2.05 (s,3), 2.22 (s,6) ppm.

The temperature dependence of the nmr spectrum of I is particularly striking. The C-methyl region is depicted in Figure 1. Three signals (intensity ratio 1:1:1) are observed at low temperature; two of them coalesce at 32°, and a two-signal spectrum is recorded (intensity ratio 1:2). Further raising of the temperature induces the coalescence of the remaining two signals into a singlet at 178°. The trimethylsilyl signal (not shown in Figure 1) was not affected by temperature variations. All spectral changes were found to be reversible.

Such spectral phenomena clearly indicate the occurrence of two kinetic processes which are associated with different kinetic parameters. It is now necessary to correlate the experimental results with the appropriate molecular processes. We shall first assume that all changes are intramolecular. The spectral data require that two consecutive rearrangements will scramble the three diastereotopic methyl groups of I. These reactions are of two types: a. cis - 1,5 shift of the Me_3Si group and, b. rotation about the C=C bond.

An activation free energy value of 15.4$\pm$0.5 kcal/mol was determined by us at the lower coalescence temperature (32°) of I ($\Delta\nu$ = 31 cps).[2] A cis - 1,5 shift has recently been discovered in the 2,4-pentandione systems (E_a = 15 $\pm$ 4 kcal/mol).[5] On the basis of the similarity of the above two activation values, we assigned the lower temperature kinetic process in I to the cis - 1,5 shift of the Me_3Si group. This shift can be described in terms of an equilibrium between the two indistinguishable structures I and II.[6] Consequently, such an

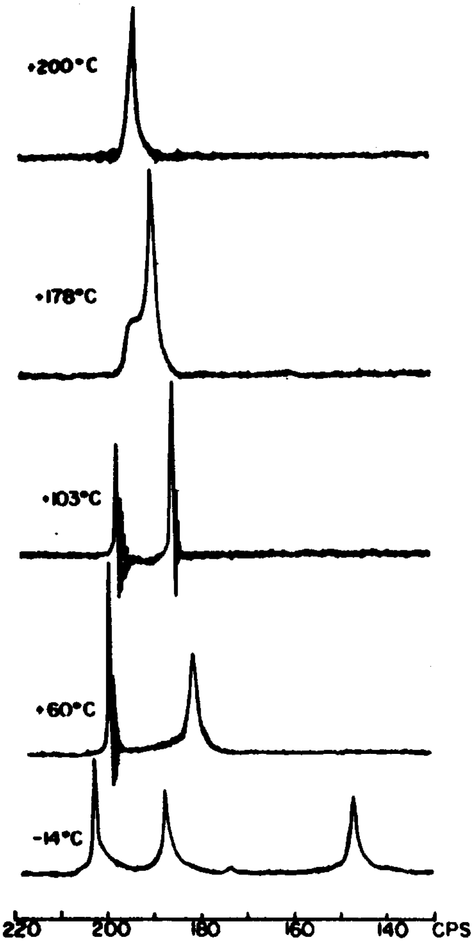
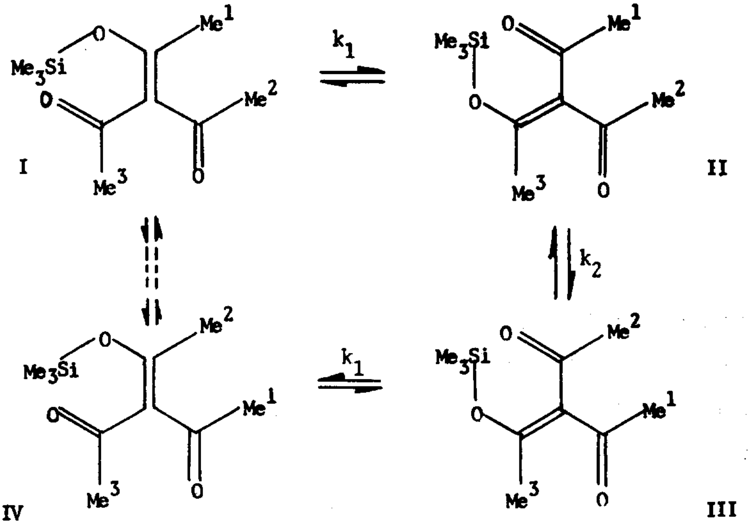


Figure 1. Variable temperature nmr spectra (100 MHz) of 0.219M solution of trimethylsilyl enol ether of triacetylmethane in 1-chloronaphthalene.

equilibrium results in the exchange of Me^1 with Me^3. The second, higher temperature, process is identified with the rotation about the C=C bond. An activation free energy value of 24.3 ± 0.5 kcal/mol was determined at the coalescence temperature (178°) of the two unequal intensity signals of I($\Delta\nu$=7 cps).[2] This process obtains also in a model compound, ethyl enol ether of triacetylmethane. Two of the three methyl singlets in its nmr spectrum ($\Delta\nu$=7 cps) coalesce at 103°(ΔG^*=20.1

The rotational process in the trimethylsilyl enol ether of triacetylmethane can be described in terms of the equilibrium II $\rightleftharpoons$ III. This equilibrium results now in the exchange of Me^1 with Me^2. An additional cis - 1,5 shift establishes an equilibrium between III and IV, and consequently Me^2 exchanges with Me^3. Since $k_1 > k_2$ the rotational process is a rate determining step for the second Me$_3$Si shift. The sequence of transformations I $\rightarrow$ IV describes the complete scrambling of the three diastereotopic methyl groups. A full cycle (I $\longrightarrow$ IV $\longrightarrow$ I), returning all labelled methyls to their original positions involves a total of six transformations. However, the three steps, mentioned above, are sufficient to describe the complete scrambling of the three methyls. Thus, the singlet of the C-methyls, observed at high temperature, reflects the fluxional nature of the compound under investigation.

The possibility of inter rather than intramolecular exchange of the Me$_3$Si group must be



given consideration. A mechanistic rationale for such an exchange involving only the acetyl group cis to the Me$_3$SiO function, can be put forward. Inasmuch as the rate of the low temperature process was unaffected by 1:4 dilution, it may indeed be concluded that the cis - 1,5 shift of the Me$_3$Si group is an intramolecular process.

It should be mentioned that all samples of I contained variable quantities (5-10%) of triacetylmethane which we could not eliminate. The intervention of triacetylmethane (enol form) as a carrier in an intermolecular transfer of the Me$_3$Si group is ruled out on the basis of the above mentioned dilution experiment. Furthermore, deliberate addition of triacetylmethane to a sample of I did not affect the free energy of activation of the low temperature process as could be determined from nmr measurements.[7]

A final point which is worthy of note is the difference in the free energy of activation for the rotational process about the C=C bond between I (24.3 kcal/mol) and the ethyl enol ether of triacetylmethane (20.1 kcal/mol). In our opinion, this is the manifestation of the O to Si electron donation which is usually attributed to p-d orbital interaction. Such an interaction would compete with the capacity of the vinylic oxygen to stabilize the positive charge which is being developed on the adjacent sp^2 carbon in the transition state for rotation, and therefore accounts for the observed energy increment.[1c,d]

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2. The free energy of activation at the coalescence temperature was evaluated using the Gutowsky-Holm relationship[3] and the Eyring activation function. It has been observed that $\Delta\nu$ at no exchange was temperature dependent. The value of $\Delta\nu$ employed in the rate calculation (and all $\Delta\nu$ values reported in the text) were obtained from extrapolation of a plot of log $\Delta\nu$ vs $10^3/T$ from the region of no exchange to the coalescence point.[4]
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6. The equivalence of structures I and II (and also of all other structures) will hold, provided that the rate of rotation of the acetyl groups is fast, and therefore cannot be detected by nmr measurements. Indeed, this must be the case under consideration since, otherwise, a completely different nmr spectrum should have resulted due to the slow interconversion of diastereomeric conformations arising from the slow rotation of the acetyl groups.
7. Throughout the whole temperature range no coalescence of the triacetylmethane signal with the signal(s) of I could be observed, thus also excluding intermolecular transfer of the Me_3Si group in the high temperature process.