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THE REARRANGEMENT OF SUBSTITUTED CYCLOPENTADIENES

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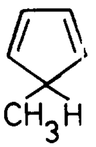
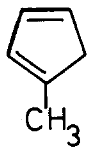
The report of Mironov et al.[1] concerning their studies of substituted cyclopentadienes has interested us since a number of their observations are similar to ours. The very recent report of Roth[2] concerning the rearrangement of isotopically-labelled cyclopentadiene has also taken our attention since we have been interested in determining how a hydrogen migrates around the cyclopentadiene ring. Mironov[1] reported that 5-methylcyclopentadiene (I) rearranges readily to 1-methylcyclopentadiene (II) which then rearranges to 2-methylcyclopentadiene (III). We also have observed this phenomenon and we have traced the course of the rearrangement using n.m.r. spectroscopy to record the change in isomer distribution directly, since each of I, II, and III has a distinctive spectrum[3]. By observing the decay of the CH_3 signal of I (8.92τ; doublet $J = 7.8$ c./s.) as a function of time we have been able to study the rearrangement of I to II; the complementary study of the rate of growth of the CH_3 signal of II (8.05τ; closely spaced doublet) was also possible and served to confirm our results. The CH_3 signal for III overlapped that of II, but examination of the rest of the spectrum showed that II was in fact the rearrangement product and that the conversion of II



I



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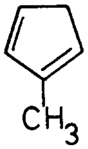

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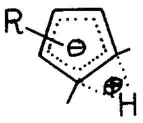

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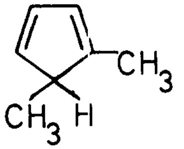

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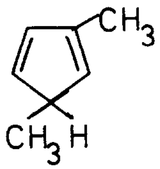

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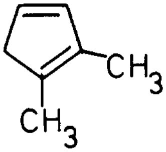

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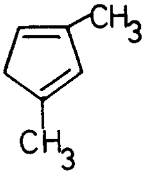

VII

to III took place considerably more slowly; this was confirmed by vapor phase chromatography and by conversion of the rearrangement products to their characteristic N-phenylmaleimide adducts. At equilibrium the composition became III:II:I = 54:45:1(v.p.c.).

The decay of undiluted I occurred at a convenient rate near room temperature, and followed first order kinetics accurately over the whole of the observable course of the reaction (effectively 100% to 0% I). This appeared to be a true homogeneous first order reaction since the rate did not change when the sample was diluted with CCl_4 (down to 10% I), or when the reaction vessel was changed from a glass spinning tube to a tube pre-treated with Me_3SiCl or a Pt vessel (from which aliquots were drawn when required). The rearrangements were normally allowed to take place in the sample tube situated in a variable-temperature probe; by varying the temperature over the range 5° to 40° rates that were conveniently measurable by the present technique were obtained (k(decay of I) varied from

5.74×10^{-5} $sec.^{-1}$ to 3.36×10^{-3} $sec.^{-1}$), and from these an Arrhenius plot led to $E_a = 20.4$ kcals. $mole^{-1}$ (standard deviation 0.3 kcals. $mole^{-1}$) and an entropy of activation of -10 e.u. for the hydrogen migration process (taking the statistical factor into account). The presence of a strong base dramatically accelerated the rearrangement. When I was allowed to rearrange in dimethoxyethane containing D_2O, it incorporated no deuterium (mass spectrum[4]).

In each of the uncatalyzed reactions the formation of II was followed concurrently; it showed the same rate as the decay of I up to about the half-life of I and then began to show divergence, but it seemed that the rate of appearance of III was too slow to measure by this method (there was always competition from the bimolecular Diels-Alder reaction). In the presence of a base such as NaC_5H_5, the sample had formed the equilibrium distribution of isomers by the time the spectrum could be recorded.

The reaction of sodium methylcyclopentadienide with Me_2SO_4 in diglyme at -10° produced a mixture that consisted almost entirely of 1,5-dimethyl-(IV) and 2,5-dimethylcyclopentadiene (V) in the ratio of 3.5:1 (some 5,5-dimethylcyclopentadiene was also formed)[3]. Both isomers rearranged spontaneously rather more slowly than I, leading to 1,2-dimethyl-(VI) and 1,3-dimethylcyclopentadiene (VII)[3]; VI eventually rearranged, at a slower but yet undetermined rate, to the equilibrium mixture of VI and 2,3-dimethylcyclopentadiene (1.35:1), but there did not appear to be any appreciable amount of the 1,4-isomer in equilibrium with VII. The rearrangement of IV was monitored using its C-5 CH_3 signal (8.95τ; doublet J = 7.8 c./s.)and once more good first order kinetic plots were obtained. The rate again showed a strong temperature dependence (k(30°) = 5.56 x 10^{-5} sec.$^{-1}$ to k(54°) = 7.34 x 10^{-4} sec.$^{-1}$) which led to E_a = 23 kcals. mole^{-1} (standard deviation 1.5 kcals. mole^{-1}) and an entropy of activation of -4 e.u. for the hydrogen migration process. The kinetic measurements were rather less accurate in this case because any fluctuation in the field during a run caused the CH_3 signal of V (8.93τ; doublet J = 7.8 c./s.) to begin to overlap that of IV. For the same reason it was not possible to obtain satisfactory kinetic data for V (the less abundant isomer at the start), but it clearly rearranged more slowly than IV; an approximate value of 5 to 6 times more slowly was obtained by direct comparison.

Our attempts to prepare a sample of cyclopentadiene-5-d by the reaction of NaC_5H_5 and D_2O at -10°[1] invariably led to material in which the deuterium had been partially scrambled by the time an n.m.r. spectrum was obtained. Instead of a vinyl:methylene proton ratio of 4:1, our samples usually started at about 3:1 and changed fairly rapidly to the equilibrium value, 2:1. We did not feel that these data were precise enough to warrant an attempt to extract rate constants, but by inspection the reaction appeared to be at least as rapid as the rearrangement of I. However, comparison with Roth's[2] results for deuterium migration in cyclopentadiene, even assuming a large isotope effect, indicates that I rearranges more rapidly than cyclopentadiene. Our own observations on an analogous pair suggest that IV rearranges more rapidly than II; we have not obtained quantitative data for II, but it appears to rearrange so much more slowly than I that it must also be slower than IV.

All available data support the postulate that these rearrangements take place by a series of intramolecular 1,2 hydrogen shifts. A similar situation has been observed in the indene system.[2,5] Although the cyclopentadienide anion has been ruled out as an intermediate (in the absence of a sufficiently strong base), it is natural to expect a transition state (e.g. VIII) in which the ring has much anionic character (pi-electron delocalization) and the migrating hydrogen resembles a proton. All available results appear to be compatible with this general picture, and we have attempted to correlate the available data[1,2] relating to the effect of methyl substituents on cyclopentadiene (including some from our own unpublished work) with a view to testing and improving the model. The following generalizations become apparent: (1) the greater the number of methyl substituents the slower the rearrangement; (2) within a set of isomers, those members having one CH_3 at C-5 rearrange most rapidly, and they are considerably less stable than their isomers (equilibrium data); (3) a 2-methyl derivative is more stable than its 1-methyl isomer; the difference is very small but it appears to be real (at least near room temperature) and it may prove all the more significant because it is unexpected. There are two principle influences of methyl substituents that can be used to account for these generalizations: firstly, a CH_3 should destabilize the transition state in this model just as it does in the corresponding ground state anions[6]; secondly, a CH_3 at a double bond would be expected to stabilize the ground state diene. Point (3) remains puzzling, and, more significantly, it is obvious that our failure to decide with certainty whether the presence of a 5-methyl substituent accelerates or decelerates the rearrangement with respect to the lower homolog represents a critical deficiency that must be rectified. If it does accelerate hydrogen migration, one would not anticipate, considering the inductive effect of CH_3, that the ground state is destabilized, and, one may seek a specific effect in a modified transition state, but such a development must await further experiment.

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4) For which we thank Dr. A.G. Harrison of this Department.

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6) S. McLean and P. Haynes, Can. J. Chem., **41**, 1231 (1963).