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MEASUREMENT OF THE RATE OF REARRANGEMENT OF BULLVALENE

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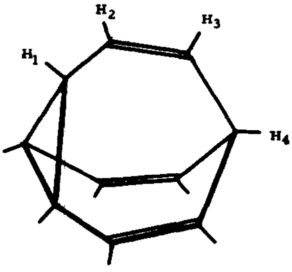
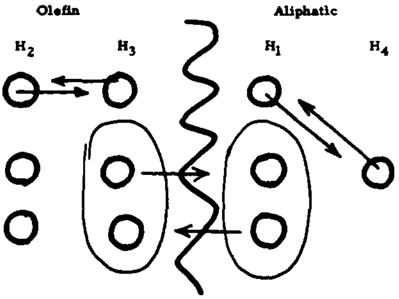
Nuclear magnetic resonance spectroscopy has proved to be a uniquely powerful tool for the study of rapid reactions which produce no net chemical change. An interesting case of this sort is the "Degenerate Cope Rearrangement" of a cis-divinyl cyclopropane(1) which was qualitatively shown to occur rapidly at elevated temperatures. The tri-vinyl cyclopropane I. suggested by Doering and Roth and named "bullvalene" by them, has recently been synthesized by Schröder in a remarkable series of reactions from cyclooctatatraene.(2) As predicted, it showed only one sharp nmr peak at high temperatures, since through a series of Cope rearrangements each hydrogen can achieve all of the chemically distinct environments. In order to obtain the rate constant and activation parameters for this interesting reaction, it was necessary to examine the factors responsible for the observed line width. The line width theory of Anderson,(3) as mathematically modified by Sack,(4) enables calculation of the nmr line shape of a system with nuclei in several environments, which have different probabilities of interconversion among these environments. Examination of the nmr spectrum of bullvalene shows that the two kinds of olefin hydrogens have chemical shift close to 4.4τ and the two kinds of aliphatic hydrogens are both close to 7.8τ (compare (2)). A single Cope rearrangement produces the interchanges diagrammatically shown below. Thus, in any one rearrangement, one H_2-type hydrogen is converted to an H_3-type and vice-versa, while the other two H_2-type hydrogens remain unchanged. The remaining two H_3-type hydrogens are converted to H_1-type hydrogens and vice-versa. Finally, the H_4 and the remaining H_1-type hydrogen are interconverted.



I.



This enables the following formula, in matrix notation, for the line shape as a function of frequency to be written:

$$I \propto \mathrm{Re}[3,3,3,1] \left| \begin{matrix} i(w_a-w)-p & 0 & \frac{2}{3}p & \frac{1}{3}p \\ 0 & -iw-\frac{1}{3}p & \frac{1}{3}p & 0 \\ \frac{2}{3}p & \frac{1}{3}p & -iw-p & 0 \\ p & 0 & 0 & i(w_a-w)-p \end{matrix} \right|^{-1} \begin{bmatrix} 1, \\ 1, \\ 1, \\ 1 \end{bmatrix}$$

where:

w= frequency in radians $\sec^{-1}$ from the olefin peak taken as origin,
w_a= chemical shift between aliphatic and olefin in radians $\sec^{-1}$, and
p= the rate constant in $\sec^{-1}$.

Carrying out the operations indicated leads to an expression which could be evaluated numerically using an IBM 709 computer. The line shapes observed using the Varian A60 and HR60 spectrometers at different temperatures were very similar to the calculated line shapes with various rate constants, except at very low temperatures where spin-spin coupling introduced additional fine structure. Since it has been demonstrated by Alexander(5) that the effect of such coupling in the two environment A-B system becomes negligible at sufficiently fast rate of A-B interconversion, and since in this case the chemical shift is so much greater than the coupling constant, it is assumed that the coupling constants will have negligible effect at rates faster than the slow limit. By fitting the calculated curves to the observed data, the rate constants in Table I were obtained.

TABLE I

T °C	line width in cps at half height	k (sec.$^{-1}$)
10.5	197	1,200
28.1	59.9	4,400
33.6	41.7	6,000
43.1	23.5	10,500
56.2	10.8	23,000
65.2	6.7	36,000
73.2	4.7	53,000
82.7	3.1	79,000

Fitting the data to an Arhenius equation gave $A = 12.3$ sec^{-1} and $E_a = 11.8 \pm 1.0$ kcal./mole. The remarkably small probability and entropy barriers to this reaction which involves the breaking of a carbon-carbon bond and the formation of another can be ascribed to the extremely favorable geometry for the reaction as well as the weakness of the bond which must be broken. Doering and Roth(1) estimate 20.6 kcal as the enthalpy required for this bond fission, however, it would be interesting to know the enthalpy of activation of the rearrangement of trans divinyl cyclopropane for comparison.

It might be noted, incidently, that the rapid reaction rate found for the bullvalene rearrangement must not be interpreted as meaning that the 1,209,600 inter-convertible permutations possible for bullvalene can be obtained from one another with comparable rapidity, since the conversion of one permutation to another involves what may be regarded as the steps of a random-walk process involving many stages. Such considerations only become of practical interest when the properties, and in particular the nmr spectrum, of substituted bullvalenes are considered. The effects of inter-conversion of positional isomers may be treated by extensions of the techniques employed here.

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