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ANOMALOUS ACTIVATION ENERGY OF THERMAL 1,5-HYDROGEN SHIFT IN 1,2-BENZOTROPILIDENE

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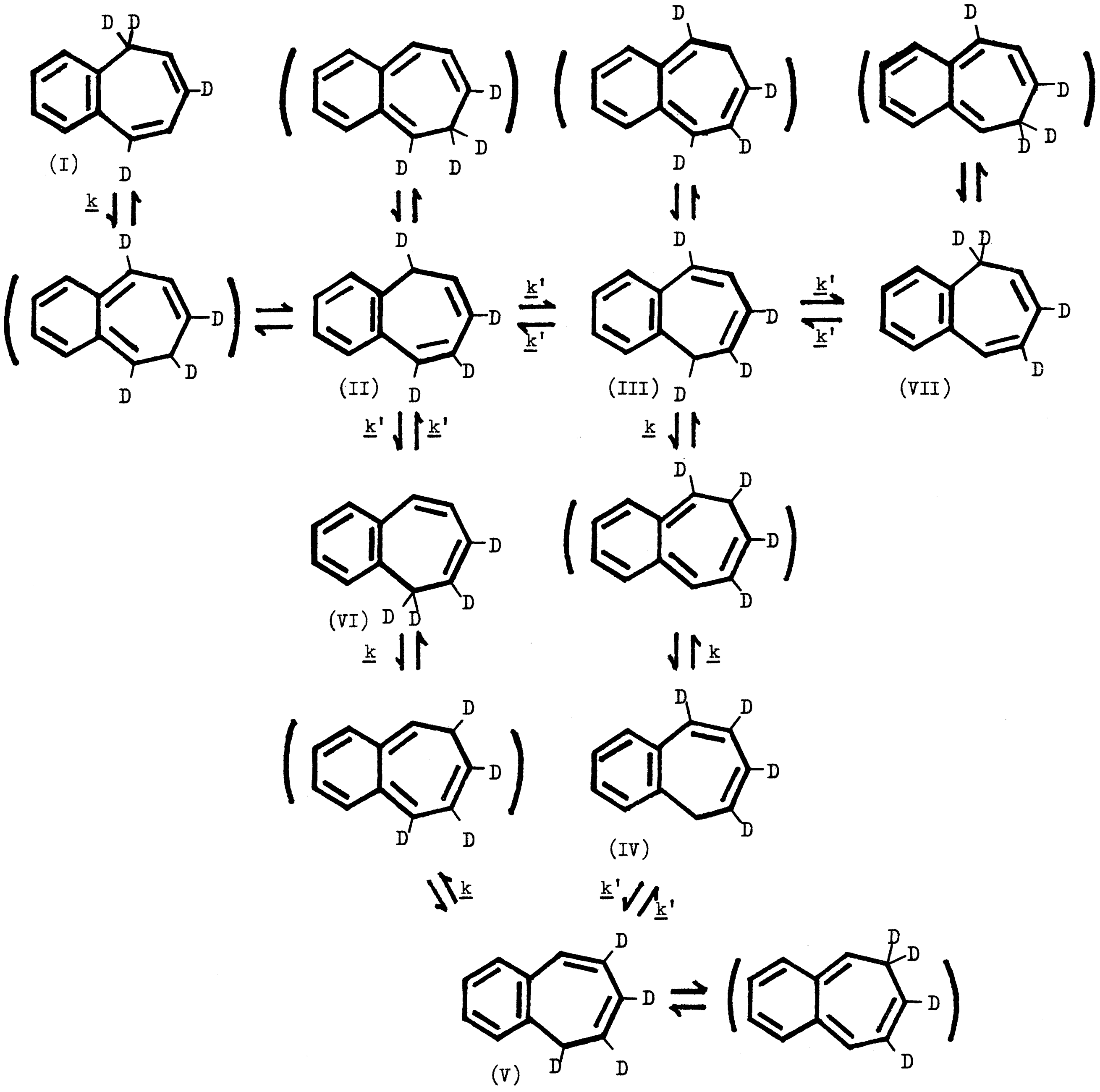
Activation energy of approximately 10 kcal/mol higher than that usually encountered in 1,5-hydrogen shifts in acyclic and cyclic 1,3-dienes was observed in the gas phase thermal reaction of 1,2-benzotropilidene. The value is attributable to the intermediary formation of 4,5-benzotropilidene in which aromatic resonance is not fully developed.

The orbital symmetry allowed thermal 1,5-hydrogen shifts have been known to occur in both acyclic and cyclic 1,3-dienes through suprafacial six-membered transition state.1) The energy of activation pertinent to this class of reactions is usually in the range between 30 and 35 kcal/mol depending on the energetics required to form the transition state. In the present paper, we report the case of 1,2-benzotropilidene, kinetic analysis of which reveals an exceptionally high energy of activation.

3,4-Benzotropilidene was prepared from _o_-phthaldialdehyde and trimethylene-bis-(triphenylphosphonium)-dibromide.2) 3,5,7,7-Tetradeuterio-1,2-benzotropilidene (I) was then prepared by equilibrating 3,4-benzotropilidene with potassium _tert_-butoxide and hexadeuterated dimethyl sulfoxide.3) Approximately 92% deuteration was thus attained. The reaction of I was carried out in gas phase in a 100-ml quartz sealed vessel at temperatures ranging from 309 to 360°C. The reaction temperature was maintained within 0.5°C of the recorded value. Products were collected by liquid nitrogen and were subjected to NMR(60-MHz) analysis as carbon tetrachloride solution. In addition to a signal at 2.9τ for four aromatic hydrogens, NMR showed signals at 3.05τ, 3.55τ, 3.9τ, 4.3τ and 7.05τ for hydrogens at positions 3, 4, 5, 6 and 7, respectively.4) Peak intensities of the latter signals were used to evaluate relative concentrations of seven tetradeuterio-1,2-benzotropilidene isomers. The 1,5-hydrogen shift of I to produce six other isomers can be schematically illustrated as follows:



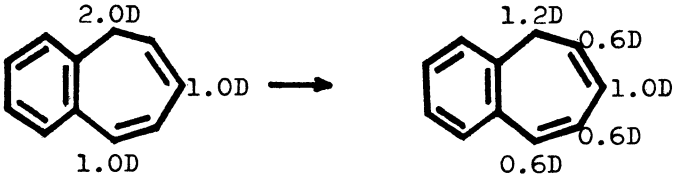
Seven tetradeuterio-4,5-benzotropilidenes indicated in parentheses in the above scheme were not detected. Simultaneous rate equations with respect to more stable seven tetradeuterio-1,2-benzotropilidenes, from I through VII, can be solved to give the following for the instantaneous mole fractions, if it is assumed that $\underline{k} \ll \underline{k}'$,

$$(\mathrm{I}) = 1/10 + 2\exp(-5\underline{k}t/3)/5 + \exp(-8\underline{k}t/3)/2$$

$$(\mathrm{II}) = (\mathrm{III}) = 2(\mathrm{VI}) = 2(\mathrm{VII}) = 1/5 + 2\exp(-5\underline{k}t/3)/15 - \exp(-8\underline{k}t/3)/3$$

$$2(\mathrm{IV}) = (\mathrm{V}) = 1/5 - 8\exp(-5\underline{k}t/3)/15 + \exp(-8\underline{k}t/3)/3$$

where $\underline{k}$ and $\underline{k}'$ are the apparent specific rates of the 1,5-hydrogen shift with and without the intermediary formation of 4,5-benzotropilidene, respectively; and t the reaction time. According to the above solution, (I) = 1.0 and the concentration of all the other isomers becomes zero at $t = 0$. At $t = \infty$, on the other hand, equilibrium scramble of deuterium atoms as indicated by the following equation should be established.



This is in agreement with the present study and also with existing literature.[3)] Reaction parameter, Y, defined by the following equation, is calculated from the observed deuterium distribution at time t, which is in turn used to evaluate intrinsic rate constant, $\underline{k}_{\mathrm{int}}$, pertinent to the rate controlling steps of the formulated reaction scheme.

$$\begin{aligned} Y &= (\text{number of D-atom at C-7})/(\text{number of D-atom at C-4 and C-6}) \\ &= \{2(\mathrm{I}) + (\mathrm{II}) + (\mathrm{III}) + (\mathrm{V}) + 2(\mathrm{VI}) + 2(\mathrm{VII})\}/\{(\mathrm{II}) + (\mathrm{III}) + 2(\mathrm{IV}) + 2(\mathrm{V}) + (\mathrm{VI}) + (\mathrm{VII})\} \\ &= \{3 + 2\exp(-5\underline{k}t/3)\}/\,3\{1 - \exp(-5\underline{k}t/3)\} \end{aligned}$$

$$\underline{k}_{\mathrm{int}} = -\,6/5t\cdot\ln\{3(Y-1)/(3Y+2)\}$$

Since any of the intermediary 4,5-benzotropilidene undergoes either 1,5-deuterium shift or 1,5-hydrogen shift with equal probability, intrinsic rate constant, $\underline{k}_{\mathrm{int}}$, is set twice the apparent rate constant, $\underline{k}$.

The results are summarized in Table 1. The least-squares fit of the listed $\underline{k}_{\mathrm{int}}$'s into the

Table 1. Rate of thermal 1,5-hydrogen shift in 1,2-benzotropilidene

Temperature °C	Reaction time min	Deuterium distribution C-3	C-4 and C-6	C-7	Y	$\underline{k}_{\mathrm{int}}$ $\mathrm{sec}^{-1}\times 10^5$
309	150	0.84	0.11	1.69	7.77	2.93 ± 0.40
312	90	0.87	0.09	1.74	9.89	3.78 ± 0.43
316	150	0.78	0.20	1.57	3.93	6.00 ± 0.84
316	200	0.77	0.22	1.54	3.46	5.28 ± 0.85
316	250	0.74	0.27	1.48	2.76	5.20 ± 0.74
332	90	0.62	0.31	1.24	1.98	19.8 ± 3.2
340	100	0.63	0.30	1.25	2.08	18.6 ± 3.0
347	61	0.70	0.34	1.41	2.09	30.5 ± 5.0
353	78	0.63	0.44	1.27	1.43	40.5 ± 8.7
360	50	0.63	0.45	1.26	1.39	66.4 ± 14.9

Table 2. Kinetic parameters for some 1,5-hydrogen shifts in cycloheptatriene system

Reaction	Phase	Log A sec^{-1}	E_a kcal/mol	Reference
7-D-1,3,5-cycloheptatriene → 3-D-1,3,5-cycloheptatriene	Liquid	11.2	32.8	5)
7-Methyl-1,3,5-cycloheptatriene → 3-Methyl-1,3,5-cycloheptatriene	Gas	12.6	33.3	6)
7-Phenyl-1,3,5-cycloheptatriene → 3-Phenyl-1,3,5-cycloheptatriene	Liquid	10.8	27.6	7)
7-Methoxy-1,3,5-cycloheptatriene → 3-Methoxy-1,3,5-cycloheptatriene	Liquid	10.0	26.4	8)

Arrhenius equation yields the following kinetic parameters: $E_a = 43.32 \pm 1.24$ kcal/mol, Log A = 11.79 ± 0.38 sec^{-1}, and $\Delta S^{\ddagger} = -7.97 \pm 1.74$ cal/°K-mol. An inspection of the values of reported E_a listed in Table 2 makes it quite clear that 1,2-benzotropilidene assumes an outstanding position among other 1,5-hydrogen shifts in cycloheptatriene system. The value obtained in the present study is approximately 10 kcal/mol higher than that reported on 7-D-1,3,5-cycloheptatriene. The discrepancy can be tentatively accounted for by the intermediary formation of less stabilized 4,5-benzotropilidene taking part in the present case. Difference in the total π-electron energy between 1,2- and 4,5-benzotropilidenes is estimated by the simple Hückel method as being $-0.404\beta \approx 8$ kcal/mol, the value which is not inconsistent with the present view.

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