An Electron Spin Resonance Study of the Kinetics of Thermal Isomerization of Bitropenyl (Bi-2,4,6-cycloheptatrien-1-yl)[1]

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Abstract: The rate constant of the intramolecular thermal isomerization of neat liquid 7-tropenylcycloheptatriene (bitropenyl; bi-2,4,6-cycloheptatrien-1-yl) to 3-tropenylcycloheptatriene has been measured over the temperature range $410 \leq T \leq 460°K$. The rate of loss of bitropenyl is determined by measuring the concentration of tropenyl radical, which is in equilibrium with bitropenyl, using electron spin resonance spectroscopy. A least-squares fit of the first-order rate constant to the Arrhenius equation yields log A (sec^{-1}) = 13.3 ± 2.2 (twice the standard deviation) and $\Delta E_a = 34.4 \pm 4.4$ kcal/mole. The transition-state-theory parameters obtained are $\Delta H^{\ddagger} = 32.8 \pm 4.3$ kcal/mole and $\Delta S^{\ddagger} = -3.2 \pm 5.0$ cal/(mole deg) (path degeneracy factor of 4). Previous studies have shown that such isomerizations proceed *via* a 1,5 hydrogen shift. A hydrogen-bridged cyclic transition state has been postulated and is consistent with the measured negative entropies of activation. The value of $\Delta S^{\ddagger}$ obtained in this work for a cyclic system is smaller in magnitude than those for typical acyclic systems. This reduction is in agreement with results of recent work on 7-methylcycloheptatriene and contrasts with results of some previous studies of 7-substituted cycloheptatrienes.

There has been considerable interest in intramolecular thermal isomerization reactions involving 1,5 hydrogen shifts in 1,3-diene systems.[3] These reactions have been studied for both linear and cyclic dienes.

Thermal isomerization of the 7-substituted cycloheptatrienes has been investigated from both the kinetic and equilibrium points of view.[3b,4] Egger[3b] has recently pointed out that there exists a discrepancy between the gas-phase and liquid-phase results on substituted cycloheptatrienes, most of the latter failing to reveal the expected difference in entropy of activation between linear and cyclic systems.

For this reason an investigation of another liquid-phase cyclic reaction system, performed using a technique different from those employed in previous work, is of interest. We have studied the kinetics of the thermal isomerization of bitropenyl (7-tropenylcycloheptatriene; bi-2,4,6-cycloheptatrien-1-yl) with the aid of electron spin resonance (esr) spectroscopy.

In the course of an investigation of the tropenyl radical ($C_7H_7\cdot$),[5] generated by thermal dissociation of the neat liquid bitropenyl, it was observed that the esr signal of $C_7H_7\cdot$ decays with time at elevated temperatures. We ascribe this decrease of radical concentration to the thermal isomerization of the dimer. The rate of loss of bitropenyl at a given temperature can be readily determined by measuring the rate of decay of the esr signal, since bitropenyl is in equilibrium with the tropenyl radical.

The isomerization of liquid bitropenyl has also been studied by Dauben and Hunter[4i,6] who used nmr. These investigators have proposed the reaction scheme shown in Figure 1[4i] in which the first two steps are essentially irreversible. We have measured the rate constant (k_{73}) for the first step in this scheme, which converts 7-tropenylcycloheptatriene to 3-tropenylcycloheptatriene.

Experimental Section

The esr measurements were performed using a Varian spectrometer and variable-temperature apparatus which have been described previously.[7,8] Samples of bitropenyl (neat) were deoxygenated and sealed under nitrogen. The spectrum of the tropenyl radical was recorded at constant temperature ($410 \leq T \leq 460°K$) and the peak-to-peak amplitudes (h) of the two central components were measured as a function of time.

Results

Order of the Reaction. It will be shown below that the reaction by which bitropenyl is consumed is *first order* in bitropenyl, a result which is consistent with the proposal of a thermal isomerization. If the process is first order, then a plot of log h *vs.* time will be a straight line; if it is second order, then $1/h^2$ *vs.* time will be linear (h is the amplitude of the esr signal and is proportional to the square root of the bitropenyl concentration). The experimental data for a typical run are graphed in Figures 2 and 3. The first-order plot is linear and the second-order plot deviates considerably from linearity.

Rate Constant. The rate constant k_{73} has been obtained for each run by means of an unweighted least-squares fit of the data to the relationship

$$\ln h = -{}^1/_2 k_{73}t + \text{constant} \qquad (1)$$

The results are listed in Table I.

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(1) Supported by the U. S. Army Research Office, Durham.

(2) Alfred P. Sloan Research Fellow.

(3) See the following papers and the references cited therein: (a) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 999 (1966); (b) K. W. Egger, *J. Am. Chem. Soc.*, **89**, 3688 (1967); (c) R. Hoffman and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(4) (a) A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962); (b) A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Rec. Trav. Chim.*, **82**, 717, 741 (1963); (c) T. J. Pratt, Ph.D. Thesis, University of Washington, 1964; (d) R. B. Medz, Ph.D. Thesis, University of Washington, 1964; (e) E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 59 (1964); (f) T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Japan*, **38**, 665 (1965); (g) A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 245 (1965); (h) A. P. ter Borg, E. Razenberg, and H. Kloosterziel, *ibid.*, **84**, 1230 (1965); (i) F. R. Hunter, Ph.D. Thesis, University of Washington, 1966; (j) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 3527 (1966); (k) K. W. Egger, *ibid.*, **90**, 1 (1968).

(5) G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, Jr., and F. R. Hunter, *ibid.*, **87**, 3527 (1965).

(6) H. J. Dauben, Jr., and F. R. Hunter, unpublished work.

(7) M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 222, 302 (1967).

(8) G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, Jr., *ibid.*, **48**, 2876 (1968).

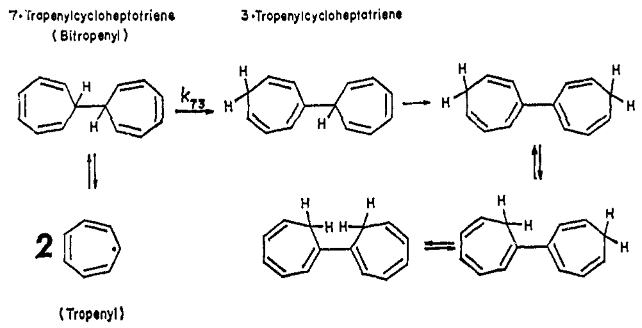

Figure 1. Reaction scheme for the thermal isomerization of bitropenyl. The homolytic thermal cleavage of bitropenyl is also shown.

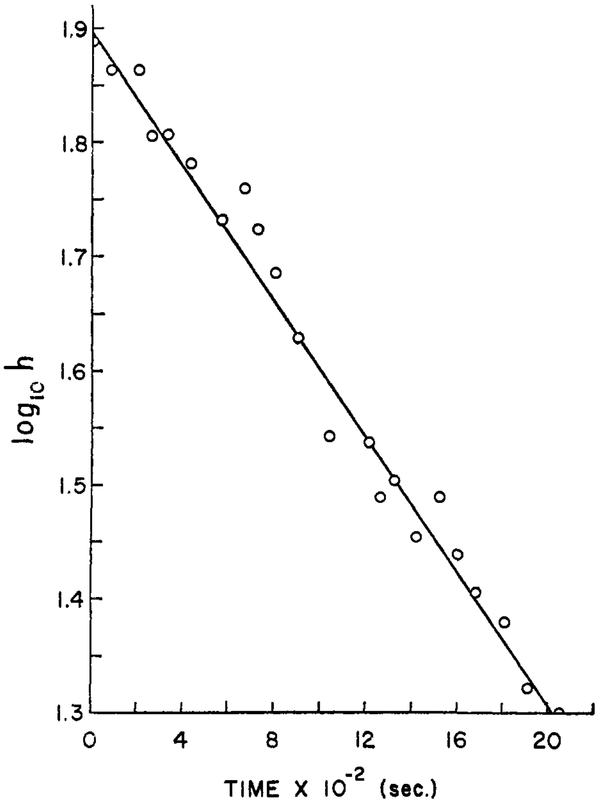

Figure 2. Plot of log *h* vs. time for a typical run (*h* is the amplitude of the esr signal).

Arrhenius Parameters. The Arrhenius activation energy (ΔE_a) and the logarithm of the frequency factor (A) have been evaluated by a least-squares fit of the rate constants presented in Table I to

$$\ln k_{73} = \ln A - \Delta E_a/RT \qquad (2)$$

The values obtained are $\Delta E_a = 34.4 \pm 4.4$ kcal/mole and $\log A$ (sec^{-1}) = 13.3 ± 2.2. A plot of $\log k_{73}$ *vs.* T^{-1} is shown in Figure 4. The straight line drawn through the points is the least-squares line.

Discussion

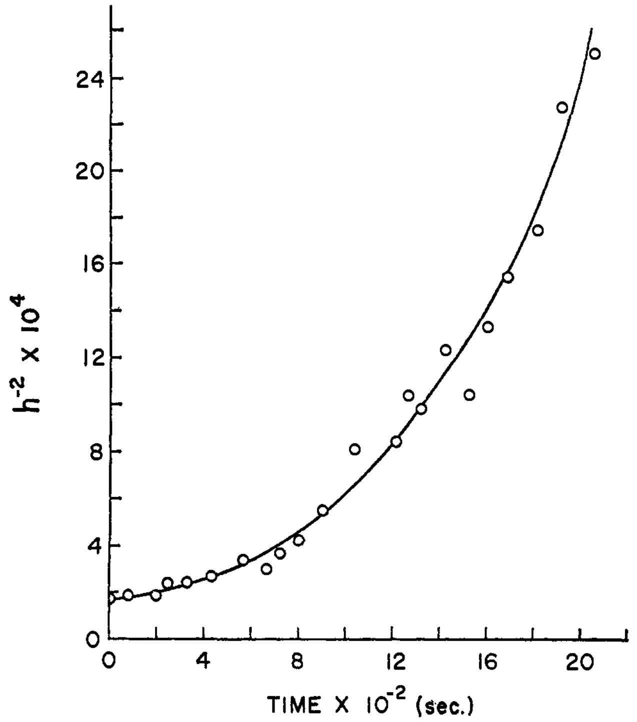

Figure 3. Plot of $1/h^2$ *vs.* time for a typical run.

We compare our kinetic data first to those obtained by Dauben and Hunter[4i,6] on the same system. Their results are in good agreement with those reported in this work. They find $k_{73} = 5.2 \times 10^{-5}$ sec^{-1} (423 °K; two runs; seven points), $k_{73} = 25 \times 10^{-5}$ sec^{-1} (441 °K; one run; eight points), and $\Delta E_a = 30.6$ kcal/mole. Corresponding values obtained in this study are $(3.4 \pm 0.3) \times 10^{-5}$ sec^{-1} (423 °K), $(22 \pm 2) \times 10^{-5}$ sec^{-1} (441 °K), and $\Delta E_a = 34.4 \pm 4.4$ kcal/mole.[9]

Table I. Rate Constant k_{73} for the Thermal Isomerization of Bitropenyl

$k_{73} \times 10^6$, sec^{-1}	No. of data points	Temp, °K	Duration of run $\times 10^{-3}$ sec
13.1 ± 4.4[a]	41	410	25.5
25.4 ± 1.6	47	419	23.8
40.4 ± 2.4	39	422	18.0
42.8 ± 7.6	37	429	17.3
116 ± 12	21	435	6.5
129 ± 19	15	437	8.8
326 ± 8	34	451	5.4
440 ± 28[b]	58	454	4.4
954 ± 88	24	457	3.4
1360 ± 82	22	457	2.0
874 ± 116	20	460	3.8

[a] The uncertainty in the rate constants is twice the standard deviation. [b] This rate constant is for the isomerization of 10% by weight bitropenyl in naphthalene. All other rate constants listed are for samples of neat bitropenyl.

It is also of interest to compare our kinetic data with that which has been obtained for other 7-substituted cycloheptatrienes. The Arrhenius and transition-state-theory parameters are listed in Table II. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for bitropenyl have been calculated using a least-squares fit of $\ln (k_{73}/T)$ *vs.* T^{-1}. A path degeneracy factor of 4 is employed. This is consistent with the preferred conformation which we have assumed for bitropenyl, namely the double boat with the methine hydrogens in axial positions.[10,11]

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[9] Rate constants at these temperatures have been obtained by interpolation.

Table II. Arrhenius and Transition-State-Theory Parameters for the Initial Step in the Thermal Isomerization of 7-Substituted Cycloheptatrienes

Compound	ΔE_a, kcal/mole	Log A	$\Delta H^{\ddagger}$,[a] kcal/mole	$\Delta S^{\ddagger}$,[b] cal/(mole deg)	Ref
Cycloheptatriene	31–32	10.9–11.5	31.6 30.2	−8.2[c] −11.5	4b
7-Phenylcycloheptatriene	27.6	10.8	26.9	−11.7	4b
1,4-Bis(7-cycloheptatrienyl)-benzene	30.6	12.5	29.8	−6.7	4j
7-Methoxycycloheptatriene	26.4	10.0	25.7	−15.0	4f
7-Methylcycloheptatriene[d]	33.3 ± 0.2	12.6 ± 0.1	32.4[e]	−4.9	3b
Bitropenyl[f]	34.4 ± 4.4	13.3 ± 2.2	32.8 ± 4.3[g]	−3.2 ± 5.0[g]	This work

[a] All transition-state-theory parameters are calculated assuming a transmission coefficient of unity. [b] Corrected for path degeneracy. The factor is 2 except for bitropenyl and 1,4-bis(7-cycloheptatrienyl)benzene in which cases it is 4. [c] Two sets of data were used. [d] This molecule was investigated in the gas phase. All others listed in the table were studied in the liquid phase. [e] Computed using $\Delta H^{\ddagger} = \Delta E_a - RT$ with $T = 450$°K. [f] All error limits cited for bitropenyl are *twice* the standard deviation. [g] Calculated by a least-squares fit of ln (k_{73}/T) *vs.* T^{-1}. The slope is $(\Delta H^{\ddagger}/R)$ and the intercept is $[(\Delta S^{\ddagger}/R) + \ln(k/h) + \ln d]$, where d is the path degeneracy factor. Essentially the same value of $\Delta S^{\ddagger}$ is obtained through the use of the equation $\Delta S^{\ddagger} = R[\ln A - \ln(kT/h) - 1 - \ln d]$.

The activation energies for the 1,5-hydrogen-shift reactions in acyclic 1,3-dienes are about 30 kcal/mole, and the entropies of activation are about −10 cal/(mole deg).[3b] In the case of the 7-substituted cycloheptatrienes, ΔE_a values are also approximately 30 kcal/mole, but the results for 7-phenylcycloheptatriene, 1,4-bis(7-cycloheptatrienyl)benzene, and 7-methoxycycloheptatriene are somewhat lower than those for cycloheptatriene, 7-methylcycloheptatriene, and bitropenyl. The 4-kcal/mole reduction in ΔE_a for 7-phenylcycloheptatriene relative to cycloheptatriene has been rationalized by the argument that the gain in stability in the product due to triene–aromatic conjugation is manifested in the transition state.[4b] Such a lowering of activation energy due to conjugation is neither expected nor observed for bitropenyl.

The −10-cal/(mole deg) entropy of activation for acyclic 1,3-dienes has been interpreted in terms of a hydrogen-bridged cyclic transition state.[3] It has been noted by Egger[3b] that (1) for such a transition state a smaller magnitude of $\Delta S^{\ddagger}$ might reasonably be expected in the case of *cyclic* systems such as 7-substituted cycloheptatrienes, and (2) gas-phase and liquid-phase results for $\Delta S^{\ddagger}$ should be similar. Such a reduction in $|\Delta S^{\ddagger}|$ has been observed in Egger's gas-phase study of 7-methylcycloheptatriene ($\Delta S^{\ddagger} = -4.9$ cal/(mole deg)) but *not* in most of the liquid-phase work summarized in Table II. Except for the case of 1,4-bis(7-cycloheptatrienyl)benzene, with $\Delta S^{\ddagger} = -6.7$ cal/(mole deg), the entropies of activation are in the range $-10 \geq \Delta S^{\ddagger} \geq -15$ cal/(mole deg). *In contrast*, the value of the entropy of activation found in this liquid-phase study of bitropenyl is only −3.2 cal/(mole deg), in excellent agreement with the result for 7-methylcycloheptatriene.

One can also compare, for the various substituted cycloheptatrienes, the rate of the transannular hydrogen shift at a given temperature. Taking proper account of path degeneracy, we find that the rate of the transannular shift for bitropenyl at 140° is about a factor of 2 greater than that for cycloheptatriene.[12] This small enhancement results from a cancellation of effects; both the frequency factor and activation energy are larger for bitropenyl. Most substituents (*e.g.*, OCH_3, CN, C_6H_5, $N(CH_3)_2$) show a much larger rate enhancement than does the tropenyl group.[4b,h,j] In the cases of 7-phenylcycloheptatriene and 7-methoxycycloheptatriene, this enhancement is due to a reduction in the activation energy.

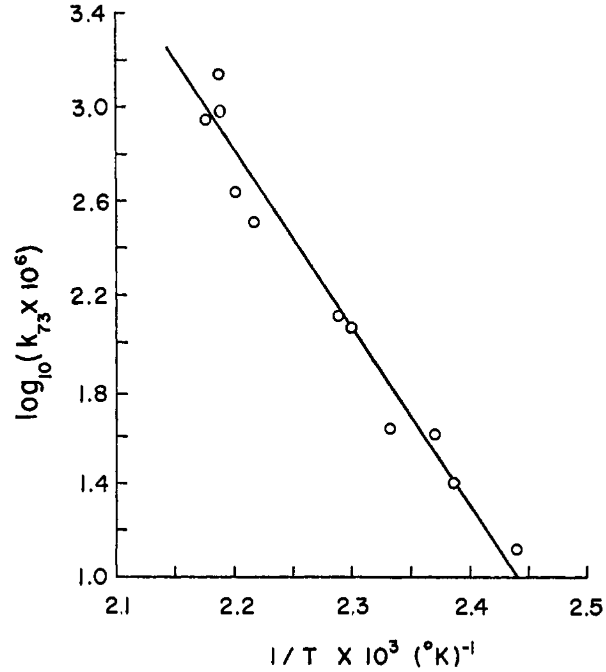

Figure 4. Plot of log k_{73} *vs.* T^{-1}. The straight line drawn through the points is the least-squares line.

Acknowledgment. We wish to thank Professor H. J. Dauben, Jr., and Dr. Frank R. Hunter for helpful discussions.

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(10) This conformation is consistent with that which has been proposed in related work. For a discussion of this point see ref 3b, 4b, and 4j.

(11) The infrared spectrum of bitropenyl indicates a conformation containing only one type of methine hydrogen, presumably axial: C. la Lau and H. de Ruyter, *Spectrochim. Acta*, **19**, 1559 (1963).

(12) It is interesting to note that the rates of isomerization for *x,x'*-di-*t*-butylbitropenyl and *x,x'*-diphenylbitropenyl are considerably greater than that for bitropenyl: L. M. Morrell and G. Vincow, unpublished work.