be very slow.[34] However, the protonation can occur through the radical anion. Since this species can exist for naphthalene in liquid ammonia, a kinetic study of the same type as that described by Szwarc[30] could provide an answer. However, in the case of benzene, it seems unlikely that it will be possible to study the mechanism of the reduction electrochemically, since it is not possible to observe the first step of the reaction to the radical anion.

Acknowledgment. We are grateful to the National Science Foundation through its U. S.-French Exchange Program for a fellowship to A. D. Support of this research by National Science Foundation Grant GP-31414X is also gratefully acknowledged.

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[34] For benzene, a 10% conversion (based on the sodium concentration) requires 2000 sec (at −45°). See Figure 3 in ref 6.

Endo- *vs.* Exocyclic Cyclopropyl Bond Rupture in Bicyclo[3.1.0]hex-2-ene

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Abstract: Highly excited bicyclo[3.1.0]hex-2-ene (BCH) produced by chemical activation isomerizes to give products arising from both endocyclic (65%) and exocyclic (35%) cyclopropyl bond rupture of BCH. Only endocyclic rupture to the diradical intermediate has been observed in thermal isomerizations, but both isomerization paths have been observed in the photoisomerization of derivatives of BCH. The results are discussed in terms of the estimated Arrhenius parameters for the two ring opening mechanisms and subsequent isomerizations.

Vinylcyclopropane isomerizations in general and bicyclo[3.1.0]hex-2-ene (BCH) rearrangements specifically are of current interest to both thermal kineticists and photochemists.[1-5] The present evidence in both thermal and photochemical reactions supports a mechanism of breaking of a bond in the cyclopropane ring to give a diradical intermediate rather than isomerization by a concerted process.[2,6,7] For BCH and its derivatives, thermally induced epimerization or structural rearrangement occurs by endocyclic bond rupture.[3,8] Photolysis of BCH derivatives in solution leads to products expected from exocyclic as well as endocyclic cyclopropane bond rupture.[4,9] No photochemical studies on the parent bicyclic molecule have been reported.

We wish to report some results on the high energy isomerization reactions of BCH using the technique of methylene chemical activation.[10,11] The results indicate that introduction into the molecule of sufficient energy by means other than a photochemical transition will lead to products arising from both types of cyclopropyl bond rupture. Since the products of exocyclic bond rupture are observed, this technique provides positive experimental data to determine the Arrhenius parameters for the reaction previously unobserved in pyrolysis. Thermochemical kinetic estimates provide an explanation why the exocyclic mechanism is not observed in thermal systems.

Experimental Section

Cyclopentadiene was prepared by cracking the commercially obtained dimer (Aldrich Chemical Co.). The starting material was stored at Dry Ice temperatures and subjected to several freeze–thaw degassing cycles before use. Gas chromatography indicated the impurities in the cyclopentadiene were less than 1%. Diazomethane was prepared by the reaction of 60% potassium hydroxide solution with *N,N'*-nitrosoylmethylurea using the procedure described by Frey.[12] It was stored at liquid nitrogen temperatures and distilled at −40° to fill the reaction vessel. The oxygen was bone dry grade (Matheson Gas) and was used without further purification.

The irradiation vessel was a 2-in. diameter 350 cm^3 cylindrical tube with Pyrex flats epoxied to the ends. The samples were filled on a greaseless, mercury-free, high-vacuum line capable of evacuating the vessel to $<10^{-4}$ Torr. The total pressure of the system was varied from 50 to 300 Torr. In most cases the ratio of diazomethane to cyclopentadiene was 1:14, but changes in this ratio by a factor of 2 did not significantly affect the relative yields. For all the results reported here, the ratio of oxygen to cyclopentadiene was 10%. The irradiations were carried out using a 200-W high-pressure mercury lamp. The light was passed through an interference filter with 40% transmission at 435.8 nm and a half-band width of 10 nm. Generally the irradiations lasted 3 hr although time dependence studies showed that the relative yields did not vary for irradiations between 0.5 and 5 hr.

The analysis of the product spectrum was done by using a gas sampling valve to inject an aliquot of the product mixture into a

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[1] H. M. Frey, *Chem. Rev.*, **69**, 103 (1969).

[2] (a) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970); (b) *J. Phys. Chem.*, 72, 1866 (1968).

[3] (a) J. S. Swenton and A. Wexler, *J. Amer. Chem. Soc.*, **93**, 3066 (1971); (b) W. E. von Doering and E. K. G. Schmidt, *Tetrahedron*, 27, 2005 (1971).

[4] H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 3648 (1972), and references therein.

[5] J. E. Baldwin and A. H. Andrist, *ibid.*, **93**, 3290 (1971).

[6] P. H. Mazzocchi and H. J. Tamburin, *ibid.*, 92, 7220 (1970); (b) R. M. Willcott and W. H. Cargle, *ibid.*, **89**, 723 (1967); **91**, 4310 (1969).

[7] There are several examples of concerted reactions, however, in substituted BCH such as bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehydes [see J. C. Gilbert, K. R. Smith, G. W. Klump, and M. Schakel, *Tetrahedron Lett.*, 125 (1972), and references therein].

[8] R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 553 (1966).

[9] (a) D. Garin and D. J. Cooke, *J. Chem. Soc. D*, 33 (1972); (b) B. Miller, *ibid.*, 574 (1971); (c) B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **89**, 1678 (1967); (d) R. A. Clark, *Tetrahedron Lett.*, 2279 (1971).

[10] B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

[11] (a) T. Rose, *J. Phys. Chem.*, **76**, 1389 (1972); (b) T. Rose, P. Crane, and R. Seyse, to be published.

[12] (a) C. S. Elliot and H. M. Frey, *Trans. Faraday Soc.*, **64**, 2352 (1968); (b) H. M. Frey, *ibid.*, **57**, 951 (1961).

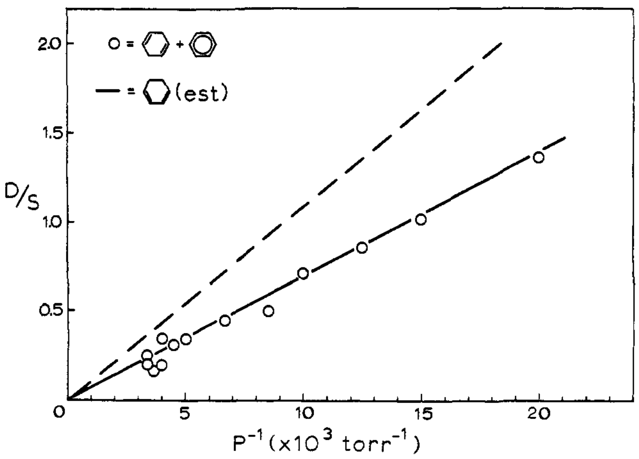


Figure 1. Plots of decomposition (D):stabilization (S) *vs.* the reciprocal of the total system pressure for the isomerization of BCH* to 1,4-cyclohexadiene and benzene. The dotted curve is the estimated isomerization to 1,3-cyclohexadiene assuming the rate is 1.5 times that to 1,4-cyclohexadiene (see text).

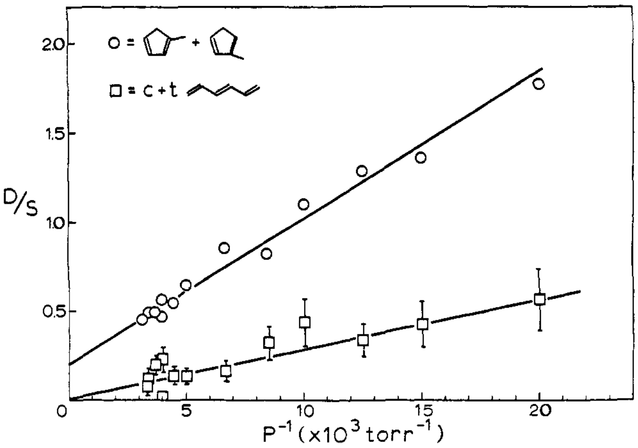


Figure 2. Plots of decomposition (D):stabilization (S) ratio *vs.* the reciprocal of the total system pressure for isomerization of BCH* to the methylcyclopentadiene (○) and hexatriene (□) isomers. The hexatriene curve has been corrected to remove the contribution to the open chain yield from isomerization of 1,3-cyclohexadiene (see text).

flame ionization gas chromatograph. The products were separated at room temperature using a serial $^1/_8$-in. stainless steel column consisting of 10 ft of 5% dimethylsulfolone, 10 ft of 20% β,β'-oxydipropionitrile, and 5 ft of 10% SF-96 silicone oil. The identity and purity of the products was confirmed by comparison of relative retention volumes with known compounds, by trapping them and reinjecting them on another column, and by either infrared or mass spectral analysis.[11b]

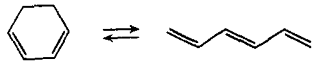
Invariably an analysis of the reaction mixture prior to the beginning of the irradiation showed some (<1%) contamination from bicyclo[3.1.0]hex-2-ene and the 1- and 2-methylcyclopentadiene isomers. The amount of these products remained fairly constant over a 3-hr period if there was no irradiation by the lamp. These "impurities" were corrected for in the calculation of the product yields resulting from the irradiation.

A second difficulty involved with the oxygen scavenged cyclopentadiene system was the formation of a fog in the reaction vessel at the beginning of the irradiation. No obvious effect on the relative products yields was evident, but the absolute yield could not be accurately compared with the unscavenged systems. The cause and effect of this fogging is being studied further.[11b]

Results

The principal product formed at high pressures from the reaction of singlet methylene with cyclopentadiene (CPD) is bicyclo[3.1.0]hex-2-ene (BCH). As the total pressure of the system decreases, the yields of seven other C_6 isomerization products become increasingly important. These products are 1,3-cyclohexadiene, 1,4-cyclohexadiene, benzene, 1- and 2-methylcyclopentadiene, and *cis*- and *trans*-1,3,5-hexatriene. Figure 1 shows a plot of the ratio of the 1,4-cyclohexadiene plus benzene yield (decomposition) to the BCH yield (stabilization) *vs.* the reciprocal of the pressure. The sum yield of 1,4-cyclohexadiene and benzene is plotted since the pyrolysis work showed that almost all the benzene arose from 1,4-cyclohexadiene decomposition.[8,13] Using the standard analysis of chemical activation data employing the steady-state condition,[10] the slope of the straight line obtained from Figure 1 can be used to calculate the unimolecular isomerization rate of BCH to 1,4-cyclohexadiene. If the strong collision assumption is valid, this rate is obtained by multiplying the slope of the line by the collisional frequency, ω. By estimating the collisional diameters of BCH and CPD as 5.5 Å the calculated bimolecular collisional frequency is $(1.2 \pm 0.1) \times 10^7$ mm^{-1} sec^{-1}. The rate of formation of 1,4-cyclohexadiene is then $(1.0 \pm 0.1) \times 10^9$ sec^{-1}.

A problem is encountered in determining the rate of formation of 1,3-cyclohexadiene because of the equilibrium with *cis*-1,3,5-hexatriene, *i.e.*



1 2 (1)

In thermal systems, this equilibrium greatly favors the cyclic structure.[14] However, at the higher energies involved in chemical activation, the open chain isomer will predominate as is observed in our experiment.[15] The dotted line in Figure 1 for the 1,3-cyclohexadiene yield, therefore, was estimated as being 1.5 times the sum of the 1,4-cyclohexadiene plus benzene yield as was obtained in the thermolysis of BCH. This assumption is reasonable because in the thermal system the activation energy, which is the temperature-dependent term in the Arrhenius equation, is the same for both cyclohexadiene isomers.[8]

The rates of formation of the methylcyclopentadiene isomers were calculated from the decomposition:stabilization plots shown in Figure 2 to give a rate constant of $(1.0 \pm 0.1) \times 10^9$ sec^{-1}. The methylcyclopentadiene curve does not pass through the origin indicating that there is another mechanism for the formation of these products other than by isomerization of BCH. This mechanism is the direct insertion of singlet methylene into the C–H bonds of cyclopentadiene. Failure to observe the 5-methylcyclopentadiene isomer is probably due to its rapid isomerization to the other two isomers as has been reported previously.[17]

(13) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, **63**, 987 (1967).

(14) K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964).

(15) By applying the methods developed by Benson[16] and coworkers to estimate the kinetic parameters for the reaction of 1,3-cyclohexadiene to *cis*-1,3,5-hexatriene, we obtain an Arrhenius equation of $k(430°\text{K}) = 10^{14.1-(44.7/\theta)}$ where θ is $2.30 \times 10^{-3}RT$. Using this equation in conjunction with the equation for the reverse reaction, $k(430°\text{K}) = 10^{11.5-(29.9/\theta)}$,[14] the ratio of open chain to cyclic isomers at the internal energy available in the chemical activation system is about 30:1!

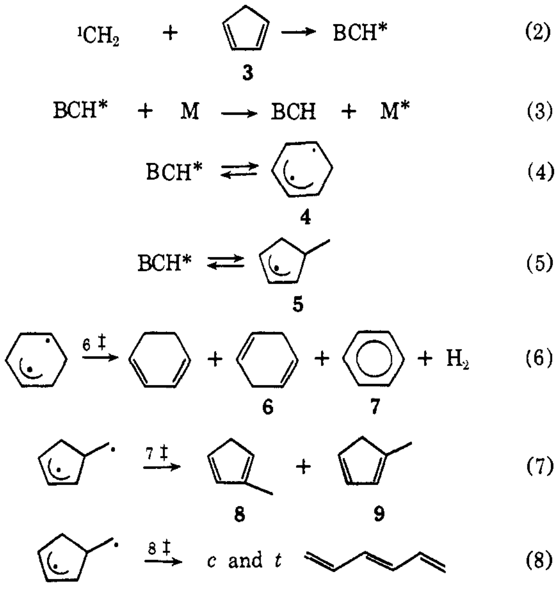
(16) (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) S. W. Benson, *et al.*, *Chem. Rev.*, **69**, 279 (1969); (c) H. E. O'Neal and S. W. Benson, *J. Chem. Eng. Data*, **15**, 266 (1970).

(17) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

The yields of the hexatriene isomers formed directly from isomerization of BCH were obtained by first taking the difference between the 1,3-cyclohexadiene yield calculated as described above and the observed yield and then subtracting this value from the measured hexatriene isomer yield. Because of this indirect evaluation, an error of ±30% is assigned to each point. The resulting kinetic plot in Figure 2, however, gives an acceptable straight line passing through the origin with a slope corresponding to a rate constant of (3.4 ± 1.0) × 10^8 sec^{-1}.

Discussion

The products arising from the isomerization of BCH can be classified into (1) those arising from endocyclic bond rupture, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and benzene, or (2) those arising from exocyclic bond rupture, 1- and 2-methylcyclopentadiene, and probably some *cis*- and *trans*-1,3,5-hexatriene. The reaction model may be outlined as follows,



The experimental rates for formation of the various isomers are presented in Table I. It is clear from the rates of methylcyclopentadiene and 1,3,5-hexatriene formation that reaction 5 is of substantial importance in the high energy isomerization of BCH. This observation is in contrast to the thermal isomerization studies of BCH in which only the cyclohexadiene isomers were found. The formation of both the cyclohexadienes and the methylcyclopentadienes involves a 1,2-hydrogen shift in the biradical. Since this shift has a higher activation energy than the ring closing activation energies,[2] $k_{-4} \gg k_7$ or k_8, epimerization will be much more rapid, therefore, than structural isomerization and will occur at a lower temperature as has been observed for substituted bicyclo[3.1.0] derivatives.[3]

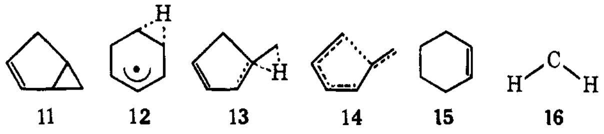
Table I. Rates for Isomerization of Bicyclo[3.1.0]hex-2-ene

Product or intermediate	Chemical activation rate, $\times 10^{-9}$ sec^{-1}	Estimated Arrhenius eq[a]
4		$k_4 = 10^{13.7-(43.3/\theta)}$
5		$k_5 = 10^{14.6-(50.0/\theta)}$
6 + **1** + **7**	2.5 ± 0.3	$K_4k_6{}^b = 10^{14.2-(50.2/\theta)}$
9 + **8**	1.0 ± 0.1	$K_5k_7 = 10^{13.6-(54.1/\theta)}$
c- and *t*-**2**	0.3 ± 0.1	$K_5k_8 = 10^{14.6-(57.3/\theta)}$

[a] Activation energy is in kcal/mol and $\theta = 2.30 \times 10^{-3}RT$. [b] Experimental value is $10^{14.5-(50.2/\theta)}$.[8]

The relative importance of k_4 and k_5 can be evaluated using the thermochemical kinetic estimation techniques developed by Benson and coworkers.[2,16] The thermochemical values used in the following calculations are given in Table II. The activation energy estimates are determined as follows

Table II. Thermochemistry Estimates of Molecules, Biradicals, and Transition States Involved in the Isomerization of Bicyclo[3.1.0]hex-2-ene



11 12 13 14 15 16

Parameter (X)[a]	**11**[b]	**5**[b]	**4**[c]	**12**[b] (6 ‡)	**13**[d] (7 ‡)	**14**[e] (8 ‡)	**9**
$S°$ (intrinsic)	71.2	77.4	73.5	71.3	71.2	77.3	76.3
$C_p°$ (300°K)	19.9	22.5	24.0	22.4	22.3	24.8	23.6
$C_p°$ (425°K)	32.2	32.8	35.0	34.5	30.4	32.0	31.4
$C_p°$ (600°K)	42.5	42.5	45.6	44.5	41.8	42.8	42.3
E (strain)	33.5	6.0	1.4	6.9	8.6	8.6	6.0

[a] Entropies and heat capacities are in units of gibbs/mol and strain energies in kcal/mol. [b] See ref 2a. [c] $X = {}^1/_2\{X°[\mathbf{1} + (\mathbf{15} - 2H)]/2 + [\mathbf{6} + (\mathbf{15} - 2H)]/2\}$. [d] $X^{\ddagger} = X°(\mathbf{9}) - X°(CH_3 \rightarrow \infty)_{2.0} + (P_{4e})_t - (\mathbf{16})_{1100\ cm^{-1}}$. [e] $X^{\ddagger} = X°(\mathbf{9}) - 2X°(550\ cm^{-1}) + 2X°(112\ cm^{-1}) - (CH_3 \rightarrow \infty)_{2.0} + (i\text{-}B_{3e})_t$.

$$E_a(\text{est}) = DH°(C{-}C) - \Delta E_{st} - E_{al} + E_{-r}^{\ddagger}$$

where DH°(C–C) is the carbon-carbon bond dissociation energy, ΔE_{st} is the difference in the ring correction strain energy for BCH and the biradical, E_{al} is the allylic resonance energy, and $E_{-r}^{\ddagger}$ is the ring closing activation energy for the biradical. For k_4 and k_5

$$E_a(k_4) = 78.7 - (33.5 - 1.4) - 12.6 + 9.3 = 43.3 \text{ kcal/mol}$$

$$E_a(k_5) = 80.8 - (33.5 - 6) - 12.6 + 9.3 = 50 \text{ kcal/mol}$$

The activation energy for k_4 is in good agreement with the recently published experimental value of 32.4 kcal/mol for *trans*-5,6-diphenylbicyclo[3.1.0]hex-3-ene if corrected by 12.5 kcal/mol for the benzylic resonance energy in the derivative system.[3a] The A factor estimates are determined by

$$A(\text{est}) = (\text{rpd})\frac{ekT_m}{h}e^{(\Delta S^{\ddagger}/R)}$$

where rpd is the reaction path degeneracy,[16] T_m is the mean temperature of the reaction, and $\Delta S^{\ddagger}$ is the entropy difference between the parent molecule and the transition state at T_m. For our reactions

$$\Delta S^{\ddagger}(\text{est}) = \Delta S°(300°) + \langle \Delta C_p° \rangle \ln \frac{T_m}{300} + \Delta S_{-r}^{\ddagger}$$

$$\Delta S^{\ddagger}(k_4, 425°K) = 2.3 + 1.2 - 2.0 = 1.5 \text{ gibbs/mol}$$

$$\Delta S^{\ddagger}(k_5, 425°K) = 6.2 + 0.6 - 1.0 = 5.8 \text{ gibbs/mol}$$

where $\Delta S_{-r}^{\ddagger}$, the reaction coordinate used for the activation energy for ring closing, is taken as a 300-cm^{-1} out-of-plane ring vibration for k_4 and a 550-cm^{-1} in-plane ring vibration for k_5.[2a] Since the reaction path degeneracy is one for both reactions, $A_4(\text{est}) = 10^{13.7}$ and $A_5(\text{est}) = 10^{14.6}$. The resulting estimates for k_4 and k_5 are $k_4(\text{est}) = 10^{13.7-(43.3/\theta)}$ and $k_5(\text{est}) = 10^{14.6-(50.0/\theta)}$ where θ is $2.30 \times 10^{-3}RT$. At 425°K, the ratio $k_4{:}k_5$ is 1000:1. These estimates are clearly in accord with the experimental observation that for isomerizations in the 400–470°K temperature range exocyclic bond rupture is not competitive with endocyclic decomposition.[3-6]

We now consider the situation at higher pyrolysis temperatures (600°K) where the cyclohexadienes are observed but no methylcyclopentadiene.[8] Since $k_{-4} \gg k_6$ and $k_{-5} \gg k_7$, $k_{\text{exp}}\,(\mathbf{6{,}1}) = K_4k_6$ and $k_{\text{exp}}(\mathbf{9}) = K_5k_7$. Accordingly the transition state is taken between the diradical and final product. For the activation energy

$$E_{\text{a}}(\text{est}) = \text{DH}^\circ(\text{C–C}) - \Delta E_{\text{st}} - E_{\text{al}} + E_{\text{h}}$$

where ΔE_{st} is now the difference in strain energy between BCH and the transition state and E_{h} is the activation energy for a 1,2-hydrogen shift which is assigned the value of 10.8 kcal/mol.[2a] For the two pathways

$$E_{\text{a}}(\mathbf{6{,}1}) = 78.7 - (33.5 - 6.9) - 12.6 + 10.7 = 50.2 \text{ kcal/mol}$$

$$E_{\text{a}}(\mathbf{9}) = 80.8 - (33.5 - 8.6) - 12.6 + 10.7 = 54.0 \text{ kcal/mol}$$

The estimate for the cyclohexadienes has been made previously by Benson and O'Neal.[2a] The estimated activation energy agrees exactly with the observed value of 50.2 kcal/mol.[8] It is assumed for this calculation that the transition states leading to both cyclohexadiene isomers have the same thermochemistry. The extra strain energy of 5.5 kcal/mol in the transition state compared to the biradical is attributed to the energy required to make the ring planar during the hydrogen migration. A similar effect was found in the formation of cyclopentene from bicyclo[2.1.0]pentane.[2a] The value of this extra strain energy in the formation of the methylcyclopentadiene isomer is unknown. A value of 2.8 kcal/mol has been assigned for the following reasons. The planarity requirement should not be so great as for the 1,2 shift on the ring itself. On the other hand, if no extra strain is assumed, the rate of methylcyclopentadiene formation is such that the products should have been observed at 600°K (see below). The value of 2.8 kcal/mol was taken as a value between 0 and 5.5 kcal/mol. This value also leads to an activation energy difference for the two pathways which is equal to the difference observed in the bicyclo[3.1.0]hexane isomerization to cyclohexene and 1-methylcyclopentene.[18]

For the A factor estimates

$$\Delta S^{\ddagger}(\text{est}) = \Delta S^\circ(300^\circ) + \langle \Delta C_{\text{p}}^\circ \rangle \ln \frac{T_{\text{m}}}{300} - S^\circ_{\text{rc}}$$

$$\Delta S^{\ddagger}(\mathbf{6{,}1},\ 600^\circ\text{K}) = 0.1 + 1.5 - 0.6 = 1.0 \text{ gibb/mol}$$

$$\Delta S^{\ddagger}(\mathbf{9},\ 600^\circ\text{K}) = 0 + 0.6 - 0.6 = 0 \text{ gibb/mol}$$

Since both cyclohexadiene isomers are being formed, the rpd is 2 and $A(\mathbf{6{,}1}, \text{est}) = 10^{14.2}$ as was estimated previously.[2a] The experimental value is $10^{14.5}$. For the methylcyclopentadiene $A(\mathbf{9}, \text{est}) = 10^{13.6}$. The resulting expressions for product formation are thus

$$k_{\text{est}}(\mathbf{6{,}1}) = 10^{14.2-(50.2/\theta)}$$

$$k_{\text{est}}(\mathbf{9}) = 10^{13.6-(54.1/\theta)}$$

Using these rate expressions at 600°K the ratio of cyclohexadiene to methylcyclopentadiene would be 100:1. A 1% product could easily have missed detection in the pyrolysis work. On the other hand if the activation energy for methylcyclopentadiene formation was lowered by 2.6 kcal/mol, the above ratio would become 10:1, and the product should have been observed.

The rate expression for formation of the hexatriene isomers is estimated as follows.

$$E_{\text{a}}(\mathbf{2}) = 80.8 - (33.5 - 8.6) - 12.6 - 14 = 57.3 \text{ kcal/mol}$$

$$\Delta S^{\ddagger}(\mathbf{2},\ 600^\circ\text{K}) = 6.0 + 1.8 - 3.2 = 4.5 \text{ gibbs/mol}$$

The value of 14 kcal/mol chosen for the activation energy for the bond rupture is taken as halfway between the value of 6 kcal/mol for formation of two olefins from a 1,4 diradical in cyclobutanes and the value of 22 kcal/mol observed for the cyclopentadiyl-1,3-biradical where there is a steric inhibition to the developing resonance.[16] This intermediate value seems reasonable because in our system the methylene radical is free to rotate to assume the geometry necessary for the electrons in the fragmenting C–C bond to interact to form the resulting π bond of the triene. The reaction coordinate used in calculating the entropy of activation is an out-of-plane ring vibration with a frequency of 225 cm^{-1}.

The resulting rate expression for *cis*-1,3,5-hexatriene is $k_{(\text{est})}(\mathbf{2}) = 10^{14.6-(57.3/\theta)}$. At 600°K, the estimated ratio of formation of cyclohexadienes to open chain isomers is 160:1. It should be pointed out, however, that even if *cis*-1,3,5-hexatriene were formed, at 600°K it would rapidly isomerize to 1,3-cyclohexadiene[14] and not be observed in the pyrolysis experiment. This observation introduces an interesting possibility. If the activation energy for hexatriene formation was in fact lower than the estimated value by 4 kcal/mol, which is probably not outside the error limits for the estimate, the ratio of cyclohexadienes to hexatriene would be decreased to 6:1. Under these circumstances there would be a significant contribution to the 1,3-cyclohexadiene *via* the hexatriene pathway. The 1,4-cyclohexadiene yield, however, would not be increased because none of this isomer is formed from the subsequent hexatriene isomerization. This mechanism may explain the higher A factor observed in the pyrolysis studies for 1,3-cyclohexadiene formation than for 1,4-cyclohexadiene.[8] The activation energy should also be slightly higher, but this change would be smaller and may not be observed over the small temperature range studied.

Table I gives a summary of the predicted rate equations for the products observed in the chemical activation work. As the temperature is increased the methylcyclopentadiene isomers and hexatrienes should be-

(18) H. M. Frey and R. C. Smith, *Trans. Faraday Soc.*, **58**, 697 (1962).

come relatively more important. The ultimate limit will be roughly the ratios of the A factors. For the rate equations estimated here the ratio of methylcyclopentadienes:cyclohexadiene:hexatrienes would be 1:4:10. As expected, the high energy chemical activation results lie between these limits and those observed at 600°K. Work is in progress to check the estimated Arrhenius parameters by comparing the RRKM predictions with the chemical activation results.[19]

Conclusions

Chemically activated bicyclo[3.1.0]hex-2-ene isomerizes by both exocyclic and endocyclic cyclopropyl bond rupture. It is shown that the high activation energy for exocyclic rupture precludes isomerization by this pathway at temperatures around 170° despite the very large A factor. At higher temperatures, 325°, the expected exocyclic bond rupture product is still not observed because of the high activation entropy associated with the hydrogen migration as well as a slightly higher activation energy. At very high energies, however, the products from both mechanisms are expected as observed in the experiment.

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[19] W. L. Hase, R. L. Johnson, and J. W. Simons, *Int. J. Chem. Kinet.*, **4**, 1 (1972), and references therein.

Gas-Phase Basicities of Amines. Hydrogen Bonding in Proton-Bound Amine Dimers and Proton-Induced Cyclization of α,ω-Diamines

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Abstract: The equilibrium constants for several gas-phase proton transfer reactions were determined as a function of temperature. This allowed the determination of $\Delta G°$, $\Delta H°$, and $\Delta S°$ of the reactions. One group of determinations dealt with the proton transfer $B_1H^+ + B_2 = B_1 + B_2H^+$, where B_1 and B_2 were various alkyl amines, substituted anilines, pyrrole, and other representative compounds. The findings follow trends reported in earlier publications. A second series of experiments dealt with the proton transfer $B_1H^+ + B_3 = B_1 + B_3H^+$, where B_1 indicates alkyl amines and B_3 indicates α,ω-diaminoalkanes. The measured ΔH values showed that the proton affinities of the diamines were very high. The reactions also showed large negative entropy changes. Both of these results are possible only if cyclization with a proton bridge occurs in the diamines. In a third series of experiments, measurement of the equilibria of $B_1H^+ + B_2 = B_1H^+B_2$ led to the enthalpy and entropy changes for these dimerization reactions. The amines involved were ammonia, methylamine, dimethylamine, and trimethylamine. The hydrogen bonds in the symmetric dimers ($B_1 = B_2$) were found not to change much with methyl substitution and were in the $\Delta H \approx 23$ kcal/mol range. Changes of the hydrogen bonds in $B_1H^+B_2$ could be qualitatively explained on the basis of the gas-phase basicities of B_1 and B_2. The hydrogen bond energies of the $B_1H^+B_1$ dimers are compared with those of the proton bridged diamines. This leads to an evaluation of ring strain in the proton-bridged diamines. The ring strain energies and the entropies of cyclization of the diamines were also compared with corresponding values for the cycloalkanes. The proton bridged 1,2-diaminoethane shows large strain energy, as would be expected for a four-membered ring. This means that the N–H⁺–N bond tends to be linear. The ΔS_{cycl} of the diamines generally follow the ΔS_{cycl} of the cycloalkanes, but the correspondence is not complete. The rate constants for the forward and reverse components of the reaction $CH_3NH_3^+ + (CH_3)_2NH = CH_3NH_2 + (CH_3)_2NH_2^+$ were determined.

Measurements of gas-phase proton transfer equilibria (eq 1) were reported earlier.[1] B's were

$$B_1H^+ + B_2 = B_1 + B_2H^+ \qquad (1)$$

nitrogen containing organic bases which were mostly various monoamines. The equilibrium constants K_1 lead to the free energy changes $\Delta G° = -RT \ln K_1$, while van't Hoff plots of the temperature dependence of K_1 allowed evaluation of $\Delta H_1°$ and $\Delta S_1°$. Such measurements are of considerable interest since they permit an understanding of basicity on a molecular level, *i.e.*, without the complex interference of the liquid solvent. The measurements were done with a "high pressure" mass spectrometer.[2] Three other groups[3–5] have also reported independent measurements of gas-

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