was controlled to ±0.5° by circulation of refrigerated methanol through the cell jacket and was measured with a thermocouple placed in the circulating liquid at the cell exit. The desired solution of LDIA or LTBA (2 ml) was equilibrated in the cell, and a solution of **1** or **2** was injected by syringe. Increasing absorbance was followed as a function of time. Rate constants were calculated by least-squares analysis with an integrated first-order rate law. Data points (14–39) were collected over 0.6–4.4 half-lives in various runs, and infinity points were obtained from absorbance either at >6 half-lives or after warming the sample until constant absorbance was observed. By far the greatest source of error in these experiments was temperature control.

Kinetics of Ring Opening of the Keteniminate of 4. Solutions of LDIA in THF in 10-mm Pyrex cells capped with silicone rubber septa were equilibrated at ambient temperature in the cell compartment of the spectrophotometer. The temperature was measured with a thermocouple in the cell compartment. Solutions of **4** in THF were added by syringe to the base solution, and absorbance at 650 or 730 nm was measured. After *ca.* 10 min the absorbance increased linearly with time. Using ϵ 7670 at 650 nm and ϵ 3600 at 730 nm [determined from generation of 2-cyanophenalenyllithium (**12**) from **6** and LDIA], the concentration of **12** (assumed to be the only species responsible for absorbance at ≥650 nm) was determined as a function of time over the first 1–4% reaction, and the initial zero-order rate constants in Table III were calculated.

Low-Temperature Photolyses. Samples of 20 mg of **1** in 20 ml of 0.10 *M* LTBA and 20 mg of **18** in 20 ml of 0.10 *M* lithium *N*-isopropylcyclohexylamide[4] (LICA) in THF were prepared and sealed into Pyrex tubes at −78° and placed in the well of a Pyrex dewar-type condenser, which was cooled with a rapid stream of cold

nitrogen. The temperature was held at <−65° at all times according to a thermometer placed in the condenser well. Condensation of atmospheric moisture on the condenser was prevented by evacuation of the condenser and direction of a stream of dry air on its outer jacket. The light source was a 450-W Hanovia high-pressure Hg lamp in a water-cooled Pyrex immersion well placed 10–15 mm from the condenser. The entire assembly was wrapped in aluminum foil.

Irradiation of an initially pale yellow solution of **1** for 15 min gave a red solution which was hydrolyzed at low temperature. A mixture of nitriles was isolated as described for deuteration experiments. Glpc (column C) of the products showed a 15:85 mixture of **1**: *cis*- and *trans*-α-benzocinnamonitriles (**11**) and a pmr spectrum showed only the same three compounds.

Irradiation of an initially pale yellow solution of **18** for 30 min gave a red solution which was hydrolyzed at low temperature. A pmr spectrum of the crude organic products showed a roughly 1:1 mixture of **18**:methyl *trans*-α-benzylcinnamate.

To determine whether keteniminates and ester enolates were the species undergoing photolyses, identically prepared control solutions were quenched with methanol at −78° and subjected to the same irradiation and isolation conditions. The starting **1** and **18** were recovered unchanged according to glpc (column C) analysis.

Thermal Rearrangements of Bicyclo[3.1.0]hex-2-ene. Studies of Degenerate Rearrangements

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Abstract: The degenerate rearrangement effecting interchange of the C_4 and C_6 positions of bicyclo[3.1.0]hex-2-ene has been examined in the vapor phase under conditions where structural rearrangements to cyclohexadiene are negligible. Thermolyses of bicyclo[3.1.0]hex-2-ene systems bearing deuterium as positional marker have demonstrated that two potentially concerted and orbital symmetry allowed mechanisms involving formal cleavage of an external cyclopropane bond are unimportant paths for the automerization. Studies of the reactivity of bicyclo[3.1.0]hex-2-ene systems bearing deuterium as stereochemical marker have provided detailed information concerning automerization through formal cleavage of the internal cyclopropane bond. The results of these experiments are consistent either with a biradical formalism involving a complex scheme of interconverting intermediates or with the competition of at least three concerted pathways.

For more than a decade the various thermal rearrangements of vinylcyclopropane systems have been subjected to intensive mechanistic scrutiny. Since the elucidation of the prototypal rearrangement of vinylcyclopropane to cyclopentene by Overberger[1] and Vogel,[2] numerous examples of this ring expansion have been investigated.[3] Most have been discussed in

terms of a biradical formalism supported by self-consistent kinetic and thermodynamic data.[3,4]

When the vinylcyclopropane is a compound such as bicyclo[3.1.0]hex-2-ene where the olefinic bond is contained in a five-membered ring fused to the cyclopropane moiety, the possibility for a degenerate rearrangement exists. The operation of this pathway in the parent example was examined by Doering and Grimme[5] where the interconversion of 4,4- and 6,6-dideuteriobicyclo[3.1.0]hex-2-ene was demonstrated. In the limited number of bicyclo[3.1.0]hex-2-ene systems

(1) C. G. Overberger and A. E. Borchert, *J. Amer. Chem. Soc.*, **82**, 1007 (1960).

(2) E. Vogel, R. Palm, and K. H. Ott, *Angew. Chem.*, **72**, 4 (1960).

(3) For reviews of the vinylcyclopropane to cyclopentene rearrangement, including extensive tabulations of kinetic data and activation parameters, see, for example (a) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 148 (1966); (b) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968); (c) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968; (d) M. R. Willcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, **9**, 25 (1972); (e) S. W. Benson and

H. E. O'Neall, "Kinetic Data on Gas Phase Unimolecular Reactions," U. S. Government Printing Office, Washington, D. C., 1970.

(4) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(5) W. von E. Doering and W. Grimme, unpublished results cited in W. von E. Doering and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **2**, 115 (1963).

where the automerization reaction has been studied,[5-10] the results have generally been interpreted in terms of a biradical formalism where the intermediates arise from cleavage of the internal cyclopropane bond. The structure and reactivity of the proposed intermediate have been the concern of recent work which has suggested that hindered rotation[10] or conformational considerations[9] influence the ratio of distinguishable products formed in the thermolyses of bicyclo[3.1.0]hex-2-ene systems bearing stereochemical markers. The distribution of isomers differs significantly from the random or thermodynamically modulated mixture expected if no stereoselectivity were operative.

The present studies of the automerization of bicyclo[3.1.0]hex-2-ene systems perturbed only by the presence of deuteriums as positional labels have assessed the importance of two alternative mechanisms which are potentially concerted and orbital symmetry allowed processes involving the formal cleavage of an external cyclopropane bond. In addition, studies of the degenerate rearrangement of bicyclo[3.1.0]hex-2-ene systems bearing deuteriums as stereochemical markers have examined in detail the stereoselectivity of a mechanistic pathway involving formal cleavage of the internal cyclopropane bond.

Results and Discussion

Alternatives to Internal Cyclopropane Bond Cleavage. Any mechanistic pathway which accomplishes interconversion of 4,4- and 6,6-dideuteriobicyclo[3.1.0]hex-2-ene upon migration of the C_5 center from the C_1 to the C_3 position predicts the permutation of positional markers shown in Scheme I. Note that markers at the

Scheme I
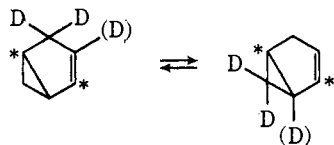
starred positions are immobile and that a planar representation of the structures avoids implications about the relative configurations of the isomers.

An alternative mechanism which also achieves interconversion of 4,4- and 6,6-dideuteriobicyclo[3.1.0]hex-2-ene proposes 5,5-dideuteriobicyclo[2.1.1]hex-2-ene as a fleeting intermediate. Formation and decomposition of the transient are envisaged as concerted and orbital symmetry allowed $_\pi 2_s + _\sigma 2_a$ processes employing the C_1—C_6 and C_2=C_3 bonds in antarafacial and suprafacial senses, respectively.[11,12] Both the disposition of markers and the relative configurations are predicted for the interrelated isomers in Scheme II.

Samples of 3-deuteriobicyclo[3.1.0]hex-2-ene contain-

(6) E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, **85**, 1788 (1963).

(7) H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965).

(8) W. von E. Doering and J. B. Lambert, *Tetrahedron*, **19**, 1989 (1963).

(9) W. von E. Doering and E. Schmidt, *Tetrahedron*, **27**, 2005 (1971).

(10) J. S. Swenton and A. Wexler, *J. Amer. Chem. Soc.*, **93**, 3066 (1971).

(11) Designations of concerted reactions follow the conventions set forth in R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, Germany, 1970. However, use of the term "concerted" in describing a reaction does not imply that the pathway is also orbital symmetry allowed.

(12) W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969).

Scheme II
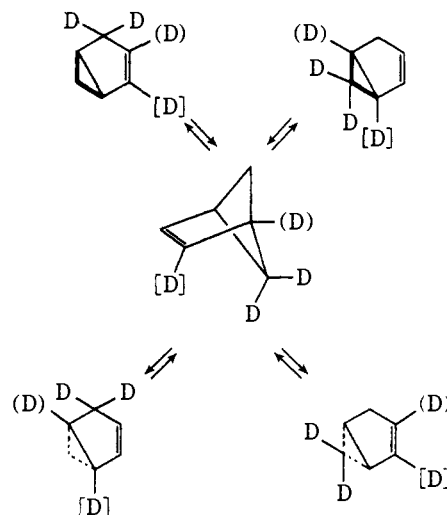
ing 0.875 ± 0.006 deuterium at the C_3 position and none elsewhere were pyrolyzed at 264.0 ± 0.5° and 32–41 Torr in a well seasoned, conventional static reactor for 3.3–5.0 hr. Qualitative examination of each of the pyrolyzed samples by proton magnetic resonance (pmr) spectroscopy revealed signal ratios consistent with predictions of the mechanism involving migration of the C_5 center from the C_1 to the C_3 position. Deuterium appeared equally distributed in the C_1 and C_3 positions without diminution of the signal due to the C_5 proton.

Simultaneous operation of both mechanisms in the thermolysis of 3-deuteriobicyclo[3.1.0]hex-2-ene predicts the interrelationship of isomers shown in Scheme III.

Scheme III
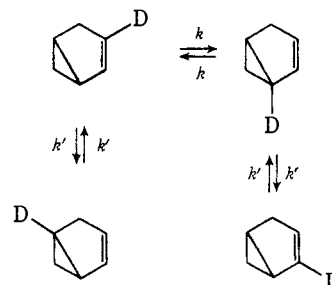
Deuterium originally in the C_3 position appears in the C_2 position in addition to the sites designated in Schemes I and II.

A sample of 3-deuteriobicyclo[3.1.0]hex-2-ene was pyrolyzed for 17.2 hr at 264.5 ± 0.5° and 45 Torr. The deuterium magnetic resonance (dmr) spectrum of 3-deuteriobicyclo[3.1.0]hex-2-ene exhibited a single resonance at 1.88 ppm upfield from $CDCl_3$. The spectrum of the pyrolysate contained this signal and an additional resonance due to the C_1 deuterium at 5.53 ppm upfield from $CDCl_3$. The ratio of the C_1 to C_3 deuterium signals was 0.993 ± 0.009, and at 1.30 ppm upfield from $CDCl_3$ there was no discernible resonance due to deuterium at the C_2 position. A conservative estimate of the limit of detection indicated that the pyrolysate contained less than 3.0 mol % 2-deuteriobicyclo[3.1.0]hex-2-ene.

An approximate computer simulation of the kinetic relationship shown in Scheme III was performed employing an estimation of $k = 2.5 \times 10^{-4}$ sec^{-1} and varying the value of k'. The pertinent results of these calculations are shown in Table I.

Table I. Mole Per Cent 2-Deuteriobicyclo[3.1.0]hex-2-ene in the Pyrolysate Predicted for Various Values of k'

| k', sec^{-1}	Predicted mole per cent 2-deuteriobicyclo[3.1.0]-hex-2-ene
1.25×10^{-7}	0.33
1.25×10^{-6}	3.04
1.25×10^{-5}	16.75

Comparison of the calculated values and experimental limit of the mole per cent 2-deuteriobicyclo[3.1.0]hex-2-ene in the pyrolysate indicates a value of $k' \leqslant 1.25 \times 10^{-6}$ sec^{-1}. Since the estimated rate constant for migration of the C_5 center from the C_1 to the C_3 position is at least 200 times the rate constant associated with the $_\pi 2_s + _\sigma 2_a$ mechanism, this latter process makes a negligible contribution to the automerization of bicyclo[3.1.0]hex-2-ene.

The interconversion of 4,4- and 6,6-dideuteriobicyclo[3.1.0]hex-2-ene is consistent with a third mechanistic pathway which may be classified as a concerted and orbital symmetry allowed $_\sigma 2_s + _\sigma 2_a$ process employing the C_1–C_6 and C_3–C_4 bonds in antarafacial and suprafacial senses, respectively. Scheme IV illustrates the

Scheme IV
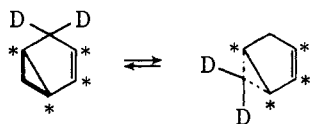
interchange of the C_4 and C_6 positions and concurrent racemization of the molecule. Note that markers at the starred positions are immobile.

The experiment described above does not provide a measure of the importance of the $_\sigma 2_s + _\sigma 2_a$ process in the automerization of bicyclo[3.1.0]hex-2-ene. However, if this mechanism operates, it must do so in conjunction with the pathway involving migration of the C_5 center from the C_1 to the C_3 position. The consequence of this combination of mechanisms is shown in Scheme V for the rearrangement of 2,3,4,4-

Scheme V
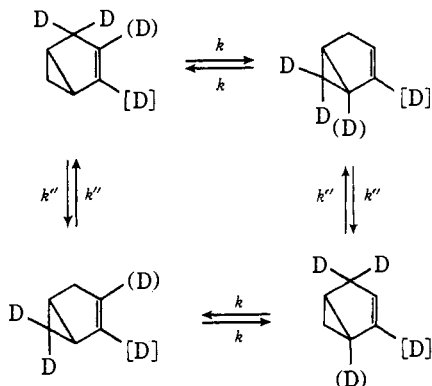
tetradeuteriobicyclo[3.1.0]hex-2-ene. Scheme V predicts that the pmr spectra of samples recovered prior to the establishment of equilibrium will exhibit C_4/C_3 proton ratios exceeding two. If the $_\sigma 2_s + _\sigma 2_a$ process is not operating, this ratio will be exactly two at all times.

Samples of 2,3,4,4-tetradeuteriobicyclo[3.1.0]hex-2-ene with a deuterium content of 0.985 ± 0.001 at the C_3

position and 1.967 ± 0.003 at the C_4 position were pyrolyzed in a well seasoned plug-flow reactor at a nominal temperature of $321.7 \pm 1.0°$. Nitrogen was employed as the carrier gas and the nominal residence time varied from 14.4 ± 0.7 to 47.0 ± 2.3 sec. Examination of the pmr spectra afforded the data shown in Table II.

Table II. Experimentally Determined C_4/C_3 Proton Ratios in the Pyrolysate from 2,3,4,4-Tetradeuteriobicyclo[3.1.0]hex-2-ene

Time, sec	C_4/C_3 proton ratio
14.4 ± 0.7	2.007 ± 0.034
24.0 ± 1.2	1.993 ± 0.044
47.0 ± 2.3	2.002 ± 0.034

An approximate computer simulation of the kinetic relationship shown in Scheme V was performed employing an estimation of $k = 9.8 \times 10^{-3}$ sec^{-1} and varying the value of k''. The pertinent results of these calculations are shown in Table III.

Table III. C_4/C_3 Proton Ratios in the Pyrolysate from 2,3,4,4-Tetradeuteriobicyclo[3.1.0]hex-2-ene Predicted for Various Values of k''

k'', sec^{-1}	C_4/C_3 proton ratio Time, sec		
	14.4	24.0	47.0
1.96×10^{-5}	2.022	2.015	2.009
1.96×10^{-4}	2.050	2.041	2.030
1.96×10^{-3}	2.319	2.288	2.218

Statistical analysis employing a Student's t test[13] demonstrates that the difference between the calculated and experimental values of the C_4/C_3 proton ratio at all residence times is significant at the 0.975 confidence level for values of $k'' \geqslant 1.96 \times 10^{-4}$ sec^{-1}. Since the estimated rate constant for migration of the C_5 center from the C_1 to the C_3 position is at least 50 times the rate constant associated with the $_\sigma 2_s + _\sigma 2_a$ mechanism, this latter process makes a negligible contribution to the automerization of bicyclo[3.1.0]hex-2-ene.
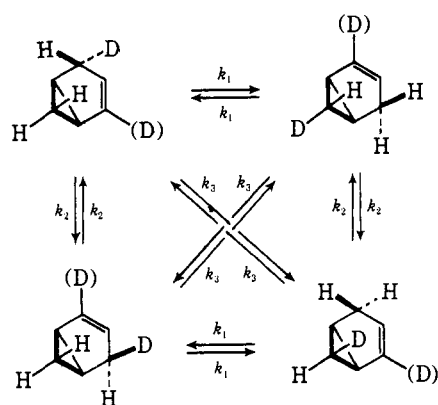
Mechanisms Involving Internal Cyclopropane Bond Cleavage. The total complexity of the automerization reaction proceeding by a mechanism which involves migration of the C_5 center from the C_1 to C_3 position is not revealed by studies of systems containing only positional labels. The interconversion of isomeric bicyclo[3.1.0]hex-2-enes bearing stereochemical markers at the C_4 or C_6 positions is shown in Scheme VI. In general, three distinct rate constants are required to describe the kinetics of this permutation of stereochemical labels and coincident interchange of relative configuration.

If the mechanism involves no intermediate, the interconversion of 2,exo-4- and 2,exo-6-dideuteriobicyclo[3.1.0]hex-2-ene may be described as a $_\sigma 2_s + _\pi 2_s$ process. Similarly, the interconversion of 2,exo-4- and 2,endo-6-dideuteriobicyclo[3.1.0]hex-2-ene is a $_\sigma 2_a + _\pi 2_a$ process and the formation of 2,endo-4-dideuteriobicyclo[3.1.0]hex-2-ene from the same starting

(13) F. L. Wolf, "Elements of Probability and Statistics," McGraw-Hill, New York, N. Y., 1962, pp 268–278.

Table IV. Mole Per Cent Dideuteriobicyclo[3.1.0]hex-2-ene Isomers from the Pyrolysis of 2,exo-4-Dideuteriobicyclo[3.1.0]hex-2-ene

Time, sec	2,exo-4-	2,endo-4-	2,endo-6-	2,exo-6-
14.4 ± 0.7	81.9 ± 1.1	6.7 ± 0.8	1.8 ± 1.6	9.5 ± 1.4
23.8 ± 1.2	68.4 ± 0.8	11.2 ± 1.5	5.6 ± 1.3	14.8 ± 1.2
48.7 ± 2.4	54.4 ± 1.1	15.9 ± 0.5	10.2 ± 1.1	19.6 ± 1.8

Scheme VI

Figure 1. Possible structures of the intermediates postulated in various automerization schemes for bicyclo[3.1.0]hex-2-ene.

isomer involves a disrotatory opening and closing of the cyclopropane ring. The relative rates of these reactions cannot be predicted from simple theory. The complementary paths described as $_\sigma 2_s + {_\pi}2_a$ and $_\pi 2_s + {_\sigma}2_a$ migrations or a conrotatory opening and closing of the cyclopropane ring must be avoided since they lead to a prohibitively strained trans-fused bicyclic system.

If a biradical formalism is invoked to describe the interconversions shown in Scheme VI, the structure and symmetry of the intermediate involved might be depicted by any of the representations in Figure 1. There is evidence[9,10] that the proposed intermediate is best described by species possessing C_s symmetry. If ring flipping is competitive with bond reclosure, this representation requires that the formation of 2,exo-6- from 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene be more rapid than the production of 2,endo-6- or 2,endo-4-dideuteriobicyclo[3.1.0]hex-2-ene. In addition, these latter two isomers must be formed at identical rates. The case of an intermediate possessing C_s symmetry where ring flipping is very rapid with respect to bond reclosure is not kinetically distinguishable from intervention of an intermediate possessing C_{2v} symmetry. In either situation all products in the automerization reaction must be formed at identical rates. A third alternative proposes an intermediate possessing C_1 symmetry in which the internal cyclopropane bond is highly distorted although there is no common nodal plane of the p orbitals at the C_1, C_2, and C_3 centers. If the formally separate processes of ring flipping and migration of the C_5 center both involve transition states possessing C_s symmetry and compete with bond reclosure, then no two of the products in the thermolysis of 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene are necessarily formed at identical rates. However, if sequential ring flipping and C_5 center migration are required to form 2,endo-6-dideuteriobicyclo[3.1.0]hex-2-ene, then this product must be formed most slowly.

Samples of 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene with a deuterium content of 0.137 ± 0.006 and 0.889 ± 0.003 in the endo- and exo-C$_4$ positions, respectively,
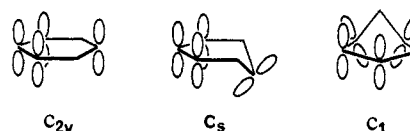
were pyrolyzed in a well seasoned plug-flow reactor at a nominal temperature of 318.3 ± 1.0°. Nitrogen was employed as the carrier gas and the nominal residence time varied from 14.1 ± 0.7 to 48.7 ± 2.4 sec. Examination of the pmr spectra of the recovered material afforded the data shown in Table IV.

An approximate computer simulation of the kinetics was fit to the disappearance or appearance of all four compounds by an iterative least-squares technique. Three rate constants were varied in the minimization execution. A plot of the experimental points[14] and the fit calculated employing rate constant values[15] (cf. Scheme VI) of $k_1 = (8.00 \pm 0.50) \times 10^{-3}$ sec^{-1}, $k_2 = (5.93 \pm 0.32) \times 10^{-3}$ sec^{-1}, and $k_3 = (1.79 \pm 0.39) \times 10^{-3}$ sec^{-1} is shown for the appearance of products in Figure 2.

Samples of (+)-2,4,4-trideuteriobicyclo[3.1.0]hex-2-ene with a deuterium content of 1.922 ± 0.037 in the C$_1$ position and a specific rotation of $[\alpha]^{25.4}$D +8.112 ± 0.037° (c 5.65, isooctane) were pyrolyzed in a well seasoned plug-flow reactor at a nominal temperature of 317.4 ± 1.0°. Nitrogen was employed as the carrier gas and the nominal residence time varied from 13.8 ± 0.7 to 40.7 ± 2.0 sec. Examination of the pmr spectra and measurement of the optical activity of the recovered material afforded the data shown in Tables V and VI.

Table V. Protium Distribution in Pyrolyzed Samples of (+)-2,4,4-Trideuteriobicyclo[3.1.0]hex-2-ene

Time, sec	Endo-C$_6$ position	C$_4$ position
0.0	1.000 ± 0.010	0.078 ± 0.037
13.8 ± 0.7	0.869 ± 0.008	0.300 ± 0.026
24.0 ± 1.2	0.770 ± 0.012	0.466 ± 0.009
40.7 ± 2.0	0.726 ± 0.038	0.628 ± 0.017

Table VI. Optical Rotations in Pyrolyzed Samples of (+)-2,4,4-Trideuteriobicyclo[3.1.0]hex-2-ene

Time, sec	$[\alpha]^{27.1}{}_{365}$	$[\alpha]^{27.1}{}_{436}$
0.0	+35.179 ± 0.065	+19.842 ± 0.072
13.8 ± 0.7	23.521 ± 0.022	13.208 ± 0.043
24.0 ± 1.2	16.026 ± 0.026	8.898 ± 0.022
40.7 ± 2.0	11.296 ± 0.117	6.463 ± 0.048

(14) For graphical clarity, error ellipses are shown for residence time fluctuations of ±1.5 sec and uncertainties of ±1.0 in the determinations of mole per cent.

(15) Rate constants cited were determined from the best fit to the complete data set. A measure of the precision was obtained by independent fitting of the data at each residence time. Quoted error limits are standard deviations of the mean.
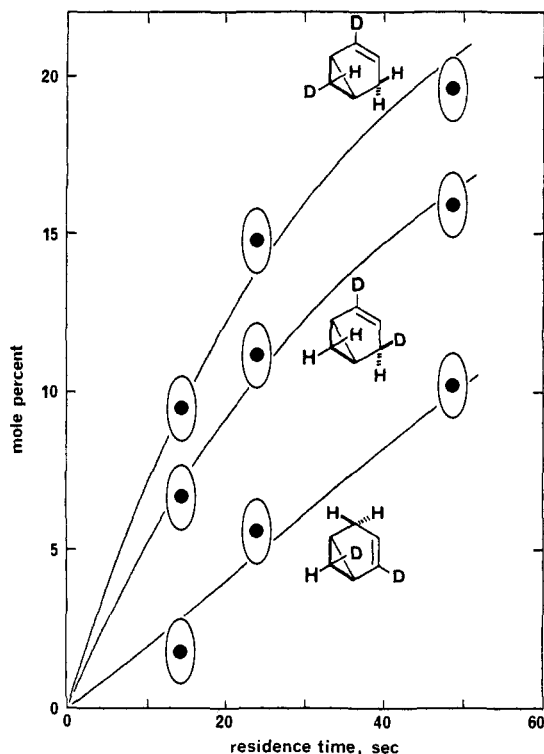
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Figure 2. Appearance of products in the gas phase pyrolysis of 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene at 318.3 ± 1.0°.

A standard kinetic analysis of these data furnished rate constants[16] for the deuterium scrambling process of k_s = (2.09 ± 0.05) × 10^{-2} and (2.13 ± 0.30) × 10^{-2} sec^{-1} determined from appearance of hydrogen at the C_4 position and disappearance of hydrogen at the endo-C_6 position, respectively. A similar treatment provided rate constants for the racemization process of k_r = (2.84 ± 0.23) × 10^{-2} and (2.81 ± 0.32) × 10^{-2} sec^{-1} determined from data measured at 365 and 436 nm, respectively. These results may be compared with values of k_s = (1.96 ± 0.13) × 10^{-2} sec^{-1} and k_r = (2.79 ± 0.12) × 10^{-2} sec^{-1} calculated[17] from the data obtained in the pyrolysis of 2,exo-4-dideuteriobicyclo-[3.1.0]hex-2-ene.

The results of these two independent experiments demonstrate both that 2,exo-6-dideuteriobicyclo[3.1.0]-hex-2-ene is formed most rapidly in the pyrolysis of 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene and that the rates of production of the other two isomers differ substantially. It is found that 2,endo-6-dideuterio-bicyclo[3.1.0]hex-2-ene is formed most slowly. Analysis employing a Student's t test indicates that at each residence time the concentration of this isomer differs from that of all other observable products by an amount that is statistically significant at the 0.975 confidence level. These data are inconsistent with models invoking intermediates possessing C_{2v} or C_s symmetry. Although in this respect they differ from the results of the solution phase automerization of 2-methyl-3,4,4-trideuterio-5-isopropylbicyclo[3.1.0]hex-2-ene at 240° where interconverting species of C_s symmetry were proposed,[9] they are in quantitative agreement with the

data observed in the vapor phase thermolysis of this compound at 485°. For both gas phase automerizations, a biradical formalism where the intermediates possess C_1 symmetry remains a mechanistic possibility. In simplest form this scheme involves four intermediates related to the isomeric dideuteriobicyclo[3.1.0]hex-2-enes by rate constants for ring opening, k_o, and bond reclosure, k_c. Although the simultaneous operation of the two processes is ignored, the intermediates are interrelated by rate constants for ring flipping, k_f, and C_5 center migration, k_m. Solution of the mechanistic scheme simplified by a steady state approximation in all intermediates and comparison with the phenomenological array provides the expression $(k_f + k_m)/k_c$ = 0.36 ± 0.10[18] describing the relationship between the rates of conformational change and of bond reclosure. From the same analysis is derived the expression k_m/k_f = 1.38 ± 0.04 which compares rates of the two types of conformational change.

The results of the pyrolysis of 2,exo-4-dideuterio-bicyclo[3.1.0]hex-2-ene are also consistent with the competition of three concerted pathways. Formation of 2,exo-6- and 2,endo-6-dideuteriobicyclo[3.1.0]hex-2-ene, the fastest and slowest processes, must transpire as orbital symmetry forbidden reactions. The disrotatory ring opening and closing which results in the formation of 2,endo-4-dideuteriobicyclo[3.1.0]hex-2-ene potentially benefits from continuous bonding throughout the reaction course.[9]

It is conceivable that the best representation of the mechanism of the automerization of bicyclo[3.1.0]hex-2-ene involves a combination of components of each of the possibilities outlined above. The simplest such synthesis proposes a competition of the concerted and orbital symmetry allowed process forming 2,endo-4-from 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene through a disrotatory ring opening and closing pathway with a biradical formalism involving intermediates possessing C_s symmetry. Comparison of the phenomenological array and the mechanistic scheme for a biradical formalism requiring two interconverting intermediates reveals the expression k_f'/k_c' = 0.57 ± 0.17 which relates the processes of ring flipping and bond reclosure.

Experimental Section

(16) Rate constants were determined from a linear least-squares analysis of the kinetic plots. The quoted error limits are standard deviations of the slopes.

(17) Inspection of Scheme VI reveals the relationships k_r = $2k_1$ + $2k_2$ and k_s = $2k_1$ + $2k_3$.

(18) Ratios cited were calculated from rate constants determined from the best fit to the complete data set. A measure of the precision was obtained from independent fitting of the data at each residence time. Quoted error limits are standard deviations of the mean.

(19) E. L. Allred, J. Sonnenberg, and S. Winstein, J. Org. Chem., 25, 26 (1960).

(20) S. Winstein and J. Sonnenberg, J. Amer. Chem. Soc., 83, 3235 (1961).

(21) E. LeGoff, J. Org. Chem., 29, 2049 (1964).

(22) E. J. Corey and R. L. Dawson, J. Amer. Chem. Soc., 85, 1782 (1963).

and the solution was stirred at 34 ± 2° for 90 min. The reaction mixture was extracted with four 30-ml portions of methylene chloride, and the combined extracts were washed with 30 ml of brine solution, dried over magnesium sulfate, and filtered. After concentration by distillation employing a 30-cm Podbielniak column, the residue was purified by preparative glpc on a 3.0 m × 7.0 mm 20% Carbowax 20M on Chromosorb W column at 150° giving 3.673 g of exo-2,exo-4-dideuteriobicyclo[3.1.0]hexan-3-one. Analysis of the pmr spectrum[23] indicated deuterium contents of 1.763 ± 0.008[24] and 0.100 ± 0.021 in the exo- and endo-$C_{2(4)}$ positions, respectively.

A 3.673-g (37.5 mmol) sample of exo-2,exo-4-dideuteriobicyclo-[3.1.0]hexan-3-one was reduced with 1.723 g (45.3 mmol) of lithium aluminum hydride according to the procedure of Winstein and Sonnenberg.[20,25] Following work-up, the ether solution of exo-2,exo-4-dideuteriobicyclo[3.1.0]hexan-3-ol was concentrated to 35 ml by distillation employing a 20-cm Vigreux column.

A 250-ml three-necked flask equipped with a stirring bar, serum cap, addition funnel and reflux condenser topped with a gas inlet/outlet system was charged with 1.145 g (47.8 mmol) of sodium hydride and 125 ml of dry ether. The stirred slurry was heated to reflux under a nitrogen atmosphere for the entire course of the reaction. The solution of alcohol from above was added dropwise, and after 3 hr, 3.16 g (41.7 mmol) of carbon disulfide was added slowly by syringe. After an additional 3 hr, 5.92 g (41.7 mmol) of methyl iodide was added slowly by syringe. After an additional 12 hr, water was added and the reaction mixture was washed with five 10-ml portions of water. The ether solution was dried over magnesium sulfate, filtered, and concentrated by distillation employing a 20-cm Vigreux column. Bulb-to-bulb distillation of the residue at 0.005 Torr gave 4.327 g of methyl 3-(exo-2,exo-4-dideuteriobicyclo[3.1.0]hexyl)xanthate[26] as a clear yellow oil.

A 25-ml flask fitted with a short-path still was charged with the xanthate mixture. The material was heated in an oil bath at 190–200°. The pyrolysate was redistilled to give 1.057 g of 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene boiling in the range 72–74°. The overall sequence from bicyclo[3.1.0]hexan-3-one was performed in 24.9% yield.

Final purification was achieved by preparative glpc on a 3.0 m × 4.5 mm 21% β,β'-oxydipropionitrile on Chromosorb P column at 50°. The material was compared with an authentic sample of bicyclo[3.1.0]hex-2-ene prepared by the method of Schneider and Crawford.[27] Examination of the pmr spectrum revealed deuterium contents of 0.804 ± 0.006 in the C_2 position and 0.889 ± 0.003 and 0.137 ± 0.006 in the exo- and endo-C_4 positions, respectively.

Preparation of (+)-2,4,4-Trideuteriobicyclo[3.1.0]hex-2-ene. A 250-ml flask equipped with a stirring bar was charged with 15.140 g (157.8 mmol) of bicyclo[3.1.0]hexan-3-one, 66.6 g (3.33 mol) of 98.0% deuterium oxide, and 60 ml of dioxane. A 1.00-g (7.24 mmol) portion of potassium carbonate was added, and the solution was stirred at 60 ± 2° for 6 hr. The reaction mixture was extracted with five 100-ml portions of ether, and the combined extracts were dried over magnesium sulfate, filtered, and freed of ether by distillation employing a 30-cm Podbielniak column. The residue was added to a 250-ml flask equipped with a stirring bar and containing a solution of 66.6 g (3.33 mol) of 99.8% deuterium oxide and 1.00 g (7.24 mmol) of potassium carbonate. The solution was stirred at 60 ± 2° for 6 hr followed by extraction, drying, and filtration as described above. Concentration by distillation employing a 60-cm spinning band column and bulb-to-bulb distillation

of the residue at 0.005 Torr gave 12.512 g of 2,2,4,4-tetradeuteriobicyclo[3.1.0]hexan-3-one as a 87.2% solution in dioxane.

Half of the sample of ketone prepared above was reduced with lithium aluminum hydride followed by isolation of 2,2,4,4-tetradeuteriobicyclo[3.1.0]hexan-3-ol as previously described. The alcohol was converted to methyl 3-(2,2,4,4-tetradeuteriobicyclo-[3.1.0]hexyl)xanthate which was purified by bulb-to-bulb distillation. Heating of the xanthate mixture as previously described and redistillation of the pyrolysate gave 3.549 g of 2,4,4-trideuteriobicyclo-[3.1.0]hex-2-ene.

A 100-ml 3-necked flask equipped with a stirring bar, serum cap, addition funnel, and reflux condenser topped with a gas inlet/outlet system was charged with 1.625 g (11.9 mmol) of α-pinene having an optical rotation of $\alpha^{23.0}$D −38.1°, 0.165 g (4.36 mmol) of sodium borohydride, and 5 ml of diglyme. The mixture was stirred at 0° under a nitrogen atmosphere for the entire course of the reaction. A solution of 0.845 g (5.95 mmol) of boron trifluoride etherate in 14 ml of diglyme was added dropwise over 15 min. After an additional 6 hr, 1.105 g (11.9 mmol) of 2,4,4-trideuteriobicyclo[3.1.0]hex-2-ene was added slowly by syringe, and the mixture was stirred overnight. The solution was poured into a separatory funnel containing 15 ml of pentane and 80 ml of ice–water. The organic layer was separated, washed with two 15-ml portions of ice–water, dried over molecular sieves, and freed of residue by bulb-to-bulb distillation at 0.005 Torr. Final purification by preparative glpc on a 3.0 m × 4.5 mm 21% β,β'-oxydipropionitrile on Chromosorb P column at 45° gave 0.3636 g of (+)-2,4,4-trideuteriobicyclo[3.1.0]-hex-2-ene. Examination of the pmr spectrum indicated a deuterium content of 1.922 ± 0.037 at the C_4 position, and measurement of the optical activity revealed a specific rotation of $[\alpha]^{25.4}$D +8.112 ± 0.037° (c 5.65, isooctane).[28] The overall sequence from bicyclo-[3.1.0]hexan-3-one was performed in 34.8% yield.

Preparation of 2,3,4,4-Tetradeuteriobicyclo[3.1.0]hex-2-ene. A 3.290-g sample of bicyclo[3.1.0]hexan-3-one was converted to 2,2,4,4-tetradeuteriobicyclo[3.1.0]hexan-3-one employing the exhaustive exchange procedure described above. Reduction with 99.0% lithium aluminum deuteride gave 2,2,3,4,4-pentadeuteriobicyclo[3.1.0]hexan-3-ol which was converted to methyl 3-(2,2,3,4,4-pentadeuteriobicyclo[3.1.0]hexyl)xanthate and purified by bulb-to-bulb distillation as previously described. Heating of the xanthate mixture and redistillation of the pyrolysate gave 0.803 g of 2,3,4,4-tetradeuteriobicyclo[3.1.0]hex-2-ene. The overall sequence from bicyclo[3.1.0]hexan-3-one was performed in 27.9% yield.

Final purification was achieved by preparative glpc on a 4.6 m × 4.5 mm 13% 1,2,3-tri(2-cyanoethoxy)propane on Chromosorb P column at 50°. Examination of the pmr spectrum indicated deuterium contents of 0.985 ± 0.001 and 1.967 ± 0.003 in the C_3 and C_4 positions, respectively.

Preparation of 3-Deuteriobicyclo[3.1.0]hex-2-ene. A 4.023-g sample[29] of bicyclo[3.1.0]hexan-3-one was reduced with 99.0% lithium aluminum deuteride, and the 3-deuteriobicyclo[3.1.0]hexan-3-ol was converted to methyl 3-(3-deuteriobicyclo[3.1.0]hexyl)-xanthate and purified by bulb-to-bulb distillation using techniques similar to those described above. Heating of the xanthate and redistillation of the pyrolysate gave 2.077 g of 3-deuteriobicyclo-[3.1.0]hex-2-ene. The overall sequence from bicyclo[3.1.0]hexan-3-one was performed in 61.9% yield.

Final purification was achieved by preparative glpc on a 3.0 m × 4.5 mm 21% β,β'-oxydipropionitrile on Chromosorb P column at 50°. Examination of the pmr spectrum revealed a deuterium content of 0.874 ± 0.006 at the C_3 position.

Pyrolysis of 2,exo-4-Dideuteriobicyclo[3.1.0]hex-2-ene. The 50-ml reaction zone of the pyrolysis apparatus was a 10-cm section of 30-mm Pyrex tubing butted to inlet and outlet tubes of 11-mm Pyrex tubing. A 7-mm Pyrex tube serving as a concentric thermocouple well ran the entire length of the apparatus permitting measurement of temperature throughout the reactor zone and minimizing dead space in the inlet and outlet tubes. The pyrolysis apparatus was centered in a 30 cm × 33 mm tube furnace so that temperature was constant to ±1.0° across the reaction zone. Temperature was controlled with a Variac and measured using a chromel–alumel

(23) All nmr spectra were run on a Varian XL-100-12 nmr spectrometer. Pmr spectra were of samples in deuteriochloroform solution. The ratios of signals in the spectra of deuterated samples were corrected by comparison with identical measurements of perprotiocompounds.

(24) Unless otherwise specified, the error limits quoted for values algebraically derived from nmr data are standard deviations of the mean. These limits were calculated from the expression $\sigma_m = (\Sigma_{i=1}^{n}(x_i - \bar{x})^2/(n - 1)n')^{1/2}$, where n is the total number of integrations and n' is the number of independent measurements of the spectrum. Since correction factors for nonintegral integration of the protons of interest and for imperfect deuterium labeling were usually known with relatively high precision, propagation of error analyses were generally not performed.

(25) S. Winstein and J. Sonnenberg, J. Amer. Chem. Soc., 83, 3244 (1961).

(26) P. K. Freeman, M. F. Grostic, and F. S. Raymond, J. Org. Chem., 30, 771 (1965).

(27) M. P. Schneider and R. J. Crawford, Can. J. Chem., 48, 628 (1970).

(28) All optical rotations were measured on a Perkin-Elmer 141 polarimeter. Determinations were performed in a temperature-controlled microcell having a path length of 1.0 dm. Quoted error limits are standard deviations of the mean of multiple measurements on a single sample.

(29) The bicyclo[3.1.0]hexan-3-one employed on the single occasion this sequence was performed was contaminated with 12.0 ± 0.2% of the corresponding alcohol.

thermocouple. Dry nitrogen was employed as the carrier gas and the flow rate was regulated by means of a needle valve. The flow rate was measured with a soap bubble flowmeter at room temperature and corrected to the temperature of the reaction zone.

The pyrolysis tube was washed with 15% ammonium hydroxide and air dried. Conditioning was achieved by pyrolysis of numerous samples of bicyclo[3.1.0]hex-2-ene under the conditions of the experiment. In a typical experiment, a 0.020-ml sample of 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene was introduced into the system through a serum cap. The pyrolysate was condensed in a trap cooled in liquid nitrogen and transferred to a storage ampoule using standard vacuum-line techniques. The nominal residence time was varied from 14.1 ± 0.7[30] to 48.7 ± 2.4 sec at a temperature of 318.3 ±1.0°.[31] In all cases, the recovery of material was close to quantitative.

Three independent measurements of the pmr spectra of each of the recovered pyrolysates were made with careful integration of the signals due to protons in the endo-C_6, exo-C_6, endo-C_4, exo-C_4, and C_3 positions at δ −0.18, 0.80, 1.56, 1.76, and 5.38, respectively. Integration of the resonance due to the olefinic hydrogen served as a constant one-proton standard. During each series of independent measurements, the spectra of bicyclo[3.1.0]hex-2-ene and of unpyrolyzed 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene were also examined. Measurements on the perprotio compound enabled correction for nonintegral integration of the various protons in the molecule, while those on the unreacted starting material permitted allowance for imperfect deuterium labeling. These data were employed in straightforward calculations utilizing a Varian 620/i laboratory computer system to determine mole percentages of 2,exo-4-, 2,endo-4-, 2,exo-6-, and 2,endo-6-dideuteriobicyclo[3.1.0]hex-2-ene in the pyrolysate. These values were compared with an approximate computer simulation of the kinetic scheme, and the best fit of rate constants was obtained using an iterative least-squares technique.

Pyrolysis of (+)-2,4,4-Trideuteriobicyclo[3.1.0]hex-2-ene. In a typical experiment, a sequence of three 0.020-ml samples of (+)-2,4,4-trideuteriobicyclo[3.1.0]hex-2-ene was heated during a nominal residence time varying from 13.8 ± 0.7 to 40.7 ± 2.0 sec at a temperature of 317.4 ± 1.0°.

Approximately 0.030-ml portions of the pyrolysates and unreacted (+)-2,4,4-trideuteriobicyclo[3.1.0]hex-2-ene were diluted to 1.0 ml with isooctane. The specific rotation of each of the samples of bicyclic olefin was determined at 436 and 365 nm. Rate constants for the loss of optical activity were determined using the normal kinetic analysis applicable to racemization processes.[32]

Three independent measurements of the pmr spectra of the remainder of each of the recovered pyrolysates were made with careful multiple integration of the signals due to the protons in the exo-C_6, C_4, and C_3 positions. Integration of the resonance due to the olefinic hydrogen served as a constant one-proton standard. During each series of independent measurements, the spectra of bicyclo[3.1.0]hex-2-ene and of unreacted (+)-2,4,4-trideuteriobicyclo[3.1.0]hex-2-ene were also examined. Rate constants for the scrambling of deuterium were determined using the norml kinetic analysis for processes involving an approach to equilibrium.[32]

Pyrolysis of 2,3,4,4-Tetradeuteriobicyclo[3.1.0]hex-2-ene. In a typical experiment, a sequence of three 0.020-ml samples of 2,3,4,4-tetradeuteriobicyclo[3.1.0]hex-2-ene was heated during a nominal

residence time varying from 14.4 ± 0.7 to 47.0 ± 2.4 sec at a temperature of 321.9 ± 1.0°.

Three independent measurements of the pmr spectra of each of the recovered pyrolysates were made with careful multiple integrations of the signals due to the protons in the C_3 and C_4 positions. During each series of independent measurements, the spectrum of bicyclo[3.1.0]hex-2-ene was measured to enable correction for nonintegral integration of the protons of interest. The C_4/C_3 proton ratios were compared with those calculated using an approximate computer simulation of the kinetic scheme to delimit the role of the proposed $\sigma 2_s + \sigma 2_a$ pathway.

Pyrolysis of 3-Deuteriobicyclo[3.1.0]hex-2-ene. The 300-ml reaction vessel was a Pyrex round-bottomed flask attached to a conventional vacuum line with a section of 9-mm Pyrex tubing. Extending from near the connecting stopcock to the center of the reaction flask was a concentric section of 5-mm Pyrex tubing serving as a thermocouple well and minimizing dead space. The entire apparatus was encased in an aluminum block surrounded by insulation of diatomaceous earth. Temperature was regulated by cartridge heaters activated by a precision proportional controller and was measured using a chromel–alumel thermocouple. Conditioning was achieved by pyrolysis of numerous samples of bicyclo-[3.1.0]hex-2-ene under the conditions of the experiment. A sample of 3-deuteriobicyclo[3.1.0]hex-2-ene was vaporized into the vacuum system, and a pressure of 45 Torr was isolated in the reaction vessel. The sample was pyrolyzed for 17.2 hr at 264.5 ± 0.5°, recovered from the reactor, and condensed in a storage ampoule using standard vacuum-line techniques. Examination of the dmr spectrum revealed no discernible deuterium at the C_2 position. An estimation of the lower limit of detection was compared with calculations using an approximate computer simulation of the kinetic scheme to delimit the role of the $\pi 2_s + \sigma 2_a$ pathway.

Computer Simulation of Complex Kinetic Schemes. To estimate the values of experimental quantities expected for simultaneous operation of a biradical formalism and either the $\sigma 2_s + \sigma 2_a$ or the $\pi 2_s + \sigma 2_a$ processes, approximate computer simulations of the appropriate kinetic schemes were undertaken. In general, the differential equations describing the behavior of each component were obtained, and values of the initial concentrations and an estimate of the rate constant[33] for the process involving migration of C_5 center from the C_1 to C_3 position were supplied. With various values of the rate constant for the competing concerted process, the concentrations of each component at experimental times were obtained employing the Euler–Cauchy method of numerical integration.[34] Computations were performed with a Varian 620/i laboratory computer system.

To fit rate constants of the experimental results obtained in the automerization reaction of 2,exo-4-dideuteriobicyclo[3.1.0]hex-2-ene, a similar procedure was used. Rate constants for each of the interconversions were estimated, and the sum of the squares of the differences between the calculated and experimental concentrations of each of the components at each experimental time was determined. Minimization of this function was achieved by independent variation of the three rate constants.

(30) The error limits for the residence times in all plug-flow pyrolyses have been uniformly quoted as ±5.0%. Experience has shown that this is a reasonable range of values for the fairly reproducible fluctuation during the pyrolysis of a 0.020-ml sample.

(31) Error limits quoted for pyrolysis temperatures are estimated ranges during an experiment. For plug-flow pyrolyses this value subsumes fluctuations from run to run in an experiment, temperature gradients along the reaction zone, and deviations at the center of the reactor during a given run.

(32) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 186.

(33) Differential secondary deuterium isotope effects have been neglected in all kinetic schemes. In experiments where such effects might have been observed this approximation appears justified within the precision of the data.

(34) E. Kreyszig, "Advanced Engineering Mathematics," Wiley, New York, N. Y., 1962, pp 91–94.