

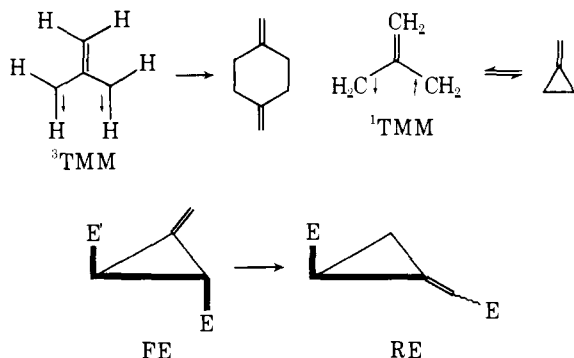
Thermal Bridgehead Double Inversion of the 6-Methylene- and 6-Ethylidene-2-methylbicyclo[3.1.0]hexanes and Related Materials. Rotational Kinetic Deuterium Isotope Effects and the Mechanism of the Thermal Interconversion of *cis*- and *trans*-2,3-Dimethylmethylenecyclopropanes via Orthogonal and Planar Trimethylenemethane Singlet Biradicals

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Contribution No. 3019 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. Received November 19, 1976

Abstract: *endo*- and *exo*-2-methyl-6-methylenebicyclo[3.1.0]hexane (N and X) interconverted at 164 °C at a rate comparable to that for *cis* to *trans* isomerization of the 2,3-dimethylmethylenecyclopropanes (C and T) allowing the possibility that the planar trimethylenemethane singlet is responsible for the racemization observed with optically active T. Pyrolysis of the four 2-methyl-6-ethylidenebicyclo[3.1.0]hexanes revealed an average of 8% preservation of the *exo* ethylidene stereochemistry in the bridgehead double inversion reaction. The kinetic deuterium isotope effect on the interconversion of *endo*- and *exo*-6,2-methyl-6-dideuteriomethylenebicyclo[3.1.0]hexanes, $k_{H_2}/k_{D_2} = 1.08 \pm 0.02$, suggests that *exo* methylene rotation occurs after rate-determining formation of a planar trimethylenemethane biradical since *exo* methylene rotation in the formation of *anti*- and *syn*-2-methylethylidenecyclopropane from *trans*-2,3-dimethyldideuteriomethylenecyclopropane has an isotope effect of 1.31 ± 0.04 . Detailed mechanisms for the stereochemical and kinetic data from pyrolysis of T and C which involve mainly orthogonal and, to a lesser extent, planar or bisorthogonal trimethylenemethane biradicals are presented. The origin and magnitude of rotational kinetic isotope effects in these interconversions is discussed.

Trimethylenemethane (TMM), a cross-conjugated π biradical, has been the object of experimental and theoretical study for two decades. The triplet appears to be the ground state, and it is planar on the basis of ESR measurements.¹ Reactions of triplet TMM consist of dimerization,^{1,2} trapping with little stereospecificity,³ and possibly ring closure to methylenecyclopropane.⁴ On the other hand, methylenecyclopropanes undergo a thermal self-interconversion without formation of dimers suggesting intermediacy of singlet trimethylenemethane.⁵ Major concerns about singlet TMM involve its geometry—the relative energies of planar, orthogonal, and bisorthogonal forms—and the energetics of closure of singlet TMM to methylenecyclopropane. The facts heretofore obtained in partial answer to the first question are that optically active Feist's ester, FE, gave optically active rearranged ester, RE,^{5a} subsequently shown to be substantially inverted,⁶ suggesting intermediacy of orthogonal TMM biradicals or a concerted 1,3-sigmatropic shift.



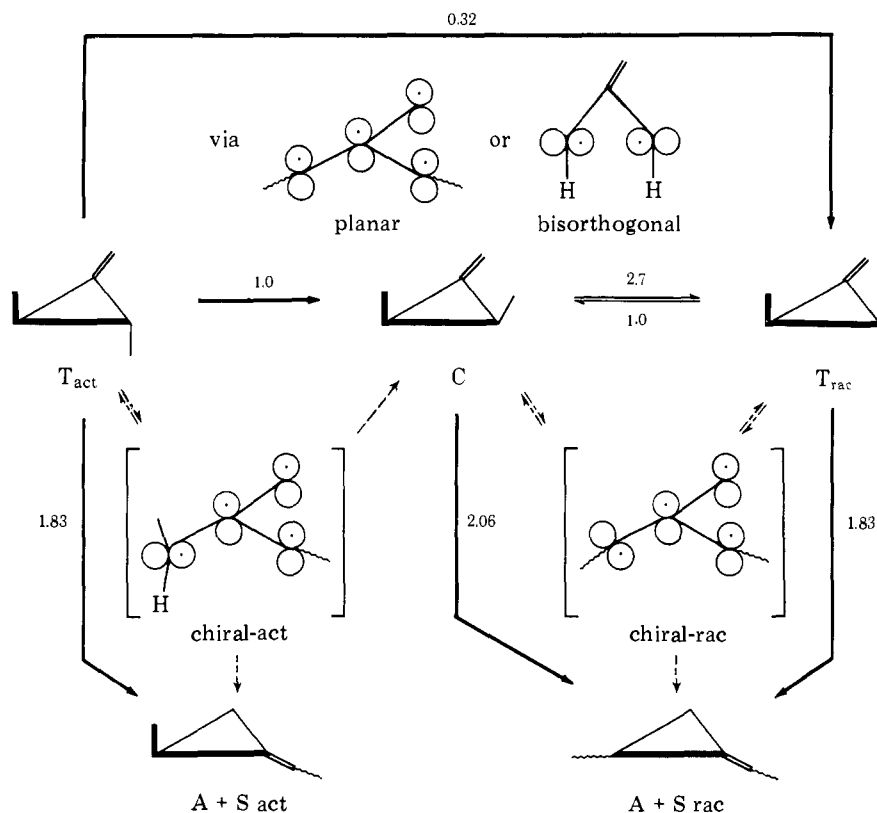
Prior to establishment of this stereo pathway,⁶ it was found that optically active *trans*-2,3-dimethylmethylenecyclopropane (T) gave both *syn*- and *anti*-2-methyl-1-ethylidenecyclopropane (S and A), with opposite optical rotation to that of T,^{5c}

subsequently found^{5d} to represent inversion, at least in the *anti* product. T also gave its *cis* isomer, C, roughly half as fast, while C gave T 1.5 times faster than it gave A + S. Moreover, T racemized during the reaction at a rate faster than it could have been reproduced from C or S or A. Integration of the differential equations for the four-component scheme T_{act} , T_{rac} , C, and A + S, with T_{rac} and A + S being formed irreversibly, revealed that 10% of the detectable ring-opening events of T_{act} proceeded via some achiral species to give T_{rac} . These data were accommodated by a mechanistic scheme involving orthogonal TMM singlets which were responsible for inversion in the allylic shift and geometric isomerization of starting T and C; the racemization of T was accommodated by a planar TMM species or a bisorthogonal form.

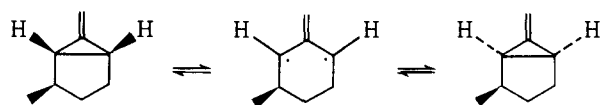
The proposition that an orthogonal TMM biradical is responsible for the allylic rearrangement and not a separate orbital symmetry controlled 1,3-sigmatropic shift with inversion at the migrating carbon was confirmed by Doering⁷ in an examination of 3-methyl-2-cyanoethylidenecyclopropane interconversions.

Theoreticians have calculated the energy gap between the planar and the orthogonal singlet TMM to be 26,⁸ 52,⁹ 2.7,¹⁰ and 6.2¹¹ kcal/mol, with the orthogonal form being more stable. In an attempt to determine experimentally whether or not the planar form was accessible in the MCP interconversions, energetics of formation of a planar form—or at least one in which the three cyclopropane carbons would be forced to have their p orbitals coplanar in the TMM species—was examined. 6-Methylenebicyclo[3.1.0]hexane appeared to be a reasonable candidate for such a study, and *exo*-*endo* isomerization of the 2-methyl derivative would be a convenient probe for the bridgehead double inversion.

While this work was in progress Roth reported that one optically active diastereomer of 3-methyl-6-ethylidenecyclo[3.1.0]hexane gave the other diastereomer with 9% of retention of stereochemistry of the *exo* ethylidene group.¹² This



was interpreted to indicate two separate pathways, with the higher energy one (by roughly 2 kcal/mol) involving a planar



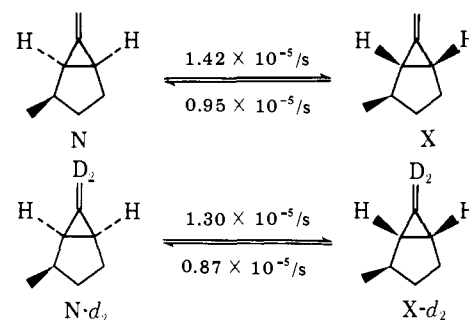
TMM species while the lower energy one involves an exo-ethylidene-rotated orthogonal TMM species. We here report our results, which are consistent with Roth's, and the substantial kinetic isotope effects due to the exo methylene rotation in the pyrolyses of T and C as well as the relatively small kinetic isotope effect in the pyrolysis of 2-methyl-6-dideuteriomethylenebicyclo[3.1.0]hexane. We also report the effect of dialkyl substitution on the exo methylene in the bicyclic system as well as a refined set of rate constants for the interconversions of T_{act} , C, T_{rac} , and A plus S which allows consideration of the mechanistic alternatives in the methylenecyclopropane thermal self-interconversions.

Results

6-Methylenebicyclo[3.1.0]hexane Interconversion. Preparation of a mixture of *endo*- and *exo*-2-methyl-6-methylenebicyclo[3.1.0]hexane (N and X, respectively) was achieved by the low-temperature coupling reaction of the dibromocarbene adducts of 3-methylcyclopentene with methyl iodide induced by butyllithium at -95°C followed by potassium *tert*-butoxide elimination in Me_2SO .¹³ The two isomers were separated by preparative VPC and characterized by NMR and equilibration studies. The major product was the *endo* isomer as deduced from the higher field methyl proton resonance (δ 0.96 vs. 1.02) and the equilibrium constant at 163.94°C : $1.49 = \text{X}/\text{N}$. The rate of approach to equilibrium at this temperature was $2.34 \pm 0.02 \times 10^{-5}/\text{s}$ while that of the 6-dideuteriomethylene material X- d_2 and N- d_2 was $2.17 \pm 0.03 \times 10^{-5}/\text{s}$. Therefore $k_{\text{H}_2}/k_{\text{D}_2} = 1.08 \pm 0.02$.

Interconversion of the 2-Methyl-6-ethylidenebicyclo[3.1.0]hexanes. *endo-syn*, *endo-anti*-, *exo-syn*-, and *exo-anti*-2-

Chart I. Rate Constants ($\pm 1\%$) for Interconversion of N and X, and N- d_2 and X- d_2 at 163.94°C .



methyl-6-ethylidenebicyclo[3.1.0]hexane (NS, NA, XS, and XA, respectively) were prepared by the method of Nozaki,¹³ and separated and identified by the higher field C_2 methyl in NS and NA relative to that in XS and XA, the absence of a high-field proton (presumably the C_1 H) in NA and NS, the higher field C_2 methyl in NS relative to that in NA, the higher field C_2 methyl in XS vs. XA, and the higher field C_2 proton resonance in XS relative to that in XA, and that in NS vs. NA (Table I). Correlation with the resonances of N and X as well as the equilibrium concentrations materially assisted assignment of the *endo* and *exo* stereochemistry.

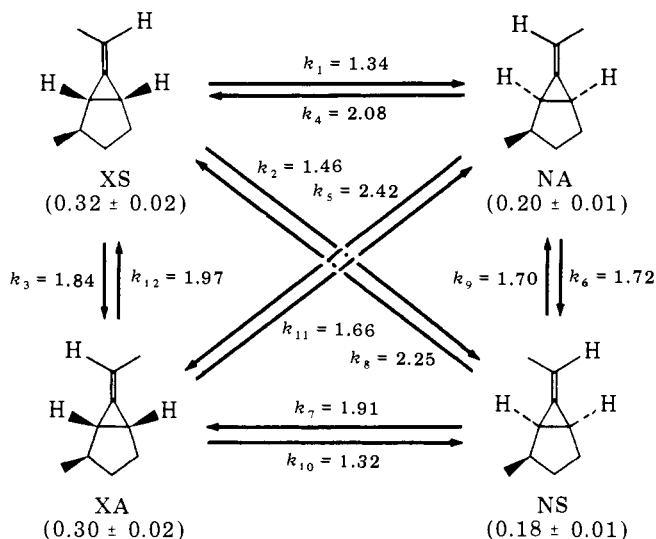
Pyrolysis of each of these isomers at 187.2°C for 10 800 s in immediate succession with multiple analyses of the starting and pyrolysate mole fractions gave the data reported in Table II. The precision with which the mole fraction of formation of each of the other three isomers from each starting material is determined is of the order of ± 0.003 to ± 0.005 (± 2 –4%) once the precision of the analysis of the starting material and pyrolysate is considered with the worst precision being in the amount of XA from XS and vice versa.

In order to determine rate constants, numerical integration of the differential equations appropriate to an array of four interconverting species (Chart II) was performed assuming values for the 12 rate constants. One set of rate constants that

Table I. Relevant NMR Shifts in the 6-Methylene- and 6-Ethylidene-2-methylbicyclohexanes^{a,b}

Compd	Vinyl H	C ₂ H	Allyl Me	C ₂ Me	C ₁ H
N	5.25	2.16		0.96	>1.1
X	5.35	2.30		1.02	0.80
XS	5.67	2.18	1.73	0.98	0.75
XA	5.68	2.23	1.75	1.01	0.75
NA	5.56	2.15	1.69	0.93	>1.0
NS	5.58	2.08	1.69	0.91	>1.0

^a At 220 MHz in carbon tetrachloride in parts per million downfield from Me₄Si. ^b Remaining resonances between δ 1 and 1.9 could not be assigned.

Chart II. First-Order Rate Constants for Interconversions of the Four 2-Methyl-6-ethylidenebicyclo[3.1.0]hexanes (in Units of 10⁻⁵/s)^a

^a The experimental equilibrium fractions are shown in parentheses. The experimental fractions of isomers and calculated fractions from the rate constants are in Table II.

provided an exact fit (within 0.0003 average deviation of the average values of the experimental mole fraction) correctly was assessed by a referee as not satisfying the constraints of microscopic reversibility, in particular, that $k_1k_6k_7k_{12}$ must equal $k_3k_{10}k_9k_4$.¹⁴ Consideration of the thermodynamic constraints on the ratio of rate constants relating any three of the four components of Chart II requires that

$$\begin{aligned} k_1k_6k_8 &= k_2k_4k_9 \\ k_6k_7k_{11} &= k_5k_9k_{10} \\ k_2k_7k_{12} &= k_3k_8k_{10} \\ k_1k_5k_{12} &= k_3k_4k_{11} \end{aligned}$$

and combination of these requires that indeed $k_1k_6k_7k_{12} = k_3k_{10}k_9k_4$ but, in addition, that $k_1k_5k_8k_{10} = k_2k_4k_7k_{11}$ and $k_3k_6k_8k_{11} = k_2k_5k_9k_{12}$. Thus three independent relationships must be satisfied in a completely interconverting four-component scheme. However, for purposes of selecting rate constants, the four relationships among triads of the four components are much more convenient to use and this leads to a new set of rate constants shown in Chart II which not only satisfies the three fundamental relationships but reproduces the experimental data within the precision limits. Just how accurate these rate constants are is very difficult to determine since there is no analytical expression relating experimental concentrations and the rate constants; however, considering that the experimental data are reproduced only at the upper and lower extreme limits of precision in most cases owing to

Table II. Fractions of XS, NA, NS, and XA after Pyrolysis of Each at 187.2 °C for 10 800 s

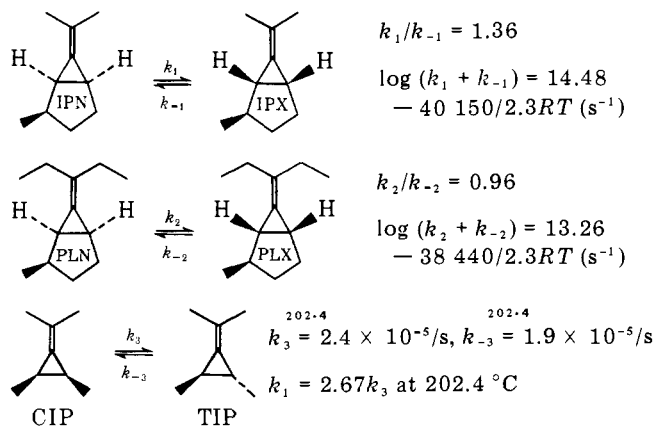
		XS	NA	NS	XA
XS	Anal. ^a	1.0	0.000	0.000	0.000
	Pyrolysis ^b	0.6436 ± 0.004	0.1051 ± 0.002	0.1115 ± 0.002	0.1399 ± 0.005
	Calcd ^c	0.6438	0.1028	0.1093	0.1440
NA	Anal. ^a	0.0159 ± 0.0025	0.8290 ± 0.0005	0.1440 ± 0.003	0.0114 ± 0.005
	Pyrolysis ^b	0.1666 ± 0.0025	0.4692 ± 0.001	0.1874 ± 0.003	0.1768 ± 0.0007
	Calcd ^c	0.1687	0.4726	0.1848	0.1741
NS	Anal. ^a	0.0094 ± 0.0005	0.1724 ± 0.0035	0.8040 ± 0.002	0.0142 ± 0.002
	Pyrolysis ^b	0.1682 ± 0.002	0.1913 ± 0.002	0.4787 ± 0.001	0.1618 ± 0.001
	Calcd ^c	0.1712	0.1935	0.4762	0.1591
XA	Anal. ^a	0.000	0.0225 ± 0.0005	0.0295 ± 0.002	0.9473 ± 0.002
	Pyrolysis ^b	0.1589 ± 0.005	0.1257 ± 0.001	0.1152 ± 0.003	0.6001 ± 0.007
	Calcd ^c	0.1545	0.1282	0.1164	0.6002

^a Analysis of starting material. ^b Analysis after 10 800 s pyrolysis. ^c Calculated fraction from rate constants of Chart II.

the constraints of the microscopic reversibility conditions, the rate constants cannot be in error more than 1% or else the thermodynamic constraints will be violated or the calculated concentrations will broach the precision limits. Thus, the microscopic reversibility conditions provide constraints on the rate constants which substantially lower the error in the rate constants.

The rate constant ratios k_1/k_2 , k_5/k_4 , k_8/k_7 , and k_{11}/k_{10} indicate the extent of preservation of stereochemistry of the exo methylene group in the exo to endo isomerizations, and these are 1.09, 1.16, 1.18, and 1.26, respectively. Thus the average percent retention is 54% and the average percent of inversion is 46%.

Interconversion of the 2-Methyl-6-dialkylmethylenebicyclo[3.1.0]hexane. In order to gauge the effect of alkyl exo methylene substitution on the bridgehead double inversion of the 6-methylenebicyclo[3.1.0]hexane, the 6-isopropylidene-, the 6-(2'-butylidene)-, and the 6-(3'-pentylidene)-2-methylbicyclo[3.1.0]hexanes (IP, BL, and PL, respectively) were prepared by the method of Newman,¹⁵ then separated and pyrolyzed. The endo-exo isomerizations of IP and PL were first order, giving $\log(k_1 + k_{-1})\text{IP} = 14.48 - 40\,151/RT$ and $\log(k_2 + k_{-2})\text{PL} = 13.26 - 38\,440/2.3RT$. At 202.4 °C the rate ratio of IP vs. PL was 2.74; at 178.8 °C this rate ratio was 2.46.

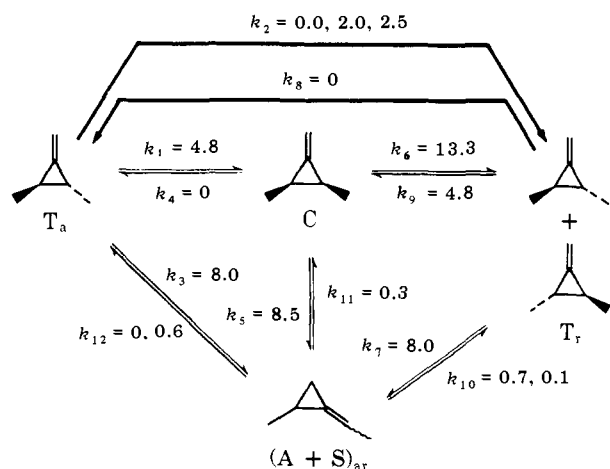


The rate of approach to equilibrium by bridgehead double inversion of IP was 2.7 times that for geometric isomerization

Table IV. Experimental^a and Calculated^b Fractions of Products from Pyrolysis of T_{act} at 152.0 °C

Time	T _{act}	C	T _{rac}	A + S
T _{act} 8430 s Exptl	0.889 ± 0.01	0.034 ± 0.01	0.0 ± 0.01	0.076 ± 0.01
k ₂ = 0, k ₁₀ = 0.7, k ₁₂ = 0	0.897	0.035	0.002	0.065
k ₂ = 2.0, k ₁₀ = 0.7, k ₁₂ = 0	0.883	0.035	0.017	0.065
k ₂ = 2.5, k ₁₀ = 0.7, k ₁₂ = 0	0.878	0.035	0.021	0.065
k ₂ = 2.5, k ₁₀ = 0.1, k ₁₂ = 0.6	0.878	0.035	0.021	0.065
T _{act} 15 450 s Exptl	0.795 ± 0.01	0.0525 ± 0.01	0.0335 ± 0.01	0.120 ± 0.01
k ₂ = 0, k ₁₀ = 0.7, k ₁₂ = 0	0.820	0.0572	0.0066	0.1155
k ₂ = 2.0, k ₁₀ = 0.7, k ₁₂ = 0	0.796	0.0573	0.031	0.115
k ₂ = 2.5, k ₁₀ = 0.7, k ₁₂ = 0	0.788	0.0572	0.038	0.116
k ₂ = 2.5, k ₁₀ = 0.1, k ₁₂ = 0.6	0.790	0.0572	0.037	0.116
T _{act} 21 350 s Exptl	0.741 ± 0.01	0.066 ± 0.01	0.0374 ± 0.01	0.155 ± 0.01
k ₂ = 0, k ₁₀ = 0.7, k ₁₂ = 0	0.761	0.072	0.0115	0.155
k ₂ = 2.0, k ₁₀ = 0.7, k ₁₂ = 0	0.728	0.072	0.043	0.156
k ₂ = 2.5, k ₁₀ = 0.7, k ₁₂ = 0	0.722	0.0716	0.051	0.155
k ₂ = 2.5, k ₁₀ = 0.1, k ₁₂ = 0.6	0.721	0.0719	0.050	0.156
T _{act} 30 400 s Exptl	0.639 ± 0.01	0.080 ± 0.01	0.071 ± 0.01	0.208 ± 0.01
k ₂ = 0, k ₁₀ = 0.7, k ₁₂ = 0	0.678	0.088	0.021	0.213
k ₂ = 2.0, k ₁₀ = 0.7, k ₁₂ = 0	0.637	0.088	0.0605	0.213
k ₂ = 2.5, k ₁₀ = 0.7, k ₁₂ = 0	0.628	0.088	0.070	0.213
k ₂ = 2.5, k ₁₀ = 0.1, k ₁₂ = 0.6	0.630	0.088	0.068	0.213
T _{act} 38 200 s Exptl	0.568 ± 0.01	0.094 ± 0.01	0.078 ± 0.01	0.260 ± 0.01
k ₂ = 0, k ₁₀ = 0.7, k ₁₂ = 0	0.613	0.098	0.029	0.26
k ₂ = 2.0, k ₁₀ = 0.7, k ₁₂ = 0	0.568	0.098	0.074	0.26
k ₂ = 2.5, k ₁₀ = 0.7, k ₁₂ = 0	0.557	0.098	0.085	0.26
k ₂ = 2.5, k ₁₀ = 0.1, k ₁₂ = 0.6	0.560	0.098	0.082	0.26

^a Reference 5d. ^b Rate constants of Chart IV were used; k₂, k₁₀, and k₁₂ (in units of 10⁻⁶/s) were varied for the calculation.

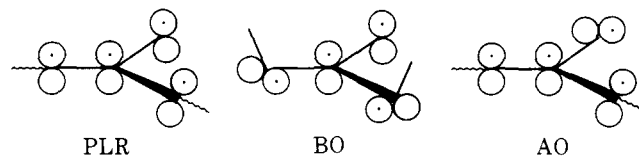
Chart IV. Kinetic Scheme and First-Order Rate Constants (in Units of 10⁻⁶/s) for Reaction of T_{act} at 152 °C

accessible in the pyrolysis of the 6-methylenebicyclo[3.1.0]-hexanes and since reasonably accurate rate constants were obtained for the rearrangement of T and T_{D2}, a comparison of these new results with the previously obtained data (Table IV)^{5d} in the pyrolysis of optically active T is essential. The rate constants for conversions of T_{act} were originally determined by assuming no reversibility in the formation of T_{rac} or of A plus S; the justification for these approximations was that the reactions were run to less than 1 half-life where subsequent reactions of products presumably occurred only to a small extent. The fractions of all products including racemic T from the pyrolysis of optically active T at 152.0 °C are given in Table IV along with calculated values for these fractions from the kinetic scheme of Chart IV with the rate constants there indicated and those that were varied for the different calculated fractions of Table IV.

The kinetic scheme of Chart IV is simplified in that optically active and racemic A plus S are considered together; this was done since there was a large uncertainty (80 ± 20%) in the relative amounts of inverted optically active and racemic structural rearrangement products. Therefore, the rate constants for conversion of these back to T_a and T_{rac} had to be varied to over extremes to determine their effect on the fractions; however, as can be gleaned from Table IV, the fractions were not sensitive to whether A plus S gave back only racemic T or mostly optically active T; the actual value of k₁₀ + k₁₂, namely, 0.7 × 10⁻⁶/s, is derived from the equilibrium data at 187 °C and the values of k₁ through k₉.

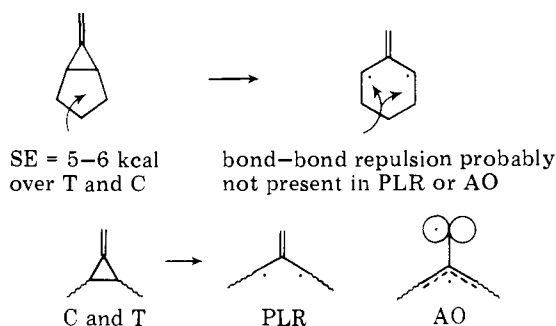
Discussion

Energetics of Formation of Planar TMM. As described in the introduction, a minor but not significant portion of the pyrolysis of optically active *trans*-2,3-dimethylmethylene-cyclopropane proceeds via an achiral biradical, the two likely candidates being a planar form, PLR, or a bisorthogonal species, BO, previously described. A third possibility that presents itself by the observed interconversions of XA, XS, NA, and NS is an achiral orthogonal species AO.



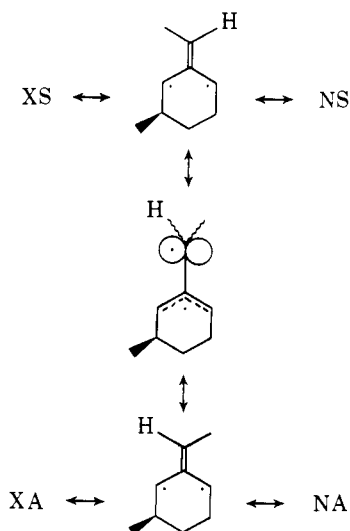
The interconversion of N and X can only occur via the PLR or AO since BO cannot account for bridgehead double inversion without passing through species PLR or AO. The average rate constant for interconversion of X and N is about one-quarter that for isomerization of C to T at 164 °C, which reveals the possibility that the planar species (PLR) or the achiral orthogonal biradical (AO) may be energetically accessible for the racemizing act in the pyrolysis of optically active T. In

addition, of course, the bisorthogonal form may also be responsible for this racemization. To quantitate the energy difference between the transition state for the X and N bridgehead double inversion and that for ring opening of C requires correction for the ground-state energy differences between the bicyclic and C. No doubt, N and X possess 5–6 kcal/mol of cyclopentane ring strain over and above that in the methylenecyclopropane which is relieved upon ring opening. Thus the transition state for formation of the planar or achiral orthogonal intermediate lies 5–6 kcal/mol higher than that for ring opening to the orthogonal form from C and T. This is about 4–5 kcal/mol higher than the transition state for formation of an achiral species in the pyrolysis of T_{act} ,^{5d} but the planar or achiral orthogonal forms from X or N may also suffer nonbonded repulsions due to a syn relationship between groups attached to the TMM biradical, a situation not necessarily encountered with the planar or achiral orthogonal form from T where alkyl groups can rotate away from one another. The



uncertainties in the strain energies therefore do not force acceptance of the planar or achiral orthogonal species in the unencumbered methylenecyclopropane pyrolysis, but no case can be made for strong rejection in favor of the bisorthogonal form.

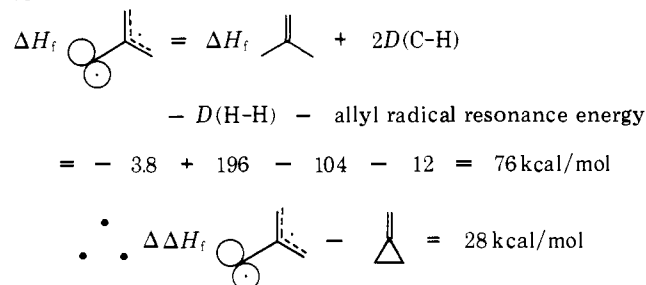
Mechanism of Interconversion of X and N. The bridgehead double inversion of X and N can occur without rotation of the exo methylene via a planar TMM species or with such a rotation to generate an orthogonal biradical like AO. A distinction between the two is possible if the exo methylene is unsymmetrically substituted. The rate constants of Chart II make it clear that the bridgehead double inversion of XS to NS and NA gives more NS than NA by a factor of 1.09. The factor for preservation of the stereochemistry of the exo methylene starting with the other isomers is 1.26 from XA, 1.16 from NA, and 1.18 from NS. Thus, an average of 54% retention and 46% inversion is observed. This can be interpreted in two ways: either a planar form is generated which rotates around the exo



methylene roughly six times faster than reclosure without exo methylene rotation or by two separate pathways, one via a higher energy planar form and one via a lower energy orthogonal form. Roth chose the latter interpretation in describing his very similar results; however, the former interpretation is more consistent with the isotope effects which will be discussed. Either interpretation, however, indicates the energetic accessibility of planar singlet trimethylenemethane, a possibility made clear in the original description of the interconversion of T, C, and A + S.^{5c,d}

Energies of Trimethylenemethane in Various Geometries.

While the observations reported here indicate that the difference in transition state energies for formation of planar and orthogonal trimethylenemethane species is small (1–4 kcal/mol) no information bears on the energy difference between the two species. That difference could be as high as 14 kcal/mol by the following logic based on the Benson noninteracting biradical hypothesis.¹⁶ The orthogonal biradical probably suffers little interaction between the nonbonding electrons, so



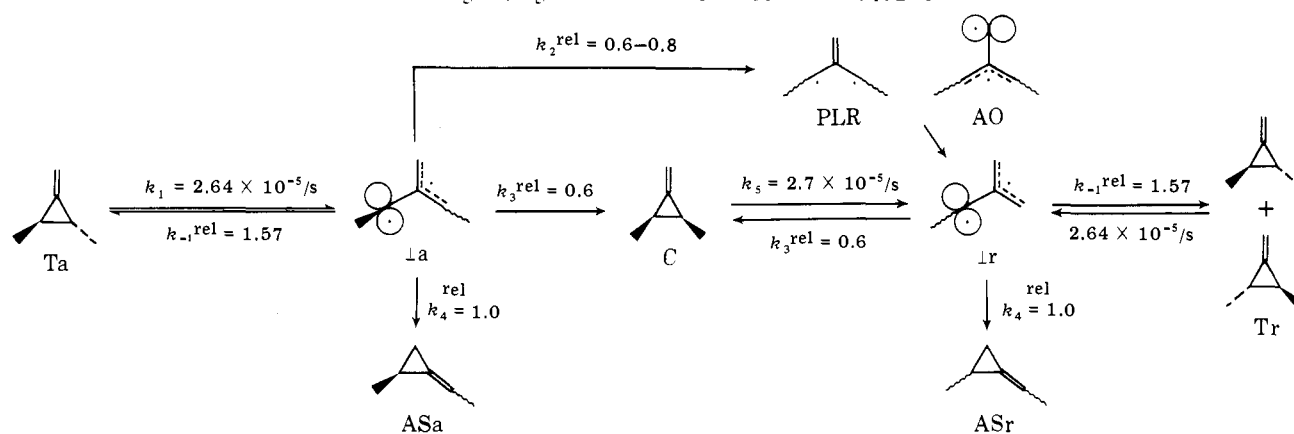
Thus, the orthogonal species resides in a 14 kcal/mol potential well since the activation energy for the methylenecyclopropane rearrangement in the unsubstituted cases is probably 2 kcal/mol higher than that for 2-methylmethylenecyclopropane ($E_{act} = 40$ kcal/mol).^{5b} However, there is no way to estimate the heat of formation of the planar singlet since the nonbonding electrons must interact, so the energy difference may be as high as 15 kcal/mol or as little as 1 kcal/mol. Clearly, the Dewar and Salem calculations, which indicate a 26 and 52 kcal/mol difference, respectively, cannot be correct, but the Schaeffer and Goddard calculations of 2.7 and 6.2 kcal/mol are not inconsistent with the data.

Finally, the heat of formation of a noninteracting bisorthogonal form can be estimated by additivity relationships and is 40 kcal/mol above methylenecyclopropane since, of course, there is no allyl radical resonance energy to stabilize the bisorthogonal form. But clearly the bisorthogonal form is accessible in the rearrangement of methylenecyclopropane.

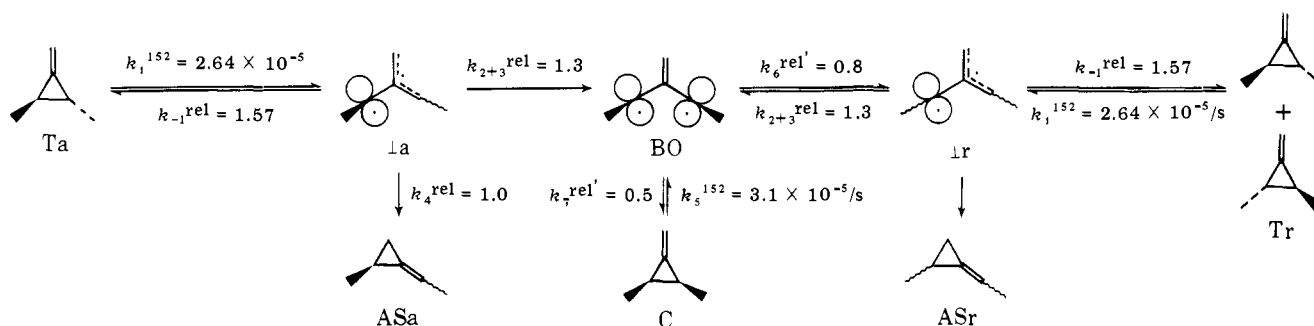
Mechanistic Schemes for the Methylenecyclopropane Self-Interconversion. The stereochemical and kinetic data obtained from pyrolysis of optically active *trans*-2,3-dimethylmethylenecyclopropane (Ta) and its *cis* isomer C require a mechanism that will account for geometric isomerization, T = C, and structural rearrangement to predominantly inverted *anti*- and *syn*-2-methylethylidenecyclopropane, A + S. The mechanism must account for racemization of Ta by a pathway other than via the *cis* isomer. Such a scheme has been proposed previously^{5c,d} which involves orthogonal trimethylenemethane biradicals responsible for preservation of optical purity in the structural rearrangement and (to a lesser extent) achiral planar or bisorthogonal species responsible for the racemization of Ta over and above that resulting from reversible formation of C. This scheme is outlined in the introduction; however, the Runge Kutta analysis of Chart IV makes assigning of relative rate constants in more detailed mechanistic schemes a worthwhile endeavor.

Various mechanistic schemes will accommodate the available data. This is because it is unknown as to which achiral

Scheme I. Mechanism for Reaction of Ta Involving Orthogonal and Planar TMM Biradicals at 152 °C



Scheme II



species, planar or bisorthogonal, is responsible for the excess racemization of Ta and whether or not this species gives products directly or merely allows interconversion of enantiomeric orthogonal species. Nonetheless, examination of these mechanistic possibilities has the virtue of establishing ranges of involvement of the achiral species because the extent of reformation of Ta after ring opening can be ascertained within various mechanistic models.

The mechanism of Scheme I represents one of the simplest of the various possibilities. Here an orthogonal biradical, $\perp a$, generated by C_2C_3 cleavage with a 90° rotation around one cyclopropane bond (via k_1), is viewed as responsible for both formation of C (via k_3) and inverted A + S (via k_4). The orthogonal species, $\perp a$, is also assumed to undergo a second 90° rotation around the same bond which rotated originally or the other to give either a bisorthogonal or planar species, respectively, via k_2 . This achiral species then undergoes a further 90° rotation around C_2 or C_3 to give a racemic set of orthogonal intermediates which partitions to racemic T, Tr, C, and racemic A + S, AS, in the same way that the optically active orthogonal species partitions to Ta, C, and ASa. In this scheme the achiral species does not give product directly but reverts to orthogonal forms. This is intuitively reasonable if the achiral species is a planar biradical: closure of the planar biradical to product requires 90° rotations around two bonds and it is easy to envision the orthogonal forms resulting from one 90° rotation as being intermediate in this process. However, if the achiral species is the bisorthogonal form then it should close to C as well as rotate to orthogonal biradicals (this possibility is outlined in Scheme II). Therefore Scheme I is most reasonably associated with a planar TMM species.

The absolute values of the rate constants k_1 and k_5 and the relative values of the mechanistic rate constants k_{-1}^{rel} , k_2^{rel} , k_3^{rel} , and k_4^{rel} can be determined by comparison of rate expressions from a steady state treatment of the mechanism of Scheme I with those from the phenomenological description of the scheme of Chart IV for which the rate constants of Chart

IV were determined. The identification equations are

$$k_1^P = (k_1 k_3 / k_{\perp a}) (1 + (k_2 / k_{\perp r}))$$

$$k_2^P = k_1 k_2 k_{-1} / (k_{\perp a} k_{\perp r})$$

$$k_3^P = (k_1 k_4 / k_{\perp a}) (1 + (k_2 / k_{\perp r}))$$

$$k_5^P = k_4 k_5 / k_{\perp r}$$

$$k_6^P = k_5 k_{-1} / k_{\perp r}$$

where k_n^P is a phenomenological rate constant of Chart IV, k_n is a mechanistic rate constant of Scheme I, $k_{\perp a} = k_{-1} + k_2 + k_3 + k_4$, and $k_{\perp r} = k_{-1} + k_3 + k_4$. Algebraic manipulation of these expressions leads to

$$\frac{k_{-1}}{k_4} = \frac{k_6^P}{k_5^P}, \quad \frac{k_3}{k_4} = \frac{k_1^P}{k_3^P}, \quad \frac{k_3}{k_1} = \frac{k_5^P k_1^P}{k_6^P k_3^P}$$

$$\frac{k_2}{k_4} = \frac{k_2^P}{k_3^P} \left(1 + \frac{k_3}{k_{-1}} + \frac{k_4}{k_{-1}} \right) / \left(1 - \frac{k_4 k_2^P}{k_{-1} k_3^P} \right)$$

$$k_1 = k_1^P \left(\frac{k_{-1}}{k_3} + \frac{k_2}{k_3} + \frac{k_4}{k_3} + 1 \right) / \left(1 + \frac{k_2}{k_{-1} + k_3 + k_4} \right)$$

$$k_5 = k_5^P \left(\frac{k_{-1}}{k_4} + \frac{k_3}{k_4} + 1 \right)$$

According to this mechanistic scheme, a comparison of k_{-1} , k_2 , k_3 , and k_4 indicates that 16–20% of opening events of Ta lead to an achiral planar trimethylenemethane species with the remainder proceeding through an orthogonal species which closes to Ta, C, or A + S_a in the ratio 1.57:0.6:1.0, respectively.

Variations in this mechanism (Scheme I) are easily envisioned. The planar biradical could also be an achiral orthogonal species with the original exo methylene twisted out of the plane. If this achiral species were formed and was not responsible for product and gave only $\perp r$, then the rate constants of Scheme I still apply. If this achiral orthogonal form did not revert to the racemic chiral orthogonal forms, $\perp r$, but gave only racemic

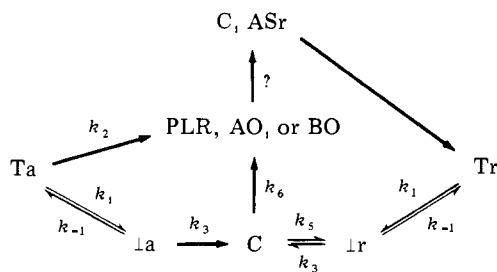
S + A_r, as is reasonable considering its geometry, then no Tr could be formed, and the fact that Tr is formed cannot be accommodated by the mechanism. If this achiral orthogonal form partitioned to give both $\perp r$ and racemic A + S, k_2 would have to be larger in proportion to the fraction of racemic A + S produced relative to $\perp r$, but an upper limit of 40% racemic A + S was generated on pyrolysis of Ta,^{5d} which therefore would substantially limit the fraction racemic A + S produced from achiral orthogonal intermediate and the value of k_2 . Thus, the planar form may be replaced by an achiral orthogonal form in Scheme I provided that this achiral orthogonal form would undergo bond rotation to the racemic chiral orthogonal forms, $\perp r$, faster than it would reclose solely to racemic A plus S.

Scheme II reveals another mechanistic possibility based on intermediacy of bisorthogonal forms which reclose and rotate to orthogonal forms which rotate back to bisorthogonal forms prior to closure. The full scheme is abbreviated in Scheme II where kinetically insignificant chiral bisorthogonal forms are ignored.

The similarity of Scheme II to Scheme I allows deduction of the rate constants k_1 , k_5 , and k_{-1}^{rel} , $k_{2,3}^{rel}$, and k_4^{rel} almost by inspection; however, k_6^{rel} and k_7^{rel} can be estimated only relative to one another, not to k_{-1}^{rel} , k_{2+3}^{rel} , or k_4^{rel} . Here it is clear that 33% of all ring opening events of Ta leads to an achiral bisorthogonal species which closes to C roughly 40% of the time it is generated.

Finally, a mechanistic possibility made likely for consideration by Berson's recent observations¹⁷ is Scheme III where

Scheme III



Ta rearranges to C and ASa by the chiral orthogonal TMM biradicals, but Ta racemizes by an independent pathway involving achiral species.

If the achiral species give only Tr then little racemization of A and S would be observed other than via intermediate formation of C. Unfortunately the experimental data are too uncertain to decide if this is a viable alternative. If the achiral species gives C and/or ASr in ratios different from the orthogonal biradicals, the values of various mechanistic rate constants are indeterminate with the current data. Only a very painful experiment, owing to difficulties in separation of sufficient amounts of A and S from a pyrolysis of optically active T, will allow a distinction between some of these mechanistic possibilities. Nonetheless, it is clear that k_2 of Scheme III can represent between 4 and 40% of the total reaction of Ta.

Deuterium Isotope Effects in Methylene-cyclopropane Pyrolyses. Since the structural rearrangements of methylene-cyclopropane involve rotation around the exo cyclic methylene and since the hybridization change at this carbon is relatively minor from starting material to product, the kinetic isotope effect in the reaction resulting from substitution of the exo methylene with deuterium is of concern, particularly in light of the observation of a normal kinetic isotope effect (1.08) in the pyrolysis of the 6-methylene- and 6-dideuteriomethylenebicyclo[3.1.0]hexanes, X, N, X-*d*₂, and N-*d*₂.

Furthermore, ring closure reactions of trimethylenemethane generated by pyrolysis of 3,3-dideuterio-4-methylene-1-pyrazoline have been shown to involve a substantial inverse deuterium isotope effect (0.75).¹⁸ The isotope effect is in a

sense opposite to that expected on the basis of the minimal hybridization change, and has been attributed to inertial effects,¹⁸ making the study reported in Table IV relevant.

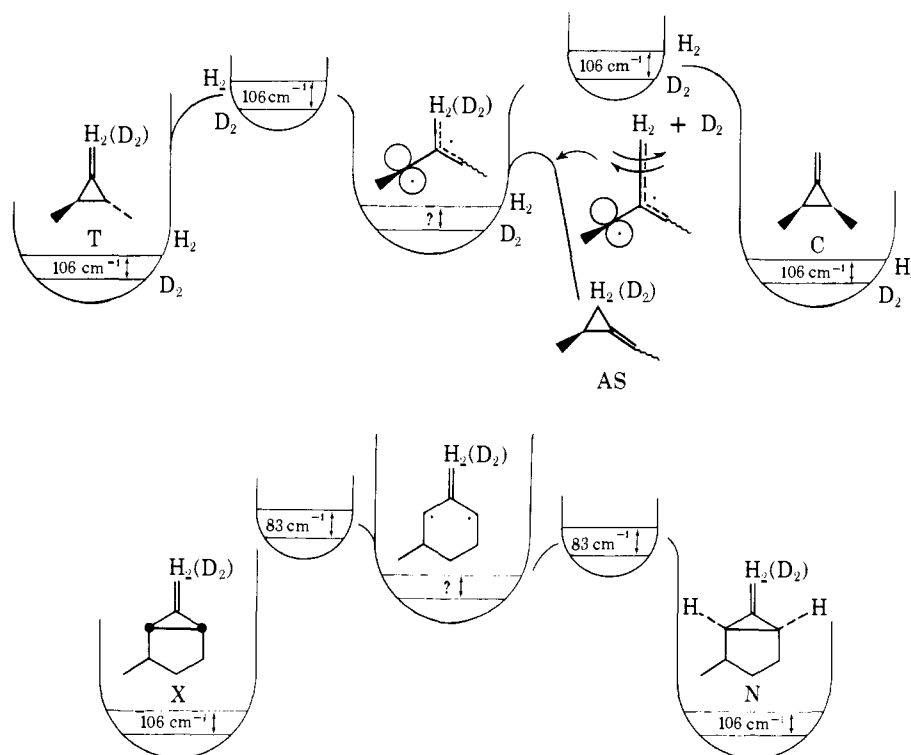
As indicated in the Results section, the effect of deuterium substitution on the exo methylene of T had little effect on trans to cis isomerization of T but retarded the structural rearrangement to A plus S. The value of k_{H_2}/k_{D_2} for formation of A plus S was $1.31 \pm 3\%$.

There are two views on the origins of this isotope effect. The first is a classical inertial argument that assumes that, for a given input of thermal energy, the ratio of rotation around groups will occur in inverse proportion to the square root of their moments of inertia. In the case of T and C, this argument suggests that the structural rearrangement to form A and S would have $k_{H_2}/k_{D_2} = 1.414$, and there should be no effect on geometric, cis-trans, isomerization. The facts with T, C, T_{D2}, and C_{D2} are reasonably consistent with this simple hypothesis. The classical inertial argument, however, ignores quantum effects and the forces acting upon the exo methylene torsional mode in the ground state and transition states for structural and geometric rearrangement of T and C. In quantum mechanical terms the substitution of deuterium for hydrogen on the exo methylene will lower the zero point energy of all vibrations associated with the exo methylene, but since the hybridization of this carbon probably changes very little from ground state to transition state in the rearrangements, the torsional vibrational mode is the one on which to focus. In methylenecyclopropane itself, the torsion has $\nu = 749 \text{ cm}^{-1}$, and in the exo dideuterio material, $\nu = 537.5 \text{ cm}^{-1}$.¹⁹ Thus, the zero point energy is lowered 106 cm^{-1} upon deuteration which corresponds to 325 cal/mol .

In the structural isomerization reaction of T where the torsional oscillation becomes part of the reaction coordinate motion in the formation of A plus S via the orthogonal biradical, the zero point energy difference is lost since the vibration becomes a translation, and the isotope effect calculated is 1.45 at $164 \text{ }^\circ\text{C}$. To calculate the isotope effect on the geometric (cis-trans) isomerization of T and C requires information about the force constant for the torsion of the exo cyclic carbon in the transition state for formation of the orthogonal biradical which is responsible for the geometric isomerization. The experimental facts suggest no change in force constant, which requires some consideration. The resonance energy of the allyl radical, which might be identified with the restoring force on the torsional vibration, is only 10–15 kcal/mol¹⁶ while the strength of the π bond in methylenecyclopropane is between 50 and 65 kcal/mol depending on how much of the extra strain in methylenecyclopropane relative to cyclopropane and a double bond is relieved in the torsional oscillation. Regardless of the latter value, a very low force constant for this torsion is expected, which is not the observation.

On the other hand, the HMO π bond order in the allyl radical is 0.707, which reflects a more substantial restoring force on the torsional oscillation than the resonance energy which therefore implies a substantial zero point energy difference between protio and dideuterio substituted orthogonal biradicals, which is roughly 70% of that in the starting material, and if there is some bonding to the exo cyclic carbon in the transition state for geometric isomerization, there may be as much zero point energy difference in the transition state as in the ground state, implying no isotope effect.²⁰

Of interest is the isotope effect with the bicyclic methylenecyclopropanes, X and N, 1.08. An interpretation, suggested by Professor L. K. Montgomery, is that loosening of the 6-methylene torsion occurs upon ring opening to a planar biradical either because it is destabilized, relative to the orthogonal species, or because the HMO π bond order in planar TMM is only 0.58. Thus, the zero point energy difference of the exo methylene torsion in the transition state for interconversion



of X and N is less than that in the ground state—by 70 cal/mol judging from the experimental results.

The magnitude of isotope effect on the interconversion of N and X also indicates that an orthogonal biradical is not formed directly in the pyrolysis as Roth suggests since the rotation becomes a reaction coordinate motion and the zero point energy difference between H₂ and D₂ is lost in the transition state, which should result in a large normal isotope effect of roughly 1.28 after correction for the fraction of reaction that proceeds with stereospecificity.

The fact that the isotope effect with X, N and X-*d*₂, N-*d*₂ is only 1.08 therefore indicates little exo methylene rotation in this rate-determining step for bridgehead double inversion requiring initial formation of a planar biradical which subsequently undergoes exo methylene rotation roughly 12 times faster than reclosure of the planar biradical. A classical description of the origin of rotational isotope effects leads to a slightly different expectation for the isotope effect resulting from the various pathways. If no exo rotation occurs in the rate-determining step then there should be no isotope effect by the classical inertial argument. If there is exo rotation, then the isotope effect should be 1.414. In either theoretical framework a large isotope effect is expected for rate-determining exo methylene rotation.

6-Dialkylidenebicyclo[3.1.0]hexane Pyrolyses. 2-Methyl-6-isopropylidenebicyclo[3.1.0]hexane (IP) undergoes the bridgehead double inversion roughly three times faster than single inversion of *cis*-2,3-dimethylisopropylidenebicyclopropane (CIP) to its *trans* isomer, TIP, at 202.4 °C. Thus, the formation of a potentially planar TMM biradical in the bicyclic case has energetics similar to that for formation of the orthogonal TMM, although, like the 6-methylenebicyclo[3.1.0]hexane system discussed previously, corrections for strain in the bicyclic case make the formation of planar TMM biradicals slightly higher in energy than formation of an orthogonal form from the monocyclic system.

Evidence for exo methylene rotation in the 6-dialkylidenebicyclics is provided by the 2-methyl-6-(2-butylidene)bicyclo[3.1.0]hexane pyrolysis where one of the isomers gave the other three in roughly comparable amounts, kinetically. Whether or not there is any preservation of stereochemistry

at the exo methylene will require a study similar to that reported in Table II with the 2-methyl-6-ethylidenebicyclo[3.1.0]hexane systems.

However, the rate effects in the 6-dialkylidene substituted bicyclo[3.1.0]hexane may suggest that exo methylene rotation occurs in the rate-determining step for bridgehead double inversion. The rate of *endo*-*exo* isomerization of 2-methyl-6-(3'-pentylidene)bicyclo[3.1.0]hexane is a factor of 2.5 ± 0.3 slower than that of 2-methyl-6-isopropylidenebicyclo[3.1.0]hexane at 178 °C. A simple calculation of the ratio of the moments of inertia of the two compounds using reasonable average geometries leads to a factor of 4, which then predicts, in a classical framework, that the isopropylidene material should isomerize twice as fast as the 3-pentylidene derivative if exo-methylene rotation occurred in the rate-determining step. The activation parameters determined for these interconversions suggest that all the rate difference is in the *A* factor, but experimental error can diminish the force of that conclusion.

Other factors may be responsible for the rate difference. Steric effects may make it more difficult for the 3-pentylidene material to undergo bridgehead double inversion. Alternatively, the double bond of the 3-pentylidene material may be more stable than that of the isopropylidene material owing to hyperconjugation. It may not be profitable to attempt to distinguish between the various hypotheses for the rate difference, although the notion of rate-determining exo methylene rotation with 6-dialkylidenebicyclo[3.1.0]hexanes due to steric effects not present in the 6-methylene- and 6-ethylidenebicyclo[3.1.0]hexanes is attractive.

Summary

trans-2,3-Dimethylmethylenebicyclopropane (T) undergoes geometric isomerization to *cis*-2,3-dimethylmethylenebicyclopropane (C), and structural rearrangement to substantially inverted *anti*- and *syn*-2-methylethylidenebicyclopropane. Racemization of T occurs by reversible formation of C and by an achiral intermediate which is formed in 15–33% of all ring-opening events of T with the major portion of the reaction proceeding via chiral orthogonal trimethylenemethane biradicals. The nature of the achiral species has not been deter-

mined. It can be a bisorthogonal form by simple thermodynamic estimates of its stability. A planar geometry is also accessible judging by the energetics and stereochemistry of the bridgehead double inversion of 6-methylene- and 6-ethylidene-2-methylbicyclo[3.1.0]hexane. The transition states for formation of the orthogonal and planar intermediates are comparable in energy, but no experimental information bears on the energy difference between planar and orthogonal trimethylenemethane singlets other than to set limits of 1–15 kcal/mol. Dideuterium substitution on the exo methylene of T resulted in a large kinetic isotope effect, 1.31, on the structural isomerization to A + S but had little effect on the geometric isomerization to C.²⁰ Deuterium substitution on the exo methylene of 6-methylenebicyclo[3.1.0]hexane resulted in a normal kinetic isotope effect of 1.08 on the bridgehead double inversion suggesting that a planar form is generated initially which subsequently undergoes exo methylene rotation competitive with ring closure to 8% exo methylene retained stereochemistry. Direct formation of an orthogonal form should have had a more substantial isotope effect.

Experimental Section

General. Nuclear magnetic resonance spectra were recorded on Varian HA 220, HA 100, and EM-360 spectrometers in carbon tetrachloride solvent. Shifts are reported in parts per million downfield from internal Me₄Si. Mass spectra were recorded on an AEI MS-9 instrument operating at 70 eV. Preparative gas chromatography was performed on a Varian Aerograph A-90P instrument with a 15 ft × 0.25 in. column packed with 20% di-*n*-butyl tetrachlorophthalate (DBTCP) on base-washed, 60/80 mesh Chromosorb P. Gas-phase pyrolyses were conducted using 2–10- μ L samples with 40–100 Torr nitrogen in a 2-L bulb which was attached to an all-Teflon stopcock vacuum line. The bulb was immersed in a well-stirred molten salt bath (KNO₃/NaNO₂) which was heated with a Variac-controlled 500-W Vycor heater; precise temperature control was provided by a Bayley Model 76-8 controller which drove a 125-W heater. The bath was immersed in a large insulated box. Temperature was read with a copper-constantan thermocouple. Temperature control was to ± 0.1 °C at 200 °C. Analysis of pyrolysis mixtures was performed on a Varian 1220-2 instrument equipped with a 200 ft × 0.1 in. i.d. stainless steel capillary column wall-coated with DBTCP. Integrations of the GC output signal were performed by a Vidar Model 6210 digital integrator.

endo- and exo-2-Methyl-6-methylenebicyclo[3.1.0]hexane (N and X). To a well-stirred, 0 °C mixture of 7.5 g (0.09 mol) of 3-methylcyclopentene, 15.6 g (0.14 mol) of potassium *tert*-butoxide, and 15 mL of *n*-pentane was added 32.8 g (0.13 mol) of bromoform under a nitrogen atmosphere at a rate so as to prevent warming the reaction mixture above 10 °C. After addition, the mixture was shaken with water, then the organic (upper) layer was removed and shaken again with water. The organic (lower) layer was washed numerous times with water, then dried over anhydrous sodium sulfate. After concentration on a rotary evaporator, distillation, bp 45–46 °C (0.1 Torr), gave 12 g (55%) of *endo*- and *exo*-2-methyl-6,6-dibromobicyclo[3.1.0]hexane: NMR δ 1.12, d ($J = 7$ Hz), 3 H; 0.9–1.6, 2 H; 1.60–2.80, 5 H. *m/e* 251.9180 (calcd for C₉H₁₀Br₂, 251.9150).

To 1.85 g (0.0073 mol) of the dibromide, 5 mL of HMPA, and 2.06 g (0.0149 mol) of methyl iodide in 40 mL of dry THF at –95 °C under a nitrogen atmosphere was added 4.5 mL of 1.67 M butyllithium in hexane slowly with stirring over a 3-h period.¹³ Cooling was provided by a methanol slush bath. After warming to room temperature, water was added and the solution was extracted with pentane. After washing the pentane extracts with water, drying over anhydrous sodium sulfate, and concentration through a Vigreux column, a residue was obtained which was distilled bulb to bulb at room temperature at 2.5 Torr to give 1.1 g of a light yellow oil: NMR δ 1.1, d ($J = 7$ Hz) superimposed on a complex multiplet at δ 1.0–2.5 from which protruded a large singlet at δ 1.7. *m/e* 188.0198 (calcd for C₈H₁₃Br, 188.0201).

To 1.1 g of the monobromide above dissolved in 3 mL of Me₂SO was slowly added 0.9 g of potassium *tert*-butoxide under nitrogen with cooling from an ice bath. After stirring at room temperature for 12 h, ice and water were added to the reaction mixture, and this was extracted with small amounts of pentane. After washing the pentane extracts with water, drying over anhydrous sodium sulfate, and con-

centration by distillation of the pentane with a Vigreux column a residue of 0.32 g was obtained which contained two GC peaks in a 15:85 ratio. This was further purified by passage through the DBTCP column; however, separation of the two isomers proved too difficult and only the *endo*-2-methyl-6-methylenebicyclo[3.1.0]hexane (N) was obtained pure.

NMR (220 MHz) of N: δ 0.96, d ($J = 7$ Hz), 3 H; 1.1–1.45, complex multiplet, 2 H; 1.48 d ($J = 6$ Hz), 1 H; 1.6–1.95, multiplet, 3 H; 2.16, pentet ($J = 7$ Hz), 1 H; 5.25, broad s, 2 H. *m/e* 108.0915 (calcd for C₈H₁₂, 108.0940).

The exo isomer, X, was obtained as a 60/40 mixture with N and its NMR could be partially deduced: NMR (220 MHz) of X δ 0.8, m, 1 H; 1.02, d ($J = 6$ Hz), 3 H; 1.1–1.8, m, 5 H; 2.3, m, 1 H; 5.35, s, 2 H.

endo- and exo-2-Methyl-6-dideuteriomethylenebicyclo[3.1.0]hexane (N-d₂ and X-d₂). The *endo*- and *exo*-2-methyl-6-dideuteriomethylenebicyclo[3.1.0]hexanes were prepared from 2-methyl-6,6-dibromobicyclo[3.1.0]hexane in a manner similar to that for preparation of N and X with the exceptions that trideuteriomethyl iodide was used in the coupling reaction and the elimination of the monobromide required heating at 45 °C for 7 days to complete the reaction. Again an 85:15 ratio of isomers was obtained. No vinyl protons were evident in the ¹H NMR spectra otherwise equivalent to N and X. *m/e* for the major, N-d₂ isomer, was 110.1039 (calcd for C₈H₁₀D₂, 110.1065).

Pyrolysis of N and X and of N-d₂ and X-d₂. An 0.8466:0.1534 mole ratio of N and X, respectively, was heated at 163.94 °C for 311.0, 355.0, 400.0, and 620.0 min, and gave 0.3122, 0.3266, 0.3592, and 0.4111 mole fraction of X, respectively. The equilibrium mole fractions were 0.5986 and 0.4014 of X and N, respectively. The average deviation in each analysis was no more than ± 0.002 , except for the 620.0-min run where it was ± 0.004 . The sums of the forward and back rate constants calculated at each time were 2.37, 2.35, 2.30, and 2.33 (in units of 10⁻⁵/s), respectively, leading to an average sum of forward and back rate constants of $2.34 \times 10^{-5} \pm 1\%$.

Pyrolysis of an 0.8450:0.1550 mole ratio of N-d₂ to X-d₂ at 163.94 °C for 345.0, 400.0, 450.0, and 605.0 min gave mole fractions of X-d₂ of 0.3052, 0.3940, 0.3507, and 0.3945, respectively, with average deviations of no more than ± 0.003 . The equilibrium constant was assumed to be the same as with N and X leading to the sums of rate constants at each point in time of 2.0, 2.20, 2.16, and 2.14 (in units of 10⁻⁵/s), respectively. The 345.0-min run was discarded leading to an average sum of forward and back rate constants of $2.17 \times 10^{-5} \pm 1\%$. Thus k^H/k^D (163.94 °C) = 1.08 ± 0.02 .

Two pyrolyses at 183.13 °C for 85.0 and 105.0 min lead to $k_+^H + k_b^H = 1.28 \pm 0.04 \times 10^{-4}$ /s. Two pyrolyses at 90.0 and 105.0 min lead to $k_+^D + k_b^D = 1.22 \times 10^{-4}$ /s, giving $k^H/k^D = 1.05 \pm 0.05$.

Preparation and Pyrolysis of endo-syn-, endo-anti-, exo-syn-, and exo-anti-2-Methyl-6-ethylidenebicyclo[3.1.0]hexane (NS, NA, XS, and XA). To 2.4 g (0.0095 mol) of 2-methyl-6,6-dibromobicyclo[3.1.0]hexane in 6 mL of HMPA, 2.9 g (0.019 mol) of ethyl iodide, and 50 mL of THF at –95 °C under nitrogen was slowly added 5.7 mol of butyllithium (1.67 M in hexane). Temperature was maintained with a methanol slush bath. Workup as described above gave 0.73 g of a liquid whose ¹H NMR indicated a doublet ($J = 7$ Hz) at δ 1.11 superimposed on a triplet ($J = 7$ Hz) at δ 1.23, 6 H; and four sharp lines at δ 1.75 superimposed on a complex multiplet at δ 1.20–2.25, 9 H. Potassium *tert*-butoxide induced elimination as described above gave 0.5 g of a yellow oil which contained four major peaks on the DBTCP preparative column, the last of which was of mass 120 and therefore ignored. The ratio of the other four was roughly 1:8:2 with the major peak having *m/e* 122.1088 (calcd for C₉H₁₄, 122.1094), but consisting of two compounds from capillary GC analysis. Repeated separation of the mixture led to four compounds, the first and fourth relatively pure and the second and third as roughly 4:1 mixtures which allowed NMR characterization and material for the pyrolyses reported in Table II.

NMR of 1 (XS): δ 0.75, m, 1 H; 0.98 d ($J = 7$ Hz), 3 H; 1.23, m, 2 H; 1.53, m, 2 H; 1.73, d ($J = 7$ Hz) superimposed on a multiplet at 1.6–1.85, 5 H; 2.18 m, 1 H; 5.67, q ($J = 7$ Hz), 1 H.

NMR of 2 (NA): δ 0.93, d ($J = 7$ Hz), 3 H; 1.0–1.5, m, 3 H; 1.69, d ($J = 6$ Hz), superimposed on a multiplet, 6 H; 2.15, pentet ($J = 6$ Hz), 1 H; 5.56, q ($J = 6$ Hz), 1 H.

NMR of 3 (NS): δ 0.91, d ($J = 7$ Hz), 3 H; 1.0–1.5, m, 3 H; 1.69, d ($J = 6$ Hz), superimposed on a multiplet 6 H; 2.08, pentet ($J = 6$ Hz), 1 H; 5.58, q ($J = 6$ Hz), 1 H.

NMR of 4 (XA): δ 0.75, m, 1 H; 1.01, d ($J = 6$ Hz), 3 H; 1.52, m,

1 H; 1.63, broad s, 2 H; 1.75, d ($J = 6$ Hz) superimposed on a multiplet, 5 H; 2.23, m, 1 H; 5.68, q ($J = 6$ Hz), 1 H.

5,5-Dimethyl-2-oxazolidone and 5,5-Dimethyl-*N*-nitrosoxazolidone.¹⁵ To 7 g (0.052 mol) of ethyl 3-hydroxy-3-methylbutyrate was added 4 g (0.125 mol) of anhydrous hydrazine. The exothermic reaction was held at 35–40 °C with cooling and then refluxed for 2 h. The excess hydrazine was evaporated with a vacuum pump to give quantitative yield of white, crystalline 5,5-dimethyl-2-oxazolidone.

To 12 g (0.09 mol) of the oxazolidone in 30 mL of 10% aqueous HCl and 50 mL of *n*-hexane was added 6 g (0.11 mol) of sodium nitrite in 15 mL of water slowly at ~0 °C. Shortly after addition, a slight amount of urea was added to destroy the excess nitrous acid; the solution was then heated to 50 °C under a reflux condenser and when N₂ gas evolved vigorously heating was stopped; the solution was cooled to room temperature and neutralized with a saturated bicarbonate solution. Most of the water was evaporated under vacuum at room temperature having a syruplike residue which was then extracted with ether. After evaporation of the ether, the residue was dissolved in an excess 30% HCl solution and 1 equiv of NaNO₂ in 10 mL of H₂O was added at 0 °C with stirring to give 7 g (54% yield) of 5,5-dimethyl-*N*-nitrosoxazolidone as light yellow crystals which were used without further purification.

5-Ethyl-5-methyl-2-oxazolidone and 5-Ethyl-5-methyl-*N*-nitrosoxazolidone.¹⁵ By using the same procedure as above for 5,5-dimethyl-2-oxazolidone and 5,5-dimethyl-*N*-nitrosoxazolidone, 7 g (54% yield) of 5-ethyl-5-methyl-*N*-nitrosoxazolidone was prepared from 12 g of ethyl 3-hydroxy-3-methylpentanoate.

5,5-Diethyl-2-oxazolidone and 5,5-Diethyl-*N*-nitrosoxazolidone. By using the same procedure as above 5,5-diethyl-*N*-nitrosoxazolidone was prepared from 23.5 g (0.15 mol) of ethyl 3-ethyl-3-hydroxypentanoate as a yellow oil which was extracted from the reaction mixture with ether. The solution was dried over sodium sulfate and evaporated to give 18 g (78% yield) of crude 5,5-diethyl-*N*-nitrosoxazolidone which was used without further purification.

General Preparation of Dialkylidenecyclopropanes. A 30% ether solution of 6.6 g (0.1 mol) of olefin, 1.5 g of tetraoctylammonium chloride, and 5 g (0.03 mol) of 5,5-disubstituted *N*-nitrosoxazolidone were stirred in a 250-mL flask at –6 °C. A solution of 5 g of sodium hydroxide in 10 mL of water was added slowly over 2 h, and the solution was stirred for another 0.5 h. It was then diluted with ether; the ether layer was washed with saturated brine and filtered through an anhydrous sodium sulfate cone, and the solvent was removed by fractional distillation, to give 20–40% yield of adducts.

endo- and exo-2-Methyl-6-isopropylidenebicyclo[3.1.0]hexane. A 66:34 mixture of *endo*- and *exo*-2-methyl-6-isopropylidenebicyclopropane (IPN and IPX, respectively) was obtained and separated by preparative GC.

NMR of IPN: δ 0.92, d ($J = 7$ Hz), 3 H; 1.15–1.30, m, 1 H; 1.45, broad s, 1 H; 1.71, singlet superimposed on a broad multiplet, 10 H; 2.11, quintet ($J = 7$ Hz), 1 H. *m/e* 136.1273 (calcd for C₁₀H₁₆, 136.1253).

NMR of IPX: δ 0.70–0.93, m, 1 H; 1.02, d ($J = 6.5$ Hz), 3 H; 1.45–1.59, m, 1 H; 1.64, broad s, 2 H; 1.74, s, 3 H; 1.78, s, 3 H; 2.08–2.28, m, 1 H. *m/e* 136.

endo- and exo-2-Methyl-6-(3'-pentyldene)bicyclo[3.1.0]hexane. A 64:36 mixture of *endo*- and *exo*-2-methyl-6-(3'-pentyldene)bicyclo[3.1.0]hexane (PLN and PLX, respectively) was obtained and separated by preparative GC.

NMR of PLN: δ 1.02, d ($J = 7$ Hz), 6 H; 0.96, d ($J = 7$ Hz), 3 H; 1.13–1.75, m, 7 H; 2.13, q ($J = 7$ Hz), 4 H. *m/e* 164.1570 (calcd for C₁₂H₂₀, 164.1566).

NMR of PLX: δ 0.85–1.30, two triplets superimposed on a doublet superimposed on a complex multiplet at δ 0.66–1.90, 16 H; 1.9–2.5, m, 4 H.

2-Methyl-6-(2'-butylidene)bicyclo[3.1.0]hexane. A 3.5:3.2:1.4:1.9 mixture of four 2-methyl-6-(2'-butylidene)bicyclo[3.1.0]hexanes (BL) resulted from base-induced decomposition of 5-methyl-5-ethyl-*N*-nitrosoxazolidone in 3-methylcyclopentene listed in order of increasing retention times on the DBTCP capillary column. The last isomer (4) was separated from the other three.

NMR (BL₄): δ 1.07, t ($J = 7$ Hz); 1.02, d ($J = 7$ Hz); 1.75, s, superimposed on a complex multiplet at δ 0.65–2.45. *m/e* 150.1406 (calcd for C₁₁H₁₈, 150.1409). NMR (BL₁ + BL₂ + BL₃) δ 0.92, d ($J = 7$ Hz); 1.11, t ($J = 7$ Hz); 1.69, s superimposed on a complex multiplet at δ 0.9–1.90, 16 H; 1.95–2.25, multiplet, 2 H. *m/e* 150.1404 (calcd for C₁₁H₁₈, 150.1409).

cis- and trans-2,3-Dimethylisopropylidenebicyclopropane. *cis*-2,3-Dimethylisopropylidenebicyclopropane (CIP) was obtained as described above using *cis*-2-butene as a substrate: NMR (CIP) δ 1.04, d ($J = 4.8$ Hz), superimposed on a multiplet, 8 H; 1.83, t ($J = 1.8$ Hz), 6 H.

trans-2,3-Dimethylisopropylidenebicyclopropane (TIP) was obtained as above from *trans*-2-butene: NMR (TIP) δ 1.02, singlet superimposed on a multiplet, 8 H; 1.73, singlet, 6 H.

Pyrolysis of IPN. A 0.9486:0.0514 mole ratio of IPN to IPX was pyrolyzed at 202.4 °C for 100.0 and 200.0 min, giving 0.3043 ± 0.008 and 0.439 ± 0.004 mole fraction of IPX, respectively; the equilibrium mole ratio was 0.4233:0.5765, respectively. The sums of forward and back rate constants were 1.10 × 10^{–4}/s and 1.12 × 10^{–4}/s, respectively, for an average of 1.11 × 10^{–4}/s.

The same mixture was pyrolyzed at 178.8 °C for 500.0 and 715.0 min, giving mole fractions IPX of 0.2006 ± 0.0013 and 0.256 ± 0.005, respectively. Using the calculated equilibrium mole fraction of 0.4196:0.5804 assuming no entropy change in the reaction gave the sum of rate constants as 1.10 × 10^{–5}/s and 1.14 × 10^{–5}/s, respectively, for an average of 1.12 × 10^{–5}/s.

The same mixture was pyrolyzed at 160.2 °C for 1330.0 min, giving 0.1241 ± 0.003 IPX. Using the calculated equilibrium mole fractions of 0.4160:0.5890 assuming no entropy change in the reaction, the sum of rate constants was equal to 1.83 × 10^{–6}/s.

A weighted least-squares analysis gave log ($k_+ + k_b$) = 14.48 ± 0.3 – 40 151 ± 700/2.3RT with an average deviation of $k_+ + k_b$ from the least-squares slope of ±4%.

Pyrolysis of PLN. A 0.9350:0.065 mole ratio of PLN to PLX was heated at 218.6 °C for 95.0 and 150.0 min, giving 0.3060 ± 0.009 and 0.3716 ± 0.015 mole fraction of PLX, respectively. The equilibrium mole fractions were 0.5104 PLN and 0.4896 PLX allowing calculation of $k_+ + k_b$ of 1.41 × 10^{–4}/s and 1.46 × 10^{–4}/s, respectively, leading to an average of 1.44 × 10^{–4}/s.

A pyrolysis of pure PLX at 202.5 °C for 208.0 min and of a 0.975:0.025 ratio of PLX to PLN for 260.0 min gave 0.2007 ± 0.007 and 0.2541 ± 0.01 mole fractions of PLN, respectively, and allowed calculation of $k_+ + k_b$ of 4.0 × 10^{–5}/s and 4.09 × 10^{–5}/s, respectively, leading to an average of 4.05 × 10^{–5}/s.

Pyrolysis of pure PLX for 1585.0 and for 2250.0 min, and of a mixture of PLN:PLX of 0.9335:0.0665 for 1385.0 and 2679.0 min, at 178.8 °C gave 0.8259 ± 0.03, 0.7620 ± 0.006, 0.1953 ± 0.006, and 0.2859 ± 0.01 mole fractions of PLX, respectively. The calculated equilibrium constant allowed calculation of $k_+ + k_b$ of 4.38 × 10^{–6}/s, 4.64 × 10^{–6}/s, 4.77 × 10^{–6}/s, and 4.41 × 10^{–6}/s, respectively, leading to an average of 4.55 × 10^{–6}/s. A least-squares analysis gave log ($k_+ + k_b$) = 13.26 ± 0.3 – 38 440 ± 700/2.3RT with an average deviation of $k_+ + k_b$ from the least-squares slope of ±4%.

Pyrolysis of 2-Methyl-6-(2'-butylidene)bicyclo[3.1.0]hexane. The isomer of 2-methyl-6-(2'-butylidene)bicyclo[3.1.0]hexane which was separable from the other three was heated at 202.4 °C for 120.0 min. The mole ratios of the four isomers in order of increasing retention times after the pyrolysis were 0.081 ± 0.008, 0.089 ± 0.006, 0.078 ± 0.005, and 0.752 ± 0.01. After 48 h the ratio of the four isomers was 1.25:1.29:1:1.30. From these data the sum of rate constants for conversion of the one isomer to the other three and back again is 5.75 × 10^{–5}/s. The sum of rate constants for overall *endo*–*exo* isomerization can be as much as 6.0 × 10^{–5}/s, or as little as 5.5 × 10^{–5} depending on which of the other three isomers is of the same stereochemistry at C₂ as the fourth isomer.

Pyrolysis of cis- and trans-2,3-Dimethyl-1-isopropylidenebicyclopropane (CIP and TIP). Pure CIP was heated at 202.4 °C for 120.0 min giving 0.742 ± 0.004, 0.158 ± 0.004, and 0.100 ± 0.003 mole fractions of CIP, TIP, and an unknown. The equilibrium fractions were 0.265, 0.55, and 0.132 of CIP, TIP, and an unknown. Pure TIP was heated at 202.4 °C for 120.0 min, giving 0.11, 0.841, and 0.049 mole fraction of CIP, TIP, and unknown. Runge-Kutta integration allowed deduction of $k_{CIP \rightarrow TIP} = 2.4 \times 10^{-5}/s$ and $k_{TIP \rightarrow CIP} = 1.9 \times 10^{-5}/s$.

Preparation of trans- and cis-2,3-Dimethylmethylenebicyclopropane (T + C) and trans- and cis-2,3-Dimethyldeuteriomethylenebicyclopropane (T-d₂ and C-d₂). To 50 mL of *trans*-2-butene, 50 g (0.48 mol) of potassium *tert*-butoxide, and 50 mL of pentane in a 1-L, three-neck flask cooled to 0 °C and equipped with a dry ice condenser under a nitrogen atmosphere was added slowly 48 g (0.19 mol) of bromoform with stirring. During the addition of bromoform 500 mL of pentane was added to dilute the mixture. After the reaction, water was added,

and the organic layer was separated and dried. Careful distillation under reduced pressure gave 34.6 g (84% yield) of dibromide, bp 57–60 °C (~15 mm).

To 8 mmol of the dibromide, 5 mL of HMPA, 2.06 g (0.014 mol) of methyl iodide, and 40 mL of THF at –98 °C in a 250-mL, two-neck flask equipped with an additional funnel was slowly added over 3.5 h 4.5 mL (7.5 mmol) of butyllithium in hexane with stirring under a nitrogen atmosphere. The mixture was stirred for 0.5 h at –95 °C after the addition. After warming to room temperature, the solution was hydrolyzed and extracted with pentane. After drying and careful evaporation of the pentane extracts, the residue was distilled bulb to bulb at 0.5 Torr to give 72% yield of alkylated product plus butyl bromide and an unknown.

NMR δ 0.18, pentet ($J = 6$ Hz), 1 H; 1.07, d ($J = 7$ Hz), 3 H; 1.22, d ($J = 7$ Hz), superimposed on a multiplet, 4 H; 1.70, s, 3 H. m/e 162.0042 (calcd for $C_6H_{11}Br$, 162.0045).

Monobromide (5 mmol) was dissolved in 9 mL of Me_2SO , 0.9 g (8 mmol) of potassium *tert*-butoxide was added slowly, and the mixture was stirred at room temperature for 14 h; the mixture was then quenched with water. After extraction with pentane and washing and drying the pentane extracts, the pentane was carefully distilled away to give crude olefin in 50–60% yield which was purified by GC. The major product was *trans*-2,3-dimethylmethylenecyclopropane (T).^{5d}

In a similar way *cis*-2,3-dimethylmethylenecyclopropane (C), as well as T- d_2 and C- d_2 were prepared with the only differences in the latter two cases being that trideuteriomethyl iodide was used in the alkylation and elimination required 7 days at room temperature to go to completion. NMR analysis revealed that 10 and 9% of two Hs were present in the exo methylene of T- d_2 and C- d_2 .

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, Professor Martin Saunders for a copy of his Runge–Kutta numerical integration program, Mr. Robert Weber for preparation of quantities of C and C_{D_2} , and Professors L. K. Montgomery, V. J. Shiner, and J. Chickos for valuable discussions.

Appendix

The deviations of the experimental concentrations from a Runge–Kutta fit to a set of interconverting species can provide information on the error limits of the rate constants used for the calculation provided that the data is taken over the first half-life of the reaction and that the reverse rate constants or those that are responsible for further reaction of product are not substantially greater than those for reaction of the species of greatest interest. Under these conditions, those rate constants for reaction of a particular species are most important in determining the mole fraction of that species and its products, and errors can be estimated by approximating the reversible system as a parallel, irreversible reaction system. In the case of the reactions of Table III and Chart III, the error

in the rate constants for loss of T_{H_2} , namely, k_1^H and k_2^H can be estimated by first assuming that the deviations in the experimental mole fractions of T_{H_2} from the calculated mole fraction of T_{H_2} is equivalent to the deviations in the experimental mole fractions of T_{H_2} from a straight line fit to a plot of $-\ln T_{H_2}/T_{H_2}^0$ vs. time where the slope is $k_1 + k_2$ so that the average deviation in $k_1 + k_2$ can be determined, and second, by assuming that the average deviation in the experimental ratio of products (A + S/C) from the calculated ratios represents the error in the ratio of k_1/k_2 .

In the case of both T_{H_2} and T_{D_2} from Table III, the average deviation in $k_1 + k_2$ is $\pm 2\%$, and the average deviation in k_1/k_2 is $\pm 2.5\%$. Since for a parallel irreversible first-order reaction $k_1 + k_2 = k_{\text{loss of T}} (\pm 2\%)$, and $k_1/k_2 = \text{ratio A + S/C} (\pm 2.5\%)$, $k_1 = k/[1 + (1/R)]$ and $k_2 = k/[1 + R]$, the average deviation in k_1 is $\pm 2.2\%$ and that in k_2 is $\pm 3\%$, and therefore, $k_1^H/k_1^{D_2} = 1.31 \pm 3\%$ since random errors in ratios and products accumulate as the square root of the sum of squares of the average deviations.¹⁴

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