# Hydrocarbon Degenerate Thermal Rearrangements. A Reinterpretation of the Data and Proposed Mechanism for the (*Z*)-2-Methylethylidenecyclobutane Self-Interconversion. Stereochemistry of Cyclobutane Ring Openings

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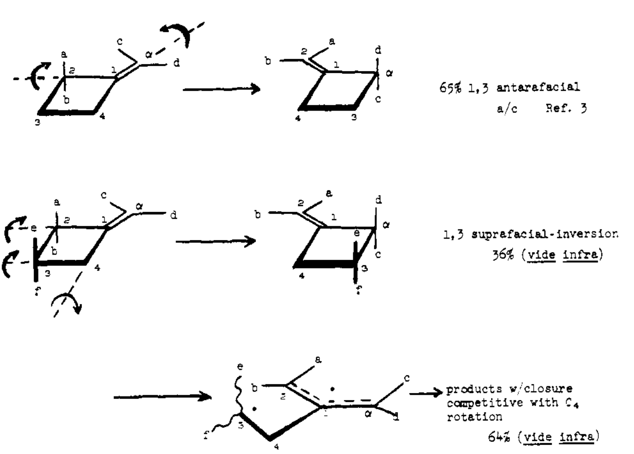
**Abstract:** Previously reported data for the racemization and deuterium scrambling of (+)-(*Z*)-(1-deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane[3] have been reevaluated by Runge-Kutta integration. Some rate constants differing by a factor of 50% from those previously reported have been obtained, leading to a fit of the data within experimental error. These new rate constants completely alter the original interpretation of 65% antarafacial allylic usage to as much as 100% suprafacial usage partially (36%) by an "allowed" 1,3-sigmatropic shift with inversion at the migrating carbon, and partially (64%) with randomization of the migrating carbon stereochemistry. This new interpretation invokes a ring opening pathway that is identical with that observed and/or calculated with other cyclobutane cleavages.

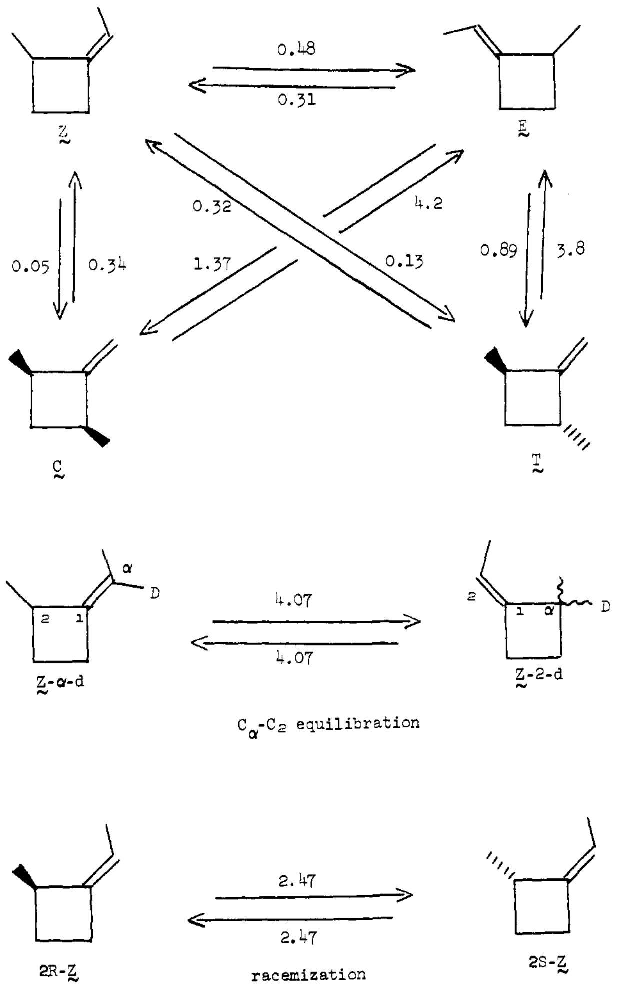
Because of our interest in the spiropentane to methylenecyclobutane thermal rearrangement energy surface,[1] the conclusion that the degenerate rearrangement of methylenecyclobutane occurred predominantly by an antarafacial 1,3-sigmatropic shift[2,3] attracted attention. As a result we have reanalyzed the published data performing Runge-Kutta integrations to evaluate other mechanistic proposals and found a self-consistent explanation based on partial involvement of a Woodward-Hoffmann allowed[4] suprafacial-inversion 1,3 pathway with the remainder involving a biradical formed by a conrotatory-bevel ring opening pathway. The biradical loses stereochemistry at C(3) due to rotation, but undergoes ring closure competitive with C(4) rotation.



Herein we report the original data, evaluate the previous interpretation, and use the new interpretation to provide a unifying hypothesis, if not explanation, for all previously reported stereochemical results in methylenecyclobutane pyrolyses and for most, if not all, other unencumbered cyclobutane thermal ring openings.

**Pyrolytic Interconversion of *cis*- and *trans*-2,4-Dimethylmethylenecyclobutane and (*Z*)- and (*E*)-2-Methylethylidenecyclobutane (Z and E).** The interconversions of the 2,4-dimethylmethylenecyclobutanes and 2-methylethylidenecyclobutanes were examined[2] with the results that: (a) the ethylidenes are more stable, $K_{eq} = 4$; (b) both *cis*- and *trans*-2,4-dimethylmethylenecyclobutane, C and T, gave roughly a 10:1 ratio of *E* to *Z* ethylidenes; (c) that *Z* and *E* isomers were comparable in stability, $K_{eq} \simeq 1.4$; (d) consistent with (b), an *E* isomer rearranged to C and T roughly ten times faster than Z rearranged to C + T; (e) Z and E interconverted slowly with respect to the E → C + T reaction, but fast with respect to the Z → C + T reaction; (f) $C_\alpha$-C(2) interchange in the *Z* isomer occurred ten times faster than the Z to E reaction; (g) $C_\alpha$-C(2) interconversion in the *E* isomer occurred at the same rate as

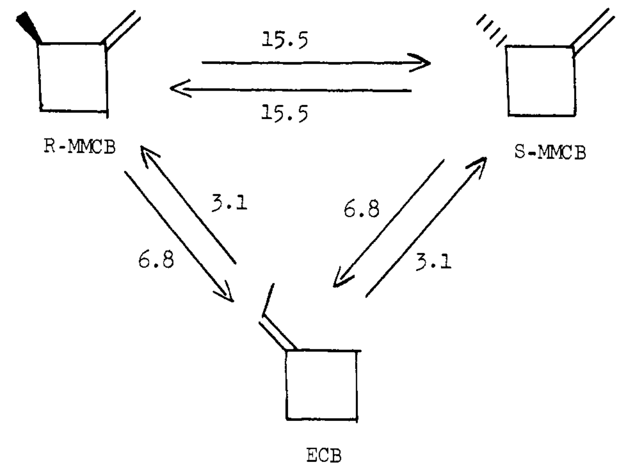
**Scheme I**



all k's x $10^{-5}$/sec at 322°C (ref 2) the E → C + T interconversion. The rate constants at 322 °C ($\times 10^{-5}$/s) are shown in Scheme I, making it clear that equilibration of $C_\alpha$ and C(2) in the *Z* isomer is much faster than the conversion of *Z* to E, C, and T. The rate constant for racemization of the *Z* isomer is only 0.62 times as fast as $C_\alpha$-C(2) interconversion.[5]

The fact that the *Z* isomer was unique in racemizing and equilibrating the vinyl carbon ($C_\alpha$) and C(2) faster than giving the other isomers made it an object for further stereochemical work,[3] but on the basis of these results it was suggested that the $Z_{\alpha d}$ and $Z_{2d}$ interconversion was at least 40% via an antarafacial use of the $C_\alpha$, C(1), and C(2) allylic system since racemization of the *Z* isomer was so slow. If a random biradical were involved, or if a 1,3-sigmatropic shift with either retention or inversion of the migrating carbon and suprafacial use of the allylic system were involved, $k_{rac}$ must equal $k_{eq}$. This startling result[6] of 40% specific antarafacial allylic usage was claimed to be a minimum value, since a process involving C(2) inversion without rearrangement could racemize the system without equilibrating deuteriums. To demonstrate this possibility, optically active 2-methylmethylenecyclobutane was heated at 333 °C to give ethylidenecyclobutane. Racemization of the starting material occurred 2.2 times faster than rearrangement even though the equilibrium constant is near unity ($K_{eq}$ = [ECB]/[MMCB] = 1.1 at 333 °C, i.e., (6.8/2) × 3.1). The derived rate constants are given in Scheme II ($\times 10^{-5}$/s).[2b]

Scheme II



k's x 10$^{-5}$/sec (ref. 2b)

Just why the results in this system are so different than those with (*Z*)-2-methylethylidenecyclobutane is unclear. If anything, they indicate a substantial sensitivity of the rearranging system to substituents, a point which is discussed later.

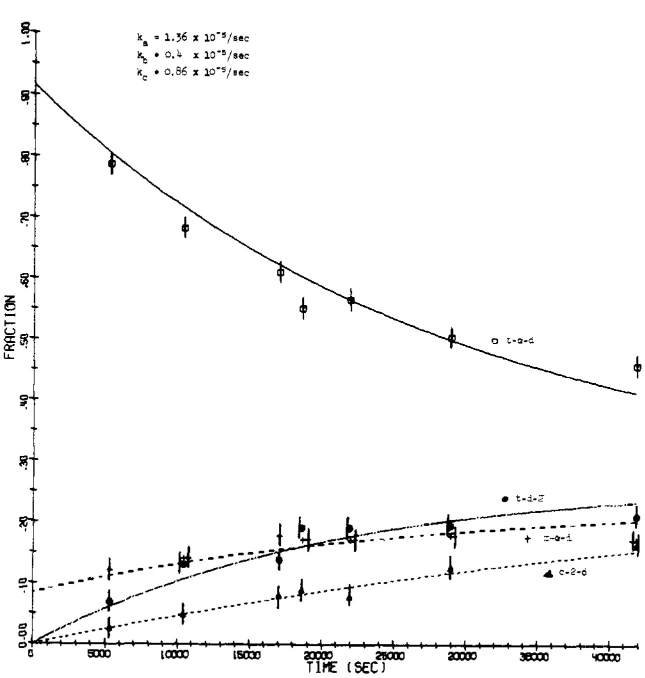
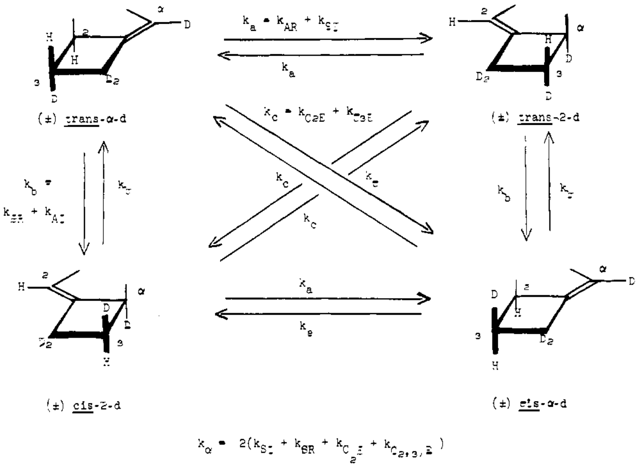


Figure 1.

Scheme III



**Interconversion of Optically Active α-Deuterio- and 2-Deuterio-, *cis*- and *trans*-3,4,4-Trideuterio-(*Z*)-2-methylethylidenecyclobutane.** In the last and most elegant and important paper of the series,[3] the deuterium scrambling of (*Z*)-(1-deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane was examined at 332 °C. The experimental values for the amount of starting material, *trans-α-d* and the three products: *trans*-2-*d*, *cis*-2-*d*, and *cis-α-d* as determined from NMR integrations are shown in Figure 1. The starting material contained 8.4% of the *cis-α-d* compound by NMR integration. Examination of the figure reveals that the experimental error in the measurements must be of the order of ±2%. The authors draw these error limits for all of the values, and considering the published spectra these error limits may be conservative. The authors' best fit of the interconversion data according to Scheme III with $k_a$ = 1.36, $k_b$ = 0.40, and $k_c$ = 0.86, all $\times 10^{-5}$/s, are also in Figure 1. From these data the rate constant for deuterium scramble ($k_{ds} = 2k_a + 2k_b$) can be calculated to be 3.52 $\times 10^{-5}$/s.[5]

In a separate experiment, optically active *trans-α-d* was pyrolyzed for 18 600 s. The extent of loss of optical activity allowed determination of $k_\alpha$ = (4.12 ± 0.46) $\times 10^{-5}$/s. Furthermore, the concentration of the products was determined by NMR integration and listed in Table I. Seeing that their derived phenomenological rate constants were too low to account for this experiment, the authors simply scaled them up by a factor of 1.37, stating that the temperature may have been higher. These "corrected" values of $k_a$, $k_b$, and $k_c$ lead to *k* deuterium scrambling equal to 4.92 $\times 10^{-5}$/s.[5]

It was then correctly pointed out[3] that there were four experimentally determined rate constants, $k_a$, $k_b$, $k_c$, plus $k_{rac}$, and that there were seven different stereochemical pathways: the W-H "allowed" suprafacial-inversion and antarafacial-retention,[4] the W-H "disallowed" suprafacial-retention and antarafacial-inversion,[4] an independent C(2) epimerization, an independent C(3) epimerization, and an independent C(2), C(3) double inversion. The possible pathways contribute to the phenomenological rate constants as shown in Scheme IV.[3] A unique interpretation of the results is impossible with seven unknowns and four equations. Thus, extremes of behavior were

Table I. Product Distribution From 18 600 s, 332 °C Pyrolysis of Optically Active (*Z*)-(1-Deuterioethylidene)-2-methyl-*trans*-3,4,4-trideuteriocyclobutane

| | Exp. | Original $k$'s[a] | Original $k$'s × 1.37[b] | New $k$'s[c] |
|---|---|---|---|---|
| *trans*-α-*d* | 0.55 | 0.60 | 0.524 | 0.577 |
| *trans*-2-*d* | 0.19 | 0.16 | 0.192 | 0.179 |
| *cis*-2-*d* | 0.09 | 0.081 | 0.107 | 0.10 |
| *cis*-α-*d* | 0.17 | 0.156 | 0.176 | 0.144 |

[a] $k_a$ = 1.36, $k_b$ = 0.40, $k_c$ = 0.86, all × $10^{-5}$/s. Original fraction of *cis*-α-*d* = 0.084. [b] $k_a$ = 1.90, $k_b$ = 0.56, $k_c$ = 1.20, all × $10^{-5}$/s. Original fraction of *cis*-α-*d* = 0.084. [c] $k_a$ = 1.60, $k_b$ = 0.6, $k_c$ = 0.6, all × $10^{-5}$/s. Original fraction of *cis*-α-*d* = 0.10.

Scheme IV

$$
\begin{aligned}
k_a &= k_{AR} + k_{SI} \\
k_b &= k_{SR} + k_{AI} \\
k_c &= k_{C(2)E} + k_{C(2)E} \\
k_\alpha &= 2(k_{SI} + k_{RS} + k_{C(2)E} + k_{C(2,3)E})
\end{aligned}
$$

calculated: an antarafacial allylic pathway with a 3.5:1 ratio of retention to inversion could account for all the allylic rearrangement, with the rest of the reaction (two-thirds) being C(2), C(3), and C(2,3) epimerization. Alternatively, only 16% of 1,3 shift need be antarafacial, the rest of the allylic shift being suprafacial, with the remainder of the reaction (one-third) being epimerization at C(3) only. A final hypothesis assumed no epimerization at C(3) giving "AR + AI = 1.6 × $10^{-5}$/s + C(2,3) double epimerization, or at least 65% of the 1,3-carbon shift is antarafacial".

**Alternative Values of $k_a$, $k_b$, and $k_c$ to Fit the Data for Interconversion of Optically Active α-Deuterio- and 2-Deuterio-, *cis*- and *trans*-3,4,4-Trideuterio-(*Z*)-2-methylethylenecyclobutane.** Considering the 2% error in NMR measured values for the amounts of the various isomers of α-deuterio- and 2-deuterio-, *cis*- and *trans*-3,4,4-trideuterio-(*Z*)-2-methylethylidenecyclobutane, different phenomenological rate constants were used to generate a fit to the interconversions of Scheme I. A set of $k_a$, $k_b$, and $k_c$ equal to 1.6, 0.6, and 0.6, respectively, all times $10^{-5}$/s, was found to give a reasonable fit to the data (Figure 2), provided 10% of the *cis*-α-*d* material was present in the starting *trans*-α-*d* material as opposed to 8.4%. Since this initial fraction of *cis*-α-*d* was also determined by NMR, it too has an error of ±2% as the other data. Furthermore, the relative amounts of products from the single run of optically active *trans*-α-*d* material could be reasonably fit without any other adjustment (Table I). Finally, the calculated rate constant for deuterium scramble ($2k_a + 2k_b$) from these new values is 4.4 × $10^{-5}$/s, which is only 12% less than the experimental value from the single run of optically active material and is certainly within experimental error. It should be emphasized that the new values of $k_a$, $k_b$, and $k_c$ are not unique. They are no better than the original values, but they do allow an interpretation of the reaction that appeals to precedence and steric reasonableness.

**Two Alternative Mechanistic Hypotheses for the Interconversion of (*Z*)-2-Methylethylidenecyclobutane.** Any mechanistic hypothesis for the interconversions of Scheme III must not only accommodate the values of $k_a$, $k_b$, and $k_c$, but must account for the observed rate constant for loss of optical activity, $k_\alpha$.

While a unique answer to the mechanistic question is not possible, as pointed out in ref 3, there are reasonable schemes that satisfy the data above. These schemes recognize that the methyl on C(2) must rotate outward to give only *Z* isomers (see below). In each scheme, 36% of a W-H allowed SI pathway is coupled with either 64% of a C(3),C(4) randomized biradical (Scheme V) or 64% of a C(3) randomized biradical formed by the same ring-opening motions as in the W-H SI pathway, but it can only close suprafacially (Scheme VI). Before discussing each Scheme it must be recognized that 36% of a W-H allowed AR pathway in place of the SI pathway would equally satisfy the data, but this process is unreasonable on steric grounds.[6] Because the migrating carbon is forced to remain on one side of the allylic system, the uncoupling of the orbitals in the AR pathway is extreme.[6]

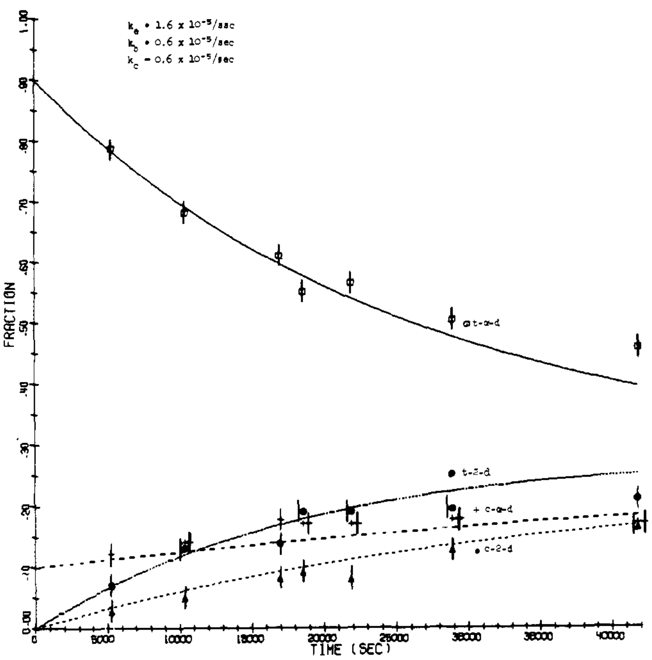


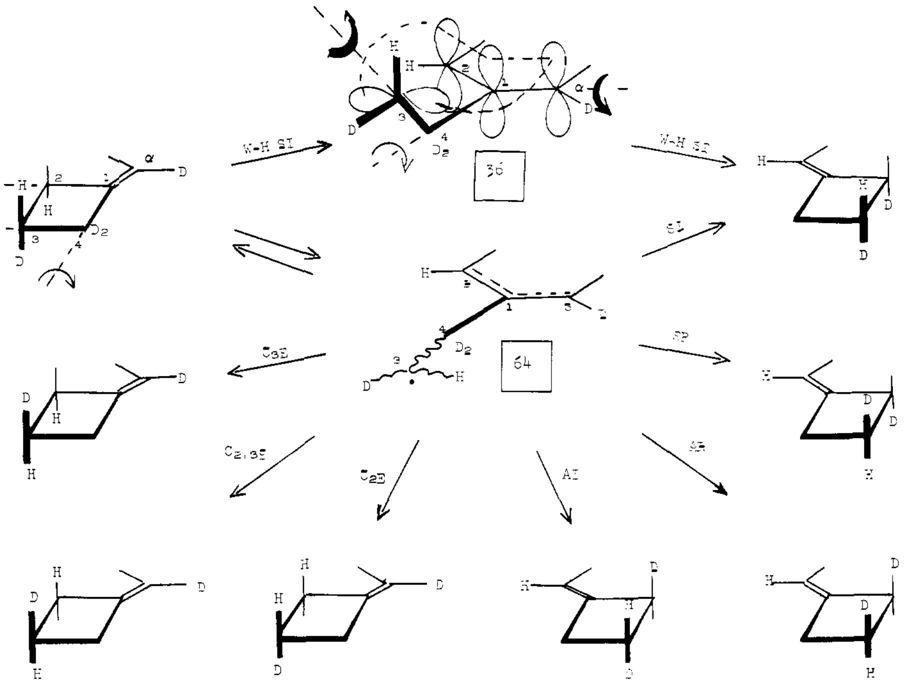
Figure 2.

The W-H allowed SI pathway requires conrotatory opening of the C(2)-C(3) bond with concomitant rotation around the C(1)-C(4) bond such that its rotation is as a meshed bevel gear with respect to the rotations around the C(1)-C(2) and the C(3)-C(4) bonds at the points of intersection of these axes. (Note that a rotation around C(1) in the opposite sense to that of C(4) is equivalent to the C(4) rotation and is itself a bevel motion with respect to the rotation of C(2) and C(3).) To complete the W-H SI-allowed reaction, bonding of C(3) to $C_\alpha$ must occur with motions that are also conrotatory bevel. Thus 2*R*-*trans*-α-*d* is converted to 2*S*-*trans*-2-*d* by this pathway.

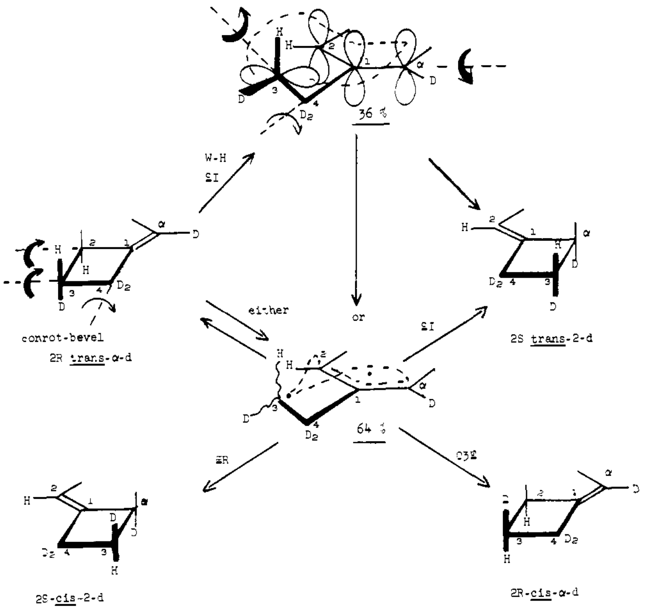
In Scheme V, 64% of the reaction proceeds via a C(3),C(4) randomized biradical. This biradical is formed by an outward rotation of the methyl at C(2), and undergoes all stereochemical modes of ring closure to **Z** materials with equal probability. (Implied here is that the biradical cannot lose allyl radical stereochemistry, i.e., ring closure is faster than rotation around the allyl radical, a most reasonable assumption.) Since all modes of isomerization are defined as equally likely via the biradical, $k_{SI} = k_{SR} = k_{AI} = k_{AR} = k_{C(2)E} = k_{C(3)E} = k_{C(2,3)E}$ = 0.3 × $10^{-5}$/s using the equations of Scheme IV and the new values of $k_a$, $k_b$, and $k_c$. To calculate $k_\alpha$, it must be recognized that the W-H SI pathway and the biradical pathway both contribute to $k_{SI}^{TOT}$, which must be equal to 1.3 × $10^{-5}$/s from the equations of Scheme IV. Thus, $k_\alpha = 2(k_{SI}^{TOT} + k_{SR} + k_{C(2)E} + k_{C(2,3)E})$ = 4.4 × $10^{-5}$/s, which is within experimental error of 4.12 × $10^{-5}$/s, the value reported in ref 3.

In Scheme VI, 64% of the reaction proceeds via a biradical formed by ring opening in the conrotatory-bevel sense, but with ultimate loss of stereochemistry only at C(3). This biradical can have the property of ring closing in a least motion sense without more than a 90° rotation around $C_\alpha$, C(2), or C(4)

Scheme V



Scheme VI

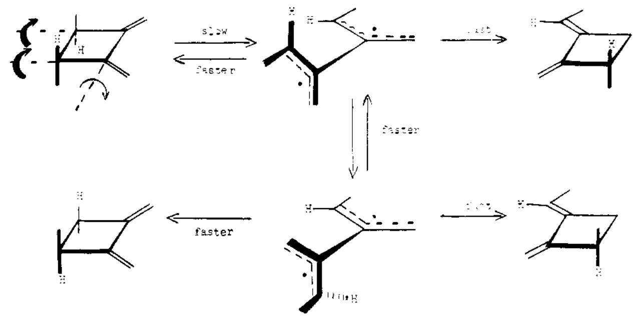


(thus reacting entirely in a suprafacial manner) leading only to *2S-trans-2-d*, *2S-cis-2-d*, and *2R-cis-α-d*, 3,4,4-trideuterio-(*Z*)-2-methylethylidenecyclobutane as well as starting *2R-trans-α-d* material. Since all four modes of ring closure are equally likely in this biradical, and because the AR, AI, C(2)E, and C(2,3)E pathways are not traversed, $k_{SI} = k_{SR} = k_{C(3)E} = 0.6 \times 10^{-5}$/s using the equations of Scheme IV. Since both the biradical pathway and the W-H allowed pathway contribute to $k_{SI}{}^{TOT}$, which must be equal to $1.6 \times 10^{-5}$/s from Scheme IV, $k_\alpha = 2(k_{SI} + k_{SR}) = 4.4 \times 10^{-5}$/s, which is also within experimental error of the value reported in ref 3.

The biradical pathway involving conrotatory, bevel opening in Scheme VI appeals to precedence in the form of experiments with 1,2-dimethylenecyclobutane thermal ring opening[7] and calculation of the cyclobutane to the tetramethylene biradical[8] and notions of minimal uncoupling of orbitals along a reaction coordinate (vide infra). However, it should be recognized that the biradical of Scheme V may also be formed by the same motions. Possibly the only difference between the biradicals of Schemes V and VI is the rate of rotation around the C(1),C(4) bond relative to ring closure. Finally, any combination of a C(3)-only randomized biradical formed by the conrotatory-bevel pathway and C(3),C(4) randomized biradical, regardless of origin, will fit the values reported herein for $k_a$, $k_b$, $k_c$, and $k_\alpha$, provided that 36% of the reaction proceeds via the W-H allowed SI pathway.

**Mechanisms of Other Methylenecyclobutane Interconversions.** The mechanistic alternatives in Schemes V and VI to account for the interconversion of (*Z*)-2-methylethylidenecyclobutane must be compared to the partial, but informative, stereochemical results of other methylenecyclobutane rearrangements. One such experiment is reported in ref 2a, namely that optically active 2-methylmethylenecyclobutane racemizes 2.2 times faster than it rearranges to ethylidenecyclobutane (ECB) (Scheme II).

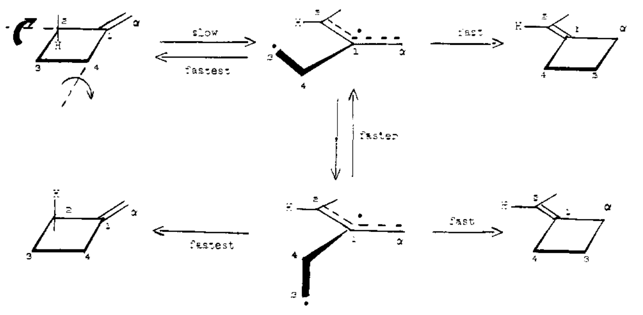
Despite the lack of appropriate labeling, it can be assumed that ring opening of the C(2)–C(3) bond occurs with rotation of the methyl on C(2) outward. (This point is discussed in a separate section below.) If, in addition to the SI concerted pathway, the ring opening generates the randomly rotating achiral biradical of Scheme V, then ring closure of C(3) on methyl-substituted C(2) faster than on $C_\alpha$ will account for the result with the appropriate adjustment rate constants for SI concerted and the biradical pathway. For comparison, optically active *trans*-3,4-dimethyl 1,2-dimethylenecyclobutane also racemizes 2.2 times faster than it rearranges to 1-methylene-*anti*-2-ethylidene-3-methylcyclobutane,[7] so there is precedence for reclosure of these types of biradicals at the more substituted carbon (Scheme VII). Moreover, in the dimethylenecyclobutane rearrangement, outward rotation of methyls also occurs and, further, an orthogonal intermediate must be generated in the rate-determining step, as judged by the small difference in rate (a factor of two) between the *trans*- and *cis*-3,4-dimethyl material, so that rapid rotation around the central bond in the bisallyl intermediate must occur to racemize the system, Scheme VII



further establishing a mechanistic link between the two systems.

The mechanistic alternative of Scheme VI, in which (*Z*)-2-methylethylidenecyclobutane ring opening rearranges partly by the SI concerted path and partly by a conrotatory-bevel pathway to a C(3)-randomized and C(4)-fixed biradical, can account for the results of the 2-methylethylidenecyclobutane racemization if the lack of a methyl substituent on $C_\alpha$ slows the reclosure rate at $C_\alpha$ so that C(4) rotation becomes competitive (Scheme VIII). Thus, neither the mechanism of

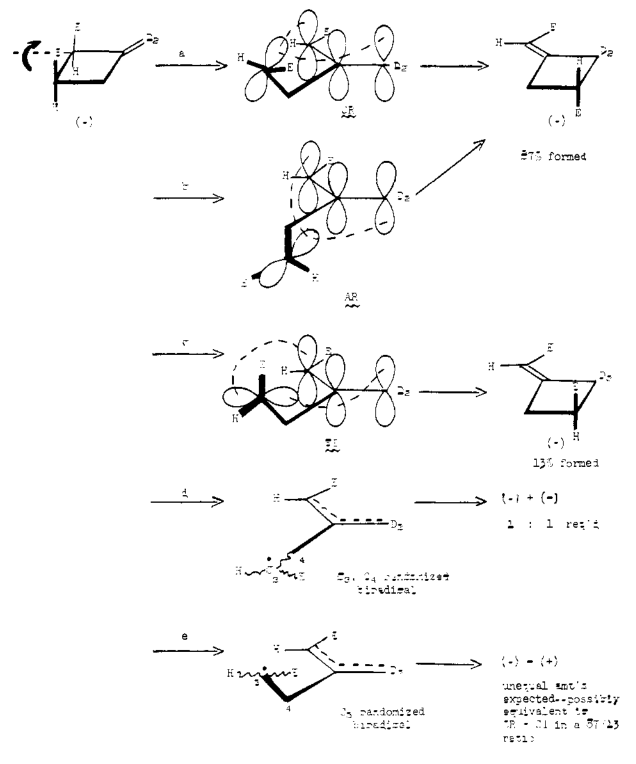
Scheme VIII



Scheme V nor Scheme VI is inconsistent or cannot be logically extended to accommodate the results in the pyrolysis of optically active 2-methylethylidenecyclobutane.

The question as to which mechanistic scheme best applies to methylenecyclobutane rearrangements appears to be answered in favor of Scheme VI. In E. Fossel's Ph.D. work with Doering, the rearrangement of optically active (2*R*,3*R*)-*cis*-2,3-dicarbomethoxy-1-dideuteriomethylenecyclobutane to 3-carbomethoxy-1-carbomethoxymethylenecyclobutane was studied.[9] The $\alpha,\beta$-unsaturated ester product was formed with only 25% racemization with the 3*R* enantiomer as the major product. Both the 3*S* and 3*R* products had the dideuteriomethylene group syn to the ester group on the exomethylene, requiring exclusive outward rotation of the C(2) ester group in the ring opening. According to Scheme IX, the major enantiomer can be formed by either (a) a W-H forbidden,[4] or Berson-Salem allowed[10] SR pathway, or (b) a W-H allowed AR pathway. The minor enantiomer can result from (c) a W-H allowed SI pathway, (d) a C(3),C(4) randomized biradical as in Scheme VI which must necessarily give a 50/50 mixture of both enantiomers, or (e) a C(4) rotation-restricted, C(3)-randomized biradical formed by conrotatory-bevel opening (Scheme VI). This last alternative has the interesting possibility that different amounts of the two enantiomers can be formed, since the biradical is not achiral because rapid rotation around C(4) is not allowed. On the basis of steric effects, it might be anticipated that the C(4) rotation-restricted biradical will close preferentially to the major isomer. Thus, the C(4) rotation-restricted biradical is an operational alternative to a mixture of W-H, forbidden SR and W-H, allowed SI pathways.

Scheme IX

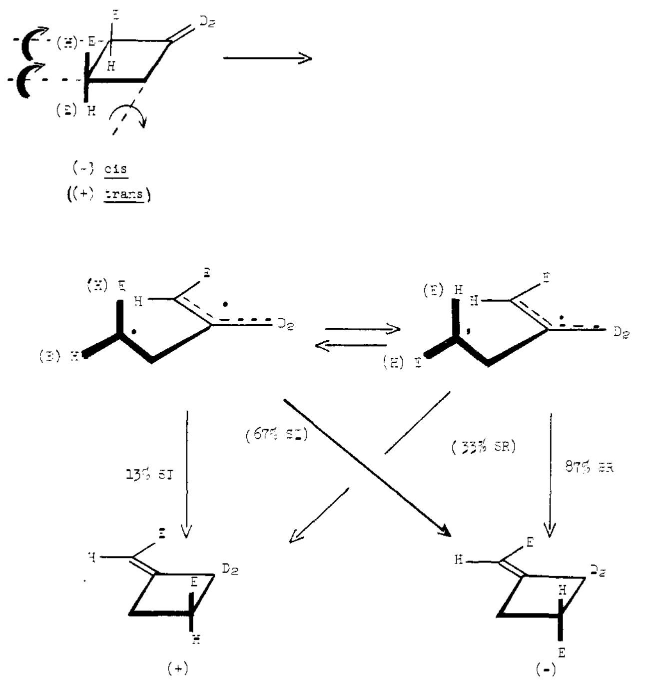


The AR pathway for the major product cannot be ruled out directly by experiment, but must be regarded as unlikely on electronic grounds: it is virtually impossible for the system to retain the Möbius overlap requisite for the allowed AR pathway.[6] The overall product ratio can be rationalized by: (1) an 87/13 ratio of SR to SI pathways; (2) as its equivalent, a C(4) rotation-restricted biradical which can close only suprafacially with the inversion or retention at C(3) in an 87/13 ratio determined by steric effects; (3) a 74/26 ratio of SR to randomized biradical paths; (4) any appropriate mixture of the alternatives 1 through 3.

The dominance of the SR stereo pathway must be closely examined. It is a W-H forbidden reaction, but Berson-Salem subjacent orbital control suggests that it may be concerted.[10] However, the C(4) rotation-restricted biradical with appendaged steric effects will also nicely rationalize this stereochemistry. The former alternative is less attractive in that the SR pathway does not dominate the less sterically encumbered (especially at C(3)) (*Z*)-2-methylethylidenecyclobutane rearrangements discussed above. Such a pathway is included in the phenomenological rate constant $k_b$, the smallest of the three rate constants of Scheme III by the values of ref 3 and is merely 21.5% of the total reaction with the new values for $k_a$, $k_b$, and $k_c$ presented here. Thus, Berson-Salem electronic control does not greatly contribute to methylenecyclobutane rearrangements in general, and so the C(4) rotation-restricted biradical pathway, subject to steric effects, is the best alternative.

To conclude, the Fossel rearrangement is best viewed as C(2),C(3) ring opening, such that the C(2) ester group rotates outward at the same time a bevel rotation around the C(1)-C(4) bond occurs to give an orthogonal biradical which can lose stereochemistry at C(3) (Scheme X). We assume (vide infra) that C(3) rotates as C(2) initially, that is conrotatory, to place the C(3) ester group inside. Least motion closure of this species is the W-H SI concerted pathway, but rotation around C(3) to give the sterically more favored species followed by closure gives the major product in what is an SR pathway overall.

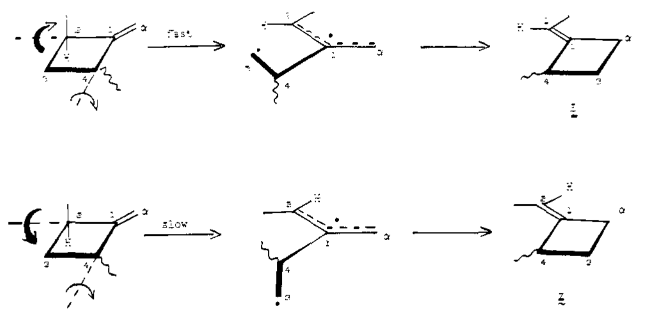
Scheme X



Supportive of this hypothesis is the fact that the *trans*-2,3-dicarbomethoxymethylenecyclobutane gave the rearrangement product with only 33% retention of optical purity, indicating that the sterically poor SI pathway from the cis diester is less encumbered and more competitive with the SR pathway from the C(4) rotation-restricted biradical. Although it is not revealed in the abstract as to which of the two pathways, SI or SR, dominates, the SI pathway is the major one if the C(2) ester group rotates outward.

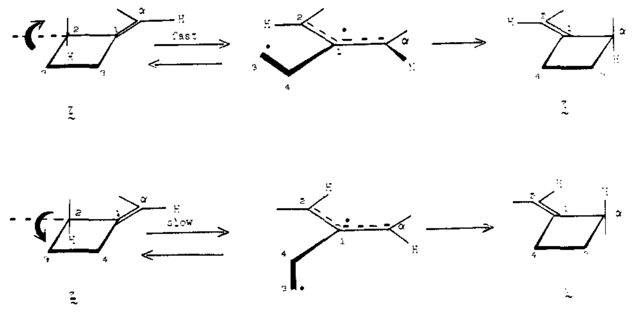
**Examination of the Direction of Rotation at C(2) in 2-Substituted Methylenecyclobutane Rearrangements.** In all of the 2-substituted methylenecyclobutane rearrangements examined, there is a preferred direction for rotation of C(2) (Scheme XI). *cis*- and *trans*-2,4-dimethylmethylenecyclobutane rearrange preferentially to the (*E*)-2-methylethylidenecyclobutane by a factor of ten over formation of the *Z* isomer.[2] This is a result of preferential rotation of C(2) to move substituents away from C(3) in the ring opening. This is a phenomena whose origins are presumably steric, and it has been observed previously in cyclobutene ring opening[11] and methylenecyclopropane[12] and 1,2-dimethylenecyclobutane[7] degenerate rearrangements. In the case at hand, no information is available on the direction of rotation of C(3) or C(4), but it is reasonable that they occur in a conrotatory-bevel sense (vide infra).

Scheme XI



Just why (*Z*)-2-methylethylidenecyclobutane undergoes $C_\alpha$,C(2) interchange roughly ten times faster than the *E*-isomer material undergoes the $C_\alpha$,C(2) interconversion also reflects the preference for outward rotation of substituents at C(2) of methylenecyclobutane (Scheme XII). In the *Z* isomer, outward rotation of the methyl at C(2) produces a cis,cis-dimethylallyl radical which may rebond on either side to C(3) by the reverse of the same motions that produced it.

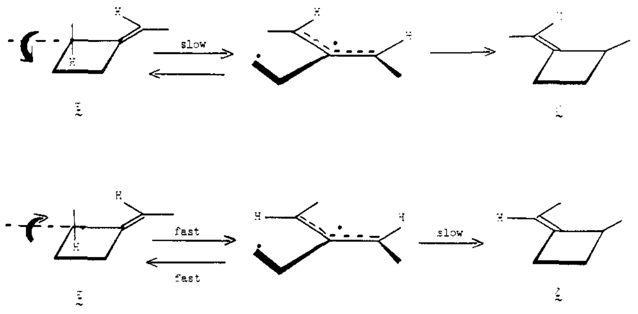
Scheme XII



Furthermore, a Z to E interconversion requires an inward rotation of the substituent at C(2) to give a cis,trans-dimethylallyl species which could then close to give the *E* isomer. But the inward rotation again is slow, judging by the fact that $C_\alpha$,C(2) interchange in the *Z* isomer is also roughly ten times faster than the Z to E rearrangement (Scheme I).

To have $C_\alpha$,C(2) interchange in the *E* isomer (Scheme XIII), the unfavorable inward rotation of the methyl at C(2) is necessary to produce a trans,trans-dimethylallyl radical which then can rebond with equal facility on either side. Thus, the E-$\alpha$-*d*/E-2-*d* interconversion should be slow with respect to the Z-$\alpha$-*d*/Z-2-*d* interchange. Finally, favorable outward rotation of the methyl at C(2) in the *E* isomer can give a cis-,trans-allyl species which could rebond to give the *Z* isomer. However, this too is slow from the data of Scheme I and is best understood in terms of preferential reclosure of the *cis,trans*-dimethylallyl species back to the *E* isomer, since this is the microscopic reverse of the outward methyl rotation ring opening. Rebonding on the other side of the allyl system to give the *Z* isomer is the microscopic reverse of inward methyl rotation opening, which must be slower than the pathway back to the *E* isomer.

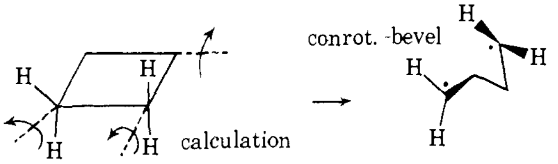
Scheme XIII



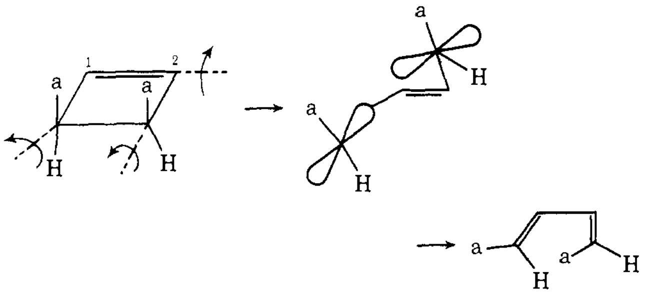
**Comparison to Other Cyclobutane Ring Cleavages.** It is important to compare the alternative mechanisms for the methylenecyclobutane rearrangement and the reasonably well-studied pathway for the degenerate rearrangement of 1,2-dimethylenecyclobutane (DMCB).[7] In a reaction with an activation energy 10 kcal/mol higher than anticipated for generation of a noninteracting 2,2′-bisallyl biradical, DMCB rearranges by a conrotatory opening of the C(3)–C(4) bond with concomitment bevel rotation around the C(1)–C(2) bond as deduced from stereochemical and kinetic studies (Scheme VII).[7]

The ring opening in both cases is virtually the same, particularly with regard to the rotation around the C(1)–C(2) bond of DMCB and the C(1)–C(4) bond of methylenecyclobutane (Schemes V, VI, and VII). After formation of the respective biradicals, differences appear. Central bond (C(1)–C(2)) rotation in 2,2′-bisallyl is fast compared with ring closure, while C(1)–C(4) rotation in the biradical from methylenecyclobutane is competitive with ring closure. This may well reflect a higher activation energy for reclosure of two more stable allyl radicals compared with reclosure of an allyl radical and an alkyl radical. Rotation around C(3) in the bisallyl species does not occur, no doubt due to allyl radical resonance energy.

In an interesting comparison, the recently calculated[8] cyclobutane to the tetramethylene biradical energy surface also follows the same rotations, namely, conrotatory bevel, to a gauche conformation. Thus, all cyclobutane ring openings appear to occur by the same pathway involving conrotatory motions and a third rotation whose axis is orthogonal to the conrotatory rotation axes. The third rotation occurs in a bevel sense as described and not as its opposite, the anti-bevel rotation (see below).

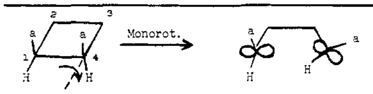
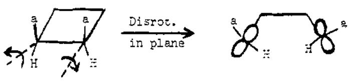
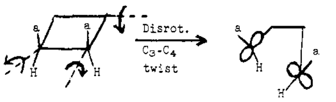
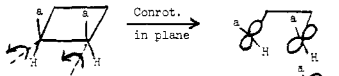
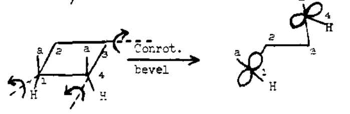
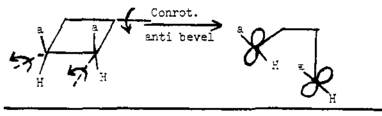


Interestingly, even the pericyclic cyclobutene ring opening requires C(1)–C(2) π-bond twisting in a bevel sense as suggested from experiments[13] and calculations.[14]



It is important to ask if the third rotation is fundamental to the motions involved in cyclobutane ring openings. Therefore, all topological possibilities for conrotatory, disrotatory, and even monorotatory processes should be analyzed from a steric and electronic point of view. In the discussion that follows, the terms dis and con refer only to rotational pathway and not to concertedness in a Woodward–Hoffmann sense (Table II).

Table II. Possible Topologies for Cyclobutane Ring Opening

| | Relative Steric Destabilization | Relative Overlap of Originally Bonded Atoms at Fixed Angles at $C_2$ and at $C_3$ |
|---|---|---|
|  Monorot. | some | minimal |
|  Disrot. in plane | some | partial |
|  Disrot. $C_3$-$C_4$ twist | some | minimal |
|  Conrot. in plane | some | partial |
|  Conrot. bevel | none | maximal |
|  Conrot. anti bevel | substantial | minimal |

If the biradical generated in the ring opening is an energy minimum, then the relative energies of different pathways to generate it will determine the favored stereochemical mode of ring opening. On the basis of steric effects alone, the conrotatory-bevel pathway is of lowest energy if reasonable distances between the groups are chosen for various transition states. Furthermore, the extent of overlap between the orbitals in the transition state should also play a role. Clearly the conrotatory-bevel pathway preserves the maximal amount of overlap between the originally bonded carbons (C(1) and C(4)) as the ∠C(1)C(2)C(3) and ∠C(2)C(3)C(4) angles open to 109°. In all other paths, including disrotatory ones, C(1) and C(4) overlap, as it appears from models, decreases faster per unit relief of strain at C(2) and C(3) than the conrotatory-bevel pathway. Thus, the conrotatory-bevel pathway should be lowest in energy, provided that the resulting biradical is lower in energy than the transition state forming it. This latter assumption has support in thermochemical calculations by Benson[15] and also has quantum theoretical support.[8] Thus, provided there is no other electronic or overwhelming steric effect operating, *thermal cyclobutane ring openings will occur by the conrotatory-bevel pathway to minimize steric repulsions and maximize overlap between the originally bonded carbons.*

**Acknowledgment.** I thank the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this work, Professor Martin Saunders for providing a copy of the Runge–Kutta Program used in this work, Mr. Robert Weber for his computer plotting expertise, and Referee I for a careful reading of the manuscript, resulting in numerous helpful suggestions.

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(6) Observation of net antarafacial use of the allylic system seems inconsistent with the severe stereoelectronic difficulties in the presumed Woodward–Hoffmann allowed antarafacial-retention pathway, particularly in the methylenecyclobutane degenerate rearrangement. The AR pathway here requires that the migrating carbon remain on the same side of the allylic moiety, thus destroying overlap at some point. By comparison, in an unencumbered 1,3-AR shift, it is possible for the system to retain overlap because the migrating group can pass through the plane of the allylic system and the termini of the three carbon units can twist sufficiently; despite this possibility, a *bona-fide* example of even a partially specific AR pathway has yet to be provided. It must also be admitted that in a concerted suprafacial-inversion methylenecyclobutane rearrangement, the distance between $C_\alpha$ and C(2) with respect to the migrating carbon C(3) is quite large so as to minimize overlap, but at least there is never a geometrically imposed null in the overlap as with the AR pathway in this system. Finally, thoughtful, but incomplete consideration of microscopic reversibility in connection with the AR pathway for the methylenecyclobutane rearrangement might seem to exclude it, but careful application of the principle reveals no prohibition on the basis of symmetry due to the presence of equivalent pathways.
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(16) Consideration of overlap alone in the reversible cyclopropane ring opening via a propane-1,3-diyl intermediate where there is no possibility of a third rotation leads to the prediction that the observed stereospecificity[17] should be due to a disrotatory pathway. The very extensive calculations[18] predict a conrotatory pathway since hyperconjugative destabilization of the orbitally symmetric biradial apparently outweighs overlap considerations.

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# Oxyfunctionalization of Hydrocarbons. 3.[1a] Superacid Catalyzed Oxygenation of Alkanes with Ozone Involving Protonated Ozone, $O_3H^+$

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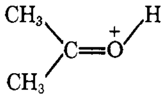
*Received October 24, 1975*

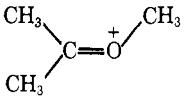
**Abstract:** The reaction of ozone with a series of alkanes in superacid-$SO_2ClF$ solution has been investigated. Product analysis reveals that the reaction pathway involves oxygenation followed by a carbon to oxygen alkyl group migration analogous to the acid-catalyzed cleavage-rearrangement reaction of hydroperoxides. Mechanistic studies are consistent with electrophilic insertion into a $\sigma$ bond by protonated ozone, $O_3H^+$.

## Introduction

In the preceding paper of this series, we demonstrated the nucleophilic nature of ozone in its reactions with alkylcarbenium ions.[1a] In these reactions, 3-5% ozone in oxygen gas was bubbled through a solution of the alkylcarbenium ion, hrepared from the corresponding alkyl halide in $SO_2ClF$ or $SO_2$ with $FSO_3H$-$SbF_5$ (magic acid) or $SbF_5$ solutions.[2] NMR analyses of the ozonation products of the dimethylcarbenium ion, trimethylcarbenium ion, and dimethylethylcarbenium ion were consistent with the formation of protonated acetone (**1**), dimethylmethoxycarbenium ion (**2**), and dimethylethoxycarbenium ion (**3**), respectively.



**1**



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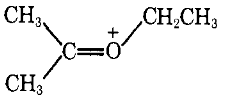
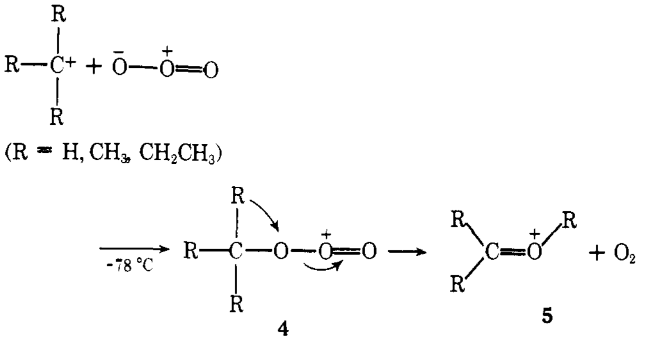


**3**

The reactions can be described as shown in Scheme I. The oxygen eliminated from the intermediate trioxide (**4**) can be considered to be in its singlet state as indicated, for example, in its ability to further oxidize products to the acetylium ion and subsequently to carbon dioxide. Such further oxidations as shown in control experiments could not be induced by ozone alone.

Scheme I



In continuation of our studies of oxyfunctionalization of hydrocarbons, we were interested in extending our investigation to the ozonation of alkanes in the presence of strong acids. We now wish to report the results of our studies of the electrophilic, magic acid catalyzed oxygenation of alkanes with ozone.

## Results and Discussion

In the reactions of propane, isobutane, and isopentane with ozone in magic acid-$SO_2ClF$ solution at −78 °C, the same products were obtained as from the reactions of the corresponding stable alkylcarbenium ions with ozone,[1a] that is **1**, **2**, and **3** in yields of 20, 45, and 40%, respectively.

It has been reported that the first step in the ozonation of alkanes has some characteristics of a radical reaction and some of an insertion reaction.[3] The most recent study[4] on the ozonation of alkanes still leaves considerable doubt as to the nature of the initial intermediate (**6**) depicted in Scheme II.

Scheme II