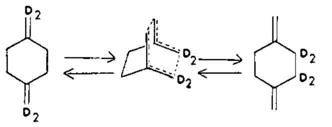
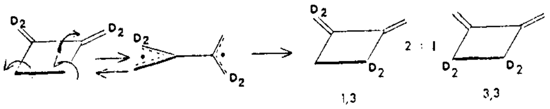
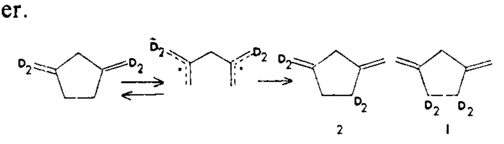
"boat"-like transition state which may resemble [2.2.2]propellane,[4] but 1,2-dimethylenecyclobutane (DMCB) cleaves to a 2,2′-bisallyl biradical which recloses to DMCB resulting in formal [1,3]- and [3,3]-shift products in a 2:1 ratio, kinetically.[5] Significantly, the latter reaction, though apparently nonconcerted, proceeds with substantial (95%) stereospecificity via a conrotatory C_3–C_4 bond rupture with simultaneous C_1C_2 rotation in a fashion that is as meshed-bevel gears at the intersection of the rotation axes. The behavior of the interfacial material, 1,3-dimethylenecyclopentane (DMCP) is therefore of concern, and we here report that it behaves as DMCB[5] does.



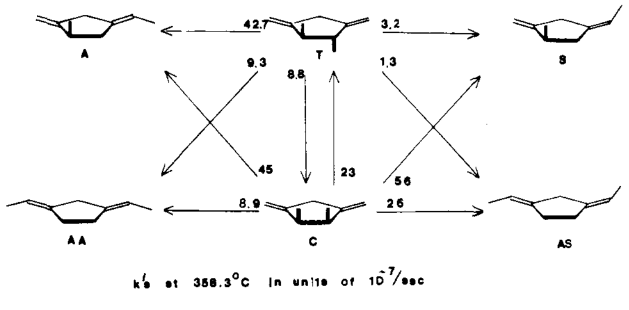


In a well-condition vessel at 370.5 °C, 1,3-bis(dideuteriomethylene)cyclopentane (DMCP-d_4,[6] ~5 Torr with 100 Torr of N_2) undergoes random methylene group scrambling as evidenced by NMR and ozonolysis. After 24 at 370.5 °C, three samples of DMCP-d_4 were individually oxidized and had a d_2:d_4 ratio of 1.99 ± 0.09 in the succinic anhydride after one-third conversion to the equilibrium mixture. Assuming a first-order reaction, a crude rate constant suggests an activation free energy of 53 kcal/mol which is about the bond dissociation energy estimated for the C_4–C_5 bond considering an allyl radical resonance energy of 12.5 kcal/mol and a reactant strain energy of 5 kcal/mol. Thus, DMCP apparently cleaves to a 2,2′-bisallylmethane which recloses in a random manner.



In an effort to determine a rotational preference in ring opening, *trans*- and *cis*-4,5-dimethyl-1,3-dimethylenecyclopentanes (T and C)[6] were pyrolyzed at 358.3 °C. T gives mostly *anti*-1-ethylidene-3-methylene-4-methylcyclopentane (A)[7] and small amounts of *anti,anti*-1,3-diethylidenecyclopentane (AA)[8], as well as C. On the other hand, C gives A, and its syn isomer (S)[7] in nearly equal quantities along with *anti, syn*-1,3-diethylidenecyclopentane (AS)[8] and some T. In order to quantitate the conversions, the first-order rate constants below for the interconversions were found to provide calculated concentrations from numerical integration of the differential rate expressions of the scheme that matched the experimental data as a function of time.[9]

These results indicate (a) that the reaction is first order; (b) that, if a single biradical is involved in the isomerization of T and a single one in the isomerization of C, each formed by the same rotational modes, then conrotatory opening of the system occurs to generate bisallylmethane biradicals which reclose faster than they undergo rotation around the methallyl radicals; and (c) that a third rotation twisting the two developing allylic system occurs since the global rate constants for reaction of T and of C are similar; an in-plane conrotatory opening of C should have been substantially retarded by steric effects.



k's at 358.3°C in units of 10^{-7}/sec

The stereospecificity in the ring opening may be attributed simply to steric effects forcing bond rotations so as to generate the most stable conformation of the transition state leading to the diradical.

A companion paper describes partial stereospecificity in the closure of the 2,2′-bisallylmethane biradical.

Acknowledgment. We thank the National Science Foundation for partial financial support and the Instituto Universitario Politecnico, Barquisimeto, Venezuela, for a predoctoral fellowship to J. S.

References and Notes

(1) For a review see S. J. Rhoads and N. R. Raulins, *Org. React.* **22,** 1 (1975).
(2) For reviews see (a) G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, **86,** 899 (1964); (b) D. J. Trecker and J. C. Henry, *ibid.*, **86,** 902 (1964); (c) J. A. Berson and M. Jones, Jr., *ibid.*, **86,** 5017, 5019 (1964); (d) J. A. Berson and E. J. Walsh, Jr., *ibid.*, **90,** 4736 (1968).
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(4) J. J. Gajewski, L. K. Hoffman, and C. N. Shih, *J. Am. Chem. Soc.* **96,** 3705 (1974).
(5) J. J. Gajewski and C. N. Shih, *J. Am. Chem. Soc.* **94,** 1675 (1972).
(6) DMCP, T, and C were prepared from the dicarboxylic acid resulting from ozonolysis of the appropriate norbornene derivative.
(7) The ^{1}H NMR values of A and S are virtually indistinguishable thus preventing rigorous assignment of stereochemistry. However, if a single intermediate is involved in the rearrangement of T and a single intermediate in the pyrolysis of C, as the d_2:d_4 ratio from DMCP-d_4 suggests, the stereochemical assignments necessarily follow from the observation of AA as the [3,3]-shift product from T, and AS as the 3,3-shift *product from* C.[8]
(8) ^{1}H NMR: AA, δ 1.54 (d, J = 7 Hz, 6 H), 2.30 (s, 4 H), 2.86 (s, 2 H), 5.20 (d, J = 7 Hz, 2 H); AS, δ 1.56 (apparent t, J = 6 Hz, 6 H), 2.27 (br s, 4 H), 2.84 (s, 2 H), 5.22 (m 2 H).
(9) The experimental and calculated mole fractions at five different reaction times over the first half-life for reaction of T and C agreed within 1–4% of one another with the rate constants cited. A table with all of the data was made available to the editor and referees.

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2,2′-Bisallylmethane: Thermal Degenerate Rearrangement of 1,3-Dimethylenecyclopentane. Partly Stereospecific Closure of a Biradical

Sir:

The 2,2′-bisallylmethane diradical (2,2′-BAM) appears to be generated as an intermediate upon thermolysis of 1,3-dimethylenecyclopentane (DMCP).[1] This conclusion derives from the finding that formal [1,3]- and [3,3]-shift products are formed in a 2:1 ratio, respectively.[1] However, pyrolysis of *cis*- and of *trans*-4,5-dimethyl-DMCP leads to stereoisomeric products from each in a manner that indicates partial stereospecificity in the formation of the biradical.[1] This communication reports stereospecificity in the closure of the biradical to the [1,3]-shift product with partial inversion of configuration of the migrating carbon. In addition, different rate- and product-determining deuterium isotope effects further substantiate the intervention of an intermediate.

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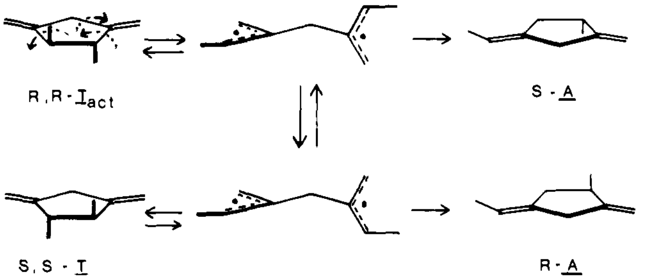
Table I

	% T	% C^a	% S^a	% A	% SA^a	% AA^a
$T^{H_4} \xrightarrow[24.00\ h]{360.4\ °C}$	52.39 ± 0.4	2.37 ± 0.03	2.47 ± 0.04	31.42 ± 0.24	1.57 ± 0.04	9.77 ± 0.1
	12.8 ± 1% rac			11.9% inv		
$T^{D_4} \xrightarrow[24.00\ h]{360.4\ °C}$	53.69 ± 0.03	2.46 ± 0.05	2.33 ± 0.05	31.08 ± 0.11	1.42 ± 0.04	9.00 ± 0.1
	16.4 ± 1% rac			10.8% inv^b		

^{a} Reference 1. ^{b} Reference 8.

Pyrolysis of (−)-(4*R*,5*R*)-*trans*-4,5-dimethyl-1,3-dimethylenecyclopentane (T_{act})[2] at 360.4 °C for 24.00 h (47.6% conversion of starting material) gives (+)-(4*S*)-4-methyl-*anti*-1-ethylidene-3-methylenecyclopentane (A)[3] with 11.9% preservation of optical purity.[4] The starting material is racemized to the extent of 12.8 ± 1% allowing calculation of a 13.5 ± 1% inversion of configuration in the formation of the [1,3]-shift product directly from T_{act}.[5]



Since the stereochemistry and kinetics for reaction of T_{rac} suggest stereospecific conrotatory-bevel ring opening to an orthogonal 2,2′-BM,[1] inversion in the [1,3]-shift product would appear to involve faster conrotatory-bevel closure than rotation about bonds to the central carbon. Overall, this corresponds formally to a Woodward–Hoffmann "allowed", suprafacial-inversion [1,3] shift, but the reaction does not appear to be concerted. This suggests that [1,3] shifts, though partly stereospecific,[6] may be so not because of concertion but because stereospecific biradical generation followed by ring closure to rearranged product via a least motion path is faster than bond rotation.

The demonstration of an intermediate in this partly stereospecific rearrangement of $T^{H_4}{}_{act}$ derives from a comparison of this pyrolysis with that under exactly the same conditions of *trans*-4,5-dimethyl-1,3-bis(dideuteriomethylene)cyclopentane, $T^{D_4}{}_{act}$, of exactly the same optical purity as $T^{H_4}{}_{act}$[7] (Table I).

The ratio of rate constants for loss of $T^{H_4}{}_{act}$ and for loss of $T^{D_4}{}_{act}$ are virtually identical (= 0.98 ± 0.03) which indicates no isotope effect on the rate-determining step, i.e., no kinetic isotope effect (KIE). However, the amount of the [1,3]- and [3,3]-shift products is less starting from T^{D_4} than from T^{H_4}, and the extent of racemization in starting material is greater starting from T^{D_4} than from T^{H_4} which indicates an isotope effect on a product-determining (PD) step.[9]

An approximation of this PDIE can be obtained by summing the rate constants[5] for formation of the [1,3]- and [3,3]-shift products ($k_{1,3+3,3}$), dividing by the sum of rate constants[5] for racemization of starting material and formation of the cis isomer ($k_{1,1}$), and comparing this ratio from T^{H_4} and T^{D_4}. From the rate constants $k^{H}{}_{1,3+3,3}/k^{H}{}_{1,1} \div k^{D_4}{}_{1,3+3,3}/k^{D_4}{}_{1,1} = 1.22 \pm 0.12$ where the error comes primarily from the uncertainty in racemization of T. The assumption here is, of course, that the [1,3] and [3,3] shifts arise from the same intermediate. A similar comparison of just the [1,3] shift to the [1,1] shift gives $k^{H}{}_{1,3}/k^{H}{}_{1,1} \div k^{D_4}{}_{1,3}/k^{D_4}{}_{1,1} = 1.21 \pm 0.12$. Thus, the PDIE, no matter how calculated, far exceeds the KIE, thus requiring an intermediate in the reaction. The origin of this PDIE appears to be a slower rate of closure of the 2,2′-BM biradical onto CD_2 groups relative to CH_2 groups in the formation of the [1,3]- and [3,3]-shift products, allowing more rotation about bonds to the central carbon racemizing the biradical and producing more racemized A^{D_4} and T^{D_4}.[10]

It is interesting to contrast these results with the pyrolysis of optically active *trans*-3,4-dimethyl-1,2-dimethylenecyclobutane which gives racemic [1,3]-shift product.[11] Here, a 2,2′-bisallyl biradical is also produced stereospecifically, but rotation about the central carbon must be faster than ring closure. This is probably a manifestation of a significant barrier to closure of a 1,4 diradical to a cyclobutane. This is in accord with the prediction derived from thermochemical estimates of the heats of formation of biradicals and comparisons of these with activation energies for ring-opening reactions.[12]

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(1) J. J. Gajewski and J. Salazar, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) The absolute configuration and optical purity was determined by analysis and formation of (+)-(2*R*,3*R*)-2,3-dimethylsuccinic anhydride. (b) E. Jonsson, *Acta Chem. Scand.*, **19**, 2247 (1965).

(3) A was obtained contaminated with 7% syn isomer since preparative VPC separation could not be achieved, but S should be formed with a specificity similar to that of A.

(4) The absolute configuration and optical purity was determined by ozonolysis and formation of (−)-(2*S*)-2-methylsuccinic anhydride, $[\alpha]_D$ −6.1° (in EtOH). The maximum rotation should be 57° since 56% optically pure diacid[4b] gives anhydride of 32.1° rotation.[4c] (b) R. Rossi, P. Diversi, and G. Ingrosso, *Gazz. Chim. Ital.*, 1391 (1968). (c) M. Naps and I. B. Jones, *J. Am. Chem. Soc.*, **62**, 2450 (1940).

(5) The differential equations for a kinetic scheme similar to that in ref 1 but with the inclusion of active T and combination of the two [1,3]-shift products and combination of the two [3,3]-shift products allowed computation of the data in Table I with appropriate rate constants that were partially derived from a fit of the data from C. The data was provided to the referees. All analyses were performed at least three times and the results of two runs each for T^{H_4} and T^{D_4} for 24.0 h are averaged.

(6) For a review see C. W. Spangler, *Chem. Rev.*, **76**, 187 (1976).

(7) Both materials were prepared from the same sample of *trans*-4,5-dimethyl-*cis*-1,3-cyclopentanedicarboxylic acid[1] which in turn was prepared from optically active *trans*-2,3-norbornenedicarboxylic acid, which was resolved using cinchonine and recrystallizing from acetone–water (2:1).

(8) A^{D_4} had a 10 ± 3% lower rotation than A^{H_4} which corresponds to a 10 ± 3% lower optical purity if the maximum rotation of tetradeuterio-A is the same as perprotio-A.

(9) W. R. Dolbier, Jr., and S.-H. Dai, *J. Am. Chem. Soc.*, **92**, 1774 (1970); S.-H. Dai and W. R. Dolbier, Jr., *ibid.*, **94**, 3846 (1972).

(10) This isotope effect appears to be due to conversion of a torsional frequency in the allyl radical into a reaction coordinate motion resulting in total loss of the zero point energy difference in the transition state.[9] For other examples see J. J. Gajewski and S. K. Chou, *J. Am. Chem. Soc.*, **99**, 5696 (1977).

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(12) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

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