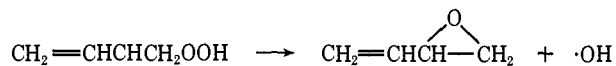
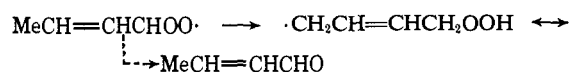


small extent, as well as at the major 2 position. This is further supported by the presence of small quantities of crotonaldehyde among the reaction products. The suggested mechanism is



Thus under our conditions $\text{RO}_2\cdot$ attack on a double bond and intramolecular proton abstraction by $\text{RO}_2\cdot$ result in different epoxides, the former mechanism occurring to a much greater extent. However, under conditions which give it greater scope, e.g., the presence of weaker C-H bonds or an increase in temperature, the latter mechanism could become more important.

Acknowledgment. We thank Dr. C. B. Thomas for the mass spectral analyses and the Science Research Council for a studentship (D. J. M. R.).

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Hydrocarbon Degenerate Thermal Rearrangements. II.¹ Stereochemistry of the Methylene-cyclopropane Self-Interconversion

Sir:

Because of the continuing interest² in the theoretically significant trimethylenemethane diradical we wish to report our recent observations concerning the nature of the species involved in the degenerate thermal rearrangement of methylenecyclopropane.^{2a,b}

trans- and *cis*-2,3-dimethylmethylene-cyclopropanes, **1** and **2**, respectively, were synthesized from Feist's ester^{3a} and the corresponding *cis* anhydride^{3b} in high yield and purity. Vapor phase pyrolysis of **1** or **2** at 225° or higher for 1 hr or longer gave a mixture of **1**, **2**, *anti*-1-ethylidene-2-methylcyclopropane (**3**), and *syn*-1-ethylidene-2-methylcyclopropane (**4**) in the ratio of 2:1:14:14, respectively. The latter two compounds were synthesized individually from *anti*- and *syn*-1-carbomethoxy-2-ethylidene-cyclopropanes.^{4a} At 170° the initial product distributions from **1** and **2** were substantially different from the equilibrium distribution (Table I). Thus, **3** and **4** did not undergo significant equilibration under the conditions of initial production at 170°.

When optically active **1** ($[\alpha]^{25}_D -59.4^\circ$ (CCl_4)) was heated at 170° to 16, 37, and 58.5% reaction, recovered **1** was 1.3, 7.4, and 23.6% racemized, respectively, and

(1) For part I see J. J. Gajewski and C. N. Shih, *J. Am. Chem. Soc.*, **89**, 4532 (1967).

(2) This list is not exhaustive; please see references contained therein: (a) E. F. Ullman, *ibid.*, **82**, 505 (1960); (b) J. P. Chesick, *ibid.*, **85**, 2720 (1963); (c) P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967); (d) P. Dowd, A. Gold, and K. Sachder, *ibid.*, **90**, 2715 (1968).

(3) (a) F. Feist, *Chem. Ber.*, **26**, 750 (1893); (b) M. G. Etlinger and F. Kennedy, *Chem. Ind.* (London), 891 (1957).

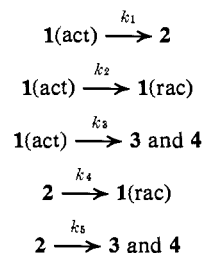
(4) (a) J. J. Gajewski, Abstracts, 155th National Meeting, American Chemical Society, San Francisco, Calif., April 1968, No. 28P; J. J. Gajewski and L. T. Burka, manuscript in preparation; (b) compounds **3** and **4** could be separated only by an efficient capillary column and not preparatively.

Table I. Product Distribution from Pyrolyses of **1** and **2**

	1	2	3	4
1 or 2 at 225°	6.5	3.5	45	45
1 at 170° ^a		34	57 ± 2	9 ± 2
2 at 170° ^a	46 ± 4		45 ± 6	9 ± 2

^a Distribution of products at ca. 10% conversion of starting material.

the rotation of **3** and **4** combined^{4b} (CCl_4) was +13.6, +12.7, and +11.5°, respectively. Integration of the first-order rate equations for the reactions

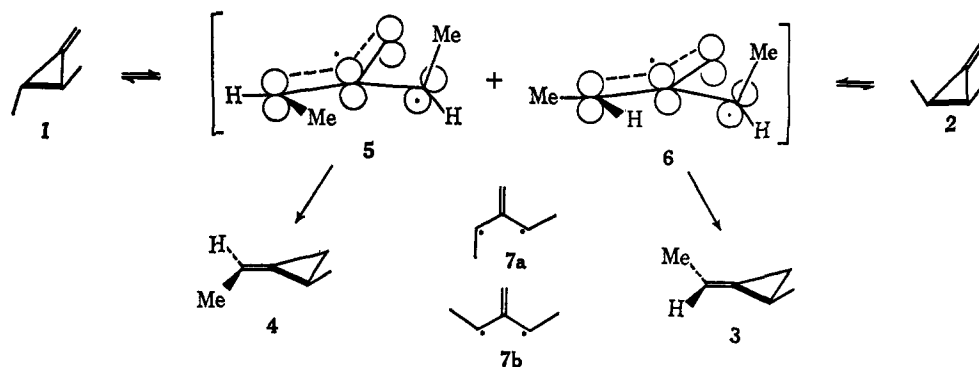


which is a good approximation during the first half-life of **1** since its racemization is relatively slow, gave the following expressions for the fraction of each material

$$\begin{aligned} \mathbf{1}(\text{act}) &= \exp\{-(k_1 + k_2 + k_3)t\} \\ \mathbf{2} &= [k_1/(k_4 + k_5 - k_1 - k_2 - k_3)][\mathbf{1}(\text{act}) - \exp\{-(k_4 + k_5)t\}] \\ \mathbf{1}(\text{rac}) &= [k_1 k_4 / (k_4 + k_5 - k_1 - k_2 - k_3)] \times \\ & \quad [1 - \mathbf{1}(\text{act}) / (k_1 + k_2 + k_3) - \\ & \quad (1 - \exp\{-(k_4 + k_5)t\}) / (k_4 + k_5)] + \\ & \quad [k_2 / (k_1 + k_2 + k_3)][1 - \mathbf{1}(\text{act})] \end{aligned}$$

Three-point kinetic runs with **1**(rac) and with **2** were performed simultaneously using separate sealed ampoules with calculated internal pressures of 150 torr in the same thermostat at 170°. First-order plots gave initial rate constants of $(8.3 \pm 0.4) \times 10^{-5}/\text{sec}$ and $(13.6 \pm 0.4) \times 10^{-5}/\text{sec}$ for disappearance of **1** and **2**, respectively. The individual constants, k_1 , k_3 , k_4 , and k_5 , could be deduced using the initial partitioning ratios of **1** and **2** (Table I). The best fit to the experimental data (racemization of **1**(act), **1**(rac))/[**1**(rac) + **1**(act)], as a function of its conversion to **2**, **3**, and **4** was provided when k_2 was set equal to $0.5 \times 10^{-5}/\text{sec}$. Thus, initially, racemization of **1** occurred *via* **2** and a direct process (k_2) to about an equal extent, and the direct racemization of **1** occurred one-eighteenth as fast as it reacted. The calculated rate constant for direct racemization of **1** was not very sensitive ($\pm 15\%$) to variations in rate constants within the indicated experimental errors. Finally, although the maximum rotations and relative configurations of **1**, **3**, and **4** are presently unknown, because of the structural similarity of **1** and **3** and **4** and the dominating electronic effect of the double bond, the relative signs and magnitudes of the rotations strongly suggest that inversion at the remaining asymmetric center in **3** and **4** occurred to a significant extent during the thermolysis.⁵

(5) For a discussion of the theory related to this conclusion see J. A. Schullman, *Accounts Chem. Res.*, **1**, 144 (1968); see also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., pp 401-412.



These results correspond to those obtained by Ullman in the pyrolysis of optically active Feist's ester^{2a} with a number of significant additions or exceptions that allow formulation of a hypothesis for the pathways involved in the thermal self-interconversion of a relatively unperturbed methylenecyclopropane system. To the small extent that **1** racemizes *via* a direct path, k_2 , and to whatever degree **3** and **4** lose optical activity when produced directly from optically active **1**, planar trimethylenemethane intermediates, **7a** and **7b**, may be envisioned. However, the simplest explanation for substantial preservation of activity of **1** and **3** and **4** and interconversion of **1** and **2** at about the same rate of rearrangement involves the postulate of two dissymmetric species, **5** and **6**, that result from allylic bond fission with a 90° rotation about only one C-C bond.⁶ Inspection of the geometry of these species reveals that so long as products are formed by a single 90° rotation about an allyl bond, **5** can form **2**, inverted **4**, and retained **1**, but not **3**; **6** can form **2**, inverted **3**, and retained **1**, but not **4**. To account for similar 3:4 ratios from **1** and **2**, **5** and **6** must be formed in nearly the same ratio from both **1** and **2**, and they must re-form the methylenecyclopropane systems faster than bond rotation to account for the stereochemical results.

If the reasonable assumption is made that all the rate constants for formation of individual products from **5** and **6** are about the same (except that **5** gives no **3** and **6** gives no **4**) and that **7** will partition itself similarly and in accord with statistical considerations, then the 3:4 ratio and the optical results suggest that **6** is about 1.7 kcal/mol more stable than **5** which in turn is about as stable as **7**. These stabilities can be calculated near quantitatively on the basis of nonbonded interactions alone using Bartell's potential functions⁷ and reasonable geometric parameters and making the assumption that the interaction of the half-filled p orbital in the nodal plane of the allyl radical in **5** and **6** with various atoms can be described by the same potential function used to calculate the interaction of a hydrogen with various

(6) (a) A variation on this mechanism which may be in accord with orbital symmetry considerations as applied to 1,3 sigmatropic shifts where the migrating orbital is antisymmetric^{6b} could be responsible for **3** and **4**. Thus, the *exo*-methylene group could twist 90° simultaneous with, but in a sense opposite to, the ring bond 90° rotation. Two such pathways are required to account for formation of both **3** and **4**. Unfortunately, this mechanism does not provide for formation of **2** from **1** or **1** from **2**, nor can a planar intermediate account solely for production of **2** and **1**; therefore **5** and **6** must still be involved. (b) See J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(7) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960). We assume that these functions apply equally to sp³- and sp²-hybridized carbon. The energy was not minimized with respect to the conformation of the methyl groups; however, the methyl position chosen reflected that indicated to be the most stable by inspection of molecular models.

atoms.^{8,9} These steric interaction calculations also suggest that the unsubstituted planar trimethylenemethane diradical is slightly more stable than the orthogonal diradical systems corresponding to **5** and **6**, a point amenable to experimental verification. Finally, if the pathways cited for the rearrangement are appropriate, and if **6** is more stable than **5** or **7** due to steric interactions, then the stabilities of the orthogonal and planar trimethylenemethane diradical systems produced in the thermolysis of methylenecyclopropane are nearly equivalent, which implies that the two systems are stabilized by electron delocalization to roughly the same extent.

Acknowledgment. We wish to acknowledge stimulating discussions with Drs. Ullman, Doering, and Crandall and the technical assistance of Mr. L. T. Burka. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support (2754-A1,4) of this research.

(8) (a) Since the lone pair of electrons on nitrogen appears to be of slightly larger "steric size" than a hydrogen,^{8b} this interaction potential may not be unreasonable. Other results suggest the opposite is true.^{8c,d} We only wish to point out that if no subtle electronic effect is operative, a destabilizing half-filled p-orbital-methyl interaction must be considered in order to account for preferential formation of **6** over **5**. (b) J. B. Lambert, *et al.*, *J. Am. Chem. Soc.*, **89**, 3761 (1967). (c) A. R. Katritzky, *et al.*, *J. Chem. Soc., B*, 550, 554 (1968). (d) See also E. L. Eliel, M. C. Knoeber, *J. Am. Chem. Soc.*, **88**, 5347 (1966), and references contained therein.

(9) There was no evidence for chemical interaction between the half-filled p orbital and the methyl group, *i.e.*, there was no transannular hydrogen shift to produce 2-ethyl-1,3-butadiene which was found to be stable under the reaction conditions.

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Benzenesulfinyl Azide and 1,3,5-Triphenyl-1,3,5,2,4,6-trithiatriazine 1,3,5-Trioxide

Sir:

Two unsuccessful attempts to prepare sulfinyl azides from *p*-toluenesulfinyl chloride and azide salts have been reported.¹ In each case, results suggested that the sulfinyl azide was a transient intermediate which disproportionates and fragments but does not undergo a Curtius-type rearrangement. Thus, considerable interest has been generated in preparing sulfinyl azides

(1) (a) M. Kobayashi and A. Yamamoto, *Bull. Chem. Soc. Japan*, **39**, 2733 (1966); (b) S. T. Purrington, 12th Annual Report on Research under the Sponsorship of the Petroleum Research Fund, American Chemical Society, Washington, D. C., 1967, p 8.