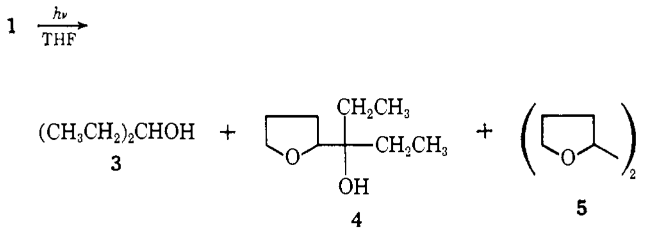
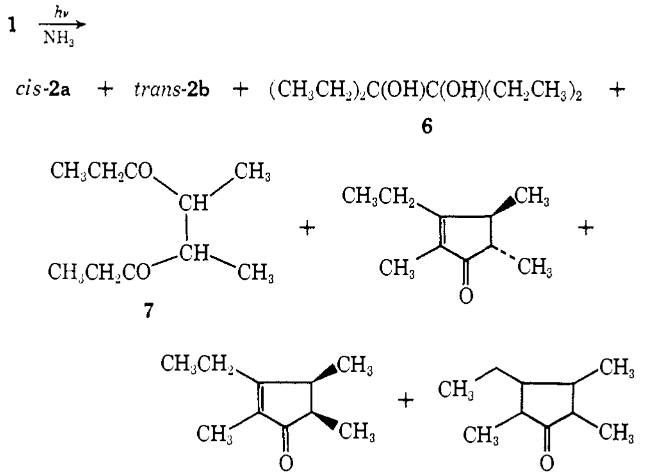
when 3-pentanone enolate (**1**) was prepared in liquid ammonia by treatment with sodium amide and irradiated at 2537 Å for 8 hr, followed by addition of 1 equiv of ammonium chloride, yields of 2% *cis*-pentene-2,3-oxide (**2a**) and 0.2% *trans*-pentene-2,3-oxide (**2b**) were realized. The products were collected by preparative vpc,[7] and identification was made by means of vpc, nmr, and mass spectral comparison with authentic material. The major products in the liquid ammonia irradiation were shown to be the pinacol **6** and the base-catalyzed cyclization products of the ketone dimer **7**. Attempts to sensitize the reaction were unsuccessful. No change in the yield of epoxides was observed when either benzophenone or naphthalene was employed as a triplet sensitizer.





Past investigations have revealed[2,3] that photochemically activated carbanions may experience enhanced basicity. In view of this possibility, we thought it especially noteworthy that the excited state of the enolate anion undoubtedly bears a substantial amount of negative charge on the carbonyl carbon.[8] Thus, in the presence of an acid too weak to protonate it in the dark, an enolate, on irradiation, could protonate at the carbonyl carbon to yield with ring closure, the corresponding epoxide. Alternatively, concerted cyclization of the enolate would produce the epoxide anion directly, a pathway analogous to the photochemical formation of oxaziranes from nitrones.[9] Epoxide anions have not been observed to ring open to enolates, but undergo slow α elimination of alkoxide to yield carbene-derived products.[10,11]

Formation of the less thermodynamically stable cis epoxide in tenfold excess over the trans isomer may be the result of preferred geometrical factors operative in the ground state or in the transition state for cyclization. Substituted allylic anions are believed to be more stable in the cis configuration,[12] and this may also be true for enolates. In regard to orbital symmetry factors, concerted photochemical cyclization could give either epoxide from either ground state, since there is no stereochemical label at the oxygen atom.

The production of epoxides thus provides evidence for the photochemical valence bond isomerization of enolates. This potentially synthetically useful reaction, then, reveals a mechanistic path available to carbonionic species, different from those outlined previously. Further work is in progress to ascertain the reasons for the predominance of the cis product.

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(7) An F and M thermal conductivity vpc with a 10 ft × $^3/_8$ in. column of 10% FFAP on Chromosorb P was used in these studies (72° oven for volatile components, 160° oven for high-boiling products).

(8) See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1967, Chapter 8.

(9) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **23**, 651 (1958); K. Shinazawa and I. Tanaka, *J. Phys. Chem.*, **68**, 1025 (1964).

(10) J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4526, 4527 (1967).

(11) Treatment of an epoxide with strong base, when a hydrogen β to oxygen is present, results in the formation of the corresponding allylic alcohol: J. K. Crandall and L. C. Lin, *J. Org. Chem.*, **33**, 2378 (1968).

(12) See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 193, for an extensive discussion.

(13) National Science Foundation Predoctoral Fellow.

(14) A. P. Sloan Fellow.

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Geometric Isomerization *vs.* Cycloreversion in the Pyrolysis of Tetramethylcyclobutane-d_6. Ponderal and Energetic Effects on the Competition Ratio in a Series of "1,4-Butanediyls"[1]

Sir:

Both thermodynamic[2] and quantum mechanical[3] arguments have been used to rationalize and predict the behavior of the high-energy species produced as intermediates or transition states in the unimolecular pyrolysis reactions of simple small-ring compounds. As part of an effort to provide experimental tests of these ideas, we report here the preparation and pyrolysis of *cis*-, racemic *trans*-, and optically active *trans*-1,1,2,2-tetramethylcyclobutane-d_6.

Stereospecific syntheses of the labeled hydrocarbons from the known[4] compounds *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylic acid and *cis*-1,2-dimethylcyclobutane-1,2-dicarboxylic anhydride followed procedures similar to those used[5] for the corresponding tetramethylcyclopropane-d_6 isomers. Optical activation of

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

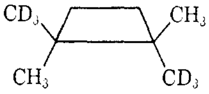
(2) (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

(3) (a) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); (b) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, in press; (c) L. Salem, *Bull. Soc. Chim. Fr.*, in press. (d) We thank Professors Hoffmann and Salem for preprints of the latter two papers.

(4) C. J. Albisetti, D. C. England, M. J. Hogsed, and R. M. Joyce, *J. Amer. Chem. Soc.*, **78**, 472 (1956).

(5) J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968).

the trans isomer was achieved by use of optically active *trans*-1,2-dimethyl-1,2-bishydroxymethylcyclobutane as an intermediate, the diol being partially resolved by fractional crystallization of the diastereomeric mixture of *d*-mandelates. Optically pure *trans*-hydrocarbon **1** was shown to have $[\alpha]_{546}$ 1.21° (CS_2) (enantiomeric configuration arbitrary).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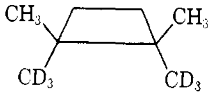
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Infrared analysis (Perkin-Elmer Model 421 spectrometer), using absorptions at 1370, 1355, 1075, and 920 cm^{-1}, permitted estimation of *trans*- and *cis*-hydrocarbons **1** and **2** to $\pm 10\%$ and detection of as little as 10% of one isomer in the other.

Pyrolysis of tetramethylcyclobutane-d_6 (**1** or **2**) in an "aged" reactor at temperatures in the range 338–401° and initial pressures between 10 and 30 mm gave isobutylene-d_3 as the major product (>99%).[6]

Tetramethylcyclobutane-d_6 recovered from varying degrees of partial pyrolysis of pure trans (or cis) hydrocarbon showed no detectable quantity (<10%) of the cis (or trans) isomer, even after 96% decomposition to isobutylene. Moreover, optically active d_6-*trans*-hydrocarbon **1** was recovered from partial pyrolysis with undiminished activity (racemization <4% after 11.7% decomposition).

Configurational inversions of each of the substituted carbons C_1 and C_2 of tetramethylcyclobutane plausibly (but not necessarily) might be achieved by rotations about the C_1–C_4 or C_2–C_3 bond axes. In the most general sense, if the number of such inversions of C_1 is r and that of C_2 is s, $(r + s)$ *odd* corresponds to the reaction trans $\rightleftharpoons$ cis, and $(r + s)$ *even*, r and s both odd, corresponds to the reaction (−)-trans $\rightleftharpoons$ (+)-trans. The experimental results show that regardless of mechanistic details, both such processes are indetectably slow relative to fragmentation. The upper limits for the amount of racemization of (−)-**1** and for the amount of conversion to **2** may be combined with the overall per cent decomposition to give minimum values for the ratio of the rate constant for the decomposition, trans → 2-isobutylene (k_d), to that for enantiomerization, (−)-trans → (+)-trans (k_e), or geometric isomerization, trans → cis (k_i). The ratios are derived from the relationship of eq 1,[7,8] where f_t, f_c, f_-, and f_+ represent

$$1 + \frac{2k_i}{k_d} = \frac{\log(f_t - f_c)}{\log(f_t + f_c)} = \frac{\log(f_- - f_+)}{\log(f_+ + f_-)} = 1 + \frac{2k_e}{k_d} \tag{1}$$

the fractions of trans, cis, −, and + components, respectively. These ratios are $k_d/k_e \geqslant 6$ (at 360°) and $k_d/k_i \geqslant 22$ (at 401°).

Although not obligatory, it is convenient to discuss the data as representative of the properties of a putative intermediate 1,4-butanediyl. Irreversible cleavage of the C_2–C_3 bond to produce olefin from this species is much faster than C_1–C_2 and C_3–C_4 bond rotation–recyclization. This behavior is in sharp contrast to that of the corresponding 1,3-propanediyl derived from tetramethylcyclopropane, in which the ratio of rates of irreversible intramolecular olefin-forming hydrogen transfer[9] and bond rotation–recyclization[5] at 401° is about four orders of magnitude smaller than the value k_d/k_i in the present case. The result is at least qualitatively concordant with the estimate[2a] of a substantially higher activation energy for hydrogen shift in 1,3-propanediyl than for 2,3-bond cleavage in 1,4-butanediyl, a bias that should be accentuated by the substitution in the tetramethyl cases.

Table I. Ratio of Rate Constants (k_d/k_i) for 2,3 Cleavage *vs.* Geometric Isomerization in Intermediates of the Type $R_1R_2C–CH_2–CH_2–CR_3R_4$

R_1	R_2	R_3	R_4	k_d/k_i	Temp, °C	Ref
H	CH_3	H	CH_3	4	401[j]	*a*
H	CH_3	H	CH_3	8	401[k]	*a*
H	CH_3	OH	CH_3	8	381[j]	*b*
CD_3	CH_3	CD_3	CH_3	$\geqslant 22$	401	*c*
CH_3	C_2H_5	CH_3	C_2H_5	$\geqslant 48$[d,g]	148[h]	*f*
CH_3	C_2H_5	CH_3	C_2H_5	$\geqslant 64$[e,g]	148[i]	*f*

[a] H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83,** 4884 (1961). [b] E. D. Feit, *Tetrahedron Lett.*, 1475 (1970). [c] Present work. [d] Derived from the *meso*-azo compound. [e] Derived from the *d,l*-azo compound. [f] P. D. Bartlett and N. Porter, *J. Amer. Chem. Soc.*, **90,** 5317 (1968). [g] % olefin/<2% "crossover" cyclobutane in thermal reaction. [h] At room temperature, the photolytically generated singlet diradicals show k_d/k_i ~12 and ~20 from *meso*- and *d,l*-azo compounds, respectively. [i] From the *cis*-cyclobutane. [k] From the *trans*-cyclobutane.

Table I shows that the k_d/k_i ratio for a series of 1,4-butanediyls increases with increasing terminal substitution. The effect agrees with that expected of an increase in k_d because of increasing stability of the fragment olefins and of a decrease in k_i because of the more negative entropy of activation associated with more massive rotors.[10]

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(6) Traces of tetramethylethylene-d_6 and ethylene also were observed. In an unconditioned reactor packed with glass beads, prolonged pyrolysis again produced mainly isobutylene, together with traces of tetramethylethylene, but two minor unidentified products also appeared. At least one of the latter products showed nmr absorption consistent with a terminal methylene group and may have been formed by transfer of hydrogen from a methyl group.

(7) This is a special case of the general three-component triangular kinetic system of first-order reactions covered by the Korvezee equations.[8]

(8) *Cf.* A. E. Korvezee, *Recl. Trav. Chim. Pays-Bas.*, **59,** 913 (1940).

(9) (a) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3052 (1962); (b) C. Blumstein, D. Henfling, C. Sharts, and H. E. O'Neal, *Int. J. Chem. Kinet.*, in press.

(10) This ponderal entropy effect on the rotor has been predicted[2a] and is in qualitative agreement with intermolecular[5,11] and intramolecular[11] comparisons of cyclization *vs.* rotation in 1,3-propanediyls. An increased rotational barrier would operate in the same direction, but its importance relative to the ponderal entropy effect cannot be accurately evaluated at present.

(11) W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **90,** 7345 (1968); R. G. Bergman and W. L. Carter, *ibid.*, **91,** 7411 (1969).

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1,1′-Spirobibenzocyclobutene from an Allenic *o*-Quinomethane Intermediate

Sir:

The hitherto unreported hydrocarbon 1,1′-spirobibenzocyclobutene (**1**) is of interest not only as a particu-