marked on Figure 6, the relative magnitude of these decreased to zero with approach from 40 to 100% *exo*, but were observable in samples with 5% *endo*. Pure *exo* showed no transformations from room temperature to melting at 143°. Samples with over 60% *endo* showed transitions at 75–94° (pure *endo*) but no transition at 109°. Thermal halts at 75–77° (mixtures) and 94–96° (pure *endo*) were also observable with an Aminco "Accumelt" thermocouple embedded in prefused samples.

X-Ray Diffraction Studies. A General Electric powder camera, A4969, was used with Cu Kα irradiation. Temperature control was by directing a stream of hot air over the 0.3-mm capillary containing the pulverized sample. The temperature at 110° varied by $\pm 5°$ around the critical volume of the sample, as estimated with a thermocouple. *endo* isomer at 110° gave one strong reflection $\theta = 8.28°$, and three much weaker ones, $\theta = 11.74$, 14.44, and 16.78°. These correspond to a body-centered cubic structure of cell dimensions $a_0 = 7.57 \pm 0.05$ A. (Other body-centered cubic structures were compared: camphene at room temperature also gave only four lines, $a_0 = 7.95$ A (lit.[37] *ca.* 8.00 A), and hexamethylenetetramine gave $a_0 = 7.03$ A (lit.[38] 7.02 A). The saturated compound, *endo*-norbornane-2,3-dicarboxylic anhydride, gave only four lines at 110° and a slightly larger unit cell, $a_0 = 7.63$ A, than the *endo*-norbornene anhydride.) On cooling to room temperature a complex, many-line diffraction pattern appeared which was not always identical with the equally complex, but distinct, pattern for initial *endo* isomer as obtained by crystallization from CCl_4 or benzene-petroleum ether. Apparently two forms of nonrotating *endo* isomer may exist at low temperatures; in one case recrystallization by cooling with Dry Ice occurred in a 0.3-mm capillary containing an *endo* sample which had been heated to 110°. The X-ray pattern then corresponded to a "spotty" *endo* pattern with spacings the same as obtained from an unheated sample. *exo* anhydride gave the same unique, many-line pattern at 110° as at room temperature.

Solid-State Nmr Spectra. High-resolution nmr spectra were obtained on neat, polycrystalline samples of *endo* anhydride utilizing a Japan Electron Optics Laboratories C-60H spectrometer. Samples were first melted and solidified into ordinary sample tubes. The spectrum at 115° was three broad humps with peaks at *ca.* τ 3.3, 6, and 8, standardized against external TMS. These correspond to olefinic, bridgehead and α-hydrogens, and to bridge hydrogens, respectively. A mixture of 50–50% *exo–endo* was completely melted (see Figure 6) at 115° and served as a standard of comparison. This liquid mixture gave the sharp lines (*e.g.*, the $W_{1/2}$ for the α-hydrogen signal of *exo* isomer was *ca.* 2 cps) and also gave the spin–spin splittings which are obtained from a dilute solution of the compounds in chloroform-*d*. The amplitude of the three broad signals from pure solid *endo* was about the same as from the completely liquid *exo–endo* mixture. *exo* anhydride gave no signal at this temperature.

Acknowledgment. We thank Professor T. Wells (Simon Fraser University), Professor J. Trotter, Dr. J. Passmore, and Miss C. Burfitt (University of British Columbia) for assistance and suggestions concerning the operation of equipment.

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Base-Catalyzed Isomerization of Bicyclic Olefins[1]

Shelton Bank,[2] Charles A. Rowe, Jr.,[3] A. Schriesheim,[3] and L. A. Naslund[3]

Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York, and the Esso Research and Engineering Company, Linden, New Jersey. *Received June 13, 1967*

Abstract: The rates of base-catalyzed isomerization of three bicyclic olefins in which the double bond is exocyclic have been studied. Using the system potassium *t*-butoxide–dimethyl sulfoxide, the rate constants, activation enthalpies, and entropies for the isomerization of 2-methylenebicyclo[2.2.1]heptane, 2-methylenebicyclo[2.2.2]octane, and β-pinene were obtained. The observed relative rates (statistically corrected) at 55° are β-pinene, 43; 2-methylenebicyclo[2.2.2]octane, 3.9; 2-methylenebicyclo[2.2.1]heptane, 2.6; and methylenecyclohexane, 1.0. In addition, the rates of the base-catalyzed endocyclic to exocyclic olefin isomerization have been calculated for the cyclic and bicyclic olefins. From the relative rates of the exocyclic compounds the relative importance of angle strain contributions is assessed to be minor. By contrast, angle strain factors are important in the endocyclic isomerization. The principal factors governing the rate of isomerization of the exocyclic olefins are the torsional effects.

Structural influences on the physical and chemical properties of cyclic and bicyclic compounds have been investigated in considerable detail during the last 20 years.[4] The fixed and known geometries of these readily available systems provide the framework for attempts to derive predictive relationships governing their behavior. As a result, considerable information about the factors influencing the rate-determining step(s) of a variety of reactions has been derived from studies of the rate variation with change in ring size.[5]

For some time we have been interested in the base-catalyzed isomerization of olefins. Previously, the effect of ring size on the rate of isomerization of monocyclic compounds was investigated.[6] In the present study, the base-catalyzed isomerizations of several bicyclic olefins are determined, and these are compared with the monocyclic compounds to provide insights into the factors governing reactivity.

Mechanistic studies of the base-catalyzed olefin isomerization have provided some detail on the nature

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(2) Address inquiries to Department of Chemistry, State University of New York at Albany, Albany, N. Y. 12203.

(3) Esso Research and Engineering Company.

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of the reactive intermediate.[7] In sum, an allylic ion tightly bound in an ion pair is depicted as the reactive intermediate. The principal evidence supporting this conclusion includes a large carbon–hydrogen isotope effect,[7] a linear free energy relationship with ketone bromination,[6] the marked influence of strongly electron-donating substituents on the rate,[7] and finally, the high degree of intramolecularity.[7] The effect of ring size upon the rate of base-catalyzed isomerization of the various methylenecycloalkanes demonstrated that structural effects were important, and that stereoelectronic factors governing the case of rehybridization contributed to the marked rate variations. This paper describes a study of the base-catalyzed isomerization of select bicyclic olefins of varying angle and eclipsing strain. Further, the relative importance of angle and torsional strain is assessed by relating the relative rates of these olefins and the monocyclic compounds with computed angle and torsional strain energy terms.

Results and Discussion

The bicyclic olefins 2-methylenebicyclo[2.2.1]heptane and 2-methylbicyclo[2.2.1]heptene-2 were prepared by conventional reactions as described in the Experimental Section. α- and β-pinene are commercially available, and 2-methylenebicyclo[2.2.2]octane and 2-methylbicyclo[2.2.2]octene-2 were made available from Professor Schleyer's laboratory.

The olefins were isomerized in 0.7 *M* potassium *t*-butoxide in dimethyl sulfoxide. The exocyclic olefins isomerized to equilibrium mixtures of *exo*- and *endo*-bicyclic olefins. The compositions of equilibrium mixtures of these various bicyclic *exo–endo* pairs were obtained and discussed elsewhere.[8] That there was no loss of olefin due to side reactions was established through the use of internal standards and gas chromatographic techniques. The disappearance of starting olefin was followed gas chromatographically as a function of time. First-order rate constants were obtained from these data as described in the Experimental Section. Table I records the pertinent rate data as well as the enthalpies and entropies of activation.

Table I. Rate Constants and Derived Data for the Isomerization of the Bicyclic Olefins

Olefin	10^6k, sec^{-1} [a]	ΔH^{+}, kcal/mole	$\Delta S^{\pm}$, eu
2-Methylenebicyclo-[2.2.1]heptane	5.58	20.5 ± 0.4	−20.0 ± 1.0
2-Methylenebicyclo-[2.2.2]octane	16.9	22 ± 2	−17 ± 2
β-Pinene	172.5	19.4 ± 0.4	−16.5 ± 1.2

[a] At 55° using 0.7 *M* KO-*t*-Bu in DMSO.

Comparison of these rate constants with the cyclic compounds is made convenient by expressing the rate constants on a per hydrogen basis. For methylenebicyclo[2.2.2]octane and β-pinene this merely requires division of the observed rate constant by two. In contrast, there is good reason to conclude that only one hydrogen is involved in the isomerization of methylenebicyclo[2.2.1]heptane. For example, only one hydrogen is readily exchanged in the base-catalyzed deuteration of 2-norbornanone[9] and other bicyclo[2.2.1]heptanones.[10] In the comparison of rate constants we assume only one hydrogen is involved in the isomerization of methylenebicyclo[2.2.1]heptane.

To facilitate discussion of the several factors influencing base-catalyzed olefin isomerization, the rates and the relative rates of the exocyclic to endocyclic isomerization are summarized in Table II and rates and relative rates of isomerization of the reverse reaction are summarized in Table III.

Table II. Rates of Base-Catalyzed Isomerization of Cyclic and Bicyclic *exo*-Olefins at 55°

Compound	10^6k, sec^{-1} [a]	Rel rate[a]
Methylenecyclobutane	2300[b]	1070
Methylenecyclopentane	973[b]	454
Methylenecyclohexane	2.15[b]	1.0
Methylenecycloheptane	12.5[b]	5.8
Methylenecyclooctane	36.6[b]	17.0
Methylenebicyclo-[2.2.1]heptane	5.58[c,d]	2.6
Methylenebicyclo-[2.2.2]octane	8.5[c]	3.9
β-Pinene	86.3[c]	43.0

[a] Per hydrogen, using potassium *t*-butoxide in dimethyl sulfoxide solution. [b] See ref 6. [c] This work. [d] Assuming only one hydrogen is involved in isomerization *vide supra*.

Table III. Rates of Base-Catalyzed Isomerization of Cyclic and Bicyclic *endo*-Olefins at 55°

Compound	10^6k, sec^{-1} [a]	Rel rate
1-Methylcyclobutene	1990.0[c]	38,300
1-Methylcyclopentene	6.24[c]	120
1-Methylcyclohexene	0.052[c]	1.0
1-Methylcycloheptene	0.96[c]	18.5
1-Methylcyclooctene	0.24[b]	4.6
2-Methylbicyclo[2.2.1]heptene-2	64.1[d]	1,230
2-Methylbicyclo[2.2.2]octene-2	2.09[e]	40
α-Pinene	3.37[e]	65

[a] First-order rate constant using potassium *t*-butoxide in dimethyl sulfoxide solution. Rate constants are the observed since no statistical correction is required. [b] Obtained from the rate constants for the exocyclic isomerization at 55° [6] and the equilibrium constants at 55°.[8] [c] Obtained from the rate constants for the exocyclic isomerization at 55° [6] and the equilibrium constants at 55° calculated from the data given in A. C. Cope, *et al.*, *J. Am. Chem. Soc.*, **82**, 1750 (1960); and J. Herling, J. Shabtai, and E. Gil-Av, *ibid.*, **87**, 4107 (1965). [d] Measured directly in this work. [e] Obtained from the rate constants for the exocyclic isomerization at 55° (this work) and the equilibrium constants at 55°.[8]

Quantitative determinations of the effect of strain upon the equilibria[11] and rates of reactions[12,13] essentially employ application of the Westheimer treatment of steric effects.[14] The steric effects are considered as

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(7) (a) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **85**, 2115 (1963); (b) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *ibid.*, **87**, 3244 (1965), and other papers in this series.

(8) P. von R. Schleyer, S. Bank, W. F. Watts, and A. Schriesheim, *ibid.*, in press.

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(10) (a) A. F. Thomas and B. Willhalm, *ibid.*, 1309 (1965); (b) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Am. Chem. Soc.*, **89**, 68 (1967); (c) P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

(11) E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **87**, 505 (1965).

(12) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *ibid.*, **87**, 2932 (1965).

(13) G. J. Gleicher and P. von R. Schleyer, *ibid.*, **89**, 582 (1967).

(14) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.

Table IV. Angle Strain Energies

Compound	θ, deg	Ew,[a] kcal/mole	θs, deg	Ews,[a] kcal/mole
Methylenecyclobutane	90[b]	6.8	90[b]	4.5
Methylenecyclopentane	107[c]	0.97	103.3[d]	0.46
Methylenecyclohexane	116[c]	0.0	109.5[d]	0.0
Methylenecycloheptane	116,[e] 122[c]	0, 0.43	112[d]	0.075
Methylenecyclooctane	116,[e] 123[c]	0, 0.59	112[d]	0.075
Methylenebicyclo[2.2.1]heptane	103[c,f]	2.04	102.9,[f] 104.2[f]	0.52, 0.34
Methylenebicyclo[2.2.2]octane	110[c,f]	0.43	109.9[f]	0.002
β-Pinene	120[c]	0.20	109.5	0.0
		Ew', kcal/mole		
1-Methylcyclobutene	90[b]	18.0		
1-Methylcyclopentene	111.5[e]	2.65		
1-Methylcyclohexene	120[e]	0.01		
1-Methylcycloheptene	122[e]	0.0		
1-Methylcyclooctene	122[e]	0.0		
2-Methylbicyclo[2.2.1]heptene-2	103[g]	8.7		
2-Methylbicyclo[2.2.2]octene-2	112[g]	2.4		
α-Pinene	115[g]	1.2		

[a] Calculated from the equation $Ew = {}^1/_2A(\theta - \theta e)^2$, where A, the apparent bending force constant is a function of the displacement, the value of which was taken from H. Dauben, Jr., as quoted in M. E. H. Howden and J. D. Roberts, *Tetrahedron*, **18**, *Suppl.*, **2**, 403 (1963), where $\theta e = 116°$ for exocyclic compounds and 122° for endocyclic compounds (for discussion of this, see ref 12). [b] Assumed from value of 90° for cyclobutanone: K. A. Bauden, T. Gäuman, and F. Tank as quoted in K. Frei and H. H. Gunthard, *J. Mol. Spectry.*, **5**, 218 (1960). [c] Calculated from relationship between *exo*-olefin stretching frequencies and bond angle (S. Bank, W. D. Closson, and L. T. Hodgins, *Tetrahedron*, in press). [d] C. S. Foote, *Tetrahedron Letters*, 579 (1963), and references cited therein. [e] See ref 12. [f] See ref 13. [g] Calculated from a derived linear relationship between olefin stretching frequencies and the bond angle for the unsubstituted olefins (S. Bank, unpublished results). This makes the reasonable assumption that the bond angles of the unsubstituted and methyl-substituted olefins are similar.

the sum of the various independent strain-producing mechanisms, expressed as

$$E(\text{total strain}) = E(\text{bond length strain}) + E(\text{bond angle strain}) + E(\text{torsional strain}) + E(\text{nonbonded interaction strain}) \quad (1)$$

Garbisch[12] and Gleicher and Schleyer[13] calculated the several strain effects and correlated the results with the rates of diimide reduction of olefins and the solvolysis of bridgehead-substituted polycyclic bromides, respectively.

This study includes analysis of only the bond angle strain and the torsional strain. Neglect of the bond length strain terms is not serious since bond deformation in both the ground state and the transition state are relatively unimportant.[13]

The nonbonded interaction terms, at best difficult to estimate, probably do not significantly differ among the compounds investigated. Hence differences in reaction rates are correlated with the calculated strain effects of bond angle and bond torsion; other possible effects are not included.[15]

Bond Angle Bending Strain. The contribution of bond angle bending strain to the rate is expressed in eq 2, where Ew^* and Ew are the angle strain energies

$$\Delta Ew = Ew^* - Ew \quad (2)$$

of the transition state and the ground state, respectively. Angle strain energies can be readily calculated from eq 3, where k is the bending force constant, θe is the unstrained angle value, and θ is the actual angle. Estimation of Ew is straightforward since for the ground state the geometry is either known or reasonable estimates can be obtained. Estimation of Ew^* requires more complex treatment. For solvolysis reactions with a transition state resembling the carbonium ion, Gleicher and Schleyer[13] estimated the strain energies by application of the Wiberg[16]–Harris[17] programs to the relevant carbonium ion. For diimide reductions Garbisch[12] used a disposable parameter to define the optimal geometry of the transition state. In view of our ignorance of the structure of the allylic anion the latter approach was adopted for the present study.

$$E(\text{angle strain}) = (k/2)(\theta - \theta e)^2 \quad (3)$$

The strain energy of the transition state (Ew^*), the structure of which resembles the allylic anion, is assumed to lie between that of the exo- and endocyclic olefins as given by eq 4 and 5, where Ew is the angle strain energy of the *exo*-olefin, Ew' the angle strain energy of the *endo*-olefin, and x^* is the fractional contribution of the endocyclic olefin to the transition state. Substitution of eq 4 into eq 2 yields eq 6. Similarly,

$$Ew^* = Ew - x^*(Ew - Ew') \quad (4)$$

$$Ew^* = Ew' - (1 - x^*)(Ew' - Ew) \quad (5)$$

$$\Delta Ew = x^*(Ew' - Ew) \quad (6)$$

for the isomerization of endo- to exocyclic olefin substitution of eq 5 into eq 7 yields eq 8.

$$\Delta Ew' = Ew^* - Ew' \quad (7)$$

$$\Delta Ew' = (x^* - 1)(Ew' - Ew) \quad (8)$$

If we assume that x^* remains constant throughout the series, then the contributions of bond angle bending strains to the reaction rates can be determined from the differences between the angle strain energies of the endo- and exocyclic olefins. Therefore, a plot of the log of the rates *vs.* ($Ew' - Ew$) would reveal whether angle strain makes significant contributions to the rate. Table IV tabulates the values of the angle strain for

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(15) See, however, P. Coppens, E. Gil-Av, J. Herling, and J. Shabtai, *J. Am. Chem. Soc.*, **87**, 4110 (1965).

(16) K. Wiberg, *ibid.*, **87**, 1070 (1965).

(17) H. A. Harris, Ph.D. Thesis, Yale University, 1966.

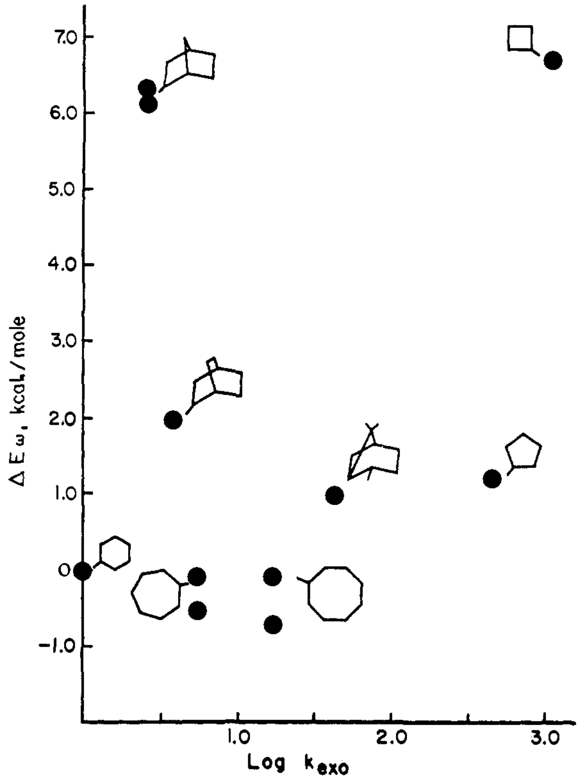


Figure 1. Plot of $\Delta E\omega$ *vs.* log k_{exo}.

the exo- and endocyclic olefins for the part of the system undergoing structural change. This includes one unsaturated and one saturated valence angle for the exocyclic compound (θ and θs, respectively) and two unsaturated angles for the endocyclic compound. Table V records the differences between the various exo- and endocyclic compounds as well as the logs of the relative rates.

Table V. Angle Strain Energy Differences and Relative Rates of Olefins

	System	$Ew' - Ew - Ews$, kcal/mole	log k, *exo*	log k, *endo*
1.	Cyclobutyl	6.72	3.03	4.58
2.	Cyclopentyl	1.22	2.66	2.08
3.	Cyclohexyl	0.01	0.0	0.0
4.	Cycloheptyl	−0.08, −0.51	0.76	1.27
5.	Cyclooctyl	−0.08, −0.67	1.23	0.66
6.	Bicyclo[2.2.1]heptyl	6.15, 6.33	0.42	3.09
7.	Bicyclo[2.2.2]octyl	2.0	0.59	1.60
8.	Pinene	1.0	1.63	1.81

Figures 1 and 2 depict the relationship between the differences in angle strain and the relative rates of the exo- and endocyclic olefins, respectively. For the exocyclic olefins (Figure 1) clearly there is no obvious relationship, and the points represent an essentially random array. The least-squares correlation is 0.03; a perfectly random array would give a least-squares correlation of 0.0. Consequently, angle strain factors are not of major importance in the rate of base-catalyzed isomerization of the exocyclic compounds.

By contrast, the relationship depicted in Figure 2 shows a reasonably good linear correlation between the log of the rates of the endocyclic compounds and the difference in angle strain. The least-squares correlation is 0.82. While the linear relationship is not perfect, indicating that other factors are involved, clearly angle strain is the major factor in the isomerization of the endocyclic compounds.

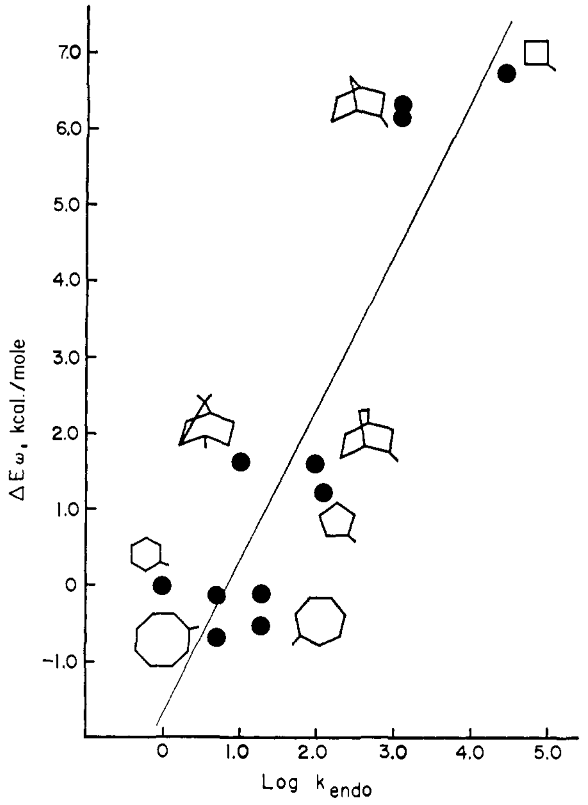


Figure 2. Plot of $\Delta E\omega$ *vs.* log k_{endo}.

In sum, angle strain factors are of prime importance for the *endo* to *exo* isomerization, but of minor importance for the *exo* to *endo* isomerization. What bearing these conclusions have on the transition state and the allylic anion will be considered after discussion of the effect of torsional strain.

Torsional Strain. A treatment similar to that given for the angle bending strain contribution leads to a comparable relationships

$$\Delta E\phi = x^*(E\phi' - E\phi) \qquad (9)$$

$$\Delta E\phi' = (x^* - 1)(E\phi' - E\phi) \qquad (10)$$

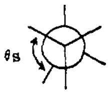
where x^* is the fractional contribution of the endocyclic olefin to the transition state, and $E\phi$ and $E\phi'$ are the torsional strain energies of the exo- and endocyclic olefins, respectively. Again, assuming that x^* for the series remains constant, a plot of the logs of the relative rates and the energy differences reveals the importance (or lack) of torsional strain contributions to the rate.

Torsional potential differences for the various *exo–endo* pairs were calculated from eq 11 and 12, where

$$E\phi = K/2(1 + \cos 3\phi) \qquad (11)$$

$$E\phi s = Ks/2(1 + \cos 3\phi s) \qquad (12)$$

K = 2.0 kcal/mole for olefins and Ks = 2.8 kcal/mole for saturated bonds and angles θs and θ are those defined in structures I and II, respectively.



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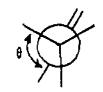

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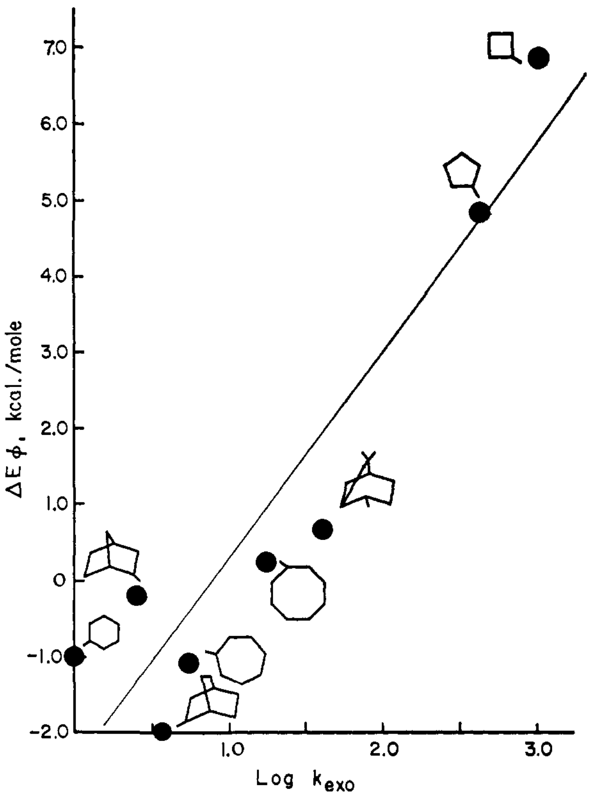

Figure 3. Plot of $\Delta E\phi$ *vs.* log k_{exo}.

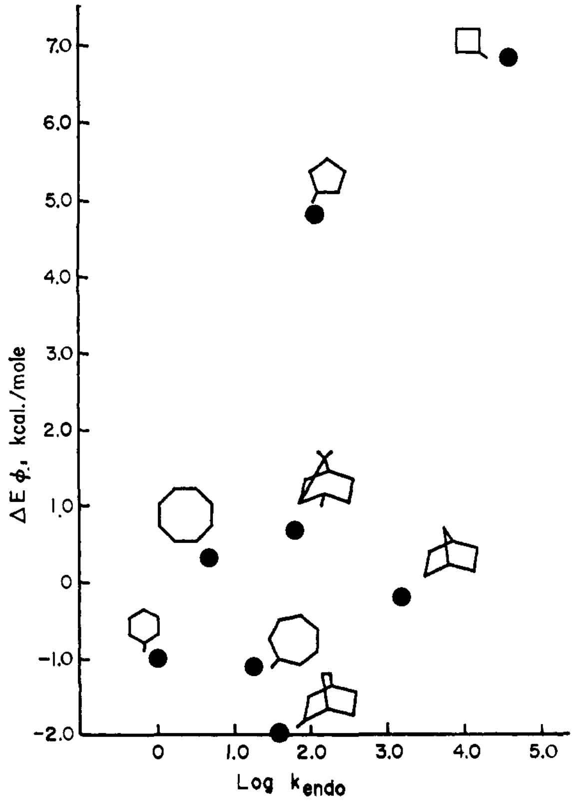

Figure 4. Plot of $\Delta E\phi$ *vs.* log k_{endo}.

The change in torsional strain ($\Delta E\phi$) includes the difference in olefinic torsional strain for the *exo* and *endo* compounds as well as the saturated torsional energies associated with the loss of a methylene group in going from the exo- to the endocyclic compounds. The over-all change is given by 13, where $\Delta E\phi$ is the

$$\Delta E\phi = E\phi_{exo} - E\phi_{endo} + E\phi s \qquad (13)$$

over-all change, $E\phi_{exo}$ and $E\phi_{endo}$ are the olefinic torsional energies of the exo- and endocyclic compounds, respectively, and $E\phi s$ is the saturated torsional strain energy of the α-methylene group in the exocyclic compound. Strictly, the difference in saturated torsional barriers will involve more than this one group. However, this approximation which greatly simplifies analysis, includes most of torsional strain differences.

Table VI. Calculated Torsional Strain Energies

Compound	θ, deg	$E\theta$, kcal/mole	θs, deg	$E\theta s$, kcal/mole
Methylenecyclobutane	0, 0	4.0	0	2.8
Methylenecyclopentane	15, 15	3.41	15	2.4
Methylenecyclohexane	60, 60	0.0	60	0.0
Methylenecycloheptane	23, 45	1.65	40	0.7
Methylenecyclooctane	43, 15	2.08	40	0.7
Methylenebicyclo[2.2.1]heptane	40, 0	2.50	40	0.7
Methylenebicyclo[2.2.2]octane	60, 0	2.00	60	0.0
β-Pinene	25, 25	2.50	50	0.2
Methylcyclobutene	60, 60	0.0		
Methylcyclopentene	40, 40	1.0		
Methylcyclohexene	40, 40	1.0		
Methylcycloheptene	15, 5	3.41		
Methylcyclooctene	25, 25	2.51		
Methylbicyclo[2.2.1]heptene	20, 20	3.00		
Methylbicyclo[2.2.2]octene	0, 0	4.0		
α-Pinene	0, 60	2.0		

For each set, $E\phi$ and $E\phi s$ were calculated using the angles determined by Dreiding models. Table VI records the relevant values of the angles θ and θs as well as the torsional potentials calculated from eq 11 and 12. Table VII records the over-all differences calculated by 13.

Table VII. Torsional Strain Energy Differences

System	$\Delta E\phi$, kcal/mole
Cyclobutyl	+6.8
Cyclopentyl	+4.8
Cyclohexyl	−1.0
Cycloheptyl	−1.06
Cyclooctyl	+0.27
Bicyclo[2.2.1]heptyl	−0.20
Bicyclo[2.2.2]octyl	−2.00
Pinene	+0.70

Figures 3 and 4 depict the relationship between the difference in torsional strain and the log of the relative rates of the *exo* and *endo* compounds, respectively. For the exocyclic going to endocyclic (Figure 3) a reasonably good linear correlation is obtained; the least-squares correlation coefficient is 0.88. In essence those *exo*-olefins with the most to gain by reduction of torsional interactions isomerize fastest and *vice versa*. We conclude, accordingly, that torsional effects are the principal factors governing the rate of

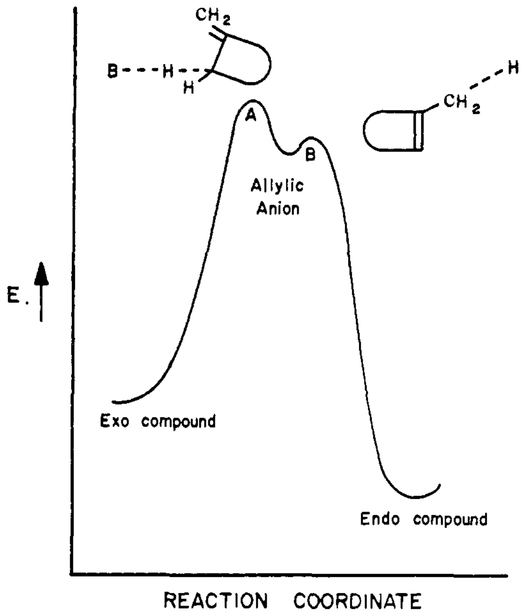

Figure 5. Free-energy reaction coordinate profile.

isomerization of exo- to endocyclic olefins. By contrast the random array in Figure 4 (least-squares correlation 0.49) suggests that for the endo- going to exocyclic isomerization torsional effects are not of major importance in determining the rate.

Thus, we may conclude that for the exo- to endocyclic isomerization, torsional strain factors are of prime importance whereas angle strain factors are relatively unimportant. Conversely, the endo- to exocyclic isomerization has a marked dependency on angle strain but is much less sensitive to torsional strain factors. Because the transition state is the same for each reaction, according to the principle of microscopic reversibility, these strain factors have bearing on the structure of the transition state.

The Structure of the Allylic Anion in Strained Systems. The essential features of the energy diagram for the isomerizations are depicted in Figure 5. The violations of the Ingold[18] protonation rules are derived from extension of the collapse ratios recently obtained by Cram.[19] In essence alkyl-substituted carbanions protonate to give the thermodynamically more stable tautomer. Thus transition state A is the one that governs the reaction. This is reasonable since primary carbanions are more stable than secondary and on this basis B would be expected to be of lower energy than A.

The conclusions of the previous sections as regards the effects (and lack thereof) of the several strain terms on the rates of the *exo*- and *endo*-olefins result from a common phenomenon, namely, the strain factors present in the transition state. The absence of relationship between angle strain differences and rates for the exocyclic compounds indicates that x^* is small. Confirmingly, the presence of a relationship between angle strain differences and rates for the *endo* isomerization indicates that $1 - x^*$ is large. Since x^* is the fractional contribution of the angle strain of the *endo* isomer to the angle strain of the transition state, it must follow that the angle strain of the transition state is comparable to that of the exocyclic compound.

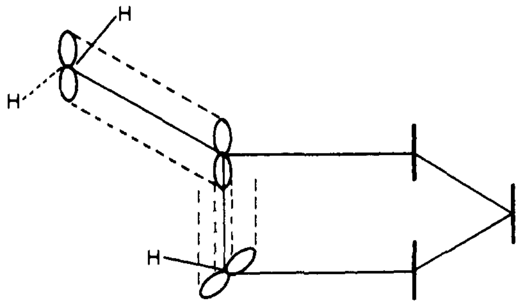

Figure 6. Strained allylic anion.

By a similar analysis we can deduce that the torsional strain factors of the transition state compare with those of the endocyclic compound. And, since the transition state resembles the allylic anion the structure of the anion may be expected to have a geometry consistent with these conclusions.

A coplanar allylic anion with three sp^2 carbon atoms does not fulfill these requirements. This structure has two trigonal carbon atoms in the ring, and, therefore angle strain factors are analogous to the endocyclic compound, in direct contrast to the observations. Allinger[20,21] and co-workers have shown that the planar geometry favored by the π system may not be in fact encountered because of strain associated with the σ portion of the molecule in the planar structure. A calculated structure which agrees with the electronic spectrum was obtained by balancing strain in the σ system with the energy of the π system.

While a similar quantitative treatment is beyond the scope of this work, one can reasonably account for the results in a qualitative manner, using the model depicted by Figure 6. In this strained allylic ion, the angle strain in the σ system is considerably diminished. This structure might be viewed as comprising two sp^2 carbon orbitals and a third carbon orbital approaching sp^3 hybridization. Although some delocalization energy is lost by the deviation from coplanarity, zero-order calculations[22] indicate that $\sim$90% of the resonance energy remains in the ammonia-like structure. This loss would be more than compensated for by the reduction in angle strain present in the coplanar model.

The anion depicted in Figure 6 has two sp^2 carbons and one *endo* sp^3 carbon. From that geometry, eq 4 and 5 are applicable since the angle strain of the *exo*-alkene is a good model for the angle strain in this anion.[23] However, for torsional strain calculations eq 9 and 10 are not strictly applicable since the torsional strain in this anion is not closely approximated by either the *exo*- or *endo*-alkene. Nevertheless, we can estimate the torsional strain contributions in the following manner.

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[18] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 10, says, "When a proton is supplied by acids to the mesomeric anion of weakly ionizing tautomers of markedly unequal stability, then the tautomer which is most quickly formed is the thermodynamically least stable."

[19] S. W. Ela and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 5777, 5791 (1966).

[20] N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *ibid.*, **87**, 3430 (1965).

[21] N. L. Allinger, *Tetrahedron*, **22**, 1367 (1966).

[22] Calculated assuming that the deviation from planarity is $\sim$20° using the equation $E = E_0 \cos^2 \theta$.

[23] We gratefully acknowledge the valuable suggestions of a referee in bringing these and the following considerations to our attention.

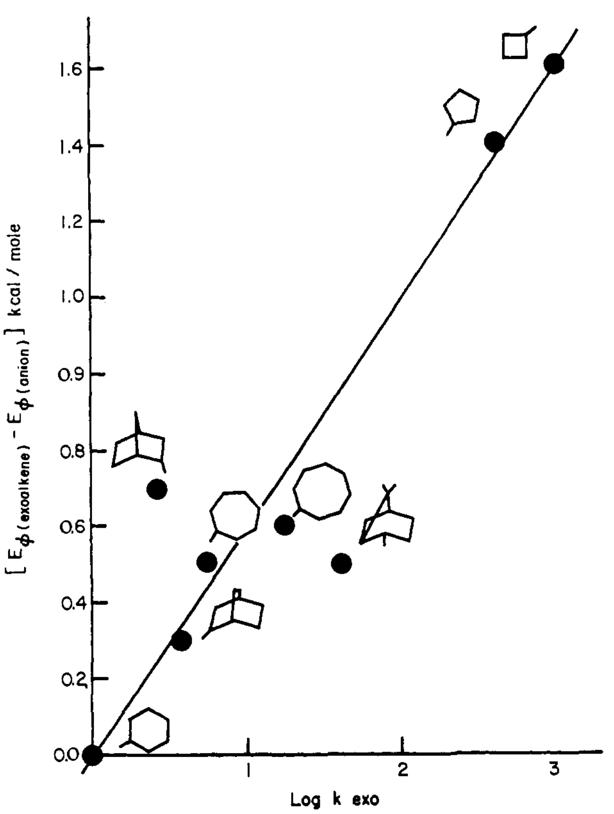

Figure 7. Plot of $E_{\phi(exo\text{-alkene})} - E_{\phi(\text{anion})}$ *vs.* log k_{exo}.

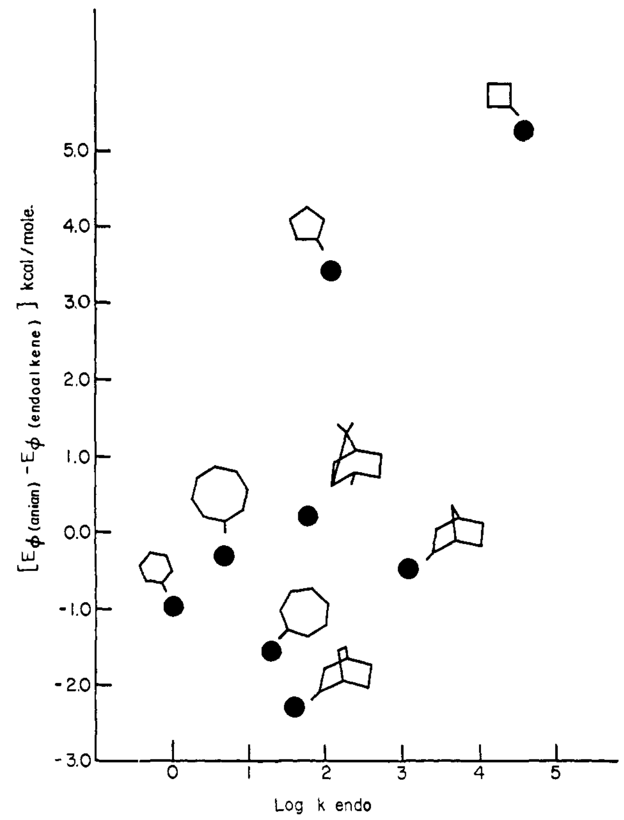

Figure 8. Plot of $E_{\phi(\text{anion})} - E_{\phi(endo\text{-alkene})}$ *vs.* log k_{endo}.

The torsional strain contributions for the *exo*- and *endo*-alkene and the anion are given by eq 14 and 15,

$$\Delta E\phi = \gamma^*(E\phi_{\text{anion}} - E\phi_{exo}) \qquad (14)$$

$$\Delta E\phi = \gamma^*(E\phi_{\text{anion}} - E\phi_{endo}) \qquad (15)$$

where γ^* is the fractional contribution of the anion to the transition state. The torsional strains for the anion can be estimated from the torsional strains of the *exo*-alkenes and eq 16. This relationship arises because

$$E\phi_{\text{anion}} = [0.5E\theta + (0.51)(0.66)E\theta + 0.66E\theta s] \qquad (16)$$

torsional potentials are reduced upon exchange a C–H bond for a lone pair, which is the change in going from the *exo*-alkene to the anion. The figure of 0.66 is taken from the series CH_3CH_3, CH_2NH_2, and CH_3OH with barriers of 3, 2, and 1 kcal/mole, respectively.[24] Table VIII records the torsional strain of the anions as well as the values of $\Delta E\phi$ and $\Delta E\phi'$. Figures 7 and 8 depict the relationship between the difference in torsional strain and the log of the relative rates of the *exo* and *endo* compounds, respectively. Figure 7 gives a good linear relationship since the angle strain energy change is near zero and the torsional strain energy change dominates the reaction profile. On the other hand, Figure 8 gives a poorer linear relationship as torsional strain changes contribute but do not dominate the total strain change. The better linear relationship found in Figure 2 indicates that angle strain changes contribute more substantially to the total energy change in this case. Accordingly the depicted anion accounts for the observations.

Table VIII. Torsional Strain Energies

System	$E\phi_{\text{anion}}$, kcal/mole	$\Delta E\phi$, kcal/mole	$\Delta E\phi'$, kcal/mole
Cyclobutyl	5.17	1.63	5.20
Cyclopentyl	4.42	1.39	3.40
Cyclohexyl	0.0	0.0	−1.0
Cycloheptyl	1.83	0.52	−1.58
Cyclooctyl	2.19	0.59	−0.30
Bicyclo[2.2.1]heptyl	2.54	0.66	−0.50
Bicyclo[2.2.2]octyl	1.66	0.34	−2.30
Pinene	2.21	0.49	0.21

Experimental Section

Materials. Potassium *t*-butoxide was obtained from Mine Safety Appliance, Inc., as the sublimed powder. Analyses showed this material to be 98.5% pure with the major impurity being potassium carbonate. Dimethyl sulfoxide was dried and distilled over Linde 13X molecular sieves. α- and β-pinene were obtained from the Hercules Chemical Co., and were used without further purification. Gas chromatographic analysis (21-ft Carbowax 20M at 120°) indicated that the materials were >99% pure. 2-Methylenebicyclo[2.2.2]octane and 2-methylbicyclo[2.2.2]octene-2 were kindly furnished by Professor Schleyer and Dr. Watts. These materials were 99 and 98% pure, respectively (gas chromatographically determined using 21-ft Carbowax 20M at 185°), and were used without further purification.

2-Methylenebicyclo[2.2.1]heptane. Methyltriphenylphonium bromide (107.1 g, 0.03 mole) was treated with phenyllithium (25.2 g, 0.03 mole) in ether (300 ml) with stirring for 3 hr. Norbornanone (11.0 g, 0.10 mole) was then added, and the solution was refluxed overnight. After being washed with water the ethereal solution was dried (magnesium sulfate) and treated with excess lithium aluminum hydride. After work-up in the usual way and solvent removal there was obtained by distillaton 7.6 g of 2-methyl-

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[24] For a discussion of this, see ref 13 and references cited therein.

enebicyclo[2.2.1]heptane, bp 123–125° (755 mm) (lit.[25] bp 123° (760 mm)), $n^{25}\text{D}$ 1.4725 (lit.[26] $n^{25}\text{D}$ 1.4719).

The infrared determined without solvent showed peaks characteristic of $R_1R_2C{=}CH_2$ at 3080 and 880 cm^{-1} (lit.[27] 881 cm^{-1}); nmr showed a complex multiplet, τ 8.2–9.1 (six protons, β-methylene hydrogens); multiplet, τ 7.9–8.2 (two protons, α-methylene hydrogens); single peaks at τ 7.72 and 7.40 (one proton each, bridgehead hydrogens); and peaks at τ 5.47 and 5.20 (one proton each, vinyl hydrogens).

2-Methylbicyclo[2.2.1]heptene-2. This compound was prepared by the Diels–Alder reaction of ethylene and commercial methylcyclopentadiene dimer (~35% 1-methylcyclopentadiene and 65% 2-methylcyclopentadiene) according to the procedure described by Schleyer.[28] Fractional distillation of the resulting mixture of isomers gave 1-methylbicyclo[2.2.1]heptene-2, bp 105°, and the desired 2-methylbicyclo[2.2.1]heptene-2, bp 118° (760 mm) (lit.[22] bp 118°) (760 mm). Final purification was accomplished by preparative-scale gas chromatography (20-ft Carbowax 20M at 185°); $n^{25}\text{D}$ 1.4623 (lit.[22] $n^{20}\text{D}$ 1.4632). The infrared determined without solvent has a maximum at 805 cm^{-1} (lit.[24] 805 cm^{-1}).

The nmr spectrum showed a complex multiplet from τ 7.9–9.1 (six protons, methylene protons); with superimposed sharp doublet at 8.3 (three protons, methyl protons); two peaks at 7.25 and 7.45 (one proton each, bridgehead protons); and a broadened singlet at 4.52 (one proton, vinyl hydrogen).

Kinetic Procedure. A 0.70 *M* solution of potassium *t*-butoxide in dimethyl sulfoxide was prepared in a nitrogen-blanketed drybox. Isomerization experiments were conducted using 7.0 ml of this solution in a small vial capped with a self-sealing neoprene stopper and preheated in a constant temperature bath (±0.2°). A thermally equilibrated equimolar mixture of the bicyclic olefin and a reference olefin, 2-methyl-1-pentene, were injected into the base solution. The inclusion of 2-methyl-1-pentene serves as a convenient internal standard since the rate of isomerization of a given olefin is independent of added olefin.[7a]

After agitation the vial was returned to the bath, and samples (0.50 cc) were taken at suitable intervals by inserting a hypodermic syringe through the self-sealing neoprene stopper. Samples were quenched in 5.0 cc of ice-water containing 0.5 cc of cyclohexane. The aqueous dimethyl sulfoxide layer was frozen, and a sample of the supernatant cyclohexane extract was analyzed by gas chromatography. The 2-methyl-1-pentene, 2-methyl-2-pentene analyses were performed on 21 ft of 20% D.C. 200 on Chromosorb P 60–80 mesh. The bicyclic olefin analyses were performed on 21 ft of Carbowax 20M at temperatures from 125–185°.

For methylenebicyclo[2.2.2]octane and β-pinene first-order plots of log concentration remaining *vs.* time were linear using conversions up to 20%. The first-order rate constants were obtained on an IBM 1620 computer using a least-squares program. For methylenebicyclo[2.2.1]heptane, first-order plots of log concentration remaining *vs.* time were not linear. This is due to the high concentration of *exo* isomer at equilibrium. Adequately linear lines were obtained from the plot of log concentration remaining minus concentration at equilibrium *vs.* time.[29] The desired rate constant of isomerization of the *exo* compound (*kf*) was obtained from the slope of this line (obtained by a least-squares computer program) which is *kf* + *kr* and the equilibrium constant, *kf*/*kr*.

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Cage Reactions in the Thermal Decomposition of Acetyl Peroxide[1]

James W. Taylor[2] and J. C. Martin[3]

Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. *Received June 26, 1967*

Abstract: Isotopic tracer methods provide evidence for an unexpectedly large amount (*ca.* 38%) of cage recombination of acetoxy radicals in the thermal decomposition of acetyl peroxide in isooctane at 80°. The reactions leading to ethane and methyl acetate are shown to be very cleanly intramolecular (>99 and >99.8%, respectively) using deuterium-labeling techniques. This result combines with the observation that methyl acetate is formed from acetyl-carbonyl-^{18}O peroxide with complete scrambling of label to confirm earlier conclusions that these are products of cage reactions. These results are compatible with a mechanism involving simple O–O bond cleavage to yield a pair of acetoxy radicals which can recombine or decarboxylate (followed by recombination of the product radicals) in reactions competitive in rate with diffusion from the cage. Ratios of rate constants for these processes are deduced from the product distribution.

The decomposition of acetyl peroxide may be visualized as proceeding by single O–O bond cleavage (1a), by concerted two-bond cleavage (1b), or by concerted three-bond cleavage (1c) leading directly to the methyl radicals which are precursors of most of the observed products. The consideration of the latter routes received its major impetus as a way of accounting for the repeated failure of efforts to trap acetoxy radicals with conventional radical scavengers.[4-8] An alterna-

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[1] For a preliminary report of this work, see J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3650 (1966); taken in part from the Ph.D. thesis of J. W. T., University of Illinois, 1964.

[2] Rohm and Haas Co. Fellow, 1962–1963; National Institutes of Health Predoctoral Fellow, 1963–1964.

[3] Fellow of the Alfred P. Sloan Foundation, 1962–1966; Fellow of the John Simon Guggenheim Memorial Foundation, 1966.

[4] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 491.

[5] M. Szwarc in "Peroxide Reactions Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 153.

[6] H. J. Shine, J. A. Waters, and D. M. Hoffman, *J. Am. Chem. Soc.*, **85**, 3613 (1963), report a reduction in carbon dioxide solution in the presence of diphenylpicrylhydrazyl (DPPH) or galvinoxyl, which they attribute to scavenging of the acetoxy radical. It is, however, difficult to rule out a direct reaction between the added scavenger and acetyl peroxide, which would give the same result, particularly for the scavenger, DPPH, yielding the most dramatic reduction. The reaction re-