

studies, and decoupling experiments. The infrared spectrum (CCl_4) has significant absorption at 3060, 3030, 2950, 2870, 1775, and 1759 cm^{-1} . The doublet carbonyl band is similar to that observed in nortricyclanone (1768 and 1755 cm^{-1}).¹² The mass spectrum of **1** shows the molecular ion as the parent peak at m/e 94, and only two other peaks with intensity over 10% at m/e 66 (31%) and m/e 65 (25%). The ultraviolet spectrum (cyclohexane) has λ_{max} at 254 $m\mu$ (ϵ 30).

The structure of **1** was proven chemically by cleavage¹³ with potassium *tert*-butoxide in dimethyl sulfoxide–water to give in high yield the known¹⁴ *endo*-bicyclo[2.1.0]pentane-2-carboxylic acid (**8**).

Acknowledgments. We are grateful to Dr. John Wright for extensive assistance with the spectroscopy experiments and to the National Science Foundation (Grant GP-33278) for financial support.

References and Notes

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Received August 29, 1974

Competitive Dissociation and Rearrangements of 1,5-Hexadiene¹

Sir:

The complete elucidation of a reaction mechanism, like that of a molecular structure, first requires a complete list of alternative possibilities. One or more of these can then be excluded, most often by successive appropriately designed experiments, until the correct one is revealed. Trivial as this logical prerequisite might appear, it has only recently been made explicit.²

For example, the pioneering stereochemical analysis of the Cope rearrangement³ is now recognized to have been both ambiguous and incomplete. It was ambiguous because the experimental data agreed equally well with a twist transition state as they did with a chair (Figure 1).^{2b,4} It was incomplete because an appropriately labeled precursor (and 11 kcal/mol more in activation enthalpy) subsequently revealed a second rearrangement mechanism—perhaps the boat or the plane.⁵

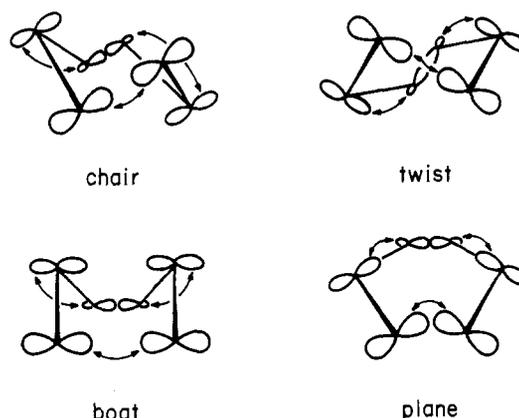


Figure 1. The symmetry-allowed [3,3]sigmatropic transition states—supra-supra (chair and boat) and antara-antara (twist and plane).^{2b}

The data, then available, could not distinguish these latter two alternative [3,3]sigmatropic possibilities. Neither could they exclude any of four [1,3]sigmatropic mechanisms. To confound matters still further, several critical colleagues have since expressed the view that yet another possibility—homolytic dissociation to allyl free radicals—had prematurely been rejected. Empirical generalizations^{6a} and/or extrapolation from higher temperature data^{6b} suggest homolytic rate constants which fall dangerously close to those that were observed.^{2b}

We are therefore particularly pleased to report new experimental results that exclude both the [1,3]sigmatropic and the dissociative possibilities. In this way, the higher temperature Cope rearrangement is now rigorously restricted to being either the boat or the plane—a level of ambiguity which still characterizes the first discovered, lower temperature process.^{3,4}

1,5-Hexadiene-*d*₂, the 1:1 mixture of 1*Z*, 6*E* and 3*R*, 4*S* isomers obtained by pyrolysis of *exo*-bicyclo[2.2.0]hexane-2,3-*d*₂⁷ at 207°, served as starting material for each of two different approaches. In the first (a classical⁹ crossover experiment), it was diluted with an equal quantity of undeuterated diene and pyrolyzed at ~600 Torr and 282° for 48 hr (2.0 half-lives of the higher temperature rearrangement). Diimide reduction, followed by mass spectrometric analysis of the resulting *n*-hexanes, provided results that were indistinguishable from the 1:1 superposition of identically obtained data but from *separate* dideuterated and undeuterated samples.¹⁰

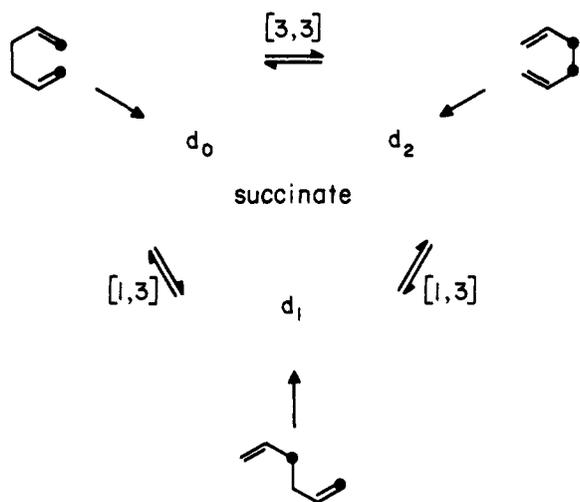
Unambiguous in excluding dissociation to allyl radicals, such data are less suited to more quantitative scrutiny. Neither can they distinguish the [1,3]- from the [3,3]sigmatropic possibilities. Both reservations are satisfied by the alternative approach, one that was explicitly suggested by the rigorous analysis of tetradeuterio- and dideuterio-1,5-hexadiene rearrangement possibilities.¹¹

As illustration, oxidative degradation of equilibrating 1,6- and 3,4-dideuterio-1,5-hexadienes provides succinic-*d*₁ acid only to the degree that [1,3]sigmatropy competes with [3,3] (Scheme I). (Here and subsequently, closed circles label a monodeuterated carbon.)

In algebraic detail, the linear analysis of labeling experiments approach^{2b} subjects each of the ten accessible dideuterio-1,5-hexadienes to the operation of nine possible reaction mechanisms: all five [3,3]sigmatropics (of rate constants k_C , k_T , k_B , k_P , and k_A) and all four [1,3]sigmatropics (of rate constants k_V , k_S , k_H , and k_D). Symmetrization¹² and symmetry-assisted diagonalization¹³ of the mechanism matrix generates the ten equations (eq 1):

$$\chi_i = \chi_i(0)e^{-\lambda_i t} \quad (1)$$

Scheme I



A mass spectrometric analysis of succinate- d_1 in the presence of d_0 and d_2 corresponds to a unique eigenfunction (eq 2) of the 1,5-hexadiene- d_2 isotopic isomer concentra-

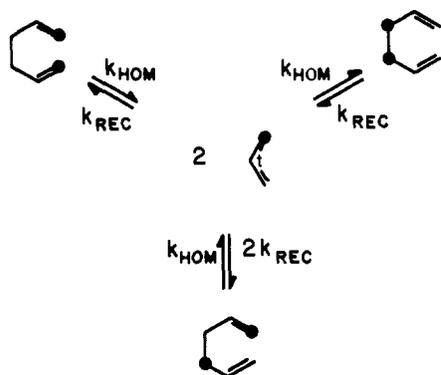
$$\begin{aligned} \chi_4 = & [3R, 4R] + [3R, 4S] + [3S, 4S] \\ & - [1E, 4R] - [1Z, 4R] - [1Z, 4S] - [1E, 4S] \\ & + [1E, 6E] + [1E, 6Z] + [1Z, 6Z] \end{aligned} \quad (2)$$

tions. The corresponding eigenvalue is then an unweighted sum of all the [1,3]sigmatropic possibilities.

$$\lambda_4 = 8(k_V + k_S + k_H + k_D) \quad (3)$$

In experimental detail, extensively jeopardized 1,5-hexadiene- d_2 was oxidized,¹⁴ the succinic acid was methylated with diazomethane, and the mass spectra of the resulting ester were calibrated with mixtures of authentic dimethyl succinate- d_0 , - d_1 , and - d_2 .¹⁵ No succinate- d_1 could be detected until 1,5-hexadiene- d_2 had been subjected either to 11.5 half-lives of the higher temperature Cope rearrangement at 283° or to 6.8 half-lives at 293°. Even then, such 1:1 d_0 : d_2 samples were contaminated only by $1.6 \pm 0.4\%$ of succinate- d_1 . Statistically greater than zero beyond the 99% confidence limits, the resulting (single point) rate constants ($k_{\text{obsd}}^{283^\circ} = 3.5 \times 10^{-8}$ and $k_{\text{obsd}}^{296^\circ} = 1.0 \times 10^{-7}$ sec⁻¹) reveal processes that are 245 and 145 times slower than the higher temperature Cope rearrangement.

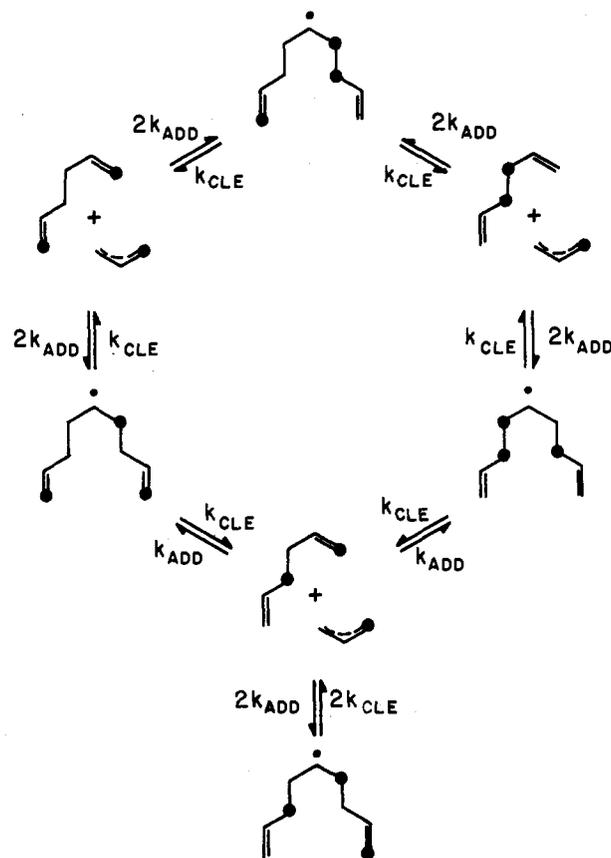
Scheme II



At present, such contaminating processes may either be regarded as [1,3]sigmatropic, as homolysis and then recombination (Scheme II), or as bimolecular addition and then cleavage (Scheme III). Most cogently

$$k_{\text{obsd}} = \lambda_4 + k_{\text{HOM}} + k_{\text{ADD}}(k_{\text{HOM}}[\text{diene}]/k_{\text{REC}})^{1/2} \quad (4)$$

Scheme III



In any case, it is now quite clear that thermal activation provides 1,5-hexadiene with two stereochemically distinct [3,3]sigmatropic rearrangements before either [1,3]sigmatropy or homolytic dissociation intrude. The more facile of these may be either chair or twist, the less facile either boat or plane. The dramatically different behavior of 2,5-dimethyl-1,3,4,6-tetraoxa-1,5-hexadiene, the isoconjugate acetyl peroxide, is described in the accompanying communication.¹⁷

Acknowledgment. We are grateful for the stimulating comments of S. W. Benson and D. C. Wigfield as well as for the partial financial support provided by the National Science Foundation (GP-24938).

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Received May 22, 1974

Competitive Dissociation and Rearrangements of Acetyl Peroxide¹

Sir:

Hardly a corner of organic chemistry remains untouched by the idea of incomplete dissociative return.² In the case of acetyl peroxide^{3a} (or, more generally, of any acyclic precursor of free radicals^{3b,c}) it appears clothed as the solvent cage model.⁴ Thermal isomerizations of cyclic hydrocarbons similarly have their biradicals, anionic rearrangements and solvolytic transformations their ion pairs.

Only rarely has it explicitly been recognized that such observations are often equally well understood to result from concerted reaction mechanisms.^{5,6} Only once to our knowledge, in the particular case of azomethane photolysis, has such an alternative unambiguously been excluded.⁷

We here report a similarly designed experiment which, no less unambiguously, requires precisely the opposite conclusion. The ¹⁸O scrambling of acetyl peroxide (Figure 1) is now most simply understood to result exclusively from competing [1,3]- and [3,3]sigmatropic shifts both in solution and in the gas phase. The alternative hypothesis—geminate recombination within a solvent cage—was previously shown to be neither necessary nor sufficient to account for ¹⁸O scrambling in solution.^{6a} We now demonstrate that this hypothesis also grossly misjudges the possibility of ¹⁸O scrambling in the gas phase.

The earlier investigation had successfully isolated the contribution of [3,3]sigmatropy, both in cumene and in isooctane solution. But it could not distinguish the two possible supplementary contributors (solvent cage recombination and/or [1,3]sigmatropy). This failure is now recognizable within a more general context.

Applying the linear analysis of labeling experiments,⁸ any mechanistic subgraph like Figure 1 requires

$$\chi_t = \chi_t(0)e^{-\lambda t} \quad (1)$$

Its twofold symmetry defines the eigenfunctions

$$\begin{aligned} \chi_1 &= [A_1] + [A_2] + [A_3] \\ \chi_2 &= [A_1] - [A_2] + [A_3] \\ \chi_3 &= [A_1] \quad \quad \quad - [A_3] \end{aligned} \quad (2)$$

Although the product vertex ($2\text{CH}_3 \cdot + 2\text{CO}_2^{46}$) is omitted,⁹ the corresponding eigenvalues (eq 3) must still include the formation of product—either by the dissociation of solvent-caged radical pair (k_{DIS}) and/or by the irreversible trans-

formation of acetyl peroxide to product (k_{PRO}); f_{R} is the fraction of return from radical pairs ($f_{\text{R}} \equiv 4k_{\text{REC}}/(4k_{\text{REC}} + k_{\text{DIS}})$).¹⁰

$$\lambda_1 = k_{\text{PRO}} + k_{\text{HOM}}(1 - f_{\text{R}})$$

$$\lambda_2 = k_{\text{PRO}} + k_{\text{HOM}} + 4k_{1,3} \quad (3)$$

$$\lambda_3 = k_{\text{PRO}} + k_{\text{HOM}} + 2k_{1,3} + 2k_{3,3}$$

The previous discovery—that λ_3 uniformly exceeds λ_2 —could therefore only require that $k_{3,3}$ exceed $k_{1,3}$. Neither the absolute nor the relative values of five mechanistic parameters can ever be defined by three experimental ones ($\lambda_i, i = 1, 3$).

The present investigation simplifies matters by contending that any semantically unambiguous model of a solvent cage⁴ must include a solvent.¹¹ In the gas phase, k_{HOM} must vanish. Three experimental rate constants can then provide three mechanistic ones.

As before,^{6a} the two isotope ratios ($R_1 = I_{34}/I_{32}$, $R_2 = I_{36}/I_{34}$) of molecular oxygen (derived exclusively from the peroxidic positions) were used to obtain two of the three experimental rate constants—"total scrambling" ($\lambda_{\text{TS}} \equiv \lambda_3 - \lambda_1$) and "random scrambling" ($\lambda_{\text{RS}} \equiv \lambda_2 - \lambda_1$). The third ("decomposition," λ_1) was concurrently obtained by gas chromatography. With acetyl peroxide at ~ 7 Torr and isopentane at ~ 600 Torr, the CO_2 yield was $99 \pm 1\%$.¹² Rate constants were insensitive to either a 15-fold increase in glass surface area or to tenfold dilution.

Perhaps the most decisive results of Table I are the dis-

Table I. Experimental Rate Constants^a

		Cumene ^b	Isooctane ^b	Gas
$10^4\lambda_1$ Decom- position	44.1°	0.49 ± 0.02	0.64 ± 0.06	0.45 ± 0.01
	55.0°	1.79 ± 0.04	2.75 ± 0.05	2.29 ± 0.06
	65.5°			9.48 ± 0.64
	75.5°			41.0 ± 5.6
$10^4(\lambda_2 - \lambda_1)$ Random scrambling	44.1°	0.10 ± 0.05	0.11 ± 0.05	0.27 ± 0.01
	55.0°	0.75 ± 0.08	1.18 ± 0.21	1.58 ± 0.14
	65.5°			5.54 ± 0.15
	75.5°			20.20 ± 0.41
$10^4(\lambda_3 - \lambda_1)$ Total scrambling	44.1°	0.21 ± 0.03	0.37 ± 0.04	0.38 ± 0.02
	55.0°	1.29 ± 0.05	1.61 ± 0.13	1.67 ± 0.17
	65.5°			7.93 ± 0.41
	75.5°			28.4 ± 1.0

^a Each rate constant derives from nonlinear least-squares fitting of 4–13 experimental points; uncertainties are standard deviations; ¹⁸O-enrichment: 10% for the 55° run, 45% for the others.
^b Reference 6a.

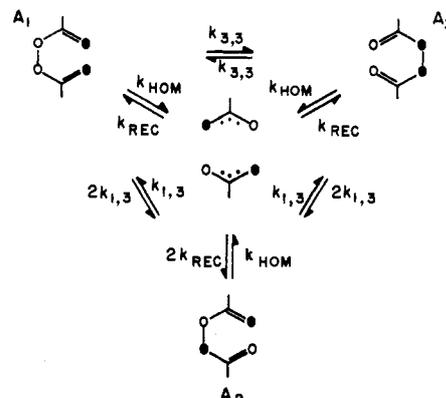


Figure 1. Three mechanisms for the ¹⁸O scrambling of acetyl peroxide. Others are possible.¹⁰