

Since $\delta \approx 0$ for simple hydrolysis, an intermediate with no covalent bond to H_2O could be present; however, the CBr bond could not be ionic. Although all tabulated reactions have $X = Br$, qualitatively identical conclusions result when $X = F, Cl, I$.

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(20) Small charges on the central carbon such as are present in conventional descriptions of SN_2 activated complexes (e.g., J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 170) are consistent with the observed pK_a^\ddagger values; charges of the magnitude required by an ion-pair mechanism are not. Further work may allow quantitative assignment of charges from pK_a^\ddagger values.

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The Degenerate [3,3]Sigmatropic Shift of Acetyl Peroxide

Sir:

Almost invariably, the [3,3]sigmatropic shift¹ of a 1,5-diene (the Cope rearrangement) predominates over its two potential competitors: [1,3] shift of either allyl moiety or homolytic cleavage into two such fragments² (Figure 1, $X = CH_2$). Current understanding of this preference is as yet less useful in heteroatomic systems. There, inversion of configuration is more difficult to detect; profound thermodynamic biases are more common.^{2d-4}

To avoid the latter problem, one need only demand a choice among three such mechanisms in a degenerate transformation, here that of the π -isoelectronic diacyl peroxide (Figure 1, $X = O$). In this way we now demonstrate the [3,3]sigmatropic path to be the dominant (though not exclusive) one for the scrambling of carbonyl and peroxidic oxygens in acetyl peroxide. While confirming a prior speculation,⁵ this too shifts the focus of current experimental disagreement.⁶

Acetylcarbonyl-¹⁸O peroxide was prepared from acetonitrile and "10%" enriched $H_2^{18}O$ by wholly conventional means.⁷ Recrystallized first from ether and

(1) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(2) (a) S. J. Rhoads in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Wiley, New York, N. Y., 1963, Chapter 11; (b) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962); (c) R. Malojčić, K. Humski, S. Borčić, and D. E. Sunko, *Tetrahedron Lett.*, 2003 (1969); (d) exceptions are reported by J. A. Berson and E. J. Walsh, Jr., *J. Amer. Chem. Soc.*, **90**, 4729, 4730, 4732 (1968).

(3) Such systems might well also lie beyond the reach of otherwise useful approximation. Cf. M. J. S. Dewar, *Tetrahedron, Suppl.*, **8** (1), 75 (1966).

(4) For recent comparisons of Claisen with Cope rearrangements, see M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **48**, 1985 (1965); S. J. Rhoads and R. D. Cockcroft, *J. Amer. Chem. Soc.*, **91**, 2815 (1969). Other recent heterosigmatropics are reported by R. W. Jemison and D. G. Morris, *Chem. Commun.*, 1226, 1345 (1969); J. M. Vernon and D. J. Waddington, *ibid.*, 623 (1969); J. E. Baldwin and J. E. Brown, *J. Amer. Chem. Soc.*, **91**, 3647 (1969). The classical studies of Claisen and benzidine rearrangements are summarized by H. J. Shine, "Aromatic Rearrangements," Elsevier, Amsterdam, 1967.

(5) A. T. Balaban, D. Fărcașiu, and R. Bănică, *Rev. Roum. Chim.*, **11**, 1205 (1966).

(6) (a) L. Herk, M. Feld, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 2998 (1961); (b) J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (c) J. C. Martin and S. A. Dombchik, *Advan. Chem. Ser.*, No. 75, 269 (1968).

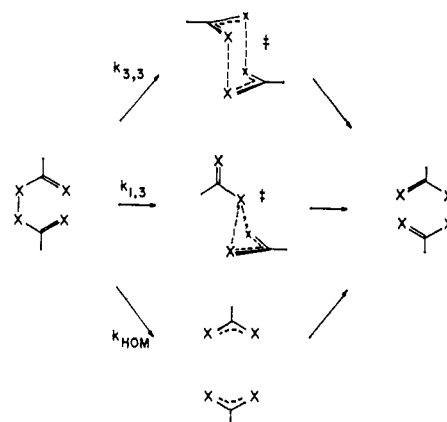


Figure 1. Competing mechanisms for a degenerate transformation.

then from its solutions in isooctane and cumene, its 0.1 *M* solutions were found to be contaminated by less than 0.002 *M* ether (by gas chromatography) and by less than 0.001 *M* acetic acid (by infrared). The two peroxidic oxygen atoms could be converted intact to those of molecular oxygen in over 90% yield by the sequence: alkaline hydrolysis, acid hydrolysis, and Ce^{IV} oxidation. The expected⁸ retention of isotopic integrity throughout both synthesis and degradation paths was confirmed by the identity (within 0.5%) of the 34/(33 + 32) *m/e* ratios of O_2 derived from enriched initial peroxide, from isotopically normal peroxide degraded in 1.5% ¹⁸O enriched media, or from a commercial cylinder.

Corresponding degradation of partially decomposed acetyl peroxide, recovered from its cumene or isooctane solutions at 44.4 or 55.1°, provided O_2 whose increasing 34/32 and 36/34 *m/e* ratios (R_1 and R_2) were fitted to eq 1-4⁹ by a nonlinear least-squares program.¹⁰ The two experimentally distinguishable scrambling rate constants, λ_{TS} ("total scrambling")

$$R_1 = N_1/(1 - N_1 - N_2) \quad (1)$$

$$R_2 = N_2/N_1 \quad (2)$$

$$N_1 + 2N_2 = (c + p) - (c - p)e^{-\lambda_{TS}t} \quad (3)$$

$$N_2 = [(c + p)^2/4] - [(c^2 - p^2)/2]e^{-\lambda_{TS}t} + [(c - p)^2/4]e^{-\lambda_{RS}t} \quad (4)$$

and λ_{RS} ("random scrambling"), listed in Table I, are related by Figure 2 to the three possible mechanistic hypotheses.¹¹ In this way, exclusive dom-

(7) S. Oae, T. Kitao, and Y. Kitaoka, *J. Amer. Chem. Soc.*, **84**, 3359 (1962); E. M. Schantz and D. Rittenberg, *ibid.*, **68**, 2109 (1946); J. R. Slagle and H. J. Shine, *J. Org. Chem.*, **24**, 107 (1959).

(8) C. A. Bunton, T. A. Lewis, and D. R. Llewellyn, *J. Chem. Soc.*, 1226 (1956); A. E. Cahill and H. Taube, *J. Amer. Chem. Soc.*, **74**, 2312 (1952).

(9) N_1 and N_2 are the mole fractions of ³⁴ O_2 and ³⁶ O_2 ; c and p are the initial atom fractions of ¹⁸O in one carbonyl and in one peroxidic oxygen. Experimentally determined rate constants are denoted by λ ; k is reserved for those defined by a reaction mechanism.

(10) Details of both the mass spectral analysis and the statistical evaluation of its results may be found in the Ph.D. thesis of H. A. Judson, Cornell University, Ithaca, N. Y., Jan 1970, and will be elaborated in the full publication.

(11) The important alternative, an irreversible decomposition that entirely bypasses the acetoxy radical pair,¹² is implicitly included as the kinetically indistinguishable consequence of $f_R = 0$. Less plausible scrambling alternatives that require bimolecular intervention of free acetoxy radicals are ignored in view of the general consensus^{6,13} that such radicals never escape their cage of birth.

(12) M. J. Goldstein, *Tetrahedron Lett.*, 1601 (1964).

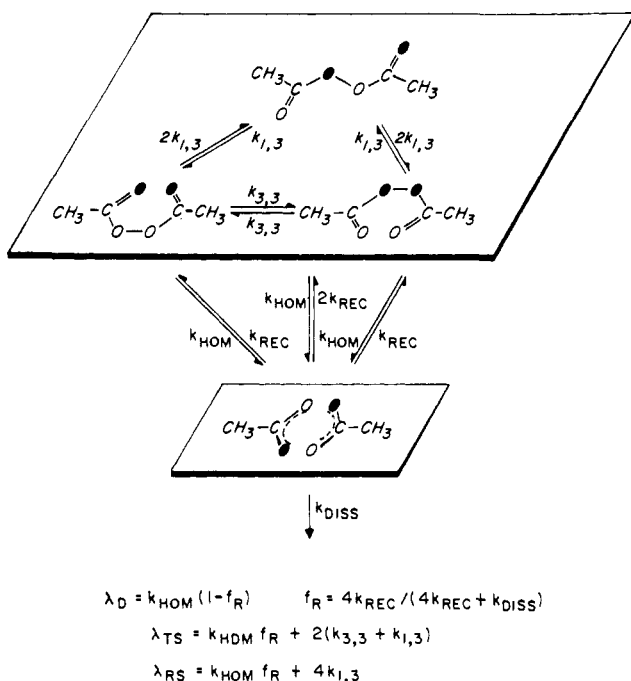


Figure 2. Oxygen scrambling in acetyl peroxide.

ination by any one path can be detected (homolysis, $\lambda_{\text{RS}} = \lambda_{\text{TS}}$; [1,3]sigmatropy, $\lambda_{\text{RS}} = 2\lambda_{\text{TS}}$; [3,3]sigmatropy, $\lambda_{\text{RS}} = 0$). The relative contributions of two (but not all three) can be evaluated.¹⁴

Table I. Oxygen Scrambling of Acetyl Peroxide^a

Solvent	Temp, °C	n ^b	10 ⁶ λ _{TS}	10 ⁶ λ _{RS}	10 ⁶ λ _D	f _R ^c
Cumene	44.4	4	0.21 ±0.03	0.10 ±0.05	0.49 ^d ±0.02	0.19 ±0.10
	55.1	13	1.29 ±0.05	0.75 ±0.08	1.78 ±0.04	0.30 ±0.04
Isooctane	44.4	5	0.37 ±0.04	0.11 ±0.05	0.64 ^e ±0.06	0.15 ±0.07
	55.1	12	1.61 ±0.13	1.18 ±0.21	2.75 ±0.05	0.30 ±0.06

^a Uncertainties are standard deviations.¹⁰ ^b Number of independent samples subjected to ¹⁸O analysis. ^c Fractional extent of acetoxy return if $k_{1,3} = 0$. ^d Obtained by M. Yoshida. ^e Obtained titrimetrically by J. D. Lassila. All other λ_D's were obtained manometrically.

That [3,3]shifts are important in this system is thus required by the observation that $(\lambda_{\text{TS}} - \lambda_{\text{RS}}) [= 2(k_{3,3} - k_{1,3})] > 0$ in all investigated environments. That these cannot constitute the sole path for oxygen scrambling is required by the observation that $\lambda_{\text{RS}} > 0$. Less certain, thus far, are the relative contributions of [1,3]shift and acetoxy recombination to the remaining ("random") scrambling. Considering the matter further elsewhere,¹⁵ we now merely note the consequences of the two extreme hypotheses. (a)

(13) (a) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962); (b) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1741 (1967); (c) T. Koenig, *ibid.*, **91**, 2558 (1969); (d) W. G. Bentrude, *Ann. Rev. Phys. Chem.*, **18**, 283 (1967).

(14) Aliphatic displacement stereochemistry is precisely analogous; the relative contributions of distinct inversion, retention, and racemization mechanisms can never all be completely determined.

(15) M. J. Goldstein and H. A. Judson, *J. Amer. Chem. Soc.*, **92**, 4120 (1970).

Should acetoxy radical pairs be absent or (equivalently) produced irreversibly ($f_R = 0$), [3,3]sigmatropy would account for 63–85% of oxygen scrambling. Alternatively (b), should [1,3]shifts be entirely absent, the [3,3] mechanism would contribute 25–54% of the scrambling. This latter possibility would then require $f_R = \lambda_{\text{RS}}/(\lambda_{\text{D}} + \lambda_{\text{RS}})$. Such values of f_R (Table I) are more generally to be regarded as *upper limits* to the fraction of acetoxy pairs that may recombine. In either case, as expected, [3,3]sigmatropy contributes less at the higher temperature.

Finally, we note the gratifying agreement between our isooctane ratios of $\lambda_{\text{TS}}/(\lambda_{\text{TS}} + \lambda_{\text{D}})$, 0.37 at either 44.4 or 55.1°, and that reported by Martin, *et al.*, 0.38 at 80°.^{6b,c} Their premature identification of this ratio as f_R followed (in part) from their belief that "no more than 1% of the reaction can proceed by mechanism A" (the [3,3]sigmatropic shift). Whether their failure to detect this mechanism is best ascribed to (a) their higher reaction temperature (80°), (b) their lower ¹⁸O enrichment (3.6%), or (c) the fewer samples they felt obliged to analyze (1) is as yet unclear. Much more puzzling is the failure of Szwarc, *et al.*,^{6a} to detect *any* scrambling under conditions where the concordant data would have predicted 38%.

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[1,3]Sigmatropic Shifts in Peroxidic Compounds

Sir:

The mechanistic ambiguities of oxygen scrambling in peroxidic compounds¹ could not be appreciated, much less disentangled, until the early consistent failures even to detect the reaction were rectified. With two such claims^{2a,b} now disposed of,^{1,3} we here remove the third and last^{2c} by reporting oxygen scrambling of *t*-butyl perbenzoate. Extending this pattern also to include *t*-butyl peracetate⁴ and perpivalate, we now find quantitative disagreement with expectations to be derived from current mechanistic thinking.

Each of the three carbonyl ¹⁸O-enriched peresters was prepared from the sodium salt of *t*-butyl hydroperoxide and the appropriate acid chloride which derived, in turn, from the nitrile and "1.5%" enriched H₂¹⁸O. Concordant assays of >98% were obtained by nmr, by CO₂ evolution (peracetate and perpivalate), and by titration⁵ (peracetate and perbenzoate). Deg-

(1) M. J. Goldstein and H. A. Judson, *J. Amer. Chem. Soc.*, **92**, 4119 (1970).

(2) (a) Acetyl peroxide, L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961); (b) benzoyl peroxide, M. Kobayashi, H. Minato, and Y. Ogi, *Bull. Chem. Soc. Jap.*, **41**, 2822 (1968); (c) *t*-butyl perbenzoate, J. C. Martin and T. W. Koenig, *J. Amer. Chem. Soc.*, **86**, 1771 (1964), footnote 21.

(3) (a) Acetyl peroxide, J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (b) benzoyl peroxide, J. C. Martin and J. H. Hargis, *ibid.*, **91**, 5399 (1969).

(4) T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968), have independently discovered oxygen scrambling accompanying peracetate decomposition in paraffin oil solution.