enebicyclo[2.2.1]heptane, bp 123–125° (755 mm) (lit.[25] bp 123° (760 mm)), $n^{25}D$ 1.4725 (lit.[26] $n^{25}D$ 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°); $n^{25}D$ 1.4623 (lit.[22] $n^{20}D$ 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.

Acknowledgment. The authors are pleased to acknowledge helpful discussions with Professor Paul von R. Schleyer during the preparation of the manuscript for this paper.

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

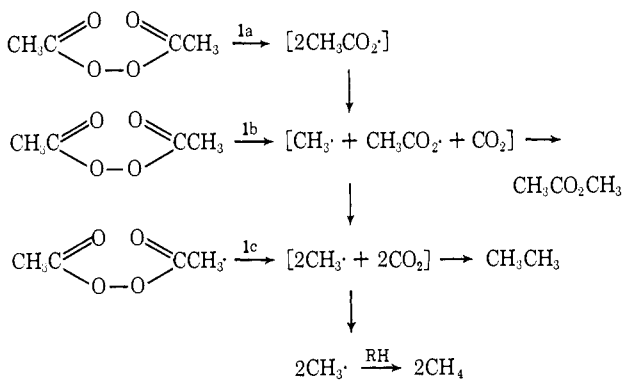
James W. Taylor[2] and J. C. Martin[3]

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-

(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-



tive rationale explains this failure by postulating the decarboxylation of initially formed acetoxy radical to be too rapid to allow competitive reaction with scavenger. Szwarc[5] has pointed to the near identity of the decomposition rates and activation parameters for acetyl peroxide (E_a, 29.5 kcal/mole), propionyl peroxide (30.0), and benzoyl peroxide (30.0) as good evidence against the operation of concerted multiple bond cleavages in this series. Such reactions leading directly to the very dissimilar methyl, ethyl, and phenyl radicals would be expected to show very different rates, by analogy with the many examples of concerted multiple bond cleavages demonstrated by Bartlett[9] and co-workers to be important in the series of *t*-butyl peresters.

Mechanism 1c recently became the object of renewed consideration as a result of the observation of a rather large kinetic isotope effect[10] (for carboxyl carbon $k_{12}/k_{13} = 1.023$, 45°) reflected in the carbon dioxide evolved in the decomposition of acetyl peroxide. This was interpreted in terms of predominant importance of the three-bond cleavage mechanism, 1c. It was suggested[10] that the product methyl acetate, *ca.* 15%, might be formed by a methyl radical induced decomposition of acetyl peroxide. The failure of added scavengers to reduce the amount of this product[7,8] makes this very unlikely. This conclusion was based on the assumption that the cage return of acetoxy radicals to acetyl peroxide is not important, in keeping with earlier work[8] applying oxygen-18 tracer techniques to this problem.

Koenig and Brewer[11] report that the decomposition of diacetyl-d_6 peroxide proceeds at the same rate as isotopically normal peroxide. This failure to observe a secondary deuterium kinetic isotope effect suggests that C–C bond cleavage is not appreciably developed in the transition state.

A comparison[8] of products from the decomposition of acetyl peroxide in the gas phase and the liquid phase, and in the presence and absence of iodine scavenger, has led to the acceptance of the idea that ethane and methyl acetate are formed in geminate recombination reactions. Applying the theory of cage reactions to the mechanism for ethane and methyl acetate formation, it has been found possible[12] to relate semiquantitatively the variation in amounts of these products, formed in decomposition in straight-chain hydrocarbon solvents, with changes in solvent viscosity and to use this variation to calculate a rate constant for decarboxylation of the acetoxy radical, 1.6×10^9 sec^{-1}, at 60° (neglecting the possibility of cage return to regenerate acetyl peroxide).

Experimental Section[13]

Reagents. The preparation of acetyl-carbonyl-^{18}O peroxide and the purification of cyclohexene have been described previously.[7] Three low-temperature recrystallizations of the peroxide were used to remove the last traces of ether, and the 1120-cm^{-1} infrared band was used to monitor the ether decrease. Isooctane was Eastman Spectrograde dried over silica gel.

Oxygen-18 Analyses. The details of the procedure used for analysis have been reported previously.[7,14] Analyses of the second and successive samples of the labeled compounds always checked to better than ±1%, relative, and are the ones reported in the tables of data. The condition of the combustion tube was monitored by direct oxygen analysis of the respective unlabeled compounds as well as by blank determinations with only the helium sweep gas flowing. The correction for blanks was negligible, and the values for the oxygen content were scattered randomly about the theoretical value.

Specificity of Carbonyl Labeling. Starting with acetic anhydride containing 1.124 atom % excess oxygen-18 per labeled oxygen, acetyl peroxide was prepared. Since an explosion resulted from the attempted direct pyrolysis of a very small sample of acetyl peroxide, the isotopic analyses were carried out on a sample of the peroxide in isooctane, *ca.* 0.5 *M*. This sample gave a value of 1.096 atom % excess per labeled oxygen. To 2 ml of isooctane containing 0.2 mmole of acetyl peroxide was added 1 ml of methanol 0.5 *M* in sodium methoxide. The cooled reaction mixture was placed in a small round-bottomed flask equipped for magnetic stirring and attached for distillation to the high vacuum line. About 60% of the liquid reaction mixture was distilled at room temperature using liquid nitrogen to facilitate the transfer. Methyl acetate was isolated from the distillate by glc using Apiezon L (James G. Biddle and Co., Philadelphia, Pa.) 20% on 80–90 mesh Analabs ABS (Analabs Inc., Hamden, Conn., designation of a diatomaceous earth which has been washed with concentrated HCl, washed with alcoholic KOH, and then vacuum siliconized to yield a nonreactive support surface) to separate the isooctane from the methanol and methyl acetate. Ucon polar (a designation of a Union Carbide water-soluble polyalkylene glycol which is sold by Micro-Tek, Baton Rouge, La., as Ucon 50 HB 280X), 20%, on Analabs ABS was used to separate the methanol from the methyl acetate. After three passes through each 10-ft column at 40–45°, the purity of methyl acetate was judged to be greater than 99% by peak height measurements. The purified methyl acetate showed 1.124 atom % excess oxygen-18 per labeled oxygen.

Kinetics of Peroxide Decomposition. The rate of disappearance of the peroxide in various solvents was determined by observing the decrease of the carbonyl absorption at 1800 cm^{-1}. Solutions of the peroxide were degassed by three freezing–thawing cycles and aliquots were sealed in vials. In each case it was shown that the solutions followed Beer's law.

Detection of Isotopic Scrambling during the Decomposition of Acetyl-carbonyl-^{18}O Peroxide. A treatment similar to that used for the kinetics experiments was followed with the exception that bulbs of 100–300-ml size were used instead of the vials. At appropriate intervals these bulbs were removed for the bath, quenched at −80°, and allowed to come to room temperature before opening. The volume of the solution was then reduced by one-half us-

ported by H. J. Shine and J. R. Slagle, *J. Am. Chem. Soc.*, **81**, 6309 (1959), forming cyclohexyl acetate from the decomposition of acetyl peroxide in cyclohexene solvent, probably does represent the scavenging of acetoxy radicals by reaction with solvent cyclohexene.[7]

(7) J. C. Martin, J. W. Taylor, and E. H. Drew, *ibid.*, **89**, 129 (1967), suggest that the scavenging of acetoxy radical responsible for the ester products formed in olefinic solvent occurs through the rapid formation of a π complex with olefin, which stabilizes the acetoxy radical toward decarboxylation.

(8) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).

(9) For a review with leading references, see P. D. Bartlett in "Peroxide Reaction Mechanisms," J. E. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 1.

(10) M. J. Goldstein, *Tetrahedron Letters*, 1601 (1964).

(11) T. Koenig and W. Brewer, *ibid.*, 2773 (1965).

(12) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, 66, 1591 (1962).

(13) We wish to thank Mr. Josef Nemeth for the microanalytical determinations and the oxygen-18 determinations, Mrs. S. Nanousi for the isotope ratio mass spectral measurements, Mr. R. Johnson for the infrared and nmr spectra, and Dr. T. Kinstle and Mr. G. Sanzone for mass spectra of the deuterated samples.

(14) J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, **83**, 1234 (1961).

ing a rotary evaporator. This served to remove a large portion of the methyl acetate resulting from peroxide decomposition. At this point in one series of runs the solutions were washed three times with a 10% sodium bicarbonate solution, then three times with water, and dried over magnesium sulfate before proceeding. Identical results were obtained in runs where this step was omitted. Identical treatment was afforded each sample from a particular run. The peroxide was recrystallized at −80° and the solvent removed through a filter stick. Fresh solvent was added and the process repeated two more times. In some cases careful centrifugation of the cold solvent was used to speed filtration. Infrared monitoring of the final solution was used to check for residual methyl acetate and traces of acetic acid. Sodium methoxide in anhydrous methanol was added in excess and the resulting solution treated as described above to isolate the methyl acetate.

Determination of Isotopic Scrambling of the Label in the Product Methyl Acetate. A sample of acetyl-carbonyl-^{18}O peroxide prepared from labeled anhydride (0.630 atom % excess per oxygen), 0.10 *M* in isooctane, was heated at 80.0° in a 300-ml sealed bulb for 35 hr (13 half-lives). The bulb was opened and the methyl acetate flash distilled and then purified by glpc using the Apiezon L column described previously. A portion (20 mg) of the recovered and purified methyl acetate was sealed in a break-tip tube with 0.1 ml of *n*-pentane. This mixture was introduced into an evacuated vessel containing a degassed mixture of 50 mg of lithium aluminum hydride in 1.5 ml of tetrahydrofuryloxytetrahydropyran,[15,16] which had been freshly distilled from lithium aluminum hydride. The reduction slurry was frozen with a −80° bath to condense the methyl acetate and reaction occurred on the surface. After three freezing and thawing cycles, dry helium was admitted and the reaction vessel attached to the vacuum line for collection of the methanol and ethanol products. Tetrahydrofurfuryl alcohol (2 ml) was added as the exchange alcohol and the mixture heated to 140° for 2 hr. The methanol and ethanol were distilled into a container maintained at liquid nitrogen temperature. The last traces were removed under vacuum, distilled into a capillary tube receiver, and sealed. The contents of the tube were then separated by glpc using the above described Ucon polar column. Equal molar concentrations of the two alcohols were obtained, and by calibrated peak height measurements the yields were 4.5 mg of ethanol and 3.0 mg of methanol. A sample of the methyl acetate, which was not reduced, was also subjected to glpc purification yielding 15 mg.

On oxygen-18 analysis the methyl acetate yielded 0.580 atom % excess per labeled oxygen; the methanol, 0.230; and the ethanol, 0.232. These results show equivalent labeling in the two alcohols, indicating complete scrambling. The total labeling of the alcohols is low, however, compared to the methyl acetate and the methyl acetate result is low compared to the 0.630 found for the starting anhydride. These discrepancies were traced to incomplete drying of the Ucon polar column used for the final purification. Water was eluted along with the alcohols and methyl acetate samples. By the use of a calibration curve of time *vs.* weight, increase of a microanalytical drying tube filled with magnesium perchlorate[17] and by knowing the time interval required to trap each component, it was possible to calculate the amount of extraneous water in each sample. The values corrected in this fashion are: anhydride, 0.630; methyl acetate, 0.627_7; methanol, 0.314_5; and ethanol, 0.312_3. These values are thus in better agreement with the starting anhydride and indicate complete scrambling of the two oxygens in the methyl acetate product. For later studies it was found that the chromatographic column could be freed of moisture by heating at 140° for 3 hr prior to use at 40–45°.

Control Experiments. Exchange of label from equilibration on the chromatograph column and in the purification steps was shown to be minimal by the agreement of the label in the starting anhydride, 1.124%, and the carbonyl label in the methyl acetate isolated from the reaction of sodium methoxide with peroxide recovered from isooctane solvent at time zero, 1.124%.

In a test for intermolecular exchange of peroxide oxygens brought about by traces of acetic acid, 200 mg of labeled acetic acid (1.5 atom % excess oxygen-18 per oxygen) was added to 25 ml of a solution 0.05 *M* in unlabeled peroxide. This mixture was heated at 80° for the appropriate time to decompose 50% of the peroxide. The peroxide was then isolated, purified, and treated with sodium methoxide to yield methyl acetate. The resulting acetate sample showed −0.001 atom % excess oxygen-18 and a sample of Eastman unlabeled methyl acetate, −0.004%.

A test for exchange of methyl acetate oxygen with acetic acid was made by heating 100 mg of labeled acetic acid (1.5 atom % excess) at 80° for 25 hr in 2 ml of cyclohexene containing 74 mg of unlabeled methyl acetate. Isolation and analysis of the methyl acetate revealed 0.001 atom % excess oxygen-18 per labeled carbonyl oxygen.

Preparation of Acetyl Peroxide-d_6. Malonic acid-d_4 was prepared in a manner similar to that of Hadzi and Sheppard.[18] Analysis by nmr using maleic anhydride internal standard in acetone-d_6 showed 93.6% deuterium incorporation after two equilibrations. Decarboxylation of the malonic acid at 140° led to acetic acid-d_4. One portion of the acid was converted into the sodium salt using sodium carbonate and another into the acid chloride using thionyl chloride. From this point the preparation of acetic anhydride-d_6 and the corresponding peroxide was similar to the preparation of carbonyl-O^{18} labeled acetyl peroxide described earlier.[7,14] Microanalysis by the falling drop method showed 93.90 atom % deuterium in the anhydride.

Deuterium Labeling Studies. A solution containing equal concentrations, 0.015 *M*, of unlabeled peroxide and acetyl peroxide-d_6 was sealed in a tube equipped with a break-seal and heated at 80.0° for a time equivalent to 15 half-lives of the peroxide in this solvent. The gaseous components were initially separated by a vacuum line technique and further purified by vapor-phase chromatography using a silica gel column to give a mixture of carbon dioxide and ethane. Methyl acetate was flash distilled from the bulk of the solvent and purified by glpc using the previously described Apiezon L column.

The mass spectrum of the methyl acetate sample was obtained using an Atlas MAT Model CH4 mass spectrometer operated at an ionizing voltage of 15 ev. This voltage was selected experimentally using unlabeled samples and represented the best compromise between sensitivity and fragmentation of the acetate. The intensities of the individual peaks of each species were corrected for the M + 1 peaks by the method described by Biemann[19] as well as for the hydrogen in the starting labeled anhydride. Approximately equal intensities were obtained at *m/e* 74 and 80 corresponding to the unlabeled and completely deuterated acetate, respectively. The corrected intensity of the peak at *m/e* 77 corresponding to the cross product was less than 0.2% of the total intensity of the peaks at 74 and 80.

The purified ethane–carbon dioxide mixture was analyzed on a Bendix time-of-flight mass spectrometer at 10.3-ev ionization voltage. An examination of the uncorrected intensities of the peaks at *m/e* 30, 33, and 36 revealed that the intensity of the 33 peak, corresponding to the cross product, was approximately 0.6% of the combined intensities of the 30 and 36 peaks. No correction was made for the incomplete labeling in the starting peroxide.

Kinetic Isotope Effects. Isotope ratio mass spectrometry was used in a manner similar to that described for the oxygen labeling studies[7] to obtain the oxygen kinetic isotope effect reflected in the carbon dioxide product. Successive samples of carbon dioxide were isolated by three freezing–thawing cycles from a sample of acetyl peroxide in isooctane which had been heated at 80.0° for known periods of time. The carbon dioxide was transferred, using a vacuum line technique, to a gas chromatograph and purified using a 50 ft × 0.25 in. o.d. column of 5% Apiezon L on 20–30 mesh Teflon (a tetrafluoroethylene polymer manufactured by the E. I. du Pont Co.).

The carbon kinetic isotope effect reflected in the methane product was determined in a similar manner but using the ratio of the *m/e* 45 to the 44 peaks in carbon dioxide resulting from combustion of the methane utilizing the Wilzbach[20] combustion mixture of purified copper and copper oxide. Prior to combustion the methane was purified by Toepler pumping through several liquid nitrogen traps.

(15) We are indebted to Dr. R. F. Nystrom for suggesting this reduction procedure and supplying the hydride solvent. The procedure is excellent for the reduction of small samples of volatile materials and is similar to that used for the reduction of carbon-^{14}C dioxide to methanol-^{14}C as described by Cox, Turner, and Warne.[16]

(16) J. D. Cox, H. S. Turner, and R. J. Warne, *J. Chem. Soc.*, 3167 (1950).

(17) The author gratefully acknowledges the excellent suggestion of Mr. Joseph Nemeth for preventing the rate of helium diffusion from obscuring these weight measurements. A closely fitting wire effectively closed the capillary restrictions in the tube and slowed the diffusion so that reproducible weighings could be made.

(18) C. Hadzi and N. Sheppard, *Proc. Roy. Soc.* (London), A216, 247 (1953).

(19) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 223.

(20) K. E. Wilzbach and W. Y. Sykes, *Science*, 120, 494 (1954).

Mass spectrometry indicated no contamination of the methane by traces of carbon dioxide or ethane.

The carbon kinetic isotope effect reflected in the carbon dioxide product was measured similarly using acetyl peroxide enriched in carbon-13 in the carbonyl carbon. This was prepared starting with the carbonation of methyl magnesium iodide using Merck Sharp and Dohme $BaCO_3$ (54% excess carbon-13) as the source of carbon dioxide. Using 9.62 mmoles of carbon dioxide, 0.365 g (15 mg-atoms) of magnesium, and 1.25 ml (20 mmoles) of methyl iodide, a yield of 8.84 mmoles of sodium acetate was finally obtained (92% yield). The sodium acetate was converted into acetyl chloride using Eastman phthaloyl chloride (25-mmole excess). Using high vacuum dried silver acetate (12-mmole excess) and vacuum line distillation it was possible to obtain 0.779 g (7.62 mmoles) of acetic anhydride from the silver acetate–acetyl chloride reaction mixture (over-all yield of 79% anhydride based on the generated CO_2). The labeled anhydride was accurately mixed with unlabeled material to yield a final stock solution of acetic anhydride with 5.890 atom % carbon-13 per carbonyl carbon. This anhydride mixture was used to prepare acetyl peroxide as described previously.[7]

The evolved carbon dioxide was purified using the previously described Teflon column, after initial separation from solvent was accomplished on the vacuum line.

Results

The procedure for determining the specificity of carbonyl oxygen labeling in acetyl peroxide involved the reaction of sodium methoxide in anhydrous methanol with the peroxide to produce methyl acetate. The results of these experiments are shown in Table I.

Table I. Specificity of Oxygen-18 Labeling in Acetyl-carbonyl-^{18}O Peroxide

Sample	^{18}O[a]	Excess/labeled atom	Carbonyl labeled, %
Starting anhydride	1.124	1.124	100.0
Acetyl peroxide[b]	0.548	1.096	97.5
Methyl acetate[c]	0.562	1.124	100.0

[a] Per cent excess oxygen-18 atom in the compound. [b] Analysis of a sample dissolved in isooctane. [c] Isolated and purified by glpc.

The analysis reported for peroxide in Table I is taken from a concentrated (*ca.* 0.5 *M*) solution of the peroxide in isooctane solvent. Considering the large volume of solvent present with the possible trace contamination of oxygen-containing impurities, all three results can be said to be in agreement. The initial oxygen-18 content of the anhydride, therefore, is specifically retained in the carbonyl oxygen of the peroxide. The data of Table I also serve to show that the purification, reaction, and isolation procedures used in obtaining the methyl acetate from the acetyl peroxide are free of equilibration steps which, if operative, would lead to a lower level of label in the methyl acetate than seen in the starting anhydride. As an added precaution several controls were performed to test for potential difficulty from equilibration. The low-temperature thermal equilibration of methyl esters is known to be slow.[21] In this procedure the methyl acetate was isolated from the mixture of methoxide in methanol by a high vacuum line technique which allowed the reaction mixture to be maintained below 10°. The chromatographic isolation was performed at 40–45° on a column prepared from a support which, according to the supplier, had been both acid and base washed and then vacuum siliconized. In earlier results, small but detectable equilibration on regular firebrick support had been noted.[7] The support treatment used here appeared to eliminate this source of difficulty.

Although infrared spectroscopic examinations of the peroxide solutions were made to test for the presence of residual acetic acid or anhydride, there was the possibility that traces of these materials not detected by this method could cause a reduction in specificity. Labeled acetic acid was, therefore, deliberately added to a solution of the peroxide in isooctane and the mixture heated for 8700 sec at 80°. The peroxide was then isolated, purified, and converted into methyl acetate. The excess labeling in the acetate was found to be negligible, showing no exchange of the peroxide with the acid. Similarly when unlabeled methyl acetate was heated with labeled acetic acid for 25 hr at 80°, no incorporation of label was detected in the methyl acetate.

When these techniques for detecting the extent of carbonyl labeling were applied to samples of the peroxide which had been heated in kinetic bath for approximately one half-life of the peroxide at 80°, the results shown in Table II were obtained from single runs of the peroxide in isooctane and cyclohexene solvents.

Table II. Scrambling of the Carbonyl Label of Acetyl Peroxide during Decomposition at 80°

Sample	Excess/labeled atom	Fraction of carbonyl specifically labeled
Run A[a]		
Starting anhydride	1.124	1.000
Peroxide, time zero	1.124	1.000
Peroxide, 8700 sec	0.984	0.751[c]
Run B[b]		
Starting anhydride	1.448	1.000
Peroxide, time zero	1.443	0.993
Peroxide, 9000 sec	1.257	0.736

[a] 0.05 *M* in isooctane. [b] 0.05 *M* in cyclohexene. [c] If both oxygens become equivalent, per cent excess would limit at 0.562. This fraction is calculated from (0.984 − 0.562)/0.562.

These results indicate that during decomposition of the peroxide there exists a mechanism for loss of specificity of the carbonyl labeling. Szwarc[8] had previously suggested the occurrence of geminate recombination of the thermally generated acetoxy radical pair as a possibility in the decomposition of acetyl peroxide. His experiments using oxygen-18 labeling and infrared spectroscopy as a probe to examine material recovered after 55% reaction led him to conclude that this recombination did not occur. We must conclude from our data that either the procedure outlined in this paper is a more sensitive method or that some mechanism for loss of carbonyl label not operative in the earlier study[8] is important under the conditions of our experiments.

In order to gain further insight into what other possibilities might exist for this scrambling, it became of interest to observe the kinetics of the loss of carbonyl label specificity. Both the rate of decrease of carbonyl labeling and the rate of disappearance of the peroxide 1800 cm^{-1} infrared band were monitored using a single stock solution of acetyl-carbonyl-^{18}O peroxide. The labeling data are shown in Table III and the kinetic plots in Figure 1.

(21) K. B. Wiberg, *J. Am. Chem. Soc.*, 75, 2665 (1953).

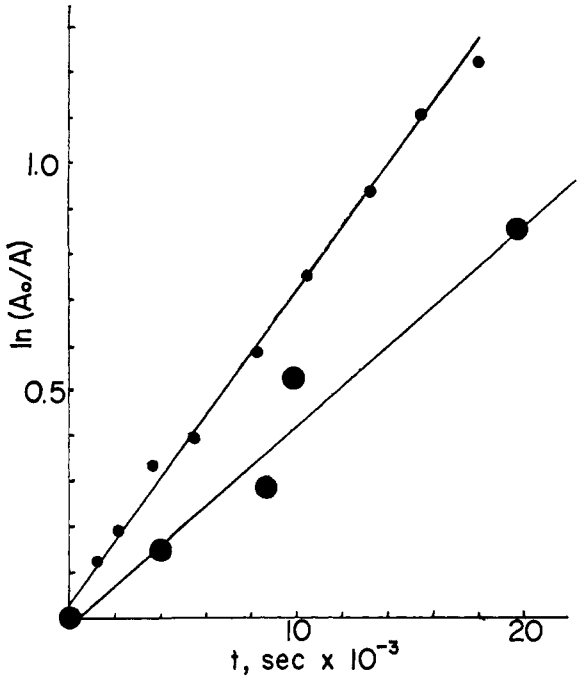


Figure 1. First-order rate plots for the disappearance of total acetyl peroxide (small circles, data obtained by infrared spectroscopy) and for scrambling of carbonyl label in recovered acetyl peroxide (large circles).

The rate constant of peroxide decomposition is found to be 7.2×10^{-5} sec^{-1}, in reasonable agreement with the values reported earlier[6,22] at this temperature. The rate of decrease of carbonyl label follows first-order kinetics and the calculated rate constant is 4.4×10^{-5} sec^{-1}.

Table III. Specificity of Labeling in Acetyl-carbonyl-^{18}O Peroxide Recovered from Partial Decomposition at 80° in Isooctane

Time, sec	Excess in carbonyl, %	Fraction of carbonyl specifically labeled[a]
0	0.618	1.000
4,800	0.574	0.857
(8,700)[b]	(0.541)[b]	(0.751)[b]
9,900	0.492	0.592
19,800	0.439	0.420

[a] If both oxygens become equivalent, the per cent excess would be expected to be 0.309. Fraction for second and subsequent entries calculated by (0.574 − 0.309)/0.309. [b] Normalized value taken from data of Table II.

Isotopic labeling data could also be used to answer some questions concerning the mechanism of formation of methyl acetate as a product from the thermal decomposition of acetyl peroxide. Reduction of the ester with lithium aluminum hydride in a manner similar to that employed in a previous study[7,23] gave the data shown in Table IV.

These data, showing equivalent labeling in the carbonyl and ester oxygens, reinforce other results in ruling out the suggestion[10] of methyl radical induced decomposition to produce the methyl acetate. This might be

(22) M. Levy, M. Steinberg, and M. A. Szwarc, *J. Am. Chem. Soc.*, 76, 5978 (1954).
(23) J. C. Martin and E. H. Drew, *ibid.*, 83, 1232 (1961).

Table IV. Distribution of the Label in Decomposition Product Methyl Acetate[a]

Sample	Excess/labeled atom, %	Total label, %
Starting anhydride	0.630	100.0
Methyl acetate[b]	0.627	99.5
Methanol[b]	0.314	49.8
Ethanol[b]	0.312	49.6

[a] Isolated from decomposition of acetyl-carbonyl-^{18}O peroxide at 80°, 0.10 *M* in isooctane. [b] These results contain a correction described in the Experimental Section.

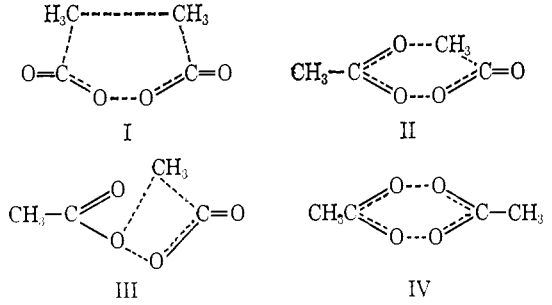
expected[24-26] to lead to a predominance of label in the carbonyl oxygens.

Since the data presented thus far are in accord with single oxygen–oxygen bond cleavage, it became of interest to examine the information gained from kinetic isotope effect (k.i.e.) data. During the course of this work, Goldstein[10] reported values for acetyl peroxide in isooctane at 45° of 1.023 ± 0.007 for oxygen (k_{16}/k_{18}) and 1.023 ± 0.003 for carboxyl carbon (k_{12}/k_{13}), as reflected in a comparison of carbon dioxide initially (0–5%) evolved and the total carbon dioxide evolved during complete decomposition. We were able to obtain satisfactory checks of these values using this same method. It has been pointed out[27,28] that the initial fraction of a product has often been found to show anomalous isotopic content. We therefore employed a method for determination of this k.i.e. using aliquots sequentially collected throughout a decomposition run. Treatment of the data after the method of Downes[29] involves a plot $\ln A \rightarrow \ln A(1 - f)$ where A is the 46/44 mass peak ratio and f is the fraction of reaction at which the sample was collected. These plots showed a considerable deviation from linearity in the later stages of the reaction for reasons as yet unknown.[30] From consideration of the slope of the line obtained from the Downes plot of data from the first 80% decomposition, we can arrive at an estimated upper limit for the carbonyl carbon value as 1.016 (k_{12}/k_{13}). The value for oxygen was 1.033 (k_{16}/k_{18}) and for the carbon in the methane, 1.005–1.010 (k_{12}/k_{13}). It is interesting to note that the carbon dioxide sample from the initial decomposition (0–5%) of the peroxide contained less carbon-13 than predicted by a linear Downes plot. The reasons for the anomalous composition of these initial samples are unknown and may be related to the presence of trace impurities, such as the peracid, at concentrations too low to be detected by our infrared method of checking for impurities. Further information to resolve this question is clearly required.

(24) W. von E. Doering, K. Okamoto, and H. Krauch, *ibid.*, 82, 3579 (1960).
(25) E. H. Drew and J. C. Martin, *Chem. Ind.* (London), 925 (1959).
(26) D. B. Denney and G. Feig, *J. Am. Chem. Soc.*, 81, 5322 (1959).
(27) C. J. Collins, *Advan. Phys. Org. Chem.*, 2, 84 (1964); V. F. Raaen, T. K. Durham, D. D. Thompson, and C. J. Collins, *J. Am. Chem. Soc.*, 85, 3497 (1963).
(28) V. F. Raaen and C. J. Collins, *Pure. Appl. Chem.*, 8, 347 (1964).
(29) A. M. Downes, *Australian J. Sci. Res.*, 5A, 521 (1952).
(30) Several possible reasons were considered, including the fact that the decomposition of one acetoxy radical within a pair prevents the return of the second acetoxy radical to acetyl peroxide, in a reaction independent of the isotopic substitution of the second acetoxy radical, and the superposition of carbonyl-^{13}C and methyl-^{13}C kinetic isotope effects. Neither of these possible complications would be expected to give effects large enough to explain the observed curvature.

Discussion

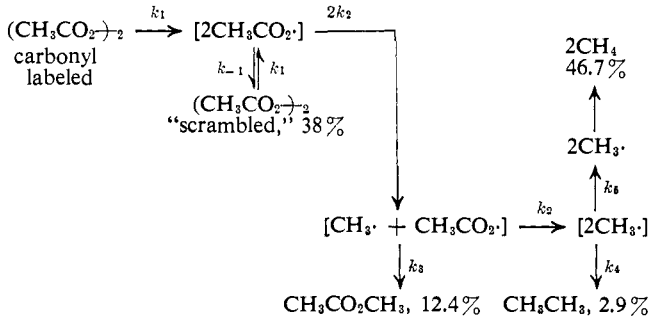
The very small amount of cross-labeled product formed in the decomposition of an equimolar mixture of diacetyl peroxide and diacetyl-d_6 peroxide provides a quantitative measure of the intramolecular nature of the reaction leading to ethane and methyl acetate (>99 and >99.8% intramolecular, respectively). This does not uniquely define the mechanism as involving cage recombination of radicals, however, since cyclic processes proceeding through transition states I, II, and III also lead to ethane and methyl acetate.[31]



I II III IV

It has been argued[5,8] that failure to observe ethane and methyl acetate as products of gas-phase decompositions of acetyl peroxide in the presence of scavengers renders unlikely the operation of such cyclic processes. While this argument is indicative it cannot be considered rigorous since, at least in principle, solvation effects could favor a cyclic process and thus make it observable in solution though unimportant in the gas phase. The small importance of the processes proceeding through II and III can be assessed, however, by isotopic tracer techniques. The complete scrambling of label in methyl acetate arising from the decomposition of acetyl-carbonyl-^{18}O peroxide in isooctane at 80° suggests the intermediacy of a species, such as the acetoxy radical, with equivalent oxygen atoms.[32] This makes the radical cage formulation, as outlined in Scheme A, an elaboration of 1a, seem very attractive for methyl acetate formation. While such a tracer experiment is not available to rule out the formation of ethane through I, the operation of such a mechanism, involving simultaneous distortions of both methyl groups, seems even less probable than the cyclic processes, II and III, which are here ruled out.

Scheme A



A similar cyclic mechanism (through IV) is available for scrambling of carbonyl-^{18}O label in acetyl peroxide. While it is possible to distinguish between scrambling *via* IV and the more random scrambling *via* acetoxy radical pairs (Scheme A) through the use of double labeling techniques, further work is required before a clear decision is possible as to the importance of IV. If we assume that all of the loss of label specificity in acetyl peroxide recovered after partial decomposition represents scrambling *via* acetoxy radical pairs, we may use the data of Table III and that from previous studies[6] to set a lower limit[33] to the amount of cage recombination. The observed scrambling of label is seen (Figure 1) to occur by a kinetically first-order process, with a rate constant ($k_s = 4.4 \times 10^{-5}$ sec^{-1}, 80°) which can be compared with the over-all rate of disappearance of acetyl peroxide, measured by disappearance of the carboxyl stretching frequency near 1800 cm^{-1} ($k_d = 7.2 \times 10^{-5}$ sec^{-1}, 80°). These measured rate constants may be related to the rate constants of the postulated Scheme A by noting that

$$k_d = \frac{2k_2k_1}{k_{-1} + 2k_2}$$

and

$$k_s = \frac{k_{-1}k_1}{k_{-1} + 2k_2}$$

therefore

$$k_d/k_s = \frac{2k_2}{k_{-1}} = 1.64$$

and

$$k_{-1} = 1.22k_2$$

Thus 38% of acetoxy radical pairs recombine with scrambling of label.

The two decarboxylation steps, which convert one radical pair into the next in line, have rate constants, k_2 and $2k_2$, which are related by the statistical factor reflecting the presence of two acetoxy radicals in the first pair. The constant k_2 is simply the conventionally defined first-order rate constant for the decarboxylation of acetoxy radical.

The radical pairs enclosed in brackets are not, in this scheme, to be considered caged radicals in the usual[34,35] sense. The brackets simply designate pairs of radicals formed in a single decomposition event. The radical pair generated in a single decomposition event is shown, by the cleanly intramolecular nature of the reaction leading to ethane and methyl acetate, to retain its identity as a distinct well-defined entity for a time long with respect to the time required for these products to

(31) See R. E. Rebbert and P. Ausloss, *J. Phys. Chem.*, 66, 2253 (1962), for a description of a detailed study of the pressure dependence of the production of ethane in the decomposition of azomethane, which suggests the small importance of a cyclic mechanism similar to that of I.

(32) The alternative explanation involving exactly equivalent contributions of processes leading through II and III is much less likely.

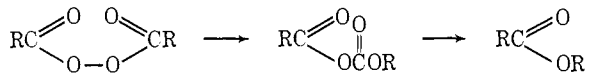
(33) It is possible to imagine cage recombination being sufficiently rapid as to prevent complete equilibration of the two types of oxygen, hence giving cage return without scrambling of label.

(34) It is probable from a consideration of product ratios that essentially all cage recombination occurs in a time shorter than one half-life for the decarboxylation of acetoxy radical. (Unpublished work of S. A. Dombchik.) The designation of the limits for the secondary recombination process of Noyes[35] becomes rather arbitrary, since one needs to decide just how near zero the probability of recombination must be before the radical pair with a given separation between the two radicals ceases to be considered as a caged pair. It is probable that the quantities within the brackets include some radical pairs which are sufficiently close to one another to be distinguishable, in principle, from other radical pairs, yet far enough apart to have a negligible probability of recombination, hence not conventionally[35] identified as cage radical pairs.

(35) R. M. Noyes, *J. Chem. Phys.*, 18, 999 (1956); *J. Am. Chem. Soc.*, 77, 2042 (1955).

be formed. Defining the bracketed quantities in this manner allows us to consider the cage reactions with rate constants k_{-1} and k_3 as rate constants for steps competitive only with decarboxylation.[36] From a consideration of product ratios we can set $k_{-1} = 1.22k_2$ and $k_3 = 0.25k_2$.

The cage recombination of methyl radicals (rate constant k_4) is competitive with diffusion from the cage (k_5). The addition of radical scavengers drastically reduces the methane yield without affecting the yield of ethane. The ratio k_4/k_5 (0.062) therefore reflects primarily the average separation of methyl radicals at the time of their formation, as this determines the probability of their ever diffusing to within a collision diameter of each other. Hydrogen abstraction is apparently too slow a process to compete effectively with the formation of ethane by primary or secondary recombination of methyl radicals in isooctane solvent.[37]



Much of the evidence concerned with the mechanism of formation of ester product in diacyl peroxide decomposition has been derived from studies of peroxides in which R is a *sec*-alkyl group. For example, Kharasch, Kudama, and Nudenberg[38] showed (for R = *sec*-butyl) that retention of configuration was seen in the alkoxyl group in the derived ester product from the decomposition of optically active peroxide. The recent observation[39] that many such decompositions proceed *via* the pictured carboxy-inversion process suggests that evidence of this sort may not be directly applicable to the analogous acetyl peroxide. The carboxy-inversion route to methyl acetate was ruled out by Greene by the observation[40] that the appropriate mixed anhydride is too stable to serve as an intermediate in the decomposition of acetyl peroxide to yield methyl acetate.

We have earlier pointed out[1] several references to observations of rate data which are more adequately explained by the postulation of appreciable cage recombination of acetoxy radicals (k_{-1}) than otherwise. That the observation[41] of $k_{gas}/k_{liq} > 1$ for the decomposition of acetyl peroxide represents a rather unusual circumstance can be seen in data tabulated[42] in a recent survey of such unimolecular decompositions. The observation of cage return of acetoxy radicals to acetyl peroxide makes it possible to suggest $k_{1,gas}/k_{1,liq} \leqslant 1$ in this case also. The cage recombination of acetoxy radicals was originally suggested by Szwarc[41b] to explain this observation but later[8] rejected by him on the basis of what proved to be erroneous data from tracer studies.

These tracer results[8] also led Braun and Eirich to reject an explanation for the observed[12] decrease in the rate of disappearance of acetyl peroxide with increased solvent viscosity[43] which was based on a postulated cage recombination of acetoxy radicals. Since our initial report[1] of the results of this paper, which again made it possible to consider cage recombination of acetoxy radicals in a mechanistic scheme, Pryor and Smith[44] have discussed these kinetic results in terms of a reduced apparent rate of decomposition resulting from an increased cage return in more viscous media. They have shown a decreased rate of decomposition of phenylazotriphenylmethane (PAT) with increased solvent viscosity which parallels the rate behavior observed by Braun and Eirich[12] for acetyl peroxide in the same media. The interesting suggestion was made[44] that this sort of kinetic criterion, used here to support the hypothesis of a cage recombination of phenylazo radicals and triphenylmethyl radicals to regenerate PAT, might be generally applied to the decompositions of radical initiators.

The appreciable k_{-1}/k_2 ratio also provides a possible rationale for the large carboxyl-^{13}C kinetic isotope effect (k.i.e.) seen by Goldstein[10] for acetyl peroxide, without postulating large contributions of (1b) or (1c) to the mechanism of decomposition. Decomposition by Scheme A under conditions which k_{-1} is larger (*i.e.*, in very viscous media) would show k_2 more nearly rate-limiting. Since k_2 reflects the rate of decarboxylation of the acetoxy radical, a reaction which might be expected to show an appreciable k.i.e., the apparent k.i.e. should increase as the k_{-1}/k_2 ratio increases. If we assume a 5% k.i.e. for the decarboxylation[45] of acetoxy radical, k_2, and use the k_{-1}/k_2 ratio derived in this paper for isotopically normal acetyl peroxide in isooctane, we would expect a k.i.e. for k_d of up to 1.8, a little smaller than the value of 2.3 reported[10] by Goldstein.

Koenig and Brewer[11] have noted essentially a zero secondary deuterium k.i.e. for the decomposition of diacetyl-d_6 peroxide. This was presented as evidence against concerted bond cleavage mechanisms 1b and 1c. It is consistent with Scheme A only if the deuterium secondary k.i.e. for decarboxylation of acetoxy radical (k_2) is very small. Since this is expected to be a very exothermic reaction with a transition state resembling

(36) In the formalism of Scheme A, k_{-1}, k_3, and k_4 are first-order rate constants representing the probability of recombination of the appropriate bracketed radical pairs. The observed order, $k_{-1} > k_3$, reflects the average greater separation of radical pairs consisting of methyl and acetoxy radicals compared with the average separation of acetoxy radical pairs. A referee has suggested that it would be more appropriate to write the mechanism in a form employing explicitly the rate constant for diffusion from the cage, k_{diff}, where the diffusive process gives noncage radical pairs which do not recombine. The simpler treatment of each geminate pair of radicals as a kinetic entity, regardless of the degree of separation of the radicals within the pair, has advantages not only in providing a rigorous definition of the bracketed species in Scheme A, but also in making it possible to express directly the rate constants for the interconversion of radical pairs in terms of the rate constant for decarboxylation of the acetoxy radical and in providing a convenient framework for further theoretical treatment of the date. (Unpublished work of S. A. Dombchik.)

(37) This is in keeping with the conclusions of R. K. Lyon, *J. Am. Chem. Soc.*, **86**, 1907 (1964), based on the numerical calculations of D. A. Flanders and H. Fricke, *J. Chem. Phys.*, **28**, 1126 (1958). In isooctane solution the value of the B value of Flanders and Fricke is 10^{-4} to 10^{-5}, suggesting less than 1–2% diversion of methyl radicals from recombination to yield ethane by the competing hydrogen-abstraction reaction yielding methane.

(38) M. S. Kharasch, J. Kudama, and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1955).

(39) F. D. Greene, H. A. Stein, C. C. Chu, and M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).

(40) Professor F. D. Greene, private communication. Confirmed in our laboratory in the work of S. Dombchik.

(41) (a) A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5975 (1954); (b) M. Levy, M. Steinberg, and M. Szwarc, *ibid.*, **76**, 5978 (1954).

(42) H. Martin, Jr., *Angew. Chem. Intern. Ed. Engl.*, **5**, 78 (1966), Table 3.

(43) A factor of nearly 2 on going from n-C_6H_{14} to n-$C_{18}H_{38}$ solvent.

(44) W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **89**, 1741 (1967).

(45) For analogies, see L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960, Chapter 7. An experimental determination of the k.i.e. for acetoxy radical decarboxylation is possible through the determination of the k.i.e. for the intramolecular competition reflected in the methyl acetate cage product.

the acetoxy radical,[46] the observation of a small k.i.e. related to k_2 would not be surprising. This would be true for the deuterium secondary k.i.e., which depends primarily on zero-point energy differences, though not true for the carbon-13 k.i.e.[45]

The various k.i.e. results are seen to be at least qualitatively in accord with Scheme A, involving a simple O–O bond homolysis as its first step. A further study of the reversibility of this process (as reflected in the ratio k_{-1}/k_2 as a function of solvent properties, viscosity, microscopic solvent structure, scavenger concentration, and temperature) should be illuminating with respect to the possibility of distinguishing between primary and secondary cage recombination processes.[35,47]

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(46) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(47) H. P. Waits and G. S. Hammond, *ibid.*, 86, 1811 (1964).

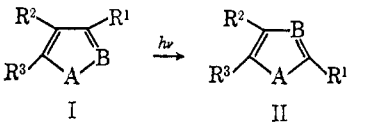
Photochemical Transposition of Ring Atoms in 3,5-Diarylisoxazoles. An Unusual Example of Wavelength Control in a Photochemical Reaction of Azirines[1]

Balwant Singh and Edwin F. Ullman

Contribution from the Central Research Division, American Cyanamid Company, Stamford, Connecticut. *Received May 19, 1967*

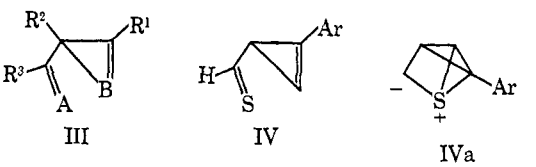
Abstract: Irradiation of 3,5-diarylisoxazoles Va and Vb with ultraviolet light results in the formation of 2,5-diaryloxazoles VIIa and VIIb. The rearrangements have been shown to proceed in two photochemical steps by way of 3-aroyl-2-aryl-1-azirines VIa and VIb. The photochemical behavior of the azirines is dramatically controlled by the wavelength of the light used. With 3130-A or shorter wavelength light the azirines rearrange almost quantitatively to the product oxazoles, whereas 3340-A or longer wavelength light caused nearly exclusive rearrangement back to the starting isoxazoles. Sensitization data suggest the possible intermediacy of triplet states of the azirines in the formation of the isoxazoles. On the other hand, the oxazoles appear to be formed from singlet azirines. The data suggest that the two reactive excited states of the azirines may undergo predissociative decay to different intermediates that can collapse to give the corresponding product or ground-state azirine. It is suggested that the two chromophores may be excited selectively with different wavelengths of light. Thus the formation of the isoxazole may occur *via* the $^3(n \rightarrow \pi^*)$ state of the carbonyl chromophore which in turn may be excited selectively with 3340-A light. On the other hand, 3130-A or shorter wavelength light may cause a selective excitation of the $n \rightarrow \pi^*$ level of the ketimine chromophore.

Recently several examples have been reported of the rearrangement of five-membered heterocyclic compounds in which two of the ring atoms appear to interchange their positions under the influence of ultraviolet light (I → II). Thus indazoles have been shown to rearrange to benzimidazoles,[2] pyrazoles to imidazoles,[2] and 2-substituted thiophenes to 3-substituted thiophenes.[3,4] The apparent similarity of these ring-atom transposition reactions with those of benzene derivatives elicited a suggestion[3,4] that these rearrangements, at least in the thiophene series, may proceed *via* bridged valence tautomers analogous to the dewar benzene, benzvalene, or prismane intermediates.



I II

However, an alternative mechanism exists[1] that is compatible with the thiophene data and provides a simple rationale for other heterocyclic rearrangements as well. This mechanism involves two allylic shifts which result in the formation of a three-membered ring intermediate III. Further evidence by Wynberg and



III IV IVa

his associates[4d,e] seems to eliminate dewar-, prismane-, or benzvalene-like intermediates. The possibility that a thioaldehyde IV may be involved in the thiophene rearrangements has recently been considered by these authors. However, they disfavor such an intermediate and

(1) A preliminary report of this work has previously appeared: E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, 88, 1844 (1966).

(2) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Tetrahedron Letters*, 2999 (1964).

(3) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, 87, 3998 (1965).

(4) (a) H. Wynberg, H. van Driel, R. M. Kellog, and J. Butler, *ibid.*, 89, 3487 (1967); (b) R. M. Kellog and H. Wynberg, *ibid.*, 89, 3495 (1967); (c) H. Wynberg and H. van Driel, *Chem. Commun.*, 203 (1966); (d) H. Wynberg, R. M. Kellog, H. van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, 88, 5047 (1966); (e) H. Wynberg, R. M. Kellog, H. van Driel, and G. E. Beekuis, *ibid.*, 89, 3501 (1967).