for this fluorescence using several other model compounds. Two working hypotheses concerning the anomalous fluorescence attribute it to (a) emission from the higher excited singlet state, analogous to the well known case of azulene,[7] and (b) conformational or tautomeric isomers which cannot be separated from the main components by chromatographic methods.[8] Photoproducts can be ruled out, since all steps of the experiments were carried out in the dark. The phytochrome spectrum was measured beginning at 14°K and up, so that the possibility of photoproduct formation can be ruled out, since at 14°K photoreactions are not likely to occur. Furthermore, biliverdins are very stable with respect to visible light.[9]

Regardless of the molecular mechanism for the short-wavelength fluorescence, the present results may have some bearing on the action spectra of the P_r–P_{fr} phototransformation and photomorphogenesis, particularly with respect to the actinic efficiency of the second absorption band of phytochrome at 380 nm.

Acknowledgment. This work was supported by the Robert A. Welch Foundation (D-182), the National Science Foundation (GB-21266 and GP-35699 to D. A. L.), and the National Institutes of Health (HD 07350 to D. A. L.).

(7) G. Viswanath and M. Kasha, *J. Chem. Phys.*, **24**, 574 (1957).

(8) The first possibility (a) is significantly lessened by the fact that near-uv excitation maxima are slightly different with respect to the long- and short-wavelength emission.

(9) D. A. Lightner and D. C. Crandall, *Tetrahedron Lett.*, 953 (1973).

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Evidence for Oxirene Intermediates in the Peroxidation of Acetylenes

Sir:

Oxirenes, potential 4π antiaromatic systems,[1] have been frequently proposed as transient intermediates in the peroxyacid oxidation of acetylenes.[2–7] The results of the earlier product[2–6] and kinetic studies[7] are consistent with but do not uniquely require the oxirene mechanism. Recent evidence seems to favor a pathway featuring ketocarbenes as reactive intermediates.[8] We now present evidence which, for the first time, compellingly implicates oxirenes as the first-formed intermediates in the peroxidation of acetylenes. The conclusion is based on the observation (Figure 1) that a strikingly close quantitative correlation exists between the logarithmic rates of acetylene oxidation and those of the peroxidation of an olefin, both in a series of solvents of diverse nature. The assumed analogy to oxirane formation in the peroxidation of olefins, which formed the principal bases for the proposal of oxirene intermediacy in the peroxidation of acetylenes, is now firmly justified. The transient existence of oxirenes has also been demonstrated recently in the photochemical Wolff rearrangement,[9] the photolysis of ketenes,[10] and the reaction of methylene with carbon monoxide.[11]

Table I. Stoichiometry for Oxidation of 4-Octyne by MCPBA in Benzene Solvent

$[\text{Octyne}]_0$[a]	$[\text{MCPBA}]_0$[a]	[Octyne consumed][a,b]
0.100	0.100	0.064
0.080	0.040	0.022
0.120	0.040	0.032
0.160	0.040	0.041
0.200	0.040	0.040

[a] In mol $l.^{-1}$. [b] When MCPBA had reacted completely.

The oxidation of 4-octyne by *m*-chloroperoxybenzoic acid (MCPBA) has been studied. Exploratory gas chromatographic analysis of the reaction mixtures revealed a 1 to 1 stoichiometry of octyne to peroxyacid when the hydrocarbon was in at least fourfold excess over MCPBA. As shown in Table I, the observed stoichiometry changed progressively toward 1 mol octyne to 2 mol peroxyacid as the ratio of initial concentrations, $[\text{octyne}]_0/[\text{MCPBA}]_0$, was reduced step by step from 5 to 1.

The data of Table I show that under conditions where the stoichiometry is 1:1, the peroxyacid participates mainly in the primary oxidation step in which an oxygen atom is transferred to the acetylenic compound;[12] its involvement in secondary oxidations becomes significant when the ratio, $[\text{octyne}]_0/[\text{MCPBA}]_0$, is less than four.

The rates of oxidation of 4-octyne by MCPBA in a series of solvents, differing widely in polarity and structure, were followed iodometrically under conditions of 1 to 1 stoichiometry. The observed second-order rate constants[13] are listed in Table II along with the literature rate constants for the epoxidation of cyclohexene by peroxybenzoic acid (PBA).[14,15]

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(1) R. Breslow, *Angew. Chem., Int. Ed. Engl.*, 7, 565 (1968).

(2) H. Schlubach and V. Franzen, *Justus Liebigs Ann. Chem.*, **577**, 60 (1952).

(3) V. Franzen, *Chem. Ber.*, 87, 1478 (1954).

(4) R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, 86, 4866 (1964).

(5) J. K. Stille and D. D. Whitehurst, *J. Amer. Chem. Soc.*, 86, 4871 (1964).

(6) J. Ciabattoni, R. A. Campbell, C. A. Renner, and P. W. Concannon, *J. Amer. Chem. Soc.*, **92**, 3826 (1970).

(7) Y. Ogata, Y. Sawaki, and H. Inoue, *J. Org. Chem.*, 38, 1044 (1973).

(8) P. W. Concannon and J. Ciabattoni, *J. Amer. Chem. Soc.*, **95**, 3284 (1973).

(9) (a) J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Amer. Chem. Soc.*, **95**, 124 (1973); (b) I. G. Csizmadia, H. E. Gunning, R. K. Gosavi, and O. P. Strausz, *ibid.*, **95**, 133 (1973).

(10) R. A. Russell and F. S. Rowland, *J. Amer. Chem. Soc.*, **92**, 7508 (1970).

(11) D. C. Montague and F. S. Rowland, *J. Amer. Chem. Soc.*, **93**, 5381 (1971).

(12) The major product of reaction in these conditions has been characterized as *trans*-5-octen-4-one based on elemental analysis, ir, and nmr. A minor product is 4-heptanone. The quantitative determination of product yields and the structure of two other hitherto unidentified products is under investigation.

(13) References 5 and 7 have shown that the peroxidation of acetylenes is governed by the second-order kinetic law. The present rate constants in the nonbasic solvents were calculated from the slopes of second-order plots which were linear to as far as the reaction was carried (usually 70–75%), while those in the basic solvents were calculated from initial rates. MCPBA decomposed in methanol, dioxane, and isopropyl alcohol solutions presumably due to trace metal catalyzed oxidations of these solvents. Dipicolinic acid ($\sim 10^{-3}$ *M*) was added for kinetic runs in these solvents which completely suppressed the decomposition of MCPBA in methanol and dioxane for more than the duration of kinetic runs. In isopropyl alcohol the trace metal catalysis could not be completely eliminated.

(14) P. Renolen and J. Ugelstad, *J. Chim. Phys. Physicochim. Biol.*, **57**, 634 (1960).

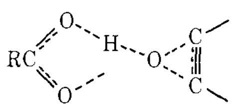
(15) R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, **35**, 2740 (1970).

Table II. Rate Constants (k_2) and Activation Parameters for the Oxidation of 4-Octyne by MCPBA in Various Solvents and the Corresponding Rate Constants (k'_2) for the Epoxidation of Cyclohexene by PBA

Solvent	ϵ	$10^4k_2{}^{a,b}$	$\Delta H^{\ddagger\,d}$	$\Delta S^{\ddagger\,d}$	$10^4k'_2{}^{a,c}$
$CHCl_3$	4.81	21.20			472.0
CH_2Cl_2	9.08	12.21			225.0
Benzene	2.28	6.93			156.0
CCl_4	2.24	5.37			77.2
		20.06^e	14.6	−24.5	
Dioxane	2.21	0.38			9.75
MeOH	32.61	0.38			5.44
		1.95^f	18.4	−17	
i-PrOH	18.6	0.33^g			6.9

[a] Second-order rate constants, in M^{-1} sec^{-1}; k_2 values are averages of two–five kinetic runs in each solvent. [b] At 24.2° unless otherwise indicated. [c] Data from ref 14 and 15 at 20°. [d] $\Delta H^{\ddagger}$ values in kcal/mol and $\Delta S^{\ddagger}$ in cal/deg mol. [e] At 40.3°. [f] At 40.15°. [g] Maximum value, k_2 containing some contribution from the trace-metal catalyzed decomposition of MCPBA in *i*-PrOH.

The linear free-energy relationship of Figure 1 has a slope of 1.0, demonstrating that the role of solvent in the two oxidations is identical and that the only important solvent–solute interactions are those involving the peroxyacid. If the solvation energy of the neutral acetylenic hydrocarbon is assumed to be small and essentially equal to that of its olefinic analog, then the transition state (TS‡) for the peroxidation of 4-octyne must closely resemble the TS‡ for the oxiranation of cyclohexene to account for the almost identical effect of solvent on the rates of the two oxidations. Thus, in a fashion completely analogous to olefin epoxidation[14] the π electrons of the acetylenic species capture the outer electrophilic peroxy oxygen from a chelated peroxyacid molecule *via* a symmetrical TS‡ which avoids charge separation by internal proton transfer.



TS‡

In support of this view the observed rates of octyne oxidation bear no relation to solvent polarity (Table II). Also there is a marked decrease in the rate of oxidation in going from a nonbasic to a basic solvent (Table II). In basic solvents, such as methanol or dioxane, with which the acidic proton of the peroxyacid forms intermolecular hydrogen bonds, RCOOOH··· O(H)–CH_3, the acts of desolvation and chelation must precede the approach of the acetylenic π system in the activation process. This predicts higher enthalpy of activation for the oxidation in a basic solvent relative to that in a nonbasic solvent where the peroxyacid already exists as a chelated monomer[16] and is set for the attack of a nucleophile. The observed enthalpies of activation ($\Delta H^{\ddagger}$ in methanol = 18.4 kcal mol^{-1}, $\Delta H^{\ddagger}$ in CCl_4 = 14.6 kcal mol^{-1} for the octyne–MCPBA reaction) are in complete accord with this prediction. The adverse entropic effect due to chelation is more than offset by the "unfreezing" of the basic solvent ($\Delta S^{\ddagger}$ in methanol = −17 eu; $\Delta S^{\ddagger}$ in CCl_4 = −24.5 eu), but the gain in the entropy of activation is not enough to counteract the

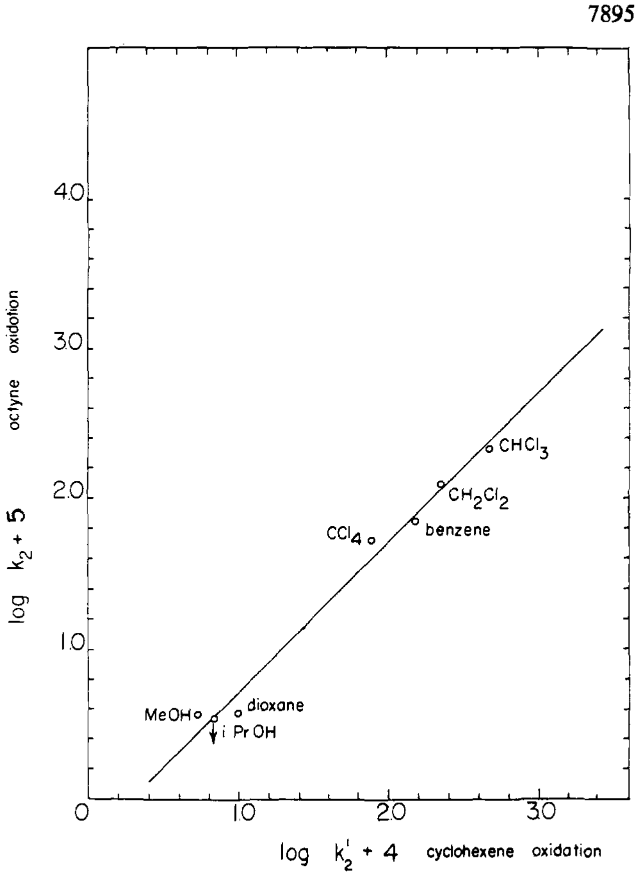
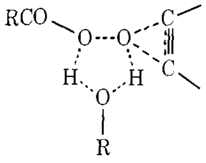


Figure 1. Linear trend in the plot of the logarithms of 3-octyne peroxidation rate constants (k_2) *vs.* the logarithms of cyclohexene epoxidation rate constants (k'_2) in various solvents.

retardation in rate due to increased enthalpy of activation when there is a change from a nonbasic to a basic solvent. The trend of activation parameters is nearly the same in the epoxidation of olefins (methanol $\Delta H^{\ddagger}$ = 12.7 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −30 eu; CCl_4 $\Delta H^{\ddagger}$ = 9.9 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −35 eu for cyclohexene–PBA reaction) and has been similarly interpreted.[15,17]

The alternative pathway for oxidation[18] in basic solvents which avoids charge separation *via* the following TS‡



is considered unlikely because it predicts dependence of rate on solvent acidity contrary to our observation ($k_{CH_3OH} \simeq k_{i\text{-}PrOH}$, although CH_3OH is more acidic by about 4 pK units)[19] and because dioxane cannot participate in such a mechanism.

The symmetrical TS‡ for olefin peroxidation breaks down to oxiranes which are generally isolatable under the conditions of peroxidation, while the TS‡ in acetylene oxidation leads to oxirenes which, being relatively less stable, rapidly transform to a variety of isolatable

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(16) D. Swern and L. S. Silbert, *Anal. Chem.*, **35**, 808 (1963), and references cited therein.

(17) D. Swern in "Organic Peroxides," Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, pp 355–533.

(18) K. M. Ibne-Rasa and J. O. Edwards, *J. Amer. Chem. Soc.*, **84**, 763 (1962).

(19) J. Hine and M. Hine, *J. Amer. Chem. Soc.*, **74**, 5266 (1952).

products directly or through other short-lived intermediates such as ketocarbenes.

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Determination of the Absolute Configuration of (+)-3-Carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy

Sir:

Nitroxides are paramagnetic compounds which have been widely used in recent years as spin-label reporter groups in biological systems.[1] The esr spectrum of a nitroxide depends on the polarity of its surroundings, its rotational mobility, its orientation with respect to an external magnetic field, and its proximity to other paramagnetic species. The esr spectrum of a chiral nitroxide species might therefore be sensitive to the chirality of the spin-labeled molecule's environment. Spin-label studies of enantiomeric specificity in biological systems have been limited because suitable optically pure chiral nitroxides of known absolute configuration have not been available. We wish to report here the X-ray crystallographic determination of the structure of the chiral nitroxide (+)-3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy ((+)I).

The (+) isomer of I was prepared as described previously, using *l*-(−)-α-methylbenzylamine as the resolving agent.[2] The circular dichroism spectrum of a solution of (+)-I in ethanol has maxima at 420 nm with $\Delta\epsilon_{\max}$ 0.34 M^{-1} cm^{-1} and at ~245 nm with $\Delta\epsilon_{\max}$ 0.6 M^{-1} cm^{-1}; the band at 245 nm is distorted by a strong negative band at lower wavelength.[3] The uv–visible absorption spectrum of an ethanol solution of (+)-I, which is similar to spectra reported for other aliphatic nitroxides,[4–6] exhibits two bands, one at 414 nm (ϵ 6.3 M^{-1} cm^{-1}) due to an n → π* transition and one at 232 nm ($\epsilon_{\max}$ 2.3 × 10^3 M^{-1} cm^{-1}) presumably due to a π → π* transition.

Crystals of the (+) isomer of I recrystallized from ethyl ether were found to be orthorhombic, space group $P2_12_12_1$ with a = 8.089 (16), b = 10.097 (10), and c = 12.404 (24) Å. The experimental density is 1.216 g/cm^3 compared with a calculated density of 1.221 g/cm^3, Z = 4.

Two axes (a, c) of diffraction data using Cu Kα radiation were collected using a Supper-Pace automated diffractometer possessing Weissenberg geometry. Following Lp corrections, the data were correlated to give the 992 independent reflections which were used in the structure determination.

Phases were obtained by direct application of the multiple tangent refinement program MULTAN.[7] An E map was calculated which clearly revealed the positions of the 13 nonhydrogen atoms. The subsequent structure-factor calculation resulted in R_1 = 0.32. Following eight cycles of refinement (R_1 = 0.11) the 16 hydrogen positions were obtained by difference synthesis. Full-matrix least-squares refinement of all positional and anisotropic thermal parameters (individual isotropic temperature factors for hydrogen) resulted in R_1 = 0.054. Final atomic positions and their estimated standard errors are given in Table I.

Table I. Atomic Positions and Estimated Standard Errors

Atom	x/a	y/b	$-z/c$
N-1	1.3586 (2)	0.2543 (3)	0.7102 (2)
C-2	1.1961 (3)	0.2543 (3)	0.6541 (2)
C-3	1.0821 (3)	0.2861 (3)	0.7516 (3)
C-4	1.1682 (4)	0.2216 (4)	0.8470 (3)
C-5	1.3536 (3)	0.2442 (3)	0.8291 (2)
O-6	1.4930 (2)	0.2554 (3)	0.6569 (2)
C-7	1.1695 (5)	0.1169 (3)	0.6049 (4)
C-8	1.1941 (5)	0.3604 (4)	0.5681 (3)
C-9	0.9067 (3)	0.2369 (3)	0.7364 (3)
O-10	0.8607 (3)	0.1283 (3)	0.7574 (5)
O-11	0.8089 (3)	0.3236 (2)	0.6914 (2)
C-12	1.4577 (4)	0.1300 (4)	0.8670 (4)
C-13	1.4157 (5)	0.3746 (4)	0.8765 (4)
H-3	1.0801 (44)	0.3796 (40)	0.7580 (35)
H-4A	1.1383 (53)	0.1308 (46)	0.8477 (37)
H-4B	1.1413 (62)	0.2653 (48)	0.9125 (48)
H-7A	1.1703 (47)	0.0497 (33)	0.6636 (32)
H-7B	1.2499 (94)	0.0862 (59)	0.5647 (64)
H-7C	1.0808 (59)	0.1161 (39)	0.5624 (41)
H-8A	1.2889 (85)	0.3287 (51)	0.5221 (51)
H-8B	1.0965 (60)	0.3692 (41)	0.5328 (42)
H-8C	1.2219 (55)	0.4492 (38)	0.6003 (37)
H-11	0.7139 (66)	0.2813 (41)	0.6884 (39)
H-12A	1.4327 (57)	0.0584 (43)	0.8340 (39)
H-12B	1.4290 (64)	0.1269 (46)	0.9428 (56)
H-12C	1.5854 (64)	0.1587 (46)	0.8614 (46)
H-13A	1.4075 (46)	0.3620 (35)	0.9619 (41)
H-13B	1.5556 (69)	0.3977 (48)	0.8477 (48)
H-13C	1.3550 (59)	0.4465 (42)	0.8571 (38)

The absolute configuration of (+)-I was determined by the direct measurement of Bijvoet differences with applied absorption corrections using a method described previously.[8] Accessible reflections with an intensity I_c greater than 2.5, calculated using the f'' values of Cromer and Liberman for oxygen, nitrogen, and carbon,[9] and a calculated $IDEL = (I_{hkl} - I_{\bar{h}\bar{k}\bar{l}})/I_c$ greater than 2.5% were ranked according to a suitability parameter $P = I_c(IDEL)^2$. The signs of the observed differences $(I_{hkl} - I_{\bar{h}\bar{k}\bar{l}})$ for the 20 reflections with the largest values of P were compared with those calculated for the S configuration. The observed signs were opposite to those calculated for all reflections, thereby establishing the configuration as R. Figure 1 is a drawing of the R configuration of (+)-I. A detailed description of the structure and absolute configuration determination will be published elsewhere.

Interatomic distances and angles and their estimated standard errors are presented in Table II. The N-1–

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[1] H. M. McConnell and B. G. McFarland, *Quart. Rev. Biophys.*, **3**, 91 (1970).

[2] (a) K. Flohr and E. T. Kaiser, *J. Amer. Chem. Soc.*, **94**, 3675 (1972); (b) K. Flohr, Ph.D. Thesis, University of Chicago, 1973.

[3] We wish to thank Professor G. Holzwarth and Mr. A. Attiah for these measurements.

[4] Y. Brunel, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1895 (1964).

[5] A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 220.

[6] E. G. Janzen, *Top. Stereochem.*, **6**, 181 (1971).

[7] P. Main, M. W. Woolfson, and G. Germain, "MULTAN: A Computer Programme for the Automatic Solution of Crystal Structures," Department of Physics, University of York, York, England, 1971.

[8] (a) J. W. Moncrief and S. P. Sims, *Chem. Commun.*, 914 (1969); (b) D. W. Engel, *Acta Crystallogr., Sect. B*, 28, 1496 (1972).

[9] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).