olefin–arene [2 + 2] cycloaddition[15] followed by ring expansion and deprotonation. Thus, the nature of the photoaddition pathways followed by **1** appears to be critically dependent on the electron-donating ability of the olefin in a way strongly suggestive of electron-transfer mechanisms for pyrrolidine ether and olefin formation. Thus, competition between addition and cycloaddition might be regulated at an olefin–iminium salt exciplex stage by the relative magnitudes of k_{et} and k_{2+2}. Also, it is quite likely that the intramolecular version of this new photochemical reaction[1] observed for *N*-allyliminium salt systems also follows an electron-transfer mechanism. Further studies are underway to probe further the mechanistic details and synthetic potential of these reactions.

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(3) (a) The iminium salt **1** is prepared in situ from 2-phenyl-1-pyrroline[3b] and 1.34 equiv of $HClO_4$ or as a crystalline substance, mp 116–117 °C.[4] Addition of $HClO_4$ to the pyrroline results in a decrease in the UV-absorption maximum at 243 nm and an increase at 264 nm (isosbestic 251 nm) which is reversible. (b) D. F. Starr, H. Bulbrook, and R. H. Hixon, *J. Am. Chem. Soc.*, **54,** 3971 (1932); S. J. Love and J. A. Moore, *J. Org. Chem.*, **33,** 2361 (1968).
(4) Spectroscopic and analytical data for all new compounds were in perfect accord with assigned structures.
(5) The mass spectra of **2, 3, 4, 7,** and **8** all show a base peak at *m/e* 146 ($C_{10}H_{12}N$ by high resolution) characteristic of the phenylpyrrolidine fragment.
(6) (a) Obtained as an ~1:1 separable mixture of diastereomers. (b) Obtained as a separable 1:1 mixture of diastereomers which can be interconverted by treatment with methanolic sodium methoxide giving the thermodynamic epimer (methoxy group exo) in a 5.9:1 excess. (c) Obtained as one diastereomer only of undetermined stereochemistry.
(7) (a) Cycloaddition of isobutylene to 6-azapyrimidines[7b] resulting in azetidine products show a reversed regiochemistry than would be required to rationalize our results. (b) J. S. Swenton and J. A. Hyatt, *J. Am. Chem. Soc.*, **96,** 4879 (1974). (c) However, cycloadditions of isobutylene and other electron-rich olefins to 3-ethoxyisoindolone[7d] follow regiochemical courses which are consistent with our results. (d) A. Howard and T. H. Koch, *ibid.*, **97,** 7288 (1975).
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(10) Internal capture of the radical cation derived from electron transfer from 1,3-butadiene to 1^{S_1} by the pyrrolidine nitrogen would lead to the diradical precursor of **9.**
(11) (a) An alternative explanation for the formation of the olefin products, via hydrogen-atom-abstraction pathways,[11b] is possible. (b) N. Toshima, S. Asao, K. Takada, and H. Hirai, *Tetrahedron Lett.*, 5123 (1970).
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(13) (a) Contributions to the free energy and, thus, rate of electron transfer due to electrostatic attraction between charged radical products were ignored since they apply only when donor and acceptor molecules are neutral. (b) Experimentally determined $E_{1/2}(-)$ of **1** is ~0.99 V vs. SCE as expected on the basis of previous measurements.[13c] (c) C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.*, **26,** 223 (1970). (d) $E_{1/2}(+)$ of olefins were calculated from known ionization potentials[13e] using the relationship of Miller.[13f] (e) K. N. Houk and L. L. Munchausen, *J. Am. Chem. Soc.*, **98,** 937 (1976). (f) L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, **37,** 916 (1972). (g) Ionization potential of this ester was estimated using a cumulative methyl substituent effect.
(14) The amines **19b–c** were formed as 1:1.5 mixtures of anti (R_1 = H; R_2 = CN or CO_2CH_3) and syn epimers and **19a** as a 4:3 epimeric mixture of unassigned stereochemistry.
(15) T. S. Cantrell, *J. Org. Chem.*, **42,** 4238 (1977), and references cited therein.
(16) Camille and Henry Dreyfus Teacher–Scholar awardee, 1975–1980.

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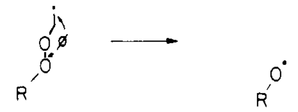
Stereochemistry of Free-Radical Substitution on the Peroxide Bond

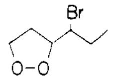
Sir:

The stereochemical course of the S_H2 reaction has been the subject of intensive theoretical interest for some 40 years.[1-3] Calculations suggest[1,3] that homolytic substitution in simple three-atom systems occurs via a colinear geometry and scattering experiments support the linear arrangement for deuterium–halogen exchange.[4] Examples of experiments designed to provide stereochemical information about the S_H2 reaction in more complicated organic systems are rare and studies have been limited to halogen atom substitution on cyclopropane carbon for the first row elements.[5-7] Homolytic substitution on phosphorus[8] and sulfur[9] has been studied and inversion of configuration is generally observed, although the possibility of a metastable radical-addition intermediate may complicate the interpretation of these results.

Carbon radical attack on the peroxide bond represents an important pathway in the autoxidation of olefins. For example, intramolecular carbon radical substitution (S_Hi) on the peroxide bond initiates the unzipping of styrene–oxygen copolymer.[10] Because of the importance of this reaction in the oxidation of polymers and natural products such as polyunsaturated lipids, we have initiated a study directed toward determining the stereochemical preference of carbon radical substitution on peroxide. We report here results of studies of the S_Hi reaction in which the orientation of the attacking radical with respect to the peroxide bond is systematically varied. This approach gives information about the stereochemical preference of the substitution reaction and the results suggest that a "back-side attack" of the carbon radical on the peroxide bond is required.



The β-bromo peroxides **1–4** were prepared by reaction of



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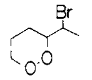

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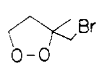

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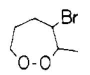

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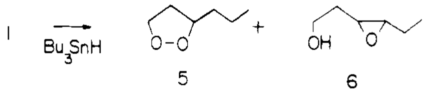
the corresponding mercuri bromides[11,12] with molecular bromine.[13] Compounds **1** and **2** are formed as threo and erythro diastereomers and **4** consists of a mixture of cis and trans isomers as prepared.[12] These diastereomers can all be separated by high pressure liquid chromatography (HPLC) on μ-Porasil with 5% ethyl acetate–hexane.

The bromo peroxides **1–4** were reacted with 1.0 equiv of tributyltin hydride in benzene at 25 °C with 2–5% *tert*-butyl hyponitrite initiator present.[14] For example, reaction of **1** (threo or erythro) with 0.455 M tin hydride leads to a mixture of cyclic peroxide **5** and epoxy alcohol **6** in a **5:6** ratio of 82:18.



5 6

The epoxy alcohol **6** was formed as a 3:1 mixture of the trans and cis geometric isomers and this product distribution was independent of the stereochemistry (threo or erythro) of the starting β-bromo peroxide. The results of analogous reactions of **2, 3,** and **4** with tributyltin hydride led to mixtures of the corresponding cyclic peroxides and epoxy alcohols.[15] The epoxy alcohol **7** derived from **2** rearranges under the conditions of analysis to the furan and pyran products **8** and **9. 7** was prepared independently from the corresponding olefin and was converted into **8** and **9** by traces of acid.

Table I. Product Distribution of 0.455 M Bromo Peroxide-Tin Hydride Reactions

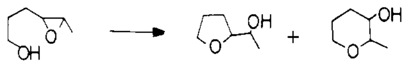
bromo peroxide	peroxide, %[a]	epoxy Alcohol, %[a,b]
1	82	18
2	17	83
3	92	8
4	100	0

[a] Product distributions are normalized to 100%; product accounted for was >80%. [b] Total epoxy alcohol **7** and furan and pyran **8** and **9** were analyzed.

Table II. r^a and k_{S_Hi} Values Found for Radicals **11-14**

radical	r	k_{S_Hi}, s^{-1}
11	0.09	7.5×10^4
12	1.05	8.7×10^5
13	0.01	1×10^4
14	$<10^{-6}$	<1

[a] $r = k_{S_Hi}/k_H$.

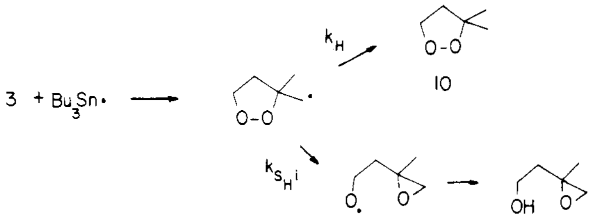


7 8 9

In Table I is presented the product composition for reaction of the bromo peroxides **1-4** with 0.455 M tributyltin hydride. Product accountability was high (85-100%) with reactions run with tin hydride concentrations >0.05 M.

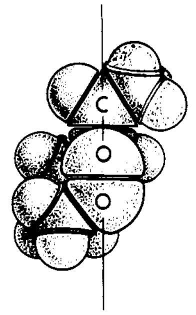
The mechanism presented in Scheme I is consistent with the products observed.[16] Further, for **1, 2,** and **3** the product distribution varies as a function of Bu_3SnH concentration as is required by this mechanism. For example, the percent yield of peroxide **10** derived from **3** is 92, 82, 78, 66, and 55% as the tin hydride concentration is reduced from 0.455 M to 0.2, 0.1, 0.05, and 0.02 M. On the other hand, no epoxy alcohol could be observed in the reaction of **4** with Bu_3SnH with concentrations of hydride as low as 0.01 M.

Scheme I



With the mechanism presented in Scheme I as a format, a kinetic expression[16-18] can be derived that gives a rate ratio of $r = k_{S_Hi}/k_H$ for the radicals **11-14** derived from **1-4.** Further, since values of k_H are known,[19] the k_{S_Hi} rate constants can be calculated (see Table II).

We suggest[11] that the dihedral angle ϕ must be 180°, or nearly so, for maximum S_Hi reactivity. For radical **12,** derived from **2,** a chair conformation[20] allows an equatorial radical to attack the peroxide bond from the back side. For the more planar dioxolanyl radicals **11** and **13** (from **1** and **3**), it is difficult to adopt conformations with the 180° preferred angle for substitution, and the rates for substitution are thus one to two orders of magnitudes slower than k_{S_Hi} for **12.** The endocyclic radical **14** formed from the seven-membered-ring peroxide, **4,** is constrained to attack the peroxide bond from the side (ϕ < 70-100°) rather than via the back-side pathway and, as a consequence, no detectable S_Hi reaction is observed. It should be noted that the transition states for S_Hi reaction of the radicals **12** and **14** are isomeric but that the rate difference for substitution between these two radicals is $>10^6$ s^{-1}. This observation supports the notion that the triangular transition state (side approach as in **14**) is not favored[1-3] and points to a preferential colinear, or back-side, substitution process.



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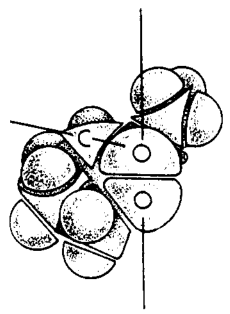

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(13) The procedure for converting the β-bromomercuri peroxide to the β-bromo peroxide is straightforward. In a typical experiment, the bromomercuri peroxide is reacted with a threefold excess of bromine in CH_2Cl_2 for 4 h. The product β-bromo peroxide is purified by preparative HPLC. See Bloodworth, A. J.; Griffin, I. M. *J. Chem. Soc., Perkin Trans. 1,* **1974,** 688, for similar reactions.

(14) To obtain reproducible results with high product accountability the degassed bromo peroxide in benzene was bulb to bulb distilled into a previously degassed tin hydride solution. An initiator solution (benzene) was then degassed and bulb to bulb distilled into the reaction mixture.

(15) Products were analyzed by gas chromatography on diisodecyl phthalate (Anachrom Q) with Teflon-lined aluminum columns.

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Chemistry at Liquid-Liquid Interfaces. Evidence for an S_N1 Reaction Occurring at a Toluene-Water Interface[1]

Sir:

Although many types of chemical and biochemical reactions are believed to take place at liquid-liquid interfaces, few examples have been well documented. It is not surprising, therefore, that only a limited understanding exists of how reactions at interfaces differ from comparable reactions carried

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