Table I. Epoxidation Reaction Yields[a] for $Q[Fe_2L(OAc)_2] + H_2O_2$

substrate	epoxide yield	byproduct yield
cyclohexene	1.6	3-cyclohexenol, 0.9; 3-cyclohexenone, 0.4
styrene	3.2	benzaldehyde, 1.5
cis-stilbene	2.5 (cis:trans, 5:95)	

[a] Yields expressed in turnover numbers, moles of product per mole of complex. Products were identified by gas chromatography. Reaction conditions: 1 mM complex + 1 M alkene under N_2 in DMF with 50 mM H_2O_2 for 45 min.

one that is also found in the active site of hemerythrin.[10]

The chloro analogue of this complex, $(Me_4N)[Fe_2L'(OAc)_2]$, exhibits a visible spectrum with a shoulder near 450 nm, due to a phenolate-to-Fe(III) charge-transfer transition (Figure 2). Its NMR spectrum shows isotropically shifted features at 48 and 88 ppm assigned by deuterium substitution to the phenolate meta and the acetate methyl protons, respectively (Figure 2). The integration shows that two acetates bind per binuclear complex as in the crystal structure. The methylene protons are not observed because of their proximity to the paramagnetic centers.

Addition of H_2O_2 to $[Fe_2L'(OAc)_2]^-$ results in the development of a new visible absorption maximum near 470 nm (Figure 2); laser excitation (514.5 nm) into this band shows the enhancement of a Raman feature at 884 cm^{-1} consistent with its assignment to the peroxide O–O stretch. Thus, this band probably arises from a peroxide-to-Fe(III) charge-transfer transition, as observed in other Fe(III)–peroxide complexes.[11-13] The NMR spectrum of the complex also reflects changes in coordination chemistry (Figure 2[14]). The acetate methyl resonance shifts to 33 ppm, and the meta protons appear as discreet features at 27 and 25 ppm. The remaining broad features are due to the methylene protons of the ligand. The integration of the meta and methyl peaks shows that only one acetate remains coordinated in this complex, suggesting that the peroxide has replaced one acetate. This replacement would also destroy the C_2 symmetry of the parent complex and explain the observed nonequivalence of the meta H's in the NMR spectrum of the peroxide complex. A possible structure for this complex is that found for $[Co_2bpmp(OAc)O_2](ClO_4)_2$ where the cobalt ions are bridged by phenolate, acetate, and peroxide.[15]

The peroxide complex can catalyze the disproportionation of H_2O_2 to O_2 and water. In the absence of an oxidizable substrate, the complex slowly destroys itself. In the presence of alkenes, epoxides along with byproducts of autoxidation are observed (Table I). The epoxide constitutes 10% of the H_2O_2 consumed in the reaction. The epoxidation of *cis*-stilbene by the binuclear complex results in 95% *trans*- and 5% *cis*-epoxide, similar to the results found for $Fe(acac)_3/H_2O_2$ epoxidation[16] but opposite to those of the Fe(TPP)Cl-, iron(III) bleomycin-, and $Fe(OTf)_3$-catalyzed reactions with PhIO where *cis*-stilbene yields predominantly or exclusively *cis*-epoxide.[17-19]

Interestingly, the mononuclear analogue, $Fe(Cl_2HDA)(H_2O)_2$,[20] binds neither acetate nor peroxide, suggesting a requirement for a binuclear unit for forming such complexes. The $Fe(Cl_2HDA)(H_2O)_2/H_2O_2$ mixture does not epoxidize alkenes but does catalyze peroxide disproportionation and one-electron oxidations such as the conversion of *o*-dianisidine and 2,4,6-tri-*tert*-butylphenol to their corresponding cation radicals. This comparison suggests that, at least for this family of ligands, a binuclear iron unit is required for the epoxidation chemistry. This is the only characterized iron(III) peroxide complex thus far shown to effect epoxidations. The other known iron(III) peroxide complexes,[21] e.g., [Fe(TPP)OOFe(TPP)],[22] $[Fe(TPP)O_2]^-$,[13] and the peroxide complex of [Fe(EDTA)],[23] have not been shown to epoxidize olefins. Efforts to understand the structure and reactivity of the binuclear peroxide complex and to compare this complex with other nonheme iron systems, such as $Fe(acac)_3$[16] and $Fe(II)/CH_3CN$,[24] that react with H_2O_2 to yield species capable of olefin epoxidation are continuing.

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Photogenerated Semi-Enone Radical Anions:[1] A New Perspective on the Reactions of 10-(Hydroxymethyl)-2-octalone Tosylate

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Since Stork's 1961 report[2] on the lithium-liquid ammonia reductive transformation of octalone tosylate **1** to the cyclopropyl ketone **6**, the nucleophilic character of the β-carbon of "semi-enone"[1] radical anions has been generally accepted. Parallel behavior would be anticipated for semi-enone radical anion of **1** generated by alternative electron-transfer processes. Indeed, electrochemical[3] and lithium dimethyl cuprate[4] reactions of octalone sulfonate esters yield the expected cyclopropyl ketones, providing experimental support for this hypothesis. In direct contrast to these results, *we report that the major product from photomediated electron-transfer to enones* **1** *–* **4** *is 10-methyl-*

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(1) The term "semi-enone" is introduced here to denote the radical anion of an α,β-unsaturated ketone, parallel to the designation of semidione and semiquinone to the corresponding diketone and quinone radical anions.

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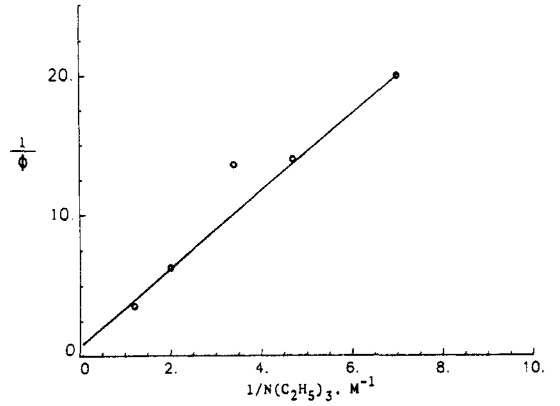


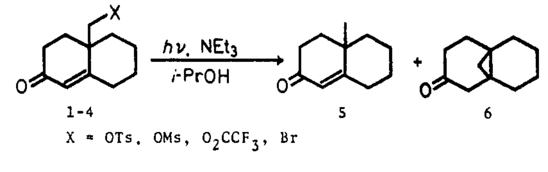
Figure 1. Reaction quantum efficiency dependence on triethylamine concentration. The slope (2.77 M) to intercept (1.36) ratio obtained from this study was 2.04 M. The limiting quantum efficiency for triethylamine (7.5 M) and **1** calculated from eq 3 is 0.57.

Scheme I. Principal Steps for the Photomediated Electron-Transfer Reactions[a] of **1–4**

$^0\mathrm{En} \xrightarrow{h\nu} {}^1\mathrm{En}$	absorption
$^1\mathrm{En} \xrightarrow{k_{st}} {}^3\mathrm{En}$	singlet–triplet crossing
$^3\mathrm{En} \xrightarrow{k_d} {}^0\mathrm{En}$	triplet decay
$\mathrm{Am} + {}^3\mathrm{En} \xrightarrow{k_{ct}} {}^3\mathrm{S}$	semi-enone formation
$^3\mathrm{S} \xrightarrow{k_r}$ products	reaction
$^3\mathrm{S} \xrightarrow{k_b} {}^0\mathrm{En} + \mathrm{Am}$	back electron transfer
$\mathrm{Q} + {}^3\mathrm{S} \xrightarrow{k_q} {}^0\mathrm{En} + \mathrm{Am} + {}^3\mathrm{Q}$	piperylene quenching

[a] En = Enones **1–4**, Am = tertiary amine, Q = quencher (piperylene), S = semi-enone–amine complex, q = quenching, ct = charge transfer (electron transfer), d = triplet enone decay, st = singlet–triplet crossing, r = reaction, b = triplet complex decay.

2-octalone (**5**, >95%) rather than the expected tricyclo[4.4.1.0^{1,6}]undecan-3-one (**6**, <3%, eq 1) when the reaction is



(1)

conducted with excess tertiary amine (triethylamine (TEA) or diazabicyclo[2.2.2]octane (DABCO)) as the electron donor.[5–7]

The bimolecular nature of the electron-transfer process for **1–4** was established through the variation of the quantum efficiency as a function of the amine concentration as shown for **1** in Figure 1. That this is a triplet process was also established by piperylene quenching of the reaction of **1** (slope = 8.6×10^2 M^{-1}; τ = 200 ns).[6]

A possible mechanistic sequence derived from these results is outlined in Scheme I and the attendant kinetic expression given in eq 2. As indicated, this mechanism correctly predicts the observed linear dependence of the reciprocal of the reaction efficiency to the reciprocal of the amine concentration. The slope to intercept ratios (eq 3 and 4) were determined for the quantum efficiency dependence on the amine and quencher concentrations, respectively. Assuming diffusion-controlled quenching, a value for the rate constant for reaction (k_r) of 10^6 s^{-1} was derived, a value which is 100 times smaller than the reported value[8–10] for electron-transfer to related α,β-enone triplets from triethylamine or DABCO. While the exact nature of the mechanistic sequence is uncertain, scission of the carbon–nucleofuge bond in the enone–amine complex represents a possible rate-determining process.

$$[\phi_r]^{-1} = [\phi_{st}]^{-1}[1 + k_b/k_r + k_q[\mathrm{Q}]/k_r][1 + k_d/(k_{CT}[\mathrm{Am}])] \tag{2}$$

$$\text{slope/intercept} = k_d/k_{CT} \quad \text{for } [\phi_r]^{-1} \text{ vs. } [\mathrm{Am}]^{-1} \tag{3}$$

$$\text{slope/intercept} = k_q/(k_r + k_b) \quad \text{for } [\phi_r]^{-1} \text{ vs. } [\mathrm{Q}] \tag{4}$$

The relative efficiencies for **1–4** at a common triethylamine concentration range (0.18 or 0.14 M) are given in Table I as well as the one-electron reduction potentials.[11] A comparison with the photochemical efficiencies for the ester nucleofuge series shows no correlation, militating against a simple rate-determining one-electron-transfer process. Indeed, the reduction potentials are more in accord with electron transfer to the common α,β-unsaturated enone moiety (cf. **5**) rather than directly to the nucleofuge or a nucleofuge–enone complex,[12,13] whereas the pho-

Table I. Reduction Potentials and Quantum Efficiencies for Enones **1–5**

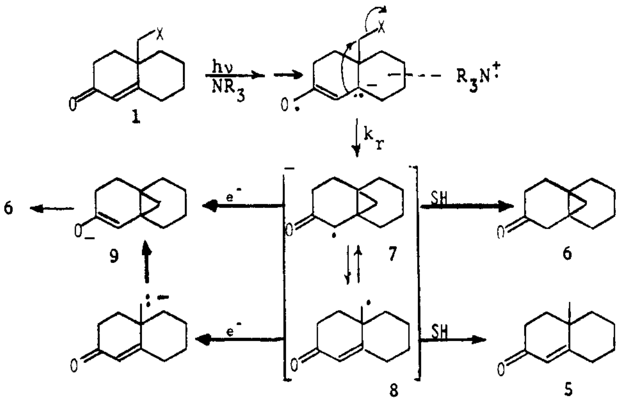
substrate	$-E_{red}$, V vs. SCE	ϕ_5	$[NEt_3]$, M
1, X = OTs	1.9	0.035	0.14
2, X = OMs	1.9	0.036	0.18
3, X = O_2CCF_3	1.9	0.0084	0.14
4, X = Br	1.5	0.22	0.14
5, X = H	2.25		

Table II. Product Ratio as a Function of the Concentration of the Hydrogen Atom Source[a]

	ratio of **5/6**			
bromide	>100[b] $[Et_2O]/[C_6H_6]$	19:1 $[Et_2O]/[C_6H_6]$	1:1 $[Et_2O]/[C_6H_6]$	1:9 $[Et_2O]/[C_6H_6]$
4	19	13.3	10	6.7
10	1		2.9	7.5

[a] Ph_6Sn_2 was employed in these experiments. [b] Diethyl ether solvent.

Scheme II. Reaction Mechanism for Semi-Enone Radical Ions



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(5) Synthetic details will be provided in our full paper. The syntheses were accomplished by the methods outlined in Stork's full paper[2b] with the appropriate modifications for introduction of the nucleofuge. All photoproducts were identified by comparison with authentic samples.

(6) Photolyses were carried out in 15 × 75 mM Pyrex test tubes at 298 K in a merry-go-round apparatus employing Corning CS 7-37 filters to isolate the 345–376-nm region from a Hanovia 450-W medium-pressure mercury lamp. For the quenching study, varying concentrations of piperylene (5×10^{-5} to 1×10^{-3} M) were added. Experimental details will be given in our full paper.

(7) Both products were also obtained in two of the three previous studies with **1**.[2,3] In each case, however, the enone product **5** was dismissed as an artifact of the workup.

(8) Schuster[9b] reported quenching rate constant of a structurally similar enone with DABCO to be 1.2×10^9 M^{-1} s^{-1}.

(9) (a) Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Rao, J. M.; Joussot-Dubien, J. *J. Am. Chem. Soc.* **1984**, *106*, 2706. (b) Dunn, D. A.; Schuster, D. I.; Bonneau, R. *J. Am. Chem. Soc.* **1985**, *107*, 2802.

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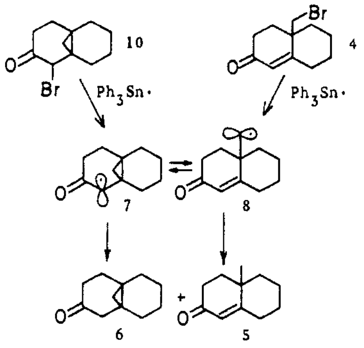
(11) Smith[4] reported reduction potentials for **1** and **5** to be 2.2 and 2.1 V (vs. SCE), respectively.

Scheme III. Ground State Generation of Equilibrating Radical Pair 7 and 8 with Ph_6Sn_2



tochemical efficiencies follow the trend expected for leaving group ability within the ester series.[14]

Scheme II depicts the molecular processes for the electron-transfer and displacement reactions adapted and extended from the original Stork mechanism.[2] The initial intermediate from internal nucleophilic displacement within the semi-enone leads to the α-keto, cyclopropylcarbinyl radical (**7**), an intermediate possessing considerable carbon radical character.[15] By analogy with other unsubstituted cyclopropylcarbinyl radicals, ring opening to the neopentyl radical **8** is expected to be very facile.[16] An alternative mechanism may involve direct formation of **8** from the triplet enone–amine exciplex.

The ring closure process from **8** back to **7** should be considerably more difficult, suggesting a large equilibrium constant for rearrangement ($K_{eq} >> 1$).[17] Hydrogen atom abstraction by **7** or **8** would then complete the reaction sequence to **5** and **6** analogous to an ECC route.[18] Alternatively, under reductive conditions, a subsequent second electron transfer to form the enolate **9**[19] and protonation completes the reaction sequence an ECE mechanism.[18]

In order to test the hypothetical intermediacy of the equilibrating radicals **7** and **8**, we have independently generated each radical from its precursor bromide (**4** and **10**) employing either $(n\text{-Bu})_3SnH$ or Ph_6Sn_2.[20] As illustrated in Scheme III and Table II, both bromides yield the same two products. Furthermore, the ratio of **5** to **6** is a sensitive function of the nature and concentration of the hydrogen atom source, whether it be $(n\text{-Bu})_3SnH$, diethyl ether, isopropyl alcohol, or $Et_3N^{\bullet+}$, and the nature of the stannane derivative, clearly demonstrating both the intermediacy of the equilibrating pair of radicals and the hydrogen atom abstraction pathway.

Thus, the dissolving metal reductions from Stork's studies[2] continue to be a successful model for reductive electron-transfer processes as well as the initial stages of the photoinduced process. Of more general interest, however, is the observation that the photochemical reaction provides critical insight into the nature of the chemical reductions and further suggests the need for additional research on the mechanism of the ground-state electron-transfer process. The work here represents our continuing effort toward that goal.

Acknowledgment. The financial support of a research grant from the University of Kansas General Research Fund is gratefully acknowledged. We thank Professor Leo Paquette, The Ohio State University, for the timely suggestion of Ph_6Sn_2 for the investigations related to the equilibration experiments.

Registry No. 1 OTS, 741-43-5; **1** OMS, 71280-42-7; **1** O_2CCF_3, 103240-06-8; **1** Br, 103240-07-9; **5**, 826-56-2; **6**, 5689-11-2; **10**, 103240-08-0.

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(12) (a) The lower reduction potential for bromide **4** is in accord with results obtained for other δ-bromo-α,β-unsaturated carbonyl derivatives.[12b] (b) Nugent, S. T.; Baizer, M. M.; Little, R. D. *Tetrahedron Lett.* **1982**, 1339.

(13) The electrochemical and dissolving metal reductions of *p*-toluenesulfonate esters result in cleavage of the O–S bond to yield the alcohol. In contrast, methanesulfonate esters are not cleaved under similar conditions. Horner, L.; Singer, R.-J. *Chem. Ber.* **1968**, *101*, 3329. Within the 2-octalone series, the 10-propyl-3′-tosylate gave only the alcohol upon treatment with lithium in liquid ammonia.[2b]

(14) Noyce, D. S.; Virgilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643.

(15) The electron density at carbon of a simple α-keto cyclohexyl radical is estimated to be 85% (Camaioni, D. M.; Walter, H. F.; Pratt, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 4057).

(16) A rate constant of 10^6 s^{-1} for ring opening of a cyclopropylcarbinyl radical to a homoallylic radical has been reported (Friedrich, E. C.; Holmstead, R. L. *J. Org. Chem.* **1972**, *37*, 2550).

(17) The equilibrium constant between the α-carbonyl, cyclopropyl radical **7** and the 10-methylene-2-octalone radical **8** can be estimated at $K_{eq} = 10^3$ by using data for the rates for cyclopropylcarbinyl ring opening (10^6 s^{-1})[16] and 10^3 s^{-1} for homoallyl radical ring closure (Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734). This analysis overestimates th K_{eq} value since **8** is stereoelectronically better suited for such a ring closure step whereas the value used for this estimate was obtained for an acyclic homoallyl radical.

(18) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcell Dekker: New York, 1969.

(19) Furthermore, the enolate of **6** is not converted to **5** under the reaction conditions.[3]

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Cycloreversion of Quadricyclane Derivative via Triplet State. Adiabatic vs. Biradicaloidal Mechanism

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Photochemically induced interconversion between norbornadiene and quadricyclane has been the focus of considerable attention in connection with the storage of solar energy.[1] A variety of sensitization methods have been applied to the valence isomerization of norbornadiene and its derivatives, including direct photolysis, triplet sensitization, complexation with metal ions, and donor–acceptor interaction.[2]

For triplet excitation, it has been reported that norbornadiene in a triplet state isomerizes efficiently to a ground state of quadricyclane through a biradicaloidal intermediate on the basis of photochemical investigation of the corresponding cyclic azoalkanes.[3] In the present paper, on the other hand, we have found that a naphthalene derivative of quadricyclane isomerizes inversely to the corresponding norbornadiene derivative via the triplet in a very high yield, and the cycloreversion has been substantiated to be an adiabatic process by convincing experimental supports. Furthermore, it might be pointed out that the conformation of the olefinic moiety of the norbornadiene in the relaxed triplet state, i.e., planar or twisted, is one of the important factors which control the reaction mechanism, i.e., adiabatic or biradicaloidal.

Benzophenone(BP) sensitization of NN and QN has been carried out by a nanosecond pulse radiolysis of the degassed benzene solution.[4,5] The transient absorption spectra recorded

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