maximum intensity at 550 nm, a region where **1** does not absorb, and decays unimolecularly with $\tau = 300$ μs. The observed signal is assigned to $M_2 \rightarrow \mu$-LCT triplet-triplet absorbance (vide infra). The transient absorbance exhibits partial saturation at high laser powers,[18-20] suggesting that the observed state is formed by a process of limited efficiency from the initial excited state, consistent with $[M_2 \rightarrow \mu\text{-LCT}]^1 \rightarrow [M_2 \rightarrow \mu\text{-LCT}]^3$ conversion. The method of Carmichael and Hug[19] was employed to fit the partial saturation of transient absorbance and obtain the triplet conversion quantum yield, $\Phi_T = 0.2$.

In the presence of CO_2, the rate of disappearance of $[M_2 \rightarrow \mu\text{-LCT}]^3$ absorbance exhibits a first-order dependence on $[CO_2]$. The photochemical kinetics of **1** with CO_2 were examined over the CO_2 pressure range 1-3 atm. Pressures of CO_2 were calibrated against $[CO_2]$ in THF solution by the method of Daniele et al.[21] The lifetime τ of $[M_2 \rightarrow \mu\text{-LCT}]^3$ absorbance exhibits an inverse linear dependence on $[CO_2]$ from which the rate constant for CO_2 addition, $k_{CO_2} = 1 \times 10^4$ M^{-1} s^{-1}, was determined. The $[M_2 \rightarrow \mu\text{-LCT}]^3$ state of **1** is also reactive with respect to the addition of a variety of other reagents. For example PhCl, which is thermally unreactive with **1** when employed as the solvent under reflux, reacts photochemically with the $[M_2 \rightarrow \mu\text{-LCT}]^3$ state with a bimolecular rate constant, $k_{PhCl} = 4 \times 10^3$ M^{-1} s^{-1}, to form the μ-phenyl amino-carbyne complex, $[Ni_2(\mu\text{-CN(Ph)Me})(CNMe)_2(dppm)_2]Cl$, **3**.[22] The dependence of $k_{obsd} = 1/\tau$ for the transient absorbance of **1** versus $[CO_2]$ and [PhCl] is given in Figure 1. The overall photochemical reactivity of **1** with CO_2 and PhCl is presented in Scheme I.

The nature of the lowest energy electronic absorption spectral band of **1** was also assessed by bridging ligand substituent and solvent effects. The electronic absorption spectrum of **1** exhibits an intense, broad band centered at $\lambda_{max} = 345$ nm ($\epsilon = 19\,000$ M^{-1} cm^{-1}) in THF. The series of μ-aryl isocyanide complexes $Ni_2(\mu\text{-L})(CNMe)_2(dppm)_2$, L = CNC_6H_6 (**4**), CN-*p*-C_6H_4Cl (**5**), and CN-*p*-C_6H_4Me (**6**), were prepared by substitution of one of the MeNC ligands of **1**.[23] Within the group of complexes **4-6** values of λ_{max} are quite insensitive to the nature of the para substituent on the aryl group but are shifted to longer wavelengths by 35 nm relative to the μ-methyl isocyanide complex **1** in THF.[23] There are also significant intensity differences between the aryl complexes **4-6** and **1**. The values of ϵ determined for the aryl complexes **4-6** are 20-100% higher than the values for **1** in THF and benzene. The bathochromic shifts and intensity increases resulting from replacement of alkyl substituent with aryl substituents are consistent with metal-to-μ-ligand charge transfer ($M_2 \rightarrow \mu$-LCT).[24] The electronic absorption spectra of the μ-isocyanide complexes **1** and **4-6** also exhibit significant solvent dependence. Hypsochromic shifts as large as 85 nm (THF/MeCN) are observed in more polar solvents. This is consistent with a Frank-Condon destabilized excited state model in which a polar solvent is unable to reorient itself in response to an excited state of polarity markedly different from the ground state. Extended Huckel calculations support the notion of metal-to-bridging ligand charge transfer. In an electronically saturated d^{10}-d^{10} configuration of nickel atoms interacting with unsaturated methyl isocyanide ligands, bridging isocyanide π^*/Ni_2 $d\pi^*$ interactions determine both the HOMO and LUMO.[25] The $\pi^*(\|)$ component of the μ-CNMe ligand and highest energy Ni_2 $d\pi^*$ combination contribute to a HOMO of metal-ligand π-bonding character. The second π^* component ($\perp$) of the μ-CNMe ligand is not disposed by symmetry to interact significantly with the Ni_2 framework and becomes the LUMO. The Huckel description thus predicts a LUMO of essentially pure μ-CNMe π^* character, consistent with the spectroscopic studies described above.

Our results suggest that a long-lived excited state of a binuclear transition-metal complex can be employed to associate with the CO_2 molecule. Previous studies from this laboratory indicate that the association of CO_2 with **1** results in the activation of CO_2 toward oxygen atom transfer reactions.[8,13] Continued studies of the photochemical activation and reduction of CO_2 are presently underway.

Acknowledgment. We are extremely grateful to Professor George McLendon (Rochester), Professors Dave McMillin and Ed Grant (Purdue), and Dr. Jay Winkler (Brookhaven) for suggestions and helpful discussions, Profesor William Jorgensen (Purdue) for assistance and support with extended Huckel calculations, and NSF (CHE-8707963) for support.

Supplementary Material Available: Description and diagrammatic layout of laser flash photolysis system; preparative details, IR, UV-vis, and $^{31}P\{^1H\}$ NMR spectroscopic data for **4**, **5**, and **6**; transient absorbance versus laser power data; and details of the determination of triplet conversion quantum yield (5 pages). Ordering information is given on any current masthead page.

(18) Transient absorbance versus laser power data and details of the determination of the triplet conversion quantum yield, Φ_T, are included as Supplementary Material.

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Transition-State Geometry in Epoxidation by Iron-Oxo Porphyrin at the Compound I Oxidation Level. Epoxidation of Alkenes Catalyzed by a Sterically Hindered (*meso*-Tetrakis(2,6-dibromophenyl)porphinato)iron(III) Chloride

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Although many studies of iron porphyrin catalyzed epoxidations have appeared in the literature,[1-3] the mechanism of epoxidation remains unresolved. The following mechanisms have been considered: (i) concerted oxygen insertion into the double bond (the oxenoid character of the iron bound oxygen atom supports this

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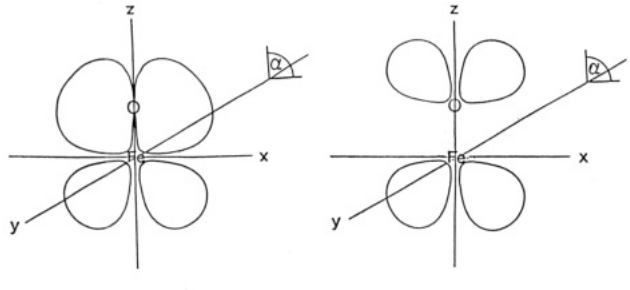
Table I. Epoxide Yields Using $(Br_8TPP)Fe^{III}(Cl)$ ($3.4–15 \times 10^{-5}$ mmol) and C_6F_5IO ($2–20 \times 10^{-3}$ mmol) in Grade A[13] CH_2Cl_2 (0.6–1.0 mL) at Room Temperature

alkene	alkene conctrtn (M)	catalyst turnover	epoxide yield[g] (%)
TME	1.0	200	99
	0.1	170	98
	0.01	200	92
	1.0		1[c]
norbornene	1.0	250	99
	0.1	140	93
	0.01	100	82
	1.0		4[c]
cis-stilbene[d]	0.25	125	99
	0.05	60	94
	0.025	45	93
	0.25		3[c]
trans-stilbene	0.14	175	4
	0.025	170	4
	0.14		3[c]

[a] The reaction times were dependent on the turnover number, typically about 10 min for 100 turnovers. [b] Yields are based on oxidant. [c] Catalyst was not present in these runs. [d] <0.1% of *trans*-stilbene and 0.5–1.5% *trans*-epoxide were observed.

view[4]), (ii) initial e^- transfer from alkene π bond to the iron–oxo porphyrin,[3a–c] or (iii) initial formation of an intermediate with Fe–O–C bonding (carbon radical, carbocation, or metallaoxetane), followed by collapse to the epoxide. Retention of stereochemistry is in accord with a concerted insertion of oxygen into the double bond,[1,2] while porphyrin N-alkylation, substrate rearrangements, and $1e^-$ oxidizability of alkenes[3c] have been offered to support nonconcerted epoxidation.[1,3] It is not clear, however, whether the N-alkylation of the porphyrin and substrate rearrangements arise from intermediates along the reaction path to the epoxide or if $1e^-$ oxidation of alkene is on the epoxidation reaction path.

On the basis of the steric selectivity observed in the epoxidation of various alkenes by iron(IV)–oxo porphyrin π-cation radical ($(^+\cdot P)Fe^{IV}{=}O$), Groves proposed a mechanism in which alkene approaches the Fe–O bond from the side and parallel to the porphyrin ring.[5] It is argued that the structure expected for Fe^{IV} in $(^+\cdot P)Fe^{IV}{=}O$ complex will have two singly occupied d_{xz} and d_{yz} orbitals considerably mixed with the filled p-orbitals on the oxygen so that the iron bound oxygen atom possesses considerable unpaired electron density and an oxenoid character.[4,6] However, the resulting Fe–O d_π–p_π bonding and antibonding orbitals would not be parallel to the porphyrin ring as depicted by Groves.[5,7] Considerable electron density on the side of oxygen distal to the porphyrin iron is expected in orbitals of this type I.[8] Thus, alkene need not approach the Fe–O bond in a perpendicular fashion but rather with the moderate optimum angle α (I).



In order to test this theory we prepared (*meso*-tetrakis(2,6-dibromophenyl)porphinato)iron(III) chloride ($(Br_8TPP)Fe^{III}Cl$),[9] a model catalyst in which the active site is encumbered by the bulky *o*-bromo substituents. The results of the epoxidation reactions are shown in Table I. Methods for product analysis have been described.[3d,13] The stability and catalytic efficiency of $(Br_8TPP)Fe^{III}(Cl)$ is shown by the 92% yield of the TME epoxide without porphyrin decomposition (determined by the comparison

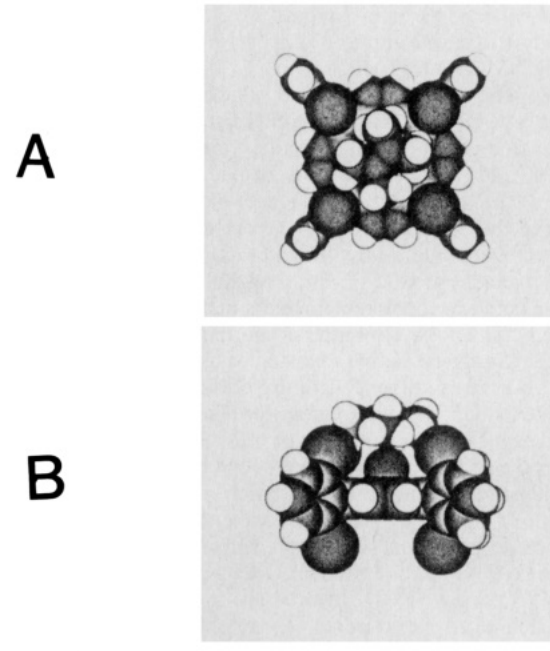


Figure 1. Space-filling models (CPK) showing the docking of 2,3-dimethyl-2-butene (TME) to (*meso*-tetrakis(2,6-dibromophenyl)porphinato)iron–oxo species. The energy of interaction is 0.6 kcal/mol. Graphics were obtained in the following manner. By using Polygen programs QUANTA and CHARMM, the structure of (*meso*-tetrakis(2,6-dibromophenyl)porphinato)iron–oxo species was created and energy minimized on the Silicon Graphics Iris 4D/60 computer. The X, Y, and Z coordinates were adjusted to match those of the X-ray coordinates of (*meso*-tetraphenylporphinato)iron(III) chloride[14] with C–Br bond lengths kept at 1.85 Å. An Fe=O bond was created with the length of 1.64 Å (as in the compound I species[15]). To minimize the steric interaction of the bromine substituents with the pyrrole hydrogens of the porphyrin moiety, the torsion angles between the phenyl and porphyrn rings were energy minimized. The structure of TME is a CHARMM minimized structure. Inspection of view A shows that TME can be fit into the niche created by the bromo substituents. Inspection of view B and real time energy calculations show that TME can be docked on top of the oxygen atom to a minimum angle $\alpha = 40°$ without serious interactions with *o*-bromines or porphyrin ring. Similar experiments were performed with norbornene and *cis*- and *trans*-stilbenes. The corresponding allowed values of α are 25–85° for norbornene, 45–60° for *cis*-stilbene, and 90° for *trans*-stilbene. None of the alkenes can approach the Fe–O bond in a perpendicular fashion suitable for interaction with both Fe and O to provide a metallaoxetane by a 2a + 2s cycloaddition.

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of UV-vis spectra before and at the completion of reaction) at a catalyst turnover numer of 200, $[(Br_8TPP)Fe^{III}(Cl)] = 4.5 \times 10^{-5}$ M, C_6F_5IO to TME is 1.0:1.1.

Computer graphics show that alkenes can approach the iron bound oxygen only from the top (Figure 1). TME requires a large value of α (I), while smaller values of α suffice for norbornene and *cis*-stilbene. Clean epoxidation of *cis*-stilbene (the substrate prone to rearrangements[3d]) indicates that the distances between the double bond and the orbitals on iron or porphyrin nitrogen are too large for the interactions which would lead to rearrangement products[3d] and that the only interaction possible is that between the alkene orbitals and orbitals on iron bound oxygen. Thus, the only interaction required for epoxidation is between the alkene double bond and oxygen.[3d] Due to severe steric hindrance *trans*-stilbene virtually does not epoxidize at all.

Taken alone, the requirement for alkene to approach the iron bound oxygen with a modest value of α allows several mechanisms. These are as follows: (i) direct oxene insertion into the alkene double bond; (ii) initial $1e^-$ oxidation of the alkene followed by collapse of the alkene π-cation radical and iron(IV)-oxo porphyrin to epoxide plus iron(III) porphyrin; and (iii) formation of a $Fe^{(IV)}$-O-C-C^+ transient species which gives way to epoxide plus iron(III) porphyrin. Disfavored are mechanisms requiring the approach of alkene to iron(IV)-oxo prophyrin π-cation radical from the side and with small values of α and the obligatory formation of a metallaoxetane (see figure legend).

Acknowledgment. This work was supported by grants from the National Insitutes of Health and the National Science Foundation.

Photo-Arbuzov Rearrangements of Benzyl Phosphites

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The *thermal* Arbuzov rearrangement is a widely known[1] reaction of organophosphorus molecules, eq 1. It classically occurs via a two-step mechanism catalyzed by R-X (X = halide, tosylate, etc.) and in certain instances can be autocatalytic.[1c] Intermolecular free-radical Arbuzov reactions are known as well.[2]

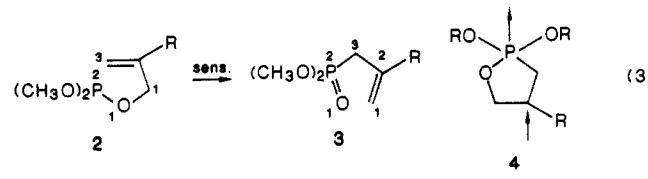
$$(RO)_3P \xrightarrow[\Delta]{R\text{-}X} (RO)_2P(O)R \qquad \Delta H^\circ \geq -40 \text{ kcal/mol}^3 \qquad (1)$$

It seemed to us possible that absorption of UV light could result in reaction 2, a *photochemical* Arbuzov rearrangement.[4] With

$$(RO)_2PO\text{-}Z \xrightarrow{h\nu} \underset{\mathbf{1}}{(RO)_2P^{*}\ {}^{*}Z} \longrightarrow (RO)_2P(O)\text{-}Z \qquad (2)$$

Z = UV chromophore

a sufficiently weak O-Z bond, useful regiospecificity might result. Radical or ion-pair intermediates (**1**) potentially could be produced. We showed recently that under conditions of triplet sensitization allyl phosphites, **2**, are photorearranged in an *intramolecular* Arbuzov-like process which is formally a cyclic 2,3-sigmatropic rearrangement, **2** → **3**, eq 3.[5] A cyclic triplet phosphoranyl 1,3-biradical (**4**) was suggested as a likely intermediate.

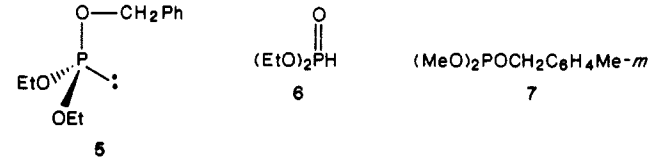


(3)

We report here the photorearrangement of benzyl dialkyl phosphites to the corresponding dialkyl benzylphosphonates, reaction 4. The specific processes examined are clean, regiospecific, and largely intramolecular. The rearrangements occur with a variety of benzylic phosphites to give potentially useful phosphonates.

$$(R^1O)_2POCHR^2Ph \xrightarrow{h\nu} (R^1O)_2P(O)CHR^2Ph \qquad (4)$$

Irradiations of 0.1-0.2 M solutions of phosphite **5** in deoxygenated benzene in quartz tubes (450-W medium pressure Hg lamp) gave $PhCH_2P(O)(OEt)_2$ in 85-95% yield at 90-100% conversion (^{31}P NMR, ^1H coupled; or ^1H NMR). Evidence for free-radical formation was found in the GLC detection, at nearly complete consumption of **5**, of 0.5-1% of bibenzyl (equivalent to

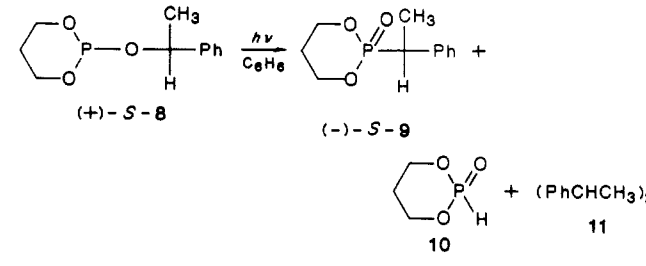


1-2% of cage-free $PhCH_2\cdot$) and 0.5-1% of phosphite **6**. Irradiation of a 1:1 mixture of **5** and **7** in benzene gave only minor amounts (1-2%) of the crossover phosphonates (^{31}P NMR). Chain reaction sequence 5 or more than minor reaction via combination of *cage-free* radical pairs is thereby excluded.

$$PhCH_2\cdot + 5 \longrightarrow PhCH_2\overset{\cdot}{O}P(OEt)_2 \longrightarrow PhCH_2P(O)(OEt)_2 + PhCH_2\cdot \qquad (5)$$

Reaction 2 (Z* = $PhCH_2\cdot$, R = Et) gives a reasonable interpretation of these results. Initial radical pair **1** is short-lived and *undergoes very predominantly cage recombination* to product benzylphosphonate, i.e., $k_{comb} \gg k_{diff}$. Cage-free radicals in minor amounts also recombine to form $(EtO)_2P(O)CH_2Ph$ and bibenzyl. (The possible formation of the dimer of $(EtO)_2P(O)\cdot$ has not been investigated.) Added MeOH failed to produce so much as 1% of $MeOCH_2Ph$ or any toluene, the trapping products of diffusive separation of $PhCH_2^+$ or $PhCH_2^-$ from potential ion-pair intermediate **1**.

The rearrangement of **8** in C_6H_6 proceeds in 84-92% yield (GLC) at 72-98% conversion with *close to complete retention of configuration of stereochemistry at the chiral carbon* (**8** → **9**). Dimer **11**, 0.2-1% yield, also is seen by GLC. Again k_{comb}



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