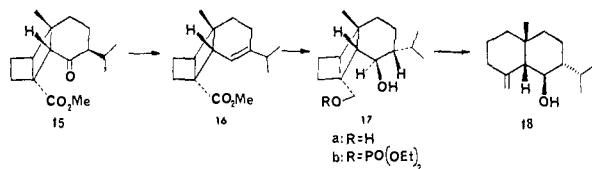


yield (distilled, mp 61–62 °C) from irradiation of piperitone in the presence of ester **1** was converted to the corresponding tosylhydrazone (65%, mp 149.5–150.5 °C dec) which reacted with sodium hydride in toluene (ambient temperature for 5 min, 110 °C for 2 h)¹⁹ to provide alkene **16** (64%, isolated).



Reaction of alkene **16** with diborane occurred with addition to the sterically less encumbered olefin face and concomitant ester reduction to afford exclusively diol **17a**⁸ (85%, mp 69.5–70.5 °C). Finally, selective esterification (1.1 equiv of BuLi; (EtO)₂POCl) of diol **17a** gave **17b** (99%) which upon reduction with lithium naphthalide²⁰ (THF, 0 °C) provided (±)-10-epijunol (**18**, 70%, isolated).^{4,21}

In addition to the above features, it is noteworthy that ester **1** and various substituted cyclobutene esters utilized as 4C components in the present annelation are readily available²² in preparative quantities (e.g., ester **1**, 60% overall yield from commercially available²³ ethyl 1-bromocyclobutanecarboxylate; 170-mmol scale) and can be stored in methylene chloride solution (–15 °C) for periods in excess of 8 months. We have also found that cyclobutenecarboxylic acid can be used in the photocycloaddition and expect that this method would be readily extended to other cyclobutene derivatives. Further studies are in progress.

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Supplementary Material Available: Structure assignments for **7a** and **7b** as determined from pyrolysis experiments, spectroscopic data on compounds **8**, **13**, and **14**, and a structure correlation which serves to independently confirm the relative stereochemistry previously assigned to 10-epijunol (2 pages). Ordering information is given on any current masthead page.

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- (17) These results in conjunction with the pyrolysis experiment⁸ lead to unique assignments of orientation.
- (18) The first step (NaOH, MeOH; RuO₂·H₂O, NaIO₄) in this transformation was based on the report of H. Gopal, T. Adams, and R. M. Moriarty (*Tetrahedron*, **28**, 4259 (1972)) while the second step (Pb(OAc)₄, Cu(OAc)₂) was modeled after the method of J. E. McMurry and L. C. Blaszcak (*J. Org. Chem.*, **39**, 2217 (1974)).
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- (24) National Science Foundation Fellow, 1975–1978.

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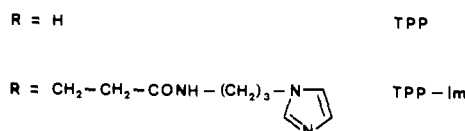
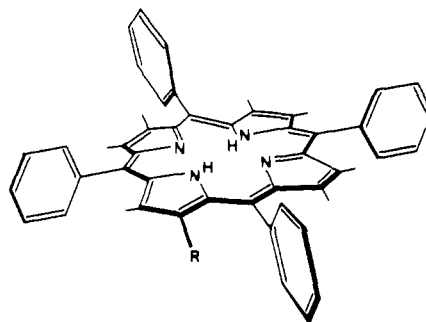
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Photodissociation of Nitrogenous Bases from Hemochromes and Kinetics of Recombination of Axial Bases

Sir:

The photodissociation of low-spin iron(II) hexacoordinate complexes of biological importance, such as carboxymyoglobin, carboxyhemoglobin, oxyhemoglobin, or of synthetic carboxyhemochromes containing porphyrin, carbon monoxide, and an additional base as ligands is well known.^{1–4} Photodissociation of other axial ligands (cyanide, isocyanide, nitric oxide) involving heterolytic bond cleavage from various d⁶ complexes has also been reported.^{5–8} We wish to present preliminary results on the photodissociation of low-spin hexacoordinate complexes of iron(II) porphyrins and nitrogenous bases as ligands (hemochromes) and on the kinetics of ligand recombination.



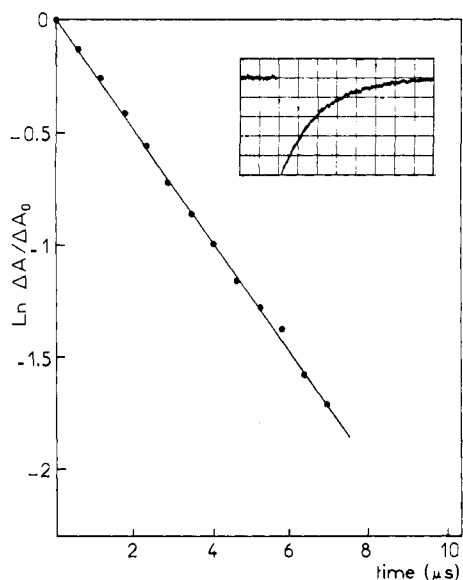


Figure 1. Decay of the bleaching of hemochrome, (pyridine)-FeTPP-Im, in toluene at 25 °C: wavelength, 530 nm; pyridine concentration, $5 \cdot 10^{-4}$ M. Inset: time scale, 2 μ s/division; absorbance scale, 0.01/division.

We have used *meso*-tetraphenylporphine (TPP) and a compound in which one axial base is covalently linked to the porphyrin, *meso*-tetraphenyl-1- β -carboxamidoethyl-*N*-[3-(1-imidazolyl)propyl]porphine⁹ (TPP-Im).

Ferric complexes of TPP and TPP-Im ($5 \cdot 10^{-5}$ M in toluene) were reduced by aqueous dithionite under anaerobic conditions,¹⁰ leading to tetracoordinate (FeTPP)¹¹ and pentacoordinate (FeTPP-Im)-iron(II)⁹ complexes, respectively. The organic phase was allowed to separate and the reduced metalloporphyrin was transferred directly into an optical cell (10 \times 5 mm) containing a known amount of ligand under an argon atmosphere. The final ligand concentration was such that 99% of the porphyrin was present as a hexacoordinate complex, as shown by the characteristic absorption spectrum in the visible range.

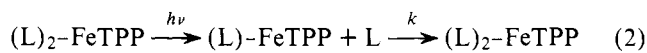
Laser photolysis was performed using the second harmonic (530 nm) of a Q-switched neodymium laser (pulse width, 15 ns). Transient absorbance changes were monitored at the wavelength of the hemochrome β band. The samples were kept at constant temperature (25 °C).

The result of a typical laser-photolysis experiment showing the transient bleaching of the 530-nm band of (pyridine)-FeTPP-Im is presented in Figure 1. For both (L)₂-FeTPP and (L)-FeTPP-Im complexes (where L refers to the ligand), the recombination reaction was found to be pseudo first order with respect to the concentration of free ligand [L] in excess, i.e., the time constant τ followed the relation

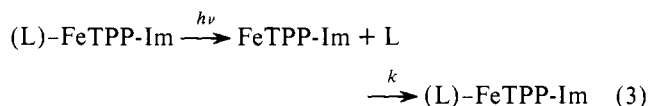
$$\tau^{-1} = k[L] \quad (1)$$

Values of the second-order rate constant k are listed in Table I. Clearly the reaction is not diffusion controlled.

Equation 1 strongly suggests that the reaction can be described by



and



in which only one ligand is removed by photolysis, leaving a pentacoordinate ferrous porphyrin.

We have determined the difference spectrum of the pri-

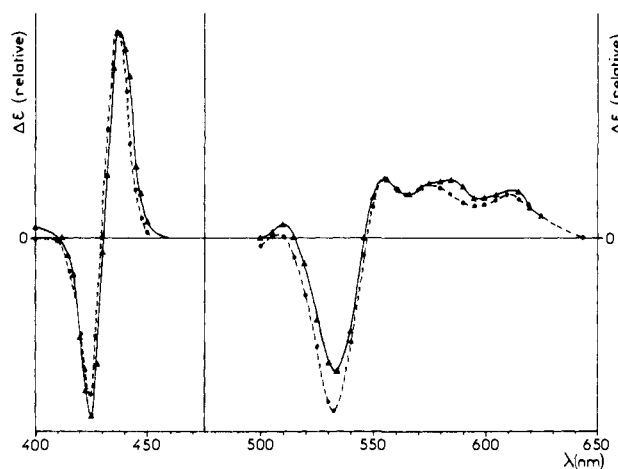


Figure 2. Initial difference spectrum following photolysis of (imidazole)₂-FeTPP, —▲—, and calculated difference spectrum for (imidazole)₂-FeTPP and (2-methylimidazole)-FeTPP, --●--. The spectra have been normalized for an easier comparison. The Soret and the visible regions are drawn at different scales.

Table I Second-Order Rate Constant for the Recombination of Various Ligands with Pentacoordinate Porphyrins and Quantum Yield (ϕ) of the Photodissociation of Hexacoordinate (L)-FeTPP-Im^a

Ligand	pK _a	(L)-FeTPP, FeTPP-Im		ϕ
		k ($\times 10^{-6}$), M ⁻¹ s ⁻¹	k ($\times 10^{-6}$), M ⁻¹ s ⁻¹	
Pyridine	5.17	370	450	0.06
Imidazole	6.95	140	190	0.05
<i>N</i> -Methylimidazole	6.95	110	180	0.04
Piperidine	11.1	50	320	0.03
2-Methylpyridine	5.96	0.7	2.6	0.08
2,6-Dimethylpyridine	6.77	13	15	0.08
2,6-Dimethylpiperidine	11.0	0.8	2.7	0.5

^a Solvent, toluene; temperature, 25 °C; pK_a values refer to water at 25 °C.

mary species formed immediately after photolysis of (imidazole)₂-FeTPP (Figure 2). Unfortunately the result cannot be compared directly with the difference spectrum for (imidazole)₂-FeTPP and (imidazole)-FeTPP, since in general pentacoordinate complexes cannot be isolated. With 2-methylimidazole as a ligand, however, only one molecule is able to bind to the heme.^{12,13} To a good approximation the optical spectra of monoimidazole- and 2-methylimidazole-iron(II) complexes are very similar; therefore we calculated the difference spectrum between (imidazole)₂-FeTPP and (2-methylimidazole)-FeTPP (Figure 2). The close similarity between the experimental difference spectrum and the calculated one clearly indicates that the only primary species formed upon photolysis of (L)₂-FeTPP complexes is the pentacoordinate ferrous porphyrin (L)-FeTPP, in agreement with the proposed reaction mechanism. No free porphyrin was formed. Indeed, attempts to photodissociate pentacoordinate complexes as (2-methylimidazole)-FeTPP or -FeTPP-Im were unsuccessful.

The quantum yield of photodissociation was determined by the relative actinometry technique used for measuring triplet yields.¹⁴ A standard solution of eosin and a solution of hemochrome were brought to equal absorbances at the excitation wavelength (530 nm). Both solutions were submitted to photolysis at equal laser energies. Excited triplet eosin was detected at 630 nm by its triplet-triplet absorption and acted as an actinometer, since triplet yield and extinction coefficient are known.¹⁵ The extinction coefficients of FeTPP-Im and (L)-FeTPP-Im were easily obtained, and the reading of the

initial absorbance change following photolysis of (L)-FeTPP-Im allowed the quantum yield to be calculated. The results are given in Table I. The quantum yield of the photolysis of hemochromes is of the same order of magnitude as the yield for photodissociation of oxyhemoglobin.¹⁶

Hemochromes were previously reported to be photoinert.^{8,17} We believe that the failure to observe any photodissociation was due to the insufficient time resolution of conventional flash photolysis techniques. At the ligand concentrations required for total complex formation, the recombination reaction is completed within a few microseconds.

The rate constants for the recombination of nonhindered ligands with (L)-FeTPP complexes is found to vary in the reverse order of their pK_a values (Table I). The recombination rates of the additional ligands are higher when imidazole occupies the fifth coordination site as in FeTPP-Im complexes. This "trans effect" is particularly marked in the case of piperidine, which presents the largest pK_a difference with respect to imidazole. On the contrary, the rate constants for the recombination of α -substituted ligands do not show a clear dependence on the pK_a and steric hindrance is probably the limiting factor responsible for their lower reactivity.

More extensive studies of these reactions with other ferrous porphyrins are in progress, principally in order to determine the various parameters involved in the recombination kinetics of the axial bases.

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Electron Paramagnetic Resonance Spectra of Carbalkoxycarbenes. Geometric Isomerism in Ground-State Triplets

Sir:

We have observed the electron paramagnetic resonance spectra of the ground-state triplets carbomethoxy- and carbethoxycarbene (**2**, R = CH₃, C₂H₅) upon direct or photosensitized decomposition of the corresponding diazo esters (**1**) in frozen solutions or in vacuum-deposited, rigid matrices. These spectra indicate the presence of two similar but nonidentical triplets, to which we assign the two rotameric structures, **2-c** and **2-t**. The carbalkoxycarbenes are the third class of methylenes to exhibit geometric isomerism, a phenomenon

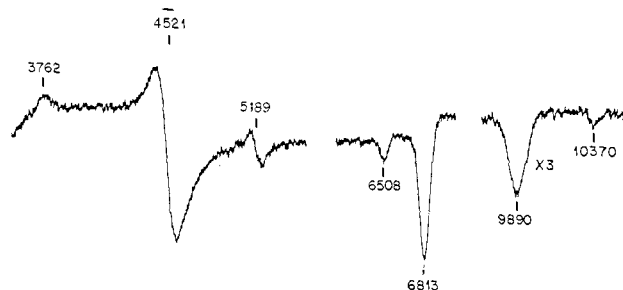


Figure 1. EPR spectrum of the isomeric carbomethoxycarbenes generated by benzophenone photosensitized irradiation of methyl diazoacetate in methylcyclohexane at 10 K. Fields are given in gauss: $h\nu/g\beta = 3305.1$ G. The low-field z line of the trans isomers is not observed. Its expected position (~ 3250 G) falls in the region of the spectrum which is obscured by an intense signal due to radicals produced during photolysis.

previously observed for the naphthylmethylenes¹ and for a series of vinylmethylenes.²

Beginning with the pioneering studies of Doering and co-workers,³ carbalkoxycarbenes have been among the most thoroughly investigated divalent-carbon intermediates.⁴ The overwhelming majority of the reported reactions are compatible with a singlet intermediate; in contrast, evidence for the involvement of the corresponding triplet states is scarce.⁵ Since no direct observation of either singlet or triplet state has been reported, the ground states cannot be identified unambiguously. The triplet state has been postulated as the ground state on the basis of extended Hückel calculations and of the nonstereospecific addition of **2** to *cis*-octene.^{5c} However, neither result is unequivocal since even sophisticated calculations substantially overestimate the relative energies of singlet carbenes⁶ and since the thermal population of a higher lying state cannot, in principle, be ruled out.⁷ The EPR data presented here provide unequivocal experimental evidence that the carbalkoxycarbenes have triplet ground states.

The EPR spectra of carbomethoxy- and carbethoxycarbene were observed upon direct irradiation or photosensitized decomposition of methyl or ethyl diazoacetate using either frozen solutions (methylcyclohexane, methyltetrahydrofuran, Nujol) or vacuum-deposited matrices (sulfur hexafluoride, acetophenone). Under comparable conditions the signal intensities of samples containing benzophenone or acetophenone were an order of magnitude higher than those of samples without a photosensitizer. The spectrum shown in Figure 1 is typical for both carbomethoxy- and carbethoxycarbene. The zero-field splittings are $D_t = 0.617$ and $E_t = 0.053$ cm⁻¹ and $D_c = 0.663$ and $E_c = 0.030$ cm⁻¹ for the two rotamers of carbomethoxycarbene and $D_t = 0.616$ and $E_t = 0.053$ cm⁻¹ and $D_c = 0.661$ and $E_c = 0.031$ cm⁻¹ for the two rotamers of carbethoxycarbene. The differences between methyl and ethyl derivatives are not significantly larger than the differences observed for any of the species in different matrices, $\Delta D \leq 0.002$ and $\Delta E \leq 0.001$ cm⁻¹. Variations of this magnitude are typical of the

