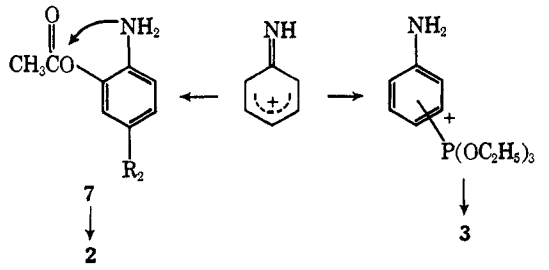
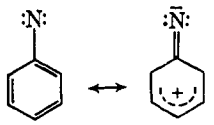
formation of **2** and **3**. The specific introduction of the acetoxy substituent in the *ortho* position in the case of **1a** and **6a** suggests an ion-pair effect and indicates that the protonation step must immediately precede product formation.[6]



Deoxygenation of aromatic nitroso compounds at 0° in solutions of triethyl phosphite containing 50% by volume acetic anhydride gives *o*-acetoxyacetanilides (**8**) as significant products (**8a**, 6%; **8b**, 16%; **8c**, 46%). While this result suggests that aryl nitrenes may be acylated by acetic anhydride, an alternative possibility involving formation of **7a–c** by reaction of the nitrene with traces of acetic acid followed by acylation of **8a–c** cannot be ruled out at present.

Extended Hückel calculations confirm the intuitive expectation that there would be extensive delocalization of the electron deficiency in phenyl nitrene and show an appreciable negative charge on nitrogen. Such delocalization would rationalize the apparent basicity of



the nitrogen atom of phenyl nitrene. Extensive delocalization of the electron deficiency at nitrogen may explain the apparent failure[9] of singlet phenyl nitrene to undergo intermolecular C–H insertion reactions. In contrast to cyanonitrene[10] or carbethoxynitrene,[11] in which the substituent groups are electron withdrawing, singlet phenyl nitrene may be less electrophilic at nitrogen than the triplet species. In the triplet species only one of the half-filled orbitals can interact with the phenyl π system to delocalize electron deficiency to the carbon atoms. Singlet phenyl nitrene may have substantial nucleophilic or dipolar properties as well as basic character, and we are investigating this possibility.

pounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, pp 225–226; H. J. Shine, "Aromatic Rearrangements," Elsevier Publishing Co., New York, N. Y., 1967, pp 182–190.

(6) An alternative mode of formation of aryl nitrenium ions in this system could involve protonation of the intermediate in the oxygen-transfer reaction, prior to expulsion of triethyl phosphate. Photolysis of aryl azides in acidic media also leads to products resulting from nucleophilic ring substitution,[7] although azides are weakly basic,[8] and protonation prior to photolytic expulsion of nitrogen is unlikely.

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(9) J. H. Hall, J. W. Hill, and J. M. Fargher, *J. Am. Chem. Soc.*, **90**, 5313 (1968).

(10) A. G. Anastassiou, *ibid.*, **89**, 3184 (1967).

(11) J. S. McConaghy, Jr., and W. Lwowski, *ibid.*, **89**, 4450 (1967).

(12) National Defense Education Act Fellow, 1966–present.

Richard J. Sundberg, Richard H. Smith, Jr.,[12] John E. Bloor
Department of Chemistry, University of Virginia
Charlottesville, Virginia 22903
Received February 26, 1969

Ligand Photoisomerization in Metalloporphyrin Complexes. A Possible Case of Photocatalysis

Sir:

Metalloporphyrins complex with a variety of axial ligands such as pyridine, ethanol, and other bases.[1] We thought that complexes containing a metalloporphyrin with the metal bound to stilbene-like ligands such as 1-(α-naphthyl)-2-(4-pyridyl)ethylene (NPE) might exhibit unusual energy-transfer phenomena. Particularly intriguing was the possibility that efficient "nonvertical" energy transfer might occur with the porphyrin as donor and the higher energy olefinic ligand as acceptor. We wish to report highly efficient photoisomerization processes for these complexes which are best described by mechanisms not involving specific electronic energy transfer.

Wavelength shifts in absorption and emission spectra indicate that *cis*- and *trans*-NPE[2] coordinate to zinc and magnesium etioporphyrin I in both ground and excited states in several solvents much the same as does pyridine.[1,3] Spectral similarities suggest that excitation in all of the complexes is largely localized in the porphyrin π electron system. The olefins quench neither the room-temperature fluorescence nor the low-temperature (EPA, 77°K) phosphorescence of the porphyrin. Irradiation of benzene solutions of *cis*- or *trans*-NPE and zinc etioporphyrin I with light absorbed only by the metalloporphyrin causes surprisingly efficient *cis–trans* isomerization of the ligand as the only detectable reaction (Table I). Similar, but less dramatic, results are obtained with magnesium etioporphyrin I–NPE solutions and with 4-stilbazole complexes. The photoisomerization is first order in light intensity; the quantum yields increase with increasing NPE concentration but show little temperature effect in the range 20–50°.[4] The isomerization is quenched by low concentrations of *p*-benzoquinone and by moderate concentrations of pyridine, which competes with NPE as a ligand. The greater than unit value for $\Phi_{c\rightarrow t}$ indicates that the reaction does not involve simple transfer of excitation from porphyrin to ligand. The strong preference for forming *trans*-NPE

Table I. Photoisomerization of Zinc Etioporphyrin I–Olefin Complexes

Sample[a]	$\Phi_{c\rightarrow t}$	$\Phi_{t\rightarrow c}$
Zn etio I–NPE[b]	6.6 ± 1	0.2
Zn etio I–stilbene	0.01	0.001
Zn etio I–NPE with 0.5 *M* pyridine[b]	0.37 ± 0.05	
Zn etio I–NPE with 10^{-4} *M* quinone[b]	0.055	

[a] Degassed benzene solutions irradiated using 405–408- and 436-nm regions of a mercury arc; porphyrin concentration 5×10^{-5} *M*; olefin concentration 5×10^{-3} *M*; temperature 25–28°; vpc analyses. [b] Photostationary state of 96% *trans*-NPE obtained.

(1) See, for example: A. H. Corwin, *et al.*, *J. Am. Chem. Soc.*, **88**, 2525 (1966); **85**, 3621 (1963); *J. Org. Chem.*, **27**, 3344 (1962); B. D. McLees and W. S. Caughey, *Biochemistry*, 7, 642 (1968), and references therein.

(2) Satisfactory analyses and spectral data were obtained for all new compounds.

(3) D. G. Whitten, I. G. Lopp, and P. D. Wildes, *J. Am. Chem. Soc.*, **90**, 7196 (1968).

(4) The lack of a temperature effect probably indicates that increases in the rates of isomerization and ligand exchange are offset by decreases in the excited-state lifetime.

suggests that some process effecting a thermodynamic equilibration is operative.

Possible mechanisms for the photoisomerization which do not involve energy transfer include eq 1–5,[5]

Path A. Ion-Chain Process

$$MPL \xrightarrow{h\nu} MPL^* \longrightarrow MP^+ + L^- \quad (1)$$

$$L^- \rightleftharpoons L'^- \quad (2)$$

$$L'^- + L \longrightarrow L' + L^- \quad (3)$$

Path B. Photocatalysis

$$MPL \xrightarrow{h\nu} MPL^* \rightleftharpoons MPL'^* \quad (4)$$

$$MPL'^* + L \rightleftharpoons MPL^* + L' \quad (5)$$

where MP = metalloporphyrin, L = *cis* ligand, L′ = *trans* ligand. Path A is reasonable since photoexcited metalloporphyrins can serve as electron donors[7] and since radical ions of olefins such as stilbene undergo *cis–trans* isomerization and electron-transfer reactions.[8] Quinone could interrupt path A by abstracting electrons from MPL* or L⁻. However, ionic processes such as reaction 1 are unlikely in nonpolar solvents such as benzene, and we see no evidence for formation of radicals upon irradiation of benzene–zinc etioporphyrin I–NPE solutions or even benzene–zinc etioporphyrin I–quinone solutions in an esr cavity.[9] Solvent effects provide evidence against path A. The reaction is less than one-tenth as fast in polar solvents such as acetonitrile and ethanol which should facilitate ionic processes. Flash spectroscopic studies (Table II) reveal no transients other than the zinc porphyrin triplet.[11]

Table II. Flash Spectroscopic Study of Zinc Etioporphyrin I Complexes

Sample[a]	Quencher	Lifetime, μsec	k_q, l. mole^{-1} sec^{-1}
Zinc etio I		200	
Zinc etio I–10^{-4} *M* pyridine		475	
Zinc etio I–10^{-4} *M* NPE[b]		480	
Zinc etio I–10^{-2} *M* piperidine		420	
Zinc etio I–10^{-4} *M* NPE[b]	4.33×10^{-6} *M* azulene	70	3×10^9
Zinc etio I–10^{-4} *M* NPE[b]	3.74×10^{-6} *M* quinone	25	1×10^{10}

[a] All samples 10^{-6} *M* in porphyrin, degassed benzene solutions, temperature 25°. [b] Starting material *cis*-NPE; initial data agree with those obtained after several flashes.

Path B seems possible since excited states of zinc porphyrin undergo rapid ligand exchange.[3] Flash studies indicate that triplets of the zinc porphyrin are not quenched by NPE; in fact the porphyrin triplets have longer lifetimes in the presence of NPE and pyridine. Triplet–triplet spectra of the zinc porphyrin are shifted to longer wavelengths with pyridine or NPE, but the change is slight. The lifetimes listed in Table II are long enough so that many exchanges occur in excess of the number required by the quantum efficiency listed in Table I. Although quinone quenches the isomerization at concentrations where fluorescence quenching is unimportant,[3] it appears unlikely that quinone, triplet energy 53 kcal/mole,[12] is quenching the 40–42-kcal/mole porphyrin triplet *via* energy transfer. A reasonable possibility is that quinone quenches the porphyrin triplet *via* charge-transfer complex formation at close to the diffusion-controlled rate.[13] If path B is operative, compounds with low-lying triplet states such as azulene and naphthacene should quench the isomerization nearly as well as quinone. Quenching by quinone and azulene is detectable in flash experiments (Table II) and correlates with isomerization experiments. In typical experiments with 10^{-4} *M* quencher, the isomerization of 5×10^{-3} *M* *cis*-NPE is 97% quenched by azulene and 99% quenched by quinone.

These results suggest that path B provides the most likely mechanism for the photoisomerization. The results are remarkable for the following reasons: spectral evidence suggests little delocalization of the porphyrin excited states to the ligand, yet isomerization occurs; *cis–trans* isomerization and ligand exchange occur in the excited state without concurrent deactivation. The observed phenomena imply that the activation barrier for *cis–trans* isomerization is sharply reduced in the excited porphyrin–NPE complexes. Results of studies with other metal complexes and kinetic details of the photoisomerization will be developed in the full paper.[14]

(14) Support of this work by the National Institutes of Health (Grant No. GM 15,238-01,2) and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(15) National Science Foundation Predoctoral Fellow, 1965–present.

David G. Whitten, Peter D. Wildes, Irene G. Lopp[15]
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

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(5) Interesting, but probably unrelated, redox and isomerization phenomena involving olefins and cobalt porphyrins have been reported.[6]

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(7) K. P. Quinlan, *J. Phys. Chem.*, 72, 1797 (1968), and earlier references; G. R. Seely, *ibid.*, 69, 2779 (1965); L. P. Vernon and E. R. Shaw, *Biochemistry*, 4, 132 (1965); V. B. Estigneev, *ibid.*, 5, 171 (1966).

(8) R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, 46, 2314 (1967); C. S. Johnson, Jr., and R. Chang, *ibid.*, 43, 3183 (1965).

(9) We have detected radicals from zinc etioporphyrin I–quinone–ethanol solutions upon irradiation in agreement with Tollin,[10] but we obtain only very weak signals from ethanol solutions of zinc etioporphyrin I–NPE.

(10) G. Tollin, K. K. Chatterjee, and G. Green, *Photochem. Photobiol.*, 4, 593 (1965); G. Tollin and G. Green, *Biochim. Biophys. Acta.*, 60, 524 (1962).

(11) A mercury–xenon flash having a fall time of *ca.* 10 μsec was used with Corning filters to activate the porphyrin visible bands. A tungsten steady-state lamp was used to monitor transients. Degassed solutions were irradiated in cylindrical cells with absorbance adjusted to low values (*ca.* 0.1) to ensure uniform production of transients.

(12) M. G. Jayswal and R. S. Singh, *Spectrochim. Acta*, 21, 1597 (1965).

(13) H. Beens and A. Weller in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 203.

Biological Demethylation of 4,4-Dimethyl Sterols. Evidence for Enzymic Epimerization of the 4β-Methyl Group Prior to Its Oxidative Removal

Sir:

In a previous report we have shown that in the oxidative demethylation of 4,4-dimethylcholestanol (**1**) to cholestanol (**9**) by enzymes of rat liver, the 4α-hydroxymethyl-4β-methyl sterol **2**, but not its 4β-hydroxymethyl isomer, behaved as an intermediate, and the conclusion was drawn that the 4α-methyl group of **1** was the first to be attacked.[1] It was noted that Gaylor and Delwiche had arrived at the opposite conclusion in

(1) K. B. Sharpless, T. E. Snyder, T. A. Spencer, K. K. Maheshwari, G. Guhn, and R. B. Clayton, *J. Amer. Chem. Soc.*, 90, 6874 (1968).