Recrystallization from chloroform–carbon tetrachloride gave an analytical sample, mp 165–166°. The spectral characteristics were ir (KBr) 3.34, 6.00, 6.20, 6.29, 6.36, 6.72, 6.95, 7.22, 7.48, 7.94, 8.29, 8.40, 8.56, 8.93, 9.36, 9.70, 10.45, 11.31, 12.19, 12.74, 13.20, 13.35, 14.32, and 14.75 μ; nmr ($CDCl_3$) τ 2.65 (partially resolved singlets, 10 H), 3.00 (mult, 1 H), 4.00 (broadened d, 1 H, J = 11 cps), 4.80 (s, 1 H), and 5.5–5.7 (mult, 2 H). The mass spectrum showed peaks for a molecular ion at 326 and 328.

Anal. Calcd for $C_{18}H_{15}OBr$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 66.19; H, 4.65; Br, 24.20.

Reduction of 6-Bromo-5,5-diphenylcyclohex-2-en-1-one. A solution of 89 mg (0.27 mmol) of 6-bromo-5,5-diphenylcyclohex-2-en-1-one in 15 ml of acetone was treated under nitrogen with 0.25 ml of 48% hydriodic acid. The solution immediately turned orange. After stirring for 1.5 hr, the mixture was added to a solution of 0.5 g of sodium thiosulfate in 50 ml of water. Extraction with ether, drying, and solvent removal *in vacuo* gave 76.8 mg of a crystallizing oil.

The oil was dissolved in chloroform–carbon tetrachloride and crystallized 19.6 mg of recovered 6-bromo-5,5-diphenylcyclohex-2-en-1-one. The mother liquor was concentrated and chromatographed on a 1 × 35 cm silicic acid column to give 31.0 mg (59%) of crystalline 5,5-diphenylcyclohex-2-en-1-one.

4,4-Diphenylcyclohexadienone was prepared from 4,4-diphenylcyclohex-2-en-1-one by enol acetate formation, bromination, and dehydrobromination using the procedure of Zimmerman, Hackett, Juers, McCall, and Schröder.[33]

2,3- and 3,4-diphenylphenols were prepared as described by Zimmerman and Schuster[3] by the dehydrogenation of 5,6-diphenylcyclohex-2-en-1-one and the acid-catalyzed rearrangement of 4,4-diphenylcyclohexadienone, respectively.

Reaction of 6-Bromo-5,5-diphenylcyclohex-2-en-1-one with Base. A solution of 107.8 mg (0.329 mmol) of 6-bromo-5,5-diphenylcyclohex-2-en-1-one in 15 ml of 50% dioxane–water was added to 365 mg (6.50 mmol) in 50 ml of 50% dioxane–water. The solution was stirred under nitrogen in the dark for 6 hr, concentrated *in vacuo* to *ca.* 10 ml, diluted with 75 ml of water, neutralized, and extracted with ether. Drying the ether extracts and solvent removal *in vacuo* gave 77.0 mg (86%) of a mixture of 2,3- and 3,4-diphenylphenols. Analysis of the mixture, *vide infra*, gave the composition as 72.5% 2,3-diphenylphenol and 27.5% 3,4-diphenylphenol. The reaction of the 6-bromo ketone with base in other solvents was performed similarly, and the results are shown in Table I.

Quantitative Analysis of the Phenol Mixture. The relative amounts of 2,3- and 3,4-diphenylphenols were determined by three methods: (1) vapor phase chromatography, (2) quantitative infrared spectroscopic analysis, and (3) isolation. The three methods gave consistently good agreement (differing at most by 3.6%) but the greatest accuracy in analysis of mixtures of known composition was obtained using vpc.

The vpc analysis was performed on a $^1/_8$ in. × 5 ft column of 5% SE-30 on Varaport 30 (100–120 mesh). Analysis of the phenol mixture at 170° gave a retention time of 9.2 min for 2,3-diphenylphenol and 18.5 min for 3,4-diphenylphenol. The quantitative infrared analysis was performed using the relative absorption at 800 and 820 cm^{-1} as described by Zimmerman.[13] The phenols were isolated by silica gel chromatography, eluting with ether–hexane.

Photolysis of 4,4-Diphenylcyclohexadienone. Dilute solutions o *ca.* 0.001 *M* were photolyzed using a 450-W Hanovia mercury lamp until no dienone or bicyclic ketone remained. The phenol mixture was isolated as described earlier[13] and analyzed by the same procedure as described above for the nonphotochemical runs. The results of these runs are shown in Table I.

Acknowledgment. Support of this research by the National Science Foundation and by the National Institutes of Health Grant GM-07487, as well as by a predoctoral fellowship to G. A. E., is gratefully acknowledged.

---

[33] H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **93**, 3653 (1971).

Photochemistry of Metalloporphyrin Complexes. Ligand Photoisomerization *via* Intramolecular Energy Transfer[1,2]

David G. Whitten,*[3a] Peter D. Wildes,[3b] and Carol A. DeRosier

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received January 17, 1972*

Abstract: An investigation of the photochemistry of complexes in which metalloporphyrins (zinc, magnesium, and cobalt etioporphyrin and mesoporphyrin complexes) are bound to reactive extraplanar ligands, isomerizable azastilbenes, is reported. Light absorbed by the long-wavelength transitions of zinc and magnesium porphyrins promotes efficient cis–trans isomerization of azastilbene ligands such as 4-stilbazole, 1-(1-naphthyl)-2-(4-pyridyl)ethylene (NPE), and 1-(1-naphthyl)-2-(4-pyridyl)propene (NPP). The extremely high quantum yields for cis to trans isomerization of several azastilbenes ($\Phi_{c\rightarrow t} = 7$ for NPE) are explained by a mechanism involving reversible intramolecular transfer of triplet excitation from porphyrin to azastilbene ligand. An intramolecular "azulene effect" involving energy transfer from a transoid azastilbene triplet to the porphyrin coupled with rapid ligand exchange during the relatively long excited state lifetime allows the operation of a photocatalytic or quantum chain process. Triplet energy transfer from porphyrin to complexed *cis*-NPE involves a surprisingly low activation energy, indicating that the excited state populated lies *at least* 8 kcal/mol below the spectroscopic or cisoid excited state. Triplet energy transfer from porphyrin to *trans*-NPE requires approximately the energy expected for vertical excitation to a transoid triplet. The high negative entropy of activation observed for triplet energy transfer from porphyrin to *cis*-NPE is consistent with several previously developed mechanisms of "nonvertical" triplet energy transfer to produce an excited state having different geometry than the *cis*-NPE ground state.

Light-induced reactions of metalloporphyrins and related compounds have been the subject of considerable attention, especially due to the importance of these compounds in photobiological and electron-transport phenomena. Due to interest in the role of chlorophyll in photosynthesis,[4] emphasis has been

---

[1] Preliminary accounts of portions of this work have appeared: (a) D. G. Whitten, P. D. Wildes, and I. G. Lopp, *J. Amer. Chem. Soc.*, **91**, 3393 (1969); (b) P. D. Wildes and D. G. Whitten, *ibid.*, **92**, 7609 (1970).

[2] Abstracted in part from the Ph.D. Thesis of P. D. Wildes.

[3] (a) Alfred P. Sloan Foundation Fellow; (b) National Defense Act Predoctoral Fellow, 1969–1970.

[4] For some reviews, see N. K, Boardman, *Advan. Enzymol.*, **30**, 1 (1968); "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press, New York, N. Y., 1966; L. P. Vernon and M. Avron, *Annu. Rev. Biochem.*, **34**, 269 (1965); J. H. Wang, *Proc. Nat. Acad. Sci. U. S.*, **62**, 653 (1969); G. N. Cheniae, *Annu. Rev. Plant Physiol.*, **21**, 2019 (1970).

placed on energy transfer, energy trapping, and photochemical electron-transfer reactions. While there has been some controversy over the exact orbital origin of porphyrin electronic transitions and the corresponding excited states, it is generally agreed that the lowest excited states of most metal complexes of chlorins and porphyrins are π,π^* states, with the electronic excitation more or less localized on the macroscopic ligand.[5-8] However, the central metal can exert strong perturbation on the π,π^* excited states, influencing such properties as its electron-donating or -accepting ability,[9] as well as rates of nonradiative decay and phosphorescence.[10] For example, it has recently been found[11] that the triplet energies of several metalloporphyrins decrease with increasing hole size or ionic radius of the central metal. On the other hand, previous studies of the emission phenomena of metalloporphyrin complexes containing extraplanar ligands indicate that metal–extraplanar ligand bonding is normally little perturbed in the metalloporphyrin singlet and triplet states;[12] thus, in zinc and magnesium complexes rapid exchange of the extraplanar ligand is indicated for the excited states,[12] as had been previously determined for the ground states of the same complexes.[13]

In the present paper we report an investigation of the photochemistry of complexes in which metalloporphyrins are bound to potentially reactive extraplanar ligands. In addition to the indications that similarly complexed metalloporphyrins might be involved in photobiological phenomena,[4] we were intrigued by the possibility that such systems might undergo efficient energy-transfer phenomena. Especially appealing was the possibility that complexes such as these, in which two chromophores are held together in a fairly well-defined geometric relationship, might provide useful systems to determine details and requirements of energy transfer, especially activated or endothermic energy transfer. We chose to initiate these investigations with isomerizable acyclic olefins, the azastilbenes, as extraplanar ligands for the metalloporphyrins. In separate studies we found excited triplet states of these azastilbenes to behave very similarly to those of stilbene and the corresponding hydrocarbons.[14,15] Since it has been well established that energy transfer to produce either singlet or triplet excited states of stilbene and similar olefins is accompanied by efficient cis–trans isomerization,[16] it was anticipated that porphyrin-to-ligand energy transfer could be followed by monitoring cis–trans isomerization of the extraplanar ligand.

The porphyrin long-wavelength transitions occur in the visible (400–600 nm) region, where the extraplanar ligands do not absorb, so that selective activation to porphyrin excited states is easily achieved. From the onset of phosphorescence,[10,12] it can be estimated that energies of the lowest triplets of the porphyrins used in this study—zinc, magnesium, and cobalt(III) etioporphyrin I complexes—are in the range 40–42 kcal/mol, while the energies of trans and cis triplets of the azastilbenes are higher by several kilocalories per mole.[1,14] Consequently, any production of ligand–olefin excited states by energy transfer from the porphyrin would be expected to be an activated process. In previous work reasonably efficient intermolecular sensitization of stilbene isomerization has been observed with triplet sensitizers having energies comparable to the metalloporphyrins.[16] Herkstroeter and Hammond[17] have measured rates of energy transfer to the stilbenes and α-methylstilbenes from triplet sensitizers having lower triplet energies than those of the olefins using flash-spectroscopic methods. For *trans*-stilbene the observed decrease in the rate of energy transfer with decreasing sensitizer energy is consistent with the requirement of an activation energy equivalent to the energy difference between donor and acceptor.[17] For *cis*-stilbene and *cis*- and *trans*-α-methylstilbene, rates of energy transfer do not fall off as fast as predicted; this observation, together with other evidence,[16,17] indicates that energy transfer to these olefins does not produce an excited state with the same geometry as the ground-state olefin but rather that a lower energy (presumably twisted) excited state is the product of energy transfer. There has been considerable interest and discussion as to the mechanism of this type of energy transfer.[16-20]

Results of the present study indicate that the molecular complexes under investigation do indeed undergo intramolecular processes which do not occur efficiently in counterpart intermolecular systems. We find that highly efficient porphyrin–olefinic ligand energy transfer does occur in both directions. The occurrence of reversible intramolecular energy transfer, together with rapid ligand exchange, permits the operation of a chain process or photocatalysis in which multiple acts of ligand isomerization can occur without necessitating excited state deactivation. Rather surprisingly, kinetic analysis reveals that the efficiency of isomerization for some zinc and magnesium complexes is limited only by the metalloporphyrin triplet lifetime and the rate of the activated energy-transfer process. A temperature study of the activated energy-transfer process indicates that "spectroscopic" states of the ligand olefin are not produced; the surprisingly low $\Delta H^{\ddagger}$ values and large negative $\Delta S^{\ddagger}$ values measured offer some interesting implications regarding energy-transfer possibilities between energy-deficient donors and nonrigid acceptors.

---

(5) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950); J. R. Platt, "Radiation Biology," Vol. III, A. Hollaender, Ed., McGraw-Hill, New York, N. Y., 1956, Chapter 2; A. H. Corwin, A. B. Chivvis, R. W. Poor, D. G. Whitten, and E. W. Baker, *J. Amer. Chem. Soc.*, **90**, 6577 (1968).

(6) I. Fischer-Hjalmas, B. Grabe, B. Roos, P. N. Shancke, and M. Sundbom, *Int. J. Quantum Chem. Symp.*, **1**, 233 (1967).

(7) R. L. Ake and M. Gouterman, *Theor. Chim. Acta*, **15**, 20 (1969); D. Eastwood and M. Gouterman, *J. Mol. Spectrosc.*, **35**, 359 (1970); M. Gouterman, *ibid.*, **6**, 138 (1961), and references cited therein.

(8) A. T. Gradyushko, V. A. Mashenkov, K. N. Solov'ev, and A. N. Sevchenko, *Sov. Phys. Dokl.*, **13**, 869 (1969); A. T. Gradyushko, V. A. Mashenkov, and K. N. Solov'ev, *Biofizika*, **14**, 827 (1969).

(9) I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970).

(10) R. S. Becker and J. B. Allison, *J. Phys. Chem.*, **67**, 2675 (1963); P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.*, **31**, 1 (1969).

(11) M. S. Fischer and C. Weiss, Jr., *J. Chem. Phys.*, **53**, 3121 (1970).

(12) D. G. Whitten, I. G. Loop, and P. D. Wildes, *J. Amer. Chem. Soc.*, **90**, 7196 (1968).

(13) C. B. Storm and A. H. Corwin, *J. Org. Chem.*, **29**, 3700 (1964).

(14) D. G. Whitten and M. T. McCall, *J. Amer. Chem. Soc.*, **91**, 5097 (1969).

(15) Y. J. Lee, D. G. Whitten, and L. Pedersen, *ibid.*, **93**, 6330 (1971); Y. J. Lee and D. G. Whitten, unpublished results.

(16) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(17) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

(18) A. Bylina, *Chem. Phys. Lett.*, **1**, 509 (1968); A. Bylina and Z. R. Grabowski, *Trans. Faraday Soc.*, **65**, 458 (1969).

(19) A. A. Lamola, *Tech. Org. Chem.*, **14**, 17 (1969).

(20) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2820 (1967).

Table I. Physical Constants and Sources of Ligand–Olefins

			% carbon		% hydrogen		Major uv absorption			
Compound	Mp, °C	Source[a]	Calcd	Found	Calcd	Found	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$
trans-4-Stilbazole	132–133	1					306	22.2	228	10.9
trans-1-(1-Naphthyl)-2-(4-pyridyl)ethylene	80–81	1					329	15.6	259	13.4
trans-4′-Methyl-4-stilbazole	147–150	1					312	17.5	231	12.0
trans-4′-Chloro-4-stilbazole	112–113	1					311	23.0	229	10.1
trans-4′-Methoxy-4-stilbazole	135–136	1					325	23.9	231	11.6
trans-4′-Cyano-4-stilbazole	139–140	1					327	22.8	227	11.8
trans-4′-Nitro-4-stilbazole	165–173	1								
trans-3′-Cyano-4-stilbazole	144–146	1					292	23.7	226	14.9
trans-1-Phenyl-2-(4-pyridyl)propene	72–73	2	86.12	86.10	6.71	6.90	285	16.6	222	9.4
trans-1-(1-Naphthyl)-2-(4-pyridyl)propene	98–99	3	88.13	87.94	6.16	6.30	304	10.8	255	79.0
cis-4-Stilbazole	Oil	4	86.15	86.02	6.12	6.24	283	9.45	223	14.3
cis-1-(1-Naphthyl)-2-(4-pyridyl)ethylene	Oil	4	88.28	88.45	5.66	5.67	305	6.47	221	38.0
cis-4′-Methyl-4-stilbazole	Oil	4	86.12	86.36	6.71	6.94	290	8.9	228	16.9
cis-4′-Chloro-4-stilbazole	Oil	4	72.39	72.46	4.67	4.89	278	10.3	227	17.4
cis-4′-Methoxy-4-stilbazole	Oil	4					302	8.65	232	15.6
cis-4′-Cyano-4-stilbazole	90–91	4	81.51	81.51	4.89	4.65	279	13.3	229	17.0
cis-4′-Nitro-4-stilbazole	100–102	4	69.00	69.09	4.46	4.61				
cis-3′-Cyano-4-stilbazole	Oil	4	81.52	81.78	4.89	5.03	274	9.85	220	18.9
cis-3-Stilbazole	Oil	5	86.12	86.32	6.71	6.78	265	7.74	233	12.8
cis-1-Phenyl-2-(4-pyridyl)propene	39–40	2, 6	86.12	86.32	6.71	6.78	265	7.74	233	12.8
cis-1-(1-Naphthyl)-2-(4-pyridyl)propene	Oil	3, 6	88.13	87.88	6.16	6.37	297	8.0	223	48.0

[a] (1) Prepared by condensation of 4-picoline with the appropriately substituted benzaldehyde or naphthaldehyde; (2) prepared by condensation of 4-ethylpyridine with benzaldehyde; (3) prepared by condensation of 4-ethylpyridine with 1-naphthaldehyde; (4) prepared by biacetyl-sensitized photoisomerization of the trans isomer; (5) prepared by the method of Clark, *et al.*;[30] (6) isolated from the condensation mixture by column chromatography on alumina, by eluting with hexane.

Experimental Section

Materials. Etioporphyrin I was prepared by the condensation of kryptopyrrole[21,22] and purified by column chromatography on alumina by elution with chloroform followed by recrystallization from chloroform–methanol. Final purity was greater than 99% as determined by visible and uv spectra and checked by liquid-liquid partition chromatography.[23] Zinc etioporphyrin I was prepared by the method of Calvin, *et al.*,[22] and purified by column chromatography. Magnesium etioporphyrin I was prepared by the magnesium hexapyridine diodide–pyridine method of Corwin, *et al.*[24]

Mesoporphyrin IX dimethyl ester was prepared by esterification of mesoporphyrin prepared by alkaline hydrogenation of protohemin.[25] Zinc mesoporphyrin IX dimethyl ester was prepared by the method of Calvin, *et al.*,[22] and purified by chromatography on alumina by elution with chloroform, followed by crystallization from chloroform–hexane. The purity of the metalloporphyrins was estimated at better than 99% from uv and visible spectra.

The trans isomers of most of the olefins used are known compounds, and literature methods of preparation are available.[26–30] 4-Stilbazole and the 4′-substituted 4-stilbazoles were prepared by condensing 4-picoline with the appropriately substituted benzaldehyde. Equimolar quantities of 4-picoline, the aldehyde, and acetic anhydride were refluxed for several days. The low-boiling components of the mixture were removed either by vacuum distillation or by rotary vacuum evaporation; a black tarry residue remained in each case. In the preparation of 4′-substituted 4-stilbazoles, the tarry residue was placed in a vacuum sublimator and heated under vacuum. White crystals were collected on a cold finger cooled by ice water. The crystals were further purified by recrystallizations from hexane–benzene.[31] *trans*-1-(1-Naphthyl)-2-(4-pyridyl)ethylene was prepared by the condensation of 4-picoline with 1-naphthaldehyde as described above; purification was by high vacuum distillation followed by several recrystallizations from hexane. *trans*-3′-Cyano-4-stilbazole was made by the condensation of 4-picoline and 3-cyanobenzaldehyde exactly as described above for the 4′-substituted 4-stilbazoles. 1-(1-Naphthyl)-2-(4-pyridyl)propene and 1-phenyl-2-(4-pyridyl)propene were prepared by the condensation of 4-ethylpyridine with 1-naphthaldehyde and benzaldehyde, respectively. Preparation and purification of the trans isomers of these compounds were accomplished exactly as described for *trans*-1-(1-naphthyl)-2-(4-pyridyl)ethylene. Table I summarizes the compounds prepared and their melting points.

Cis isomers of most of the compounds used as ligand olefins were prepared by the triplet-sensitized photoisomerization of the trans isomers using 2,3-butanedione (biacetyl) as a sensitizer. (*cis*-1-(1-Naphthyl)-2-(4-pyridyl)ethylene could also be prepared by direct photoisomerization of the trans isomer using a filter solution consisting of 1 lb of $Cu(NO_3)_2 \cdot 3H_2O$ in 3 l. of water, but the reaction is slower and the yield is poorer than that obtained by sensitized irradiation.) One gram of the trans isomer to be isomerized was dissolved in 250 ml of benzene along with 50 ml of biacetyl. The solution was irradiated with a Hanovia 450-W medium-pressure mercury lamp surrounded by a Pyrex sleeve in a quartz immersion well. A recirculating pump was used to pump a filter solution consisting of 2 g of $CuSO_4$ and 2 g of $NaNO_2$ in 3 l. of water through the lamp well. The lamp was cooled by pumping the filter solution through a copper coil immersed in ice water. The stilbazole solutions were deoxygenated by flushing with oxygen-free nitrogen gas during irradiation and for several minutes before the start of irradiation. Oxygen was removed from the nitrogen by passing it through a solution of 3.5 g of sodium metavanadate in 250 ml of 4 *N* sulfuric acid standing over zinc rods amalgamated with mercury. After 2 hr of irradiation, vpc analysis generally indicated a cis to trans ratio of about 9, and the irradiation was stopped. The solvent and most of the biacetyl were removed by rotary vacuum evaporation. The brown tarry residue remaining was dissolved in benzene and passed through a short alumina column (about 6 in. long and 0.5 in. in diameter) which removed most of the colored impurities. The product collected after removal of

---

(21) H. Fischer and H. Orth, "Die Chemie des Pyrroles," Vol. II, part 1, Akademische Verlagsgesellschaft mbH, Leipzig, Germany, 1937, p 106.

(22) G. Engelsma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, 66, 2517 (1962).

(23) E. W. Baker, M. Lachman, and A. H. Corwin, *Anal. Biochem.*, 8, 503 (1964).

(24) P. E. Wei, A. H. Corwin, and R. Arellano, *J. Org. Chem.*, 27, 3344 (1962).

(25) E. W. Baker, M. Ruccia, and A. H. Corwin, *Anal. Biochem.*, 8, 512 (1964).

(26) M. C. Chiang and W. H. Hartung, *J. Org. Chem.*, 10, 21 (1945).

(27) A. R. Katritsky, D. J. Short, and A. J. Boulton, *J. Chem. Soc.*, 1516 (1960).

(28) G. Drefahl and E. Gerlach, *J. Prakt. Chem.*, 6, 72 (1958).

(29) E. K. Fields, *J. Amer. Chem. Soc.*, 71, 1495 (1949).

(30) F. Clark, G. A. Felock, G. B. Silberman, and C. M. Watrick, *J. Org. Chem.*, 27, 533 (1962).

(31) We thank Mr. Eric Helsabeck for the preparation of 4′-chloro-4-stilbazole, 4′-methoxy-4-stilbazole, and some 4′-cyano-4-stilbazole and 4′-methyl-4-stilbazole.

the benzene was placed on a similar alumina column packed in hexane and eluted with hexane. Small fractions (10 ml) were collected, those which appeared to be greater than 99% cis by vpc analysis were combined, the solvent was removed, and the products were distilled under high vacuum. Most of the cis products were colorless or pale yellow oils; *cis*-4′-cyano-4-stilbazole and *cis*-4′-nitro-4-stilbazole crystallized and were purified by recrystallization from hexane. Significant amounts of *cis*-1-phenyl-2-(4-pyridyl)propene and 1-(1-naphthyl)-2-(4-pyridyl)propene were formed in the condensations, and these cis isomers were separated by chromatography on alumina with hexane and purified by recrystallization from cold hexane in the case of 1-phenyl-2-(4-pyridyl)propene and by distillation under high vacuum for 1-(1-naphthyl)-2-(4-pyridyl)propene. Table I includes elemental analyses on the cis isomers prepared as above. *cis*-3-Stilbazole was prepared by the method of Clark[30] and purified by preparative vapor-phase chromatography on a Hewlett-Packard Model 775 gas chromatograph.

In addition to melting points and elemental analyses, the compounds were checked by mass spectra and uv spectra. It is possible to make structural assignments for stilbazole derivatives[30] and stilbene derivatives[32-35] on the basis of their ultraviolet spectra. The band at the lower wavelength is the more intense for *cis*-stilbenes and that at the higher wavelength is more intense for the trans isomer.[30] This relationship holds even for stilbazoles with a cyano substituent on the double bond.[30] Spectral data are listed in Table I.

Benzene and toluene were purified by treatment with sulfuric acid followed by distillation from P_2O_5. Zone-refined benzene (James Hinton) was also used in several experiments. Tetrahydrofuran (Matheson Coleman and Bell) was distilled from lithium aluminum hydride before use. Pyridine and piperidine were left standing several days over potassium hydroxide and then distilled from potassium hydroxide. Ethyl iodide was distilled from silver powder and stored over copper wire. Iodobenzene and *o*-iodotoluene were treated with sodium bisulfite, filtered, then distilled under reduced pressure from silver powder, and stored in the dark. Other solvents (except spectrograde solvents) were purified by distillation before use. Azulene (Aldrich Chemical Co.) was vacuum sublimed twice before use. *p*-Benzoquinone (Columbia Chemical Co.) was twice sublimed. Benzophenone was zone refined from James Hinton. Other materials were used as received.

Photoisomerization Studies. Isomerization quantum yields were obtained by irradiating samples degassed and sealed in Pyrex ampoules. The ampoules were made from 13 × 100 mm lipless Pyrex test tubes with standard taper ground-glass joints fused at the top for connection to the vacuum line. The solutions were degassed by three or more cycles of freeze–pump–thaw on a vacuum line and sealed at a final pressure of approximately 10^{-5} mm. The solutions were irradiated with a Hanovia 450-W medium-pressure mercury lamp in a merry-go-round apparatus.[36] The following Corning glass filters were used to isolate the desired mercury emission lines: 405- and 436-nm lines, 5-58 and 3-74 filters; 546-, 577-, and 579-nm lines, 4-97 and 3-70 filters; 366-nm line, 0-52 and 7-37 filters. The intensity of exciting light was measured by potassium ferrioxalate actinometry.[37] The extent of cis-trans isomerization was determined by vapor-phase chromatography on either a Perkin-Elmer 881 or a Hewlett-Packard Model 5754 gas chromatograph, both with flame ionization detectors. The following columns were used: 8 ft × $^1/_8$ in., 5% SE-30 on Chromosorb G; 10 ft × $^1/_8$ in., 10% SE-30 on Chromosorb G; 6 ft × $^1/_8$ in., 10% W-98 on Chromosorb G. For determination of quantum yields isomerizations were carried to less than 10% conversion. Duplicate analyses were made in all cases, and many were done in triplicate.

Flash Spectroscopic Studies. Absorption spectra and lifetimes of the metalloporphyrin triplets were determined using a transient absorption spectrometer previously described.[9] Corning glass filters could be interposed between the flash lamp and the sample or between the monitoring lamp and the sample to isolate desired spectral bands. The samples were placed in cylindrical quartz cells 2.5 cm long and 2-cm i.d. A side arm attached to the cell led to an ampoule in which the samples were prepared and sealed off from the vacuum line. Solutions were degassed by several cycles of freeze–pump–thaw and sealed at a final pressure of less than 10^{-5} Torr. For measurements above room temperature the cell was placed in an insulated brass heating block with windows in the bottom and sides to admit light from the flash lamp and monitoring lamp. First-order rate constants for triplet decay (k_d) were obtained from plots of the log of the oscilloscope deflection at time t after an arbitrary time t_0 after the flash *vs.* t. Triplet lifetimes (τ) were calculated as $\tau = 1/k_d$.

Measurements of triplet decay constants were made using very dilute (*ca.* 1×10^{-6} *M*) solutions of metalloporphyrin to ensure uniform production of triplets throughout the cell. The exciting light from the flash was limited to $\lambda > 510$ nm with a Corning 3-69 filter, and the triplet absorption at $\lambda = 450$–500 nm was monitored; the problem of scattered light from the flash was thus eliminated. The use of very low porphyrin concentrations and relatively weak exciting light resulted in very low concentrations of triplets, which account for the absence of significant bimolecular quenching in the observed triplet decay.[78] Approximate triplet–triplet absorption spectra in the region between the visible and Soret absorption bands of the porphyrin were determined in the following manner. With the monochromator set at some wavelength λ, the initial intensity $V(\lambda,0)$ was recorded; the solution was flashed under the same conditions described above, and the oscilloscope deflection at some time after the flash was recorded. The time base of the oscilloscope was set at very fast time (usually 5 μsec/cm) to produce a flat curve. Similar data were collected at different wavelengths. If the intensity of the flashes is constant and the measurements are taken at the same time t for all wavelengths, a plot of log $V(\lambda,t)/(\lambda,0)$ *vs.* λ gives the relative absorbance of the triplet at different wavelengths. It was found that flashes of relatively uniform intensity (within 10%) could be produced by charging the capacitor in the lamp-firing circuit to the same voltage for each flash and allowing an equal interval of at least 4 min between flashes. The magnitude and time variation of the light intensity of the flash were found to be independent of wavelength in the range 300–600 nm. Total photon dose per flash was approximately 10^{16} photons/cm^2.

Absorption spectra were recorded on either a Cary 14 or a Unicam SP 800B spectrophotometer. Fluorescence spectra were recorded on an Aminco-Bowman or an Hitachi Model MPF-2A spectrophotofluorometer.

Results

Chart I lists structures of the compounds used in this study together with the acronyms used to identify them.

Spectra and Structure of Metalloporphyrin Complexes. The structures of metalloporphyrin complexes with extraplanar ligands have been previously investigated by a variety of techniques.[10,13,39-42] It has been established largely by the use of nmr that pyridine and similar bases bond to the metal by nitrogen such that the pyridine and porphyrin π-electron systems are mutually perpendicular.[39,40] The porphyrin electronic transitions are usually red-shifted and slightly altered upon attachment of extraplanar ligands; the extent of the alteration depends on the metal, the effective size of the ligand, the strength of the ligand–metal bond, and on the number of ligands attached to the metal.[10,12,41-44] However, there is no evidence of classical "conjugation" of porphyrin and ligand π-electron systems since unsaturated ligands such as pyridine produce essentially the same perturbation as saturated

---

(32) L. Crombie, *Quart. Rev., Chem. Soc.*, 6, 101 (1952).

(33) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Ltd., London, 2nd ed, 1957, p 269.

(34) J. F. Codington and E. Mosettig, *J. Org. Chem.*, 17, 1027, 1035 (1952).

(35) Robert S. Mulliken, *J. Chem. Phys.*, 7, 364 (1939).

(36) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

(37) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, 235, 518 (1956).

(38) L. Perkarinen and H. Linschitz, *J. Amer. Chem. Soc.*, **82**, 2407 (1960); H. Linschitz and K. Sarkanen, *ibid.*, **80**, 4826 (1958).

(39) C. B. Storm and A. H. Corwin, *J. Org. Chem.*, **29**, 3700 (1964).

(40) C. B. Storm, *J. Amer. Chem. Soc.*, **92**, 1423 (1970).

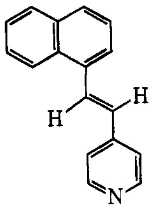
(41) B. D. McLees and W. S. Caughey, *Biochemistry*, 7, 642 (1968).

(42) A. H. Corwin, D. G. Whitten, E. W. Baker, and G. G. Kleinspehn, *J. Amer. Chem. Soc.*, **85**, 3621 (1963).

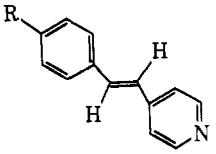
(43) E. W. Baker, M. S. Brookhart, and A. H. Corwin, *ibid.*, **86**, 4587 (1964).

(44) C. B. Storm, A. H. Corwin, R. Arellano, M. Martz, and R. Weintraub, *ibid.*, **88**, 2525 (1966).

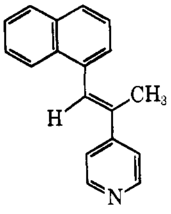
Chart I



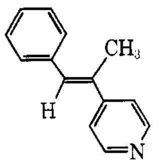
1-(α-naphthyl)-2-(4-pyridyl)ethylene
(NPE)



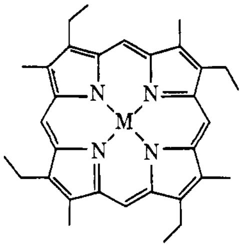
4'-R-4-stilbazole



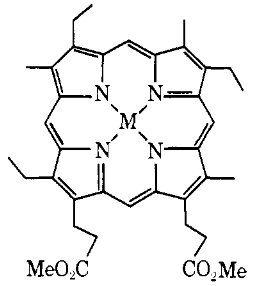
1-(α-naphthyl)-2-(4-pyridyl)propene (NPP)



1-(phenyl)-2-(4-pyridyl)propene
(PPP)



metal etioporphyrin I
(M etio I)



metal mesoporphyrin IX dimethyl ester
(M meso IX)

nitrogen bases (*e.g.*, piperidine or pyrrolidine). For the complexes used in the present study—zinc, magnesium, and cobalt(III) etioporphyrins with substituted 3- and 4-stilbazoles and NPE's as extraplanar ligands—absorption spectra show no evidence for any ground or excited state "conjugation" or delocalization of the porphyrin and extraplanar ligand π systems. The visible and near-ultraviolet (Soret) transitions of the metallophyrin are identical with those of the corresponding pyridine complexes.[12,42,44] Both room-temperature fluorescence and low-temperature total emission spectra of the zinc and magnesium etioporphyrin complexes with azastilbenes are identical with those of the corresponding pyridine complexes.[12] No new emission is observed and there is no quenching of fluorescence or phosphorescence in any case.[45] Triplet-triplet absorption spectra for zinc and magnesium complexes are the same for pyridine as a ligand as for NPE or 4-stilbazole (*vide infra*). From the above evidence the lowest excited singlet and triplet states can be identified as essentially unperturbed localized porphyrin π,π^* states.

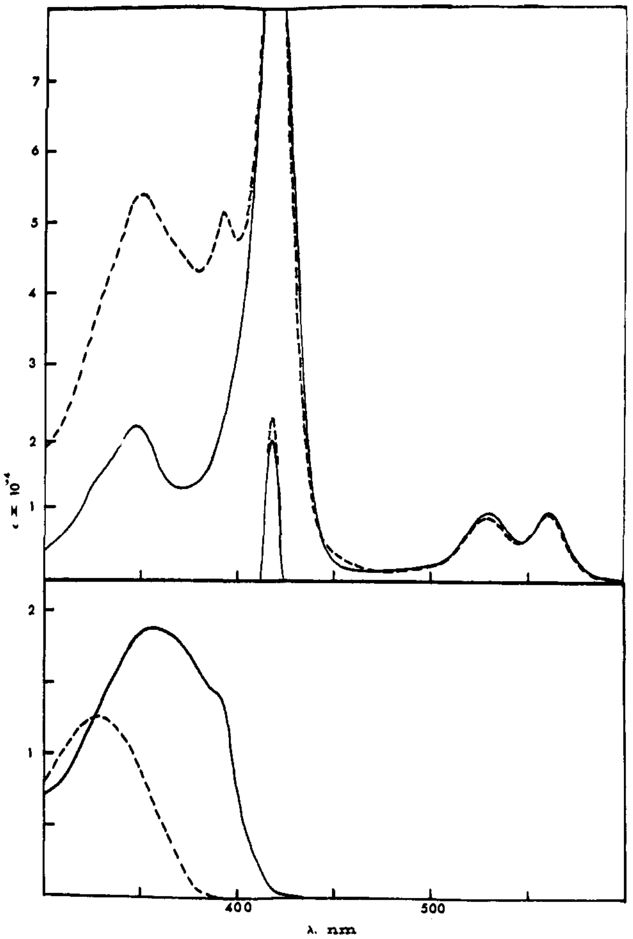


Figure 1. Absorption spectra of Co(III) etio I-*trans*-NPE complexes. Upper trace: (- - -) Co(III) etio I·(pyridine)$_2$Cl, (——) Co(III) etio I·(*trans*-NPE)$_2$Cl. Lower trace: (- - -) "free" *trans*-NPE, (——) Co(III) etio I-bound *trans*-NPE.

Although the porphyrin excited states appear to be little perturbed, it is more difficult to assess what effect complexation produces on excited states of the azastilbenes. As mentioned above, there is no detectable emission from bound azastilbenes. Rapid ligand exchange occurs for both zinc and magnesium porphyrins, and excess ligand is required to ensure complete coordination.[12,39,42,44] Consequently it is impossible to obtain a reliable spectrum of metalloporphyrin-bound azastilbene for these metals. For the trivalent cobalt etioporphyrin I complex, however, exchange is considerably slower and complexes having the structure Co(III) etioporphyrin·(ligand)$_2$Cl can be isolated.[40] Figure 1 compares electronic spectra of Co(III) etio I dipyridinate and Co(III) etio I (*trans*-NPE)$_2$. Figure 1 also compares the spectrum of Co(III) etio-bound *trans*-NPE obtained from spectral subtraction with the spectrum of free *trans*-NPE. The major obvious change in the spectrum of bound *trans*-NPE is a shift in the λ_{max} of the long wavelength transition of the ligand from 331 to 353 nm. The shift in the onset of the transition corresponds to a lowering of the singlet energy, relative to the ground state, on coordination by *ca.* 7 kcal/mol. Shifts for the other azastilbene complexes are listed in Table II. The nmr spectra of Co(III) etio-bound *cis*- and *trans*-NPE and *trans*-NPP are compared with those of the free olefins in Table III. The protons on the pyridyl ring have approximately the

---

[45] Not surprisingly[9] 4'-nitro-4-stilbazole does quench metalloporphyrin fluorescence. Consequently it could not be used in this study.

Table II. λ_{max} for Free and Bound Azastilbenes[a]

Free ligand			Bound ligand		
trans-NPE	*cis*-NPE	*trans*-NPP	*trans*-NPE	*cis*-NPE	*trans*-NPP
331 nm	319 nm[b]	310 nm	348 nm	333 nm[c]	344 nm

[a] Spectra of cobalt complexes in chloroform. [b] Onset at 390 nm. [c] Onset at 410 nm.

Table III. Nuclear Magnetic Resonance Spectra[a]

	Free ligand			Bound ligand		
	trans-NPE	*cis*-NPE	*trans*-NPP	*trans*-NPE	*cis*-NPE	*trans*-NPP
α-Pyridyl	1.38	1.69	1.39	10.00	10.22	10.00
β-Pyridyl	NR	NR	NR	5.19	5.61	5.05
1(H)-Ethylene	NR	NR	NR	4.17	4.47	3.69
	$J = 16$			$J = 16$	$J = 10$	
2(H)-Ethylene	NR	NR		3.37	4.10	
				$J = 16$	$J = 10$	
Methyl			7.92			9.04
α-Naphthyl	2.09	2.60	NR	2.74	2.61	2.93

[a] Spectra in deuteriochloroform obtained with a Varian T-60 or Jeolco A-60 spectrometer with tetramethylsilane as internal standard. The chemical shifts are reported as τ values or NR if not resolvable. The coupling constants are given in cps.

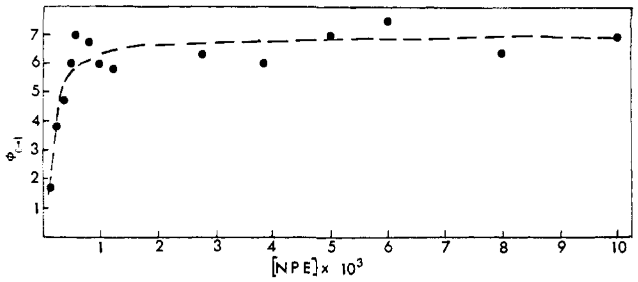


Figure 2. Quantum yield for the zinc etio I sensitized cis to trans isomerization of NPE as a function of NPE concentration.

same chemical shifts as those reported for bound pyridine,[40] the protons on the ethylene are shifted to moderately higher τ values, and naphthyl protons of the bound ligands are relatively little shifted upfield.

Photoisomerization Studies with Zinc and Magnesium Porphyrin Complexes of Stilbazoles and NPE. Results of initial photoisomerization studies for azastilbene complexes of zinc and magnesium porphyrins are summarized in Table IV. Degassed benzene solutions generally 5×10^{-5} M in porphyrin and 5×10^{-3} M in azastilbene were irradiated with light absorbed only by the porphyrin long-wavelength transitions; identical results were obtained with light absorbed either by porphyrin visible bands or by the near-ultraviolet (Soret) band. As Table IV shows, the azastilbenes, particularly NPE, undergo surprisingly efficient cis to trans isomerization, whereas stilbene, which does not coordinate to the metalloporphyrin, undergoes relatively inefficient isomerization. The isomerization quantum yields were found to vary slightly from one set of samples to another, presumably due to small differences in efficiency of degassing, solvent purity, etc. Therefore, comparisons are drawn between samples prepared at the same time and under identical conditions. Values in Table IV are averages for at least five experiments (each sample in triplicate) and for many more runs in the case of Zn etio I-NPE. Isomerization of the azastilbene was the only detectable photoreaction in degassed benzene solutions, even on prolonged irradiation. The photoisomerization of NPE is first order in light intensity and shows a very slight increase in efficiency with temperature over the range 20–60°. In one series, for example, temperatures and ($\Phi_{c\to t}$) values were 30° (6.2), 40° (6.5), and 50° (7.1) for benzene solutions 5×10^{-5} M in zinc etio I and 5×10^{-3} M in *cis*-NPE. As Figure 2 indicates, cis → trans quantum yields for zinc etio I-NPE in benzene increase with [NPE] up to a concentration of *ca.* 5×10^{-4} M. From 5×10^{-4} M to 1×10^{-2} M (the highest concentrations studied) the quantum yields remain nearly constant. At concentrations of NPE below 5×10^{-4} M, two porphyrin absorption peaks were observable, indicating the presence of significant amounts of uncomplexed porphyrin. Consequently for concentrations where the zinc porphyrin is totally in the form of the NPE complex, $\Phi_{c\to t}$ is constant.

Table IV. Photoisomerization of Olefins in Metalloporphyrin Complexes[a]

Porphyrin[b]	Olefin[c]	$\Phi_{c\to t}$	$\Phi_{t\to c}$	Photostationary state
Zn etio I	Stilbene	0.01	0.001	
Zn etio I	4-Stilbazole	0.4	0.001	99% trans
Zn etio I	NPE	6.6 ± 1	0.2	96% trans
Zn meso IX	NPE	6.6 ± 1		96% trans
Mg etio I	4-Stilbazole	0.17		99% trans
Mg etio I	NPE	3 ± 1		95% trans

[a] Degassed benzene solutions irradiated at 25–28° with 405- and 436-nm light. [b] 5×10^{-5} M. [c] 5×10^{-3} M.

The efficient cis to trans isomerization of NPE with zinc etio I is quenched by a variety of materials. As data in Table V indicate, the isomerization is quenched efficiently by substances having low-lying excited triplets at concentrations where there is no detectable quenching of zinc etio I fluorescence. The isomerization efficiency is also lowered by addition of moderate quantities of pyridine or piperidine, bases which would be expected to complete with NPE for metalloporphyrin coordination sites. Similar results were obtained in experiments with zinc etio I and 4-stilbazole. The efficiency of isomerization was also found to be strongly solvent dependent; Table VI lists comparative values for experiments with zinc meso IX and NPE.

In order to test some mechanistic hypotheses (*vide infra*), several substituted 3- and 4-stilbazoles were pre-

Table V. Zinc Etio I Sensitized Photoisomerization of Azastilbenes in the Presence of Quenchers[a] and Nitrogen Bases[b]

Olefin	"Quencher"	$\Phi_{c\to t}$
cis-NPE	None	7
cis-NPE	0.5 *M* pyridine	0.4
cis-NPE	6 *M* pyridine[c]	1
cis-NPE	4 *M* pyridine[d]	2
cis-NPE	10^{-4} *M* azulene	0.7
cis-NPE	10^{-4} *M* quinone	0.1
cis-NPE	10^{-4} *M* tetracene	0.2
cis-4-Stilbazole	None	0.4
cis-4-Stilbazole	0.5 *M* pyridine	<0.001
cis-Stilbene	None	0.01
cis-Stilbene	0.5 *M* pyridine	0.005

[a] Degassed benzene solutions irradiated at 25–28° with visible light, concentrations 5×10^{-5} *M* zinc etio I and 5×10^{-3} *M* in olefin. [b] Solution prepared as described[a] but irradiated with 405–408- and 436-nm light. [c] 50% pyridine. [d] 40% piperidine.

Table VI. Photoisomerization of Zinc Mesoporphyrin IX Dimethyl Ester–NPE Complexes[a]

Solvent	$\Phi_{c\to t}$	Photo-stationary state
Benzene	7	96% trans
Tetrahydrofuran[b]	0.9	90% trans
Acetonitrile	0.8	95% trans
Ethanol	0.1	95% trans
N-Methylformamide[c]	0	97% trans

[a] Solutions were 5×10^{-5} *M* in porphyrin and 5×10^{-3} *M* in olefin. [b] Absorption spectra showed incomplete coordination of the metalloporphyrin in tetrahydrofuran. [c] Results in this solvent are difficult to interpret; NPE absorbs strongly in the region 400–450 nm in *N*-methylformamide.

pared. In each case photoisomerization studies with the substituted stilbazoles led to qualitatively similar results;[45] $\Phi_{c\to t}$ was much greater than $\Phi_{t\to c}$ and prolonged irradiation led to stationary states of >90% trans. Cis–trans isomerization was the only detectable reaction upon irradiation into the zinc or magnesium porphyrin long-wavelength transitions. As data in Table VII indicate, initial isomerization efficiencies vary widely for the substituted stilbazoles with 4′-cyano-4-stilbazole having the highest isomerization yield for both porphyrins.

Table VII. Substituent Effects on the Metalloporphyrin-Sensitized Photoisomerization of Stilbazoles[a]

Porphyrin	Olefin	$\Phi_{c\to t}$
Zn etio I	4-Stilbazole	0.46
Zn etio I	4′-Methyl-4-stilbazole	0.83
Zn etio I	4′-Chloro-4-stilbazole	1.33
Zn etio I	4′-Methoxy-4-stilbazole	3.1
Zn etio I	4′-Cyano-4-stilbazole	6.7
Zn etio I	3′-Cyano-4-stilbazole	0.3
Zn etio I	3-Stilbazole	0.1
Mg etio I	4-Stilbazole	0.19
Mg etio I	4′-Methyl-4-stilbazole	0.22
Mg etio I	4′-Chloro-4-stilbazole	0.29
Mg etio I	4′-Methoxy-4-stilbazole	0.28
Mg etio I	4′-Cyano-4-stilbazole	1.8
Mg etio I	3′-Cyano-4-stilbazole	0.10

[a] Degassed benzene solutions; [zinc etio I] = 5×10^{-5} *M*, [stilbazole] = 5×10^{-3} *M*, irradiated at 25–28° with 405–436-nm light.

Photoisomerization Studies with Zinc Etio and α-Methylated Azastilbenes. In addition to the stilbazoles and NPE, zinc and magnesium etioporphyrin sensitized isomerization experiments were carried out with 1-(α-naphthyl)-2-(4-pyridyl)propene [NPP] and 1-(phenyl)-2-(4-pyridyl)propene [PPP], azastilbenes having a methyl group in place of one of the ethylenic hydrogens. It has been previously demonstrated that α-methyl-substituted stilbenes probably have only a single energy minimum which occurs for a twisted geometry, intermediate between cis and trans, for both excited singlets and triplets.[16,46,47] Since the photochemistry of NPP and PPP had not been previously investigated, it was necessary to carry out some preliminary experiments before proceeding with the porphyrin studies. Benzene solutions 5×10^{-3} *M* in PPP and 5×10^{-2} *M* in benzophenone were irradiated for relatively long exposures at 366 nm; similar samples containing, in addition, 0.01 *M* azulene were also irradiated. The photostationary state obtained starting with either *cis*- or *trans*-PPP was 41% cis; no other products were obtained. The presence of azulene had no effect on the photostationary state composition. For NPP we were unable to confirm that there is no "azulene effect" on the photosensitized reaction. Irradiation of solutions containing benzophenone and NPP at 336 nm leads to formation of unidentified yellow photoproducts. Presumably these arise from excited singlets of NPP since both isomers have appreciable absorption at this wavelength.

As data in Table VIII reveal, irradiation of solutions of zinc etio I with NPP or PPP led to dramatically different results from those obtained for NPE or the stilbazoles. The cis → trans efficiencies are markedly lower and the photostationary states are considerably richer in cis isomer for both NPP and PPP.

Table VIII. Photoisomerization of Zinc Etio I Complexes of α-Methylated Azastilbenes[a]

Olefin[b]	$\Phi_{c\to t}$	$\Phi_{t\to c}$	Photo-stationary state
NPP	0.4	0.2	31% cis
PPP	0.1	0.05	30% cis

[a] Degassed benzene solutions irradiated at 25–28° with 504- and 436-nm light; [zinc etio], 5×10^{-5} *M*. [b] Concentration, 5×10^{-3} *M*.

Photoisomerization of Cobalt(III) Etioporphyrin–NPE Complexes. Substitution of cobalt(III) for zinc or magnesium leads to rather different results for the photoisomerization of metalloporphyrin–NPE complexes. When 5×10^{-5} *M* cobalt(III) etio I is irradiated in degassed benzene solution in the presence of 5×10^{-3} *M* *cis*- or *trans*-NPE, very inefficient isomerization in either direction is observed ($\Phi \leq 0.002$) and a photostationary state cannot be obtained in any reasonable period of irradiation. Interestingly, irradiation of cobalt(III) etio I with *trans*-NPE does lead eventually to production of up to 2–3% *cis*-NPE. The observed

---

(46) For example no fluorescence is observed from low viscosity solutions of *trans*-α-methylstilbene or similarly substituted stilbene derivatives,[47] and no azulene effect[16] is observed in triplet sensitization of α-methylstilbene.[14]

(47) S. Sharafy and K. A. Muszkat, *J. Amer. Chem. Soc.*, **93**, 4119 (1971); D. Geglou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 3907 (1968).

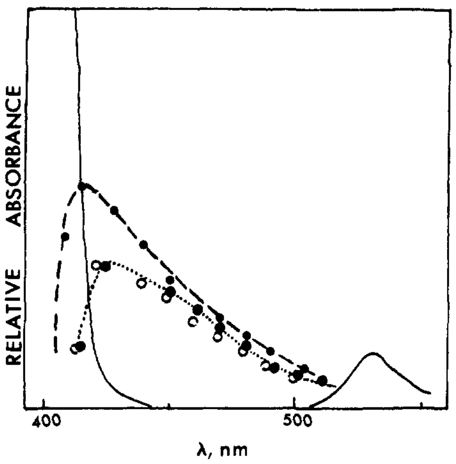


Figure 3. Singlet–singlet (——) and triplet–triplet (●, - - -) absorption spectra of zinc etio I in benzene. (····) Triplet–triplet absorption spectrum for zinc etio I-pyridine (○) and zinc etio I-*cis*-NPE (◉).

results are not surprising since cobalt(III) porphyrin complexes are relatively exchange-inert[40,48] and the lifetimes of excited singlet and triplet states of the cobalt porphyrin are indicated to be very short.[10] Irradiation of previously isolated cobalt(III) etio complexes with visible light does lead to very inefficient isomerization in both directions. Interestingly, it was found that the cobalt(III) complexes of *cis*-NPE could be prepared conveniently by treatment of cobalt(II) etio with *cis*-NPE in the presence of air and NaCl without accompanying *cis*- to *trans*-NPE isomerization.[49]

Flash Photolysis Studies. Flash photolysis of degassed solutions of zinc or magnesium porphyrins leads to transients absorbing strongly in the 400–500-nm region. These have previously been identified by Linschitz and coworkers[38] as the metalloporphyrin triplets. In the present study solutions 1×10^{-6} *M* in zinc or magnesium etio I were carefully degassed and then flashed at room temperature. No permanent changes occurred in the porphyrin spectrum; absorption spectra and lifetimes obtained after several flashes were identical with those obtained initially. Approximate triplet–triplet absorption spectra, calculated from difference spectra, are shown in Figure 3, together with ground-state absorption. The magnitude of the triplet–triplet absorption relative to the ground state singlet–singlet absorbance and the position of $\lambda_{\max}$ for the triplet–triplet transition are only approximate because of uncertainty in the extent of conversion to triplet caused by the flash. A minimum conversion of 50–60% for complexed porphyrin and 60–70% for uncomplexed porphyrin was determined by assuming a triplet absorption of zero at the point of maximum bleaching at ground-state absorption. The curves shown were calculated by arbitrarily assuming a conversion 10% greater than the minimum. Our calculated triplet–triplet absorption spectra are very similar to those reported by Linschitz, *el al.*, for zinc tetraphenylporphyrin and several other porphyrins and metalloporphyrins.[38] Triplet–triplet absorption spectra of metalloporphyrins are generally most intense between the visible and Soret bands of the porphyrin ground-state absorption spectrum. Transients produced by oxidation of metalloporphyrins such as zinc and magnesium octaethylporphyrin also absorb in the range 400–500 nm but these species generally have more intense bands in the far-red and ultraviolet regions.[50] Although a detailed investigation of these regions of the spectrum was not made, a check of several points in the range 350–400 nm showed that the transient absorption there was less intense than in the 400–450-nm range. Because of the similarity of our results to previously reported triplet–triplet absorption measurements for metalloporphyrins, we believe the transient is most likely the porphyrin triplet rather than a cation or other species.

Although the triplet–triplet absorption curves are approximate, it is noteworthy that the pyridine and NPE complexes show nearly identical behavior. Since the absorption and fluorescence of the pyridine and NPE complexes are the same, it is probably reasonable to assume that the extent of conversion to triplet is the same for these two samples. Consequently, as noted above, there appears to be little or no conjugative delocalization in the excited triplet state of the complexed metalloporphyrins. The conclusion is further supported by the finding that the difference spectrum for the piperidine complex is nearly identical with those for the pyridine and NPE complexes. The triplet–triplet absorption of magnesium etioporphyrin I is similar to that of zinc etioporphyrin I. Spectra for the magnesium porphyrin complexes were not determined, but triplet absorption observed at several wavelengths were very similar to those observed for the zinc complexes.

Addition of pyridine to zinc etioporphyrin I causes a small red shift in the triplet–triplet absorption (Figure 3); as mentioned above an identical spectrum is obtained when *cis*- or *trans*-NPE is added to zinc etio I. All of the azastilbenes investigated in this study gave similar results; spectra nearly identical with those of the pyridine complex were recorded and no new transients absorbing in other regions could be detected.

Table IX lists triplet lifetimes, τ, and $k_d = 1/\tau$ values for zinc and magnesium etioporphyrin I under various conditions. It has been shown that metalloporphyrin triplets decay according to the equation, $-dT^*/dt = k_1[T^*] + k_2[T^*]^2 + k_3[T^*][G] + \Sigma k_i[Q_i][T^*]$, where $[T^*]$ is the concentration of triplets, [G] is the concentration of porphyrin ground-state molecules, and $[Q_i]$ is the concentration of any triplet quenchers present in the solution.[38] In our experiments, however, the very low concentration of porphyrin used, *ca.* 10^{-6} *M*, and the relatively weak exciting flash resulted in such low concentrations of triplets that the second-order term was negligible, and the decay followed good first-order kinetics: $k_d = k_1 + k_3[G] + \Sigma k_i[Q_i]$. Addition of pyridine to benzene solutions of zinc or magnesium etio I caused an increase in triplet lifetime. Interestingly, triplet lifetimes were identical, within experimental error, for pyridine and NPE complexes of both metalloporphyrins. Azulene and quinone, which were found to quench NPE isomerization (*vide supra*), were also found to be efficient quenchers of metalloporphyrin triplets. Although addition of NPE and the various

---

(48) C. A. DeRosier, unpublished results.

(49) M. Tsutsui, R. A. Velapoldi, L. Hoffman, K. Suzuki, and A. Ferrari, *J. Amer. Chem. Soc.*, **91**, 3337 (1969).

(50) J. H. Fuhrhop and D. Mauzerall, *ibid.*, **91**, 4174 (1969).

Table IX. Flash Spectroscopic Study of Metalloporphyrin Complexes

Sample[a]	Quencher	Temp, °C	Lifetime, μsec	k_d, sec^{-1}	k_g, l. mol^{-1} sec^{-1}
Zn etio		25	200	5×10^3	
Zn etio–10^{-4} *M* pyridine		25	475	2.1×10^3	
Zn etio–*cis*-NPE[b]		25	480	2.1×10^3	
Zn etio–10^{-2} *M* piperidine		25	420	2.4×10^3	
Zn etio–*cis*-NPP[b]		27	73	13.7×10^3	
Mg etio		25	60	17×10^3	
Mg etio–10^{-4} *M* pyridine		25	150	6.7×10^3	
Mg etio–*cis*-NPE[b]		25	150	6.7×10^3	
Zn etio–*cis*-NPE[b]	4.3×10^{-6} *M* azulene	25	70		3×10^9
Zn etio–*cis*-NPE[b]	3.7×10^{-6} *M* quinone	25	25		1×10^{10}
Zn etio–2% pyridine in ethanol		25	147	7×10^3	
Zn etio–1% pyridine in acetonitrile		25	35	3×10^4	
Zn etio–1% pyridine in *N*-methylformamide		25	160	6×10^3	

[a] Degassed benzene (except in the last three cases) solutions, 10^{-6} *M* in porphyrin. [b] Olefin concentration, 5×10^{-3} *M*.

4-stilbazoles did not produce any quenching of the zinc etio I triplet, addition of either of the α-methylated azastilbenes, NPP or PPP, did shorten the porphyrin triplet lifetime. Table IX includes data for the lifetime of the zinc etio I triplet in several solvents. A temperature study of the triplet lifetime in the presence of pyridine, NPE, and NPP is listed in Table X.

Table X. Temperature Dependence of Triplet Decay Rates of Zinc Etio Complexes[a]

Ligand	Temp, °C	$k_d \times 10^{-3}$
Pyridine	26	5.1[b]
Pyridine	40	6.7
Pyridine	60	9.1
cis-NPE	28	6.4
cis-NPE	37	7.3
cis-NPE	50	8.0
cis-NPE	70	10.5
cis-NPP	27	13.7
cis-NPP	38	17.8
cis-NPP	62	23.5

[a] Degassed samples 10^{-6} *M* in porphyrin; the same sample was used for different temperatures; the near-room temperature value was the same in each case before and after the temperature study. [b] This value is somewhat higher than the average value listed in Table IX.

Discussion

The results of the present investigation are surprising in several respects. First of all, the measurement of quantum yields substantially greater than unity for the cis to trans isomerization of several azastilbenes (note especially NPE and 4′-cyano-4-stilbazole) was unanticipated. That photoreaction of an extraplanar ligand could occur without causing deactivation or apparent modification of the (energy-donor) porphyrin excited states was also unexpected and even more startling in view of the observed efficiency of reaction. Nevertheless from both fluorescent studies and the flash spectroscopic investigations (Figure 3 and Table IX) it is clear that the only transients observed are excited states of the porphyrin and that these are neither quenched nor apparently altered by the azastilbene ligands. The excited singlet state of the porphyrin can be excluded as the immediate precursor of the isomerization since isomerization can be sharply reduced (Table V) by quenchers without affecting fluorescence. In contrast, there is good correlation between triplet quenching from the flash studies and quenching of ligand isomerization (Tables V and IX) suggesting that the metalloporphyrin triplet is the precursor to isomerization. The fact that uncoordinated olefins do not isomerize efficiently (Tables IV, V) and that bases which can compete with the azastilbenes for coordination sites retard isomerization indicates that the isomerization is initiated by an intramolecular process.

The observation of quantum yields greater than unity for NPE cis to trans isomerization appears to preclude a simple mechanism involving triplet energy transfer from porphyrin to NPE followed by isomerization of the azastilbene triplet concurrent with decay to the ground state. The strong preference for forming the trans isomer of NPE and other azastilbenes suggests the possibility that the photoreaction could merely provide a mechanism for establishing cis–trans equilibrium for the azastilbenes. A possible mechanism for the photoisomerization which would not involve energy transfer is an ion chain process (eq 1–4), where MP =

$$\text{MP–L} \xrightarrow{h\nu} (\text{MP–L})^{1*} \xrightarrow{k_{isc}} (\text{MP–L})^{3*} \quad (1)$$

$$(\text{MP–L})^{3*} \longrightarrow \text{MP}^{+} + \text{L}^{-} \quad (2)$$

$$\text{L}^{-} \rightleftharpoons \text{L}'^{-} \quad (3)$$

$$\text{L}'^{-} + \text{L} \longrightarrow \text{L}' + \text{L}^{-} \quad (4)$$

metalloporphyrin, L = cis ligand, and L′ = trans ligand. The ion-chain process would seem reasonable since it has been well established that excited metalloporphyrins can serve as good electron donors to a variety of acceptors including electron-deficient olefins.[9,51–53] In addition, it has been demonstrated that radical anions of olefins such as stilbene undergo fairly rapid isomerization resulting in cis–trans equilibrium.[54–56] However, it is possible to exclude an ionic path for the isomerization on several grounds. The

---

(51) K. P. Guinlan, *J. Phys. Chem.*, 72, 1797 (1968), and earlier references.

(52) 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).

(53) J. K. Roy and D. G. Whitten, *J. Amer. Chem. Soc.*, 93, 7093 (1971).

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

(55) R. Dietz and M. E. Peover, *Discuss. Faraday Soc.*, 45, 154 (1968).

(56) J. W. Happ, J. A. Ferguson, and D. G. Whitten, *J. Org. Chem.*, 37, 1485 (1972).

fact that flashing benzene–zinc etio I-NPE solutions leads to no shortening of the porphyrin triplet lifetime and to no detectable new transients would indicate that an ion-chain process with the observed quantum efficiency would have a rather long chain length. A path involving generation of free ions and any kind of reasonable chain length in a nonpolar solvent such as benzene seems at best unlikely. Irradiation of benzene–zinc etio I-NPE solutions or even benzene–zinc etio I-quinone solutions in an esr cavity leads to no detectable signals under conditions where ethanol–zinc etio I-quinone solutions give a strong well-resolved spectrum.[57,58] The observed solvent (Table VI) and substituent (Table VII) effects appear to offer convincing arguments against an ionic process. Increase in solvent polarity causes only a slight reduction in the porphyrin triplet lifetime and no evident lowering of the triplet yield. Although an ionic process would be expected to be much more efficient in polar media than in benzene, quantum efficiencies for isomerization decrease as solvent polarity increases.[59] Both electron-donor substituents, such as methyl and methoxyl, and electron-acceptor substituents, such as chloro and cyano, enhance isomerization efficiency relative to unsubstituted 3- and 4-stilbazole. While the reasons for the variation in isomerization efficiency are uncertain, it is difficult to reconcile these results in terms of the mechanism outlined in eq 1–4. Although a slightly modified mechanism involving isomerization *via* an exciplex could be considered,[6,53] the evidence regarding substituent effects and the flash spectroscopic results disfavor such a mechanism.

In our initial communication[1a] we suggested that the observed results could be described as a photocatalysis accounted for by eq 1, 5, and 6. Equation 5 would involve isomerization of the ligand without loss of excitation energy; this coupled with ligand exchange during the excited state lifetime (eq 6) would allow absorption of one quantum of light to result in several isomerizations.

$$(\text{MP-L})^{3*} \rightleftarrows (\text{MP-L}')^{3*} \qquad (5)$$

$$(\text{MP-L}')^{3*} + \text{L} \rightleftarrows (\text{MP-L})^{3*} + \text{L}' \qquad (6)$$

Previous fluorescence studies have indicated that ligand exchange is very rapid for excited singlets of zinc and magnesium; rates are indicated to be very near diffusion controlled for magnesium etio I-pyridine and only slightly slower for zinc etio I complexes.[12] Consequently, during the relatively long triplet lifetimes ligand-exchange rates are expected to be such that 10^3–10^4 exchanges should occur. Clearly such rapid exchange, coupled with eq 5, makes the latter path reasonable. The obvious question arising from the photocatalysis scheme is how (in eq 5) isomerization can occur without deactivation of the porphyrin triplet, especially since the spectroscopic studies indicate insignificant delocalization of porphyrin triplet states to the ligand.

Although we dismissed a simple triplet energy-transfer mechanism followed by excitation decay concurrent with isomerization, a path involving *reversible* energy transfer can in fact explain the results. In this mechanism triplet energy transfer from porphyrin to azastilbene could be followed by isomerization of the azastilbene excited state, reverse energy transfer to regenerate the porphyrin triplet and isomerized (ground state) azastilbene, and finally ligand exchange without decay (eq 6). If the porphyrin and azastilbene are treated as separate chromophores (which appears justified from spectral evidence), the azastilbene excited triplets can be regarded as upper excited states of the metalloporphyrin–azastilbene complex. Population of azastilbene excited triplets would require an activation energy of several kilocalories per mole and although the equilibrium concentration of "ligand" excited triplets might be too small to detect, energy transfer from the porphyrin triplet could be rapid compared to radiationless decay. Several cases of activated energy transfer to upper excited states have recently been demonstrated. For example, excited singlets of heavy metal complexes of porphyrins[60,61] and benzophenone[62] can be thermally populated from the corresponding triplets so that at room temperature in solution both delayed fluorescence and phosphorescence are observed. Lamola[63] and Wagner[64] have reported phosphorescence spectra from molecules with closely spaced triplet levels which indicate in each case that the lowest triplets are in equilibrium and that the equilibrium constant follows the relationship

$$K_{\text{eq}} = e^{-\Delta E/RT} \qquad (7)$$

where ΔE is the energy separation between triplets.

Application of the above equation to the metalloporphyrin–azastilbene complexes indicates that porphyrin and azastilbene triplets should be in equilibrium. The metalloporphyrin triplet energy is 40–42 kcal/mol.[12] The energy of the olefin triplet state is not precisely known, but since photosensitized isomerization experiments with all the olefins reported using biacetyl (triplet energy 53–55 kcal/mol)[16,65] as sensitizer result in photostationary states of >90% cis, we can say that for all these compounds $E(\text{triplet})_{\text{trans}} < 53$ kcal/mol $< E(\text{triplet})_{\text{cis}}$. An assignment of triplet energies on this basis may be somewhat uncertain since it has been reported that ketonic sensitizers can effect isomerization of alkenes *via* a mechanism which does not involve triplet energy transfer.[66] Nevertheless, ketonic sensitizers such as benzophenone and biacetyl give the same results as nonketonic sensitizers of similar triplet energy in the isomerization of stilbene,[16] so our conclusion is probably justified. We attempted to measure the triplet energy of *trans*-4-stilbazole and *trans*-NPE by observing ${}^1\text{T} \leftarrow \text{S}$ absorption in *o*-iodotoluene solution. For both compounds we obtained a figure of 50 kcal/mol, but the absorption was very weak and the energy value is therefore somewhat uncertain. If we assume an energy separation $\Delta E = 8$ kcal/mol between the

---

(57) R. A. White and G. Tollin, *J. Amer. Chem. Soc.*, **89**, 1253 (1967); A. K. Bannerjee and G. Tollin, *Photochem. Photobiol.*, **5**, 315 (1966); G. Tollin, K. K. Chaterjee, and G. Green, *ibid.*, 4, 593 (1965).

(58) This does not eliminate the possibility of formation of very low concentrations of ions since the upper limit of detection is 10^{-7}–10^{-8} *M*.[9]

(59) Zinc mesoporphyrin IX dimethyl ester was used in these experiments due to its increased solubility in polar solvents.

(60) J. B. Callis, M. Gouterman, Y. M. Jones, and B. H. Henderson, *J. Mol. Spectrosc.*, **39**, 410 (1971).

(61) G. W. Sovocool and D. G. Whitten, unpublished results.

(62) J. Saltiel, *et al.*, *J. Amer. Chem. Soc.*, **92**, 410 (1970).

(63) A. A. Lamola, *ibid.*, **92**, 5045 (1970).

(64) P. J. Wagner, M. J. May, A. Haug, and D. R. Graber, *ibid.*, **92**, 5269 (1970).

(65) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

(66) N. C. Yang, J. I. Cohen, and A. Shani, *ibid.*, **90**, 3264 (1968); J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

triplet states in the complex, eq 7 yields $K_{eq} = 1.6 \times 10^{-6}$ for the equilibrium constant at 300°K and predicts $k_{et} = 1 \times 10^{7}$ sec^{-1} for the rate constant for energy transfer from the porphyrin triplet to the *trans*-azastilbene triplet. The calculated equilibrium concentration of azastilbene triplets is so low that it is not surprising that they are not detected in flash experiments. Nevertheless, the calculated rate constant for the energy transfer is high enough that olefin triplet states may be expected to be formed during the lifetime of the porphyrin triplet ($\tau = 5 \times 10^{-4}$ sec).

The situation with the metalloporphyrin-*cis*-azastilbene complex is more complicated. Biacetyl sensitization experiments indicate that E(triplet)$_{cis}$ is greater than 53 kcal/mol; the triplet energy of *cis*-stilbene has been reported as 57 kcal/mol.[16,19] Energy transfer from porphyrin triplet to *cis*-azastilbene might be much slower than energy transfer to trans, and the equilibrium concentration of *cis*-azastilbene triplets should be very low ($K_{eq} = 10^{-11}$ for $\Delta E = 15$ kcal/mol). An equilibrium involving *cis*-azastilbene triplets is probably unrealistic, however, since triplet states of cis isomers of stilbene-like olefins rapidly relax to a twisted geometry.[16,17,19] As mentioned previously, the possibility of excitation of *cis*-azastilbenes directly to a distorted triplet (Figure 4) could lower ΔE considerably.

For stilbene,[16,17,19,67] as well as several of the azastilbenes,[14] it has been shown that the excited triplet surface as a function of angle of rotation about the double bond has either two energy minima as indicated in Figure 4 or a single broad minimum intermediate between trans and twisted geometry. Substances such as azulene, having lower triplet energies than *trans*-stilbene, can selectively quench stilbene triplets to the trans ground state by energy transfer.[16,67] In the present case population of azastilbene triplets should be rapidly followed by quenching of the azastilbene triplet selectively to the trans ground state with regeneration of the porphyrin triplet. By operation of such an intramolecular "azulene effect" of the complexed porphyrin, efficient sensitized cis to trans isomerization can occur without depletion of the sensitizer (porphyrin) triplet.[68,69] The sequence of reactions for the reaction scheme outlined above is summarized in eq 1, 6, and 8–12.

$$^{3}\text{MP*–L} \xrightarrow{k_{et}} \text{MP–}^{3}\text{L}'^{*} \tag{8}$$

$$\text{MP–}^{3}\text{L}'^{*} \xrightarrow{k_r} \alpha\text{MP–L}' + (1 - \alpha)\text{MP–L} \tag{9}$$

$$\text{MP–}^{3}\text{L}'^{*} \xrightarrow{k_i} {}^{3}\text{MP*–L}' \tag{10}$$

$$^{3}\text{MP*–L}' + \text{L} \xrightarrow{k_e} {}^{3}\text{MP*–L} + \text{L}' \tag{6}$$

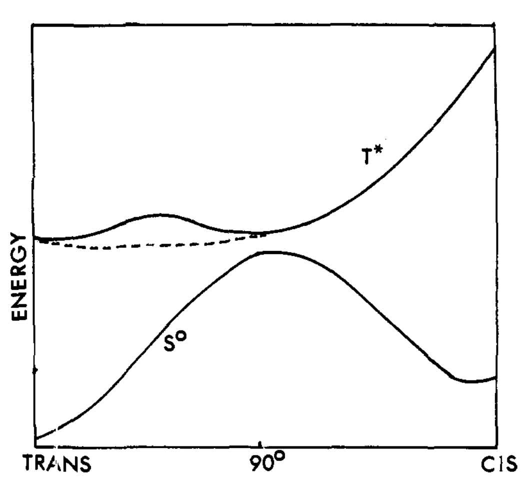


Figure 4. Probable singlet and triplet energy surfaces for stilbene and the azastilbenes.

$$^{3}\text{MP*–L} \xrightarrow{k_d} \text{MP–L} \tag{11}$$

$$^{3}\text{MP*–L}' \xrightarrow{k_{d'}} \text{MP–L}' \tag{12}$$

Making the usual steady-state approximations for intermediates and assuming $k_d = k_d'$, the scheme gives the following expression for $\Phi_{c\rightarrow t}$

$$\Phi_{c\rightarrow t} = \frac{k_{et}(k_d + k_e[\text{L}])(k_i + \alpha k_r)\Phi_{isc}}{(k_d + k_e[\text{L}])(k_i + k_r)(k_{et} + k_d) - k_e[\text{L}]k_i k_{et}} \tag{13}$$

where Φ_{isc} = the quantum yield for intersystem crossing of the metalloporphyrin.

We have previously established that $k_e[\text{L}] \gg k_d$, and with the additional assumption that $k_i \gg k_r$, eq 13 reduces to eq 14.

$$\Phi_{c\rightarrow t} = k_{et}\Phi_{isc}/k_d \tag{14}$$

Energy transfer from olefin triplet to metalloporphyrin triplet (eq 10) would be expected to have no activation energy so from absolute rate theory a predicted value $k_i = 6.25 \times 10^{12}$ sec^{-1} at 25° is obtained. The decay rate constant for stilbene triplets has been estimated as about 1×10^{8} sec^{-1}.[67] Assuming a similar rate for triplet decay of the bound azastilbenes, the assumption $k_i \gg k_r$ seems reasonable. As long as the assumptions are valid, eq 14 predicts that $\Phi_{c\rightarrow t}$ should be independent of light intensity and independent of azastilbene concentration as is observed provided the azastilbene concentration is high enough to ensure complete conversion of the metalloporphyrin to the complexed form.

According to the scheme described above, the trans-rich photostationary states obtained with 4-stilbazole and NPE are a consequence of selective quenching of the olefin triplet to trans ground state by the metalloporphyrin. As previously indicated, the result is rationalized by assuming a triplet energy surface for these olefins similar to that for stilbene (Figure 4) with an energy minimum close to trans. As a test of the proposed scheme, we prepared and investigated the behavior of *cis*- and *trans*-PPP and *cis*- and *trans*-NPP, methylated derivatives of 4-stilbazole and NPE which are not expected to have energy minima near the transoid triplet.[16,17,19] These olefins would be expected to

---

(67) J. Saltiel, *ibid.*, **90**, 6394 (1968); **89**, 1036 (1967).

(68) Saltiel has recently suggested that activated energy transfer from a low-energy donor to *cis*-stilbene could be followed by reverse energy transfer within the encounter cage resulting in reaction without depletion of sensitizer triplet and a chain process.[69] In intermolecular cases,[69] the observed effect is modest due to diffusion; the present case is therefore a particularly dramatic example because the donor and azastilbene are held together long enough for reverse energy transfer to dominate other processes. Although ligand exchange is rapid (*vide supra*), under reaction conditions the porphyrin is ~100% complexed and reverse energy transfer [$k_i > 10^{12}$ sec^{-1}] should occur prior to ligand exchange.

(69) M. Wrighton, L. Metts, and J. Saltiel, Abstracts, Joint Conference of the Chemical Institute of Canada and the American Chemical Society, Toronto, Canada, 1970, ORGN 48.

have only a single energy minimum of twisted or near-perpendicular geometry as has been observed[16,17] for 1,2-diphenylpropene (α-methylstilbene). Azulene has no effect on the sensitized photoisomerization of 1,2-diphenylpropene and we find similar behavior for PPP. According to the above scheme we would expect that with metalloporphyrin complexes of PPP and NPP, selective quenching to trans with regeneration of the porphyrin triplet should not occur; consequently $\Phi_{c\rightarrow t}$ should not exceed unity and the photostationary state should be richer in cis. As predicted, the zinc etioporphyrin I sensitized photoisomerization of NPP and PPP is markedly different from that of NPE and 4-stilbazole. In both cases $\Phi_{c\rightarrow t}$ is much lower, the stationary state is richer in cis, and addition of NPP or PPP to solutions of zinc or magnesium etio I is accompanied by a reduction in the porphyrin triplet lifetime.

Since $\Phi_{c\rightarrow t}$, k_d, and Φ_{isc} are measurable quantities eq 14 allows calculation of k_{et}, the rate constant for the activated energy transfer from the porphyrin triplet to the cis-olefin triplet. The free energy of activation for the energy transfer can then be calculated from absolute rate theory. Φ_{isc} is estimated to be 0.9 for zinc etio I in benzene based on measurements of Gurinovich, *et al.*[70,71] Using $\Phi_{isc} = 0.9$, $k_d = 2 \times 10^3$ sec^{-1} and $\Phi_{c\rightarrow t} = 7$, we obtain $k_{et} = 1.6 \times 10^4$ sec^{-1}. This corresponds to $\Delta G^{\ddagger} = 11.8$ kcal/mol from absolute rate theory. The zinc etio I–NPP system offered a convenient check on the use of eq 14 to calculate k_{et} for zinc etio I–NPE. The triplet energy of *cis*-NPP is not expected to be very different from that of *cis*-NPE. However, since triplet energy transfer from zinc etio I to *cis*-NPP is expected to be irreversible, k_{et} for the transfer to *cis*-NPP can be calculated from the reduced triplet lifetime (Table IX). The calculated value, $k_{et} = 1 \times 10^4$ sec^{-1}, is in good agreement with the above value for transfer to *cis*-NPE.

Equation 14 can also be used to calculate k_{et} for the magnesium complexes. Assuming $\Phi_{isc} \approx 0.9$ we obtain $k_{et} = 2.2 \times 10^4$ sec^{-1}; as expected, this value is very close to the value for zinc etio I. The solvent effects listed in Table VI can be at least partly explained with the present mechanism on the basis of reduced triplet lifetimes (Table IX);[72] calculated values of k_{et} for the solvents listed in Table VI are in the range 0.1–3 $\times$ 10^4 sec^{-1}.

Studies of the temperature dependence of isomerization and energy transfer reveal that reaction 8 requires a surprisingly low activation energy. Isomerization quantum yields for zinc etioporphyrin I-*cis*-NPE show very little increase with temperature (*vide supra*); an Arrhenius plot for k_{et} can be obtained from eq 14 after correcting for the measured small increases in k_d with temperature (Table X). An Arrhenius plot (correlation coefficient 0.99) so obtained gives $E_a = 3.2$ kcal/mol; using $\Delta G^{\ddagger} = 11.8$ kcal/mol, we obtain $\Delta S^{\ddagger} = -31$ eu. From k_{et} for zinc etioporphyrin I-*cis*-NPP we obtain an Arrhenius activation energy of 2.5 kcal/mol and from the preexponential term a value of $\Delta S^{\ddagger} = -34$ eu.

The low Arrhenius activation energies indicate that energy transfer to a cis-olefin triplet with energy >53 kcal/mol is not important. The high negative entropy of activation is in accord with the various interpretations of energy transfer to yield a distorted triplet. One attractive possibility is that energy transfer occurs only when thermal activation of the ground-state "cis" olefin results in specific semitwisted configurations.[19] Since the olefin has many vibrational degrees of freedom, such specific geometries would have fairly small probabilities, resulting in the high negative entropy of activation. The high negative entropy of activation might also be rationalized in terms of specific donor–acceptor interactions or by a scheme such as Bylina has proposed[18] where the $\Delta S^{\ddagger}$ term would reflect the low Franck–Condon factor for the transition to a distorted acceptor triplet. Little is known about the temperature dependence of k_{et} and the magnitude of $\Delta S^{\ddagger}$ for related intermolecular processes[17,69] and therefore it is not immediately clear whether the observed large negative $\Delta S^{\ddagger}$ will prove to be a general phenomenon or one peculiar to this system. However, examination of the situation regarding intramolecular energy transfer from zinc etio to *trans*-NPE suggests that the intramolecular system may be a good model for intermolecular energy transfer and that the large negative $\Delta S^{\ddagger}$ is due to acceptor properties rather than to other factors such as the orientation of donor and acceptor within the complex.

Photocatalytic formation of trans is not completely effective, particularly for NPE where the photostationary state composition is 4% cis, so it is possible to look more closely at the photoisomerization from trans to cis. In terms of the model which we have suggested, we might expect $\Delta S^{\ddagger}$ for the energy tranfer from porphyrin triplet to *trans*-NPE or *trans*-4-stilbazole to be very small, and $\Delta G^{\ddagger}$ for that process should be close to $\Delta H^{\ddagger}$ for the energy transfer to the cis olefin. Because of the very low percentage of cis isomer formed at the photostationary state, it is very difficult to measure $\Phi_{c\rightarrow t}$ accurately. However, knowing $\Phi_{c\rightarrow t}$ and the photostationary state composition, we can calculate $\Phi_{t\rightarrow c}$. For zinc etio I photosensitized isomerization in benzene, we obtain for NPE $\Phi_{t\rightarrow c} = 0.3$ and for 4-stilbazole, $\Phi_{t\rightarrow c} = 0.004$. These are in fairly good agreement with the measured values of 0.2 and 0.001 listed in Table IV.

The reaction sequence for conversion of trans to cis is described below.

$$\mathrm{MP\text{–}L'} \xrightarrow{h\nu} {}^1\mathrm{MP^*\text{–}L'} \longrightarrow {}^3\mathrm{MP^*\text{–}L'} \tag{1a}$$

$${}^3\mathrm{MP^*\text{–}L'} \underset{k_i}{\overset{k'_{et}}{\rightleftharpoons}} \mathrm{MP\text{–}{}^3L'^*} \tag{8a}$$

$$\mathrm{MP\text{–}{}^3L'^*} \xrightarrow{k_r} \alpha\mathrm{MP\text{–}L'} + (1-\alpha)\mathrm{MP\text{–}L} \tag{9}$$

$${}^3\mathrm{MP^*\text{–}L'} \xrightarrow{k'_d} \mathrm{MP\text{–}L'} \tag{12}$$

Making the usual steady-state approximations, we obtain the expression in eq 15 for Φ_{t-c}. We have

$$\Phi_{t-c} = \frac{(1-\alpha)k_r k'_{et}\Phi_{isc}}{k_i k'_d + k_r k'_{et} + k_r k'_d} \tag{15}$$

already discussed approximate values for k_d, Φ_{isc}, and k_i ($k_d = 2 \times 10^3$ sec^{-1}, $\Phi_{isc} = 0.9$, $k_i = 6.25 \times 10^{12}$ sec^{-1} at 300°K). For purposes of discussion we can

---

[70] G. P. Gurinovich, A. I. Patsko, and A. N. Sevchenko, *Dokl. Phys. Chem.*, 174, 402 (1967).

[71] B. Dzhagarov, *Opt. Spektrosk.*, 28, 66 (1970).

[72] However, other factors could be involved in the solvent effect; for example, rates of exchange and coordination equilibria may be dramatically altered in certain of the solvents.[10,39–44]

assume a value for k_T similar to that estimated by Saltiel[67] for stilbene triplet decay of $k_T = 1 \times 10^8$ sec^{-1}. The decay ratio, α, for 4-stilbazole is 0.5, and we can assume a similar value for NPE. Using these numbers eq 15 gives $k'_{et} = 2.5 \times 10^6$ sec^{-1} for energy transfer to *trans*-4-stilbazole and $k_{et}' = 1.1 \times 10^8$ sec^{-1} for energy transfer to *trans*-NPE. Absolute rate theory then gives $\Delta G^{\ddagger} = 9.3$ kcal/mol for 4-stilbazole and 6.0 kcal/mol for NPE. If there is no activation energy for triplet energy transfer beyond ΔE, the energy difference between the porphyrin triplet and the olefin triplet, these figures predict a triplet energy of 49–51 kcal/mol for *trans*-4-stilbazole and 46–48 kcal/mol for the triplet of *trans*-NPE; these values are very close to those expected by analogy to the case of stilbene. The fact that $\Delta G^{\ddagger}$ for energy transfer to *trans*-NPE exceeds $\Delta H^{\ddagger}$ for energy transfer to *cis*-NPE seems at first puzzling, since we have assumed that the azastilbene triplet is one state (or at least that the twisted and trans forms are nearly isoenergetic with a minimal barrier between them) and that activation of trans should have $\Delta G^{\ddagger} \sim \Delta H^{\ddagger}$. However since the *trans*-NPE ground state is more stable than the *cis*-NPE ground state, there is a 2–3 kcal/mol difference for the stilbenes,[73] such that activation to the triplet minimum from *cis*-NPE should require less energy than from *trans*-NPE by several kilocalories per mole.

From the calculated energies involved in the respective activation processes, we can conclude that energy transfer from porphyrin to complexed azastilbene yields a common excited triplet (or equilibrating, nearly isoenergetic triplets). Excitation of trans evidently yields a transoid triplet with little change in geometry; however, excitation of cis must involve a severe change in geometry or "nonvertical" process producing an excited state *at least* 8 kcal/mol lower in energy than the "spectroscopic" or cisoid excited state. Although the present results do not permit conclusions regarding the mechanism of nonvertical triplet energy transfer, the unravelling of the thermodynamic parameters provided by the intramolecular system gives a more complete and rather dramatic picture of the process and its potential.

Acknowledgment. We thank the U. S. Public Health Service (Grant No. GM 15,238) for support of this work.

---

[73] G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc. B*, 1156 (1968).

Synthesis of (±)-Prostaglandin E_1, (±)-11-Deoxyprostaglandins E_1, $F_{1\alpha}$, and $F_{1\beta}$, and (±)-9-Oxo-13-*cis*-prostenoic Acid by Conjugate Addition of Vinylcopper Reagents[1]

Francisco S. Alvarez,* Douglas Wren, and Anthony Prince

Contribution No. 405 from the Syntex Research Institute of Organic Chemistry, Palo Alto, California 94304.

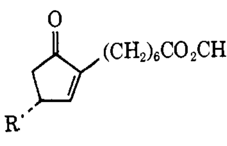
Received May 11, 1972

Abstract: The syntheses of (±)-PGE$_1$ and (±)-11-deoxyprostaglandins in the E$_1$ and F$_1$ series have been carried out by conjugate addition of bis(triethyl phosphite)copper(I) cyanide vinyllithium to the substituted cyclopentenones **1a** and **1b**, and subsequent elaboration of vinylamylcarbinol side chain *via* the intermediate carboxaldehydes **3b** and **3d**. The intermediate **3d** was also converted to (±)-9-oxo-13-*cis*-prostenoic acid (**6c**). These transformations are characterized by high yields and ease of operation.

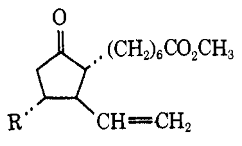
The synthesis of prostaglandins has been the subject of considerable synthetic effort during the past several years. In the course of this work a number of elegant syntheses of prostaglandins have been developed, but, in general, these approaches are lengthy and rather complex in nature.[2]

We now wish to report the synthesis of (±)-PGE$_1$ and (±)-deoxyprostaglandins which are characterized by ease of operation and high yields.

The basis of our work was the hypothesis that conjugate addition of a vinylcopper reagent to an enone such as **1a** would provide the vinylated cyclopentenone **2a** with the correct steric configuration at the three asymmetric centers of the cyclopentenone ring. (Chiral compounds are not resolved. Only one enantiomer is depicted by the structures.) This stereochemistry was expected to be a result of addition of the vinyl species to the less hindered side of the 4-oxygenated cyclopentenone **1a** and protonation of the resultant enolate to give the thermodynamically more stable trans arrangements of the alkyl and vinyl groups.[3]



1a, R = OTHP
1b, R = H
1c, R = OH
1d, R = OAc



2a, R = OTHP
2b, R = H

---

(1) Studies in Prostaglandins. IX. For part VIII see P. Crabbe, *Res. Prostaglandins*, 1 (4), 5 (1972).

(2) For recent reviews see: *Ann. N. Y. Acad. Sci.*, **180** (1971); J. E. Pike, *Fortschr. Chem. Org. Naturst.*, **28**, 313 (1971).

(3) The preparation of γ,δ-unsaturated ketones *via* conjugate addition of bisvinyl(tri-*n*-butylphosphine)copper lithium to cyclohexenones has been reported by J. Hooz and R. B. Layton, *Can. J. Chem.*, **48**, 1626