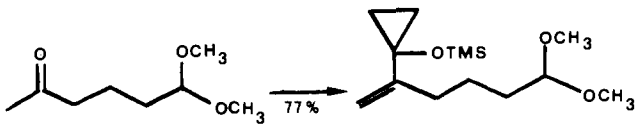
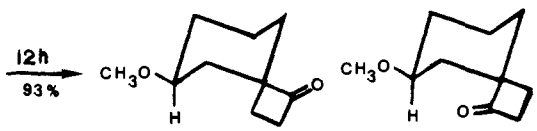
the compatibility of isolated double bonds as present in the acetal **13**.

The excellent efficiency of this new alkylation reaction (77–95% isolated yields) suggested the possibility of an intramolecular version. The keto acetal **15** was converted to the requisite vinylcyclopropanol silyl ether **16** in standard fashion in 77% yield. Exposure to a catalytic amount of **3** gave the cyclized product as a 67:33 mixture of **17**[8] and **18**[8]. The stereochemical assignment



15 **16**

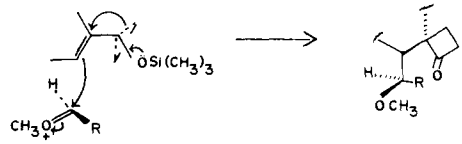


17 **18**

erythro/threo 67/33 (7)

rests upon the higher field shift for the methine proton in **18** due to the shielding by the carbonyl group (**17** 3.5, tt, J = 10.5, 4Hz; **18** 3.08, m) and the higher field for the ^{13}C shift of an axial compared to an equatorial carbonyl group (**17** 213.96; **18** 212.69).[9]

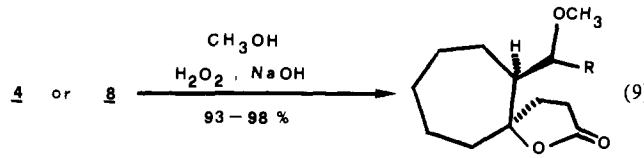
The juxtaposition of the trimethylsiloxy, cyclopropyl, and olefin groups into a composite functional group can be viewed as an extended enol silyl ether. In particular, the delocalization of additional electron density by the trimethylsiloxy group into the olefin is mediated by the cyclopropyl ring. Thus, by analogy to reaction of enol silyl ethers with acetals, an extended orientation as depicted in eq 8 would be expected. The stereochemistry



(8)

predicted by this model indeed corresponds to the major observed product in each case with selectivities as high as 8:1. The special reactivity associated with this type of composite functional group is illustrated by the failure of simple olefins to react under these conditions.

The further utility of this concept for stereocontrolled vicinal trialkylation of ketones derives from the reactivity of a cyclobutanone. For example, basic hydrogen peroxide transforms the cyclobutanones into γ-butyro lactones **19**[8] (eq 9).[11] A chemo-



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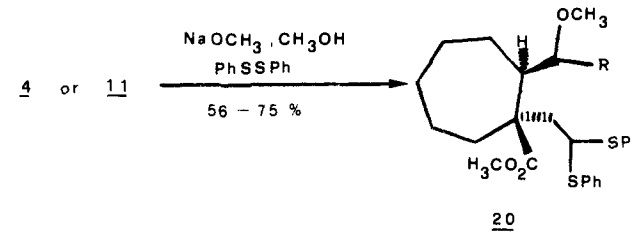
(9)

selective seco-sulfenylation[12] to **20**[8] provides clean chemodifferentiation of all three alkyl groups (eq 10). In the case of **11**, the primary ester is selectively demethylated by the liberated thiophenoxide to give the acid **20b** as the product, which was esterified with trimethylchlorosilane in methanol[13] to **20c**. This simple



20

(10)

method for the stereocontrolled introduction of three different alkyl groups into ketones and aldehydes as summarized in eq 1 offers great flexibility for further elaboration.

Acknowledgment. We thank the National Sciene Foundation and the General Medical Sciences of the National Institutes of Health for their generous support of our programs. The Italian CNR provided partial support for A.B. (NATO fellowship).

Registry No. 1, 91239-03-1; **2**, 39834-33-8; **3**, 27607-77-8; **4**, 91239-04-2; **5**, 91279-99-1; **6**, 91280-00-1; **7**, 91280-01-2; *erythro*-**8**, 91239-05-3; *threo*-**8**, 91280-02-3; **9**, 23068-91-9; **10**, 39834-29-2; *erythro*-**11**, 91239-06-4; *threo*-**11**, 91280-03-4; *erythro*-**12**, 91239-07-5; *threo*-**12**, 91239-08-6; **13**, 14152-71-7; *erythro*-**14**, 91239-09-7; *threo*-**14**, 91280-04-5; **15**, 36727-63-6; **16**, 91239-10-0; **17**, 91239-11-1; **18**, 91239-12-2; **19a**, 91239-13-3; *erythro*-**19b**, 91326-47-5; *threo*-**19b**, 91239-18-8; **20a**, 91239-14-4; *erythro*-**20b**, 91239-15-5; *threo*-**20b**, 91280-05-6; *erythro*-**20c**, 91239-16-6; *threo*-**20c**, 91280-06-7; *n*-$C_5H_{11}CH(OCH_3)_2$, 1599-47-9; $CH_3COC_6H_{13}$-*n*, 111-13-7; octahydro-1-pentalenone, 28569-63-3; *cis*-1-[1-[(trimethylsilyl)oxy]cyclopropyl]-3,3a,4,5,6,6a-hexahydropentalene, 91239-17-7.

Supplementary Material Available: Characterization data for **4**, **5**, **8**, **11**, **12**, **14**, **17**, and **18** (3 pages). Ordering information is given on any current masthead page.

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Photoinduced Electron Transfer in *meso*-Triphenyltriptycenylporphyrin–Quinones. Restricting Donor–Acceptor Distances and Orientations

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Porphyrins possessing covalent linkages to quinones have become increasingly important in the study of photoinduced electron-transfer reactions.[1] Most of these models possess flexible linkages

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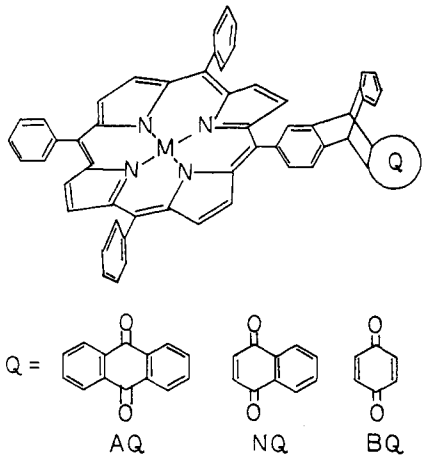

Figure 1. Structure of TPPAQ, TPPNQ, and TPPBQ (M = H_2) and ZnTPPAQ, ZnTPPNQ, and ZnTPPBQ (M = Zn).

between the porphyrin electron donor and the quinone electron acceptor which allow both the distance and the orientation between the donor and the acceptor to vary widely. This variability often leads to serious problems in interpreting the results of photochemical studies of these models. Studies of model systems possessing well-defined donor–acceptor distances and geometries are necessary to fully understand the critical role of these parameters in determining the efficiency of photoinduced charge separation. To facilitate such studies we have synthesized the three new porphyrin–quinone models illustrated in Figure 1. The center-to-center donor–acceptor distances as determined from space-filling molecular models are 10, 10.5, and 11 Å, for TPPBQ, TPPNQ, and TPPAQ, respectively.[2] Moreover, the π electronic system of the porphyrin maintains a minimum 6–7-Å edge-to-edge separation with that of the quinone, which greatly diminishes direct overlap of the π electronic system of the donor with that of the acceptor.[3] Electron-transfer processes involving radical ion to neutral and photoinduced reactions in molecules possessing very little donor–acceptor π–π overlap have recently been reported in non-porphyrin-containing systems.[4] These studies indicate that rapid exothermic electron transfer can occur over distances of >10 Å.

The porphyrin–quinones were prepared as follows: 2-anthraldehyde,[5] benzaldehyde, and pyrrole were refluxed in propionic acid[6] to yield after chromatography 25% *meso*-(2-anthracenyl)-triphenylporphyrin. The resultant porphyrin was refluxed in xylene with a 5-fold excess of benzoquinone to yield TPPBQ, 40%: mass spectrum (^{252}Cf fission fragment), m/z calcd 820.3, found 820.2.[7] Diels–Alder addition of naphthoquinone to anthracene and in situ oxidation of the corresponding adduct with an excess of naphthoquinone led to the bicyclic naphthoquinone. This naphthoquinone was alkylated with dichloromethyl methyl ether by using $AlCl_3$ in 1,2-dichloroethane.[8] Hydrolysis during workup yielded the 2-aldehyde, 30%. Porphyrin synthesis as above resulted in TPPNQ, 15%: mass spectrum, m/z calcd 870.38, found 870.5. Triptycene was acylated with phthalic anhyride by using $AlCl_3$ in 1,2-dichloroethane, 90%. The resulting keto acid was treated with polyphosphoric acid at 150 °C over night to form the bicyclic anthraquinone, 23%. Alkylation with dichloromethyl methyl ether as above yielded the 2-aldehyde, 34%. Porphyrin synthesis as above yielded TPPAQ, 18%: mass spectrum, m/z calcd 920.3, found 920.7. The respective Zn derivatives were prepared by refluxing the free base porphyrins in chloroform containing excess $ZnOAc_2$.

Table I. Energetics

compd	$E_{1/2}$,[a] V	$E_{1/2}$,[a] V	ΔE, V	$\Delta U = \Delta E - E_S$,[b] V
TPPAQ	1.05	−0.82	1.87	−0.02
TPPNQ	1.05	−0.55	1.60	−0.29
TPPBQ	1.05	−0.37	1.42	−0.47
ZnTPPAQ	0.82	−0.82	1.64	−0.43
ZnTPPNQ	0.82	−0.55	1.37	−0.70
ZnTPPBQ	0.82	−0.37	1.19	−0.88

[a] Determined by cyclic voltammetry at a Pt disk electrode. Half-wave potentials are vs. SCE. Data obtained in DMF/0.1 M tetra-*n*-butylammonium perchlorate at 20 °C. [b] The energy of the lowest excited singlet state of TPP is 1.89 V and that of ZnTPP is 2.07 V.[10]

Table II. Fluorescence Quantum Yields

compd	toluene	CH_2Cl_2	butyronitrile
TPP	0.11[a]	0.14	0.137
TPPAQ	0.128	0.119	0.138
TPPNQ	0.092	0.001	<0.001
TPPBQ	0.013	<0.001	<0.001
ZnTPP	0.03[a]	0.023	0.03
ZNTPPAQ	0.031	0.002	0.001
ZnTPPNQ	<0.001	<0.001	<0.001
ZnTPPBQ	<0.001	<0.001	<0.001

[a] The measured values are relative to these absolute values taken from ref 10. All samples were 10^{-7} M in a 1-cm path length cell. Excitation wavelengths: free bases = 515 nm, Zn derivatives = 549 nm.

One-electron redox potentials of these molecules are presented in Table I. The redox potentials of both the porphyrins and the polycyclic quinones are not altered by linking the two molecules. The sum of the one-electron oxidation potential and the one-electron reduction potential for each molecule, ΔE, yields an estimate of the free energy of the hypothetical radical ion pair state. The difference between this energy and the energy of the lowest excited singlet state of the porphyrin yields an estimate of the exothermicity, ΔU, of the electron-transfer reaction in the solvent in which the data were obtained.[9]

The ground-state optical absorption spectra and fluorescence emission spectra of the porphyrins are not perturbed by the presence of the appended quinones and are typical of TPP and ZnTPP.[10] However, the fluorescence quantum yields of these compounds diminish dramatically when ΔU becomes more negative as a result of changes in donor and acceptor redox potentials and/or an increase in the dielectric constant of the medium (Table II). The fluorescence data suggest that electron transfer is the efficient nonradiative decay pathway that depletes S_1 in these molecules.

We have obtained additional evidence supporting the electron-transfer quenching mechanism in the case of ZnTPPNQ from picosecond transient absorption and fluorescence measurements.[11] The remaining molecules are currently under investigation. The fluorescence lifetime of ZnTPPNQ in toluene is <50 ps, while that of ZnTPP is 2.0 ns as measured by the time-resolved photon-counting technique.[12] The ZnTPPNQ fluorescence lifetime measurement is instrument limited. These numbers are consistent with the observed >30-fold difference in fluorescence quantum yield of the two compounds and indicate further that the radiative decay rate of S_1 is similar in both compounds.

(2) Corey–Pauling–Koltun molecular models.
(3) The small variation is edge-to-edge distance is a result of restricted rotational motion of the hydrocarbon spacer molecule about the meso position of the porphyrin. Dynamic NMR measurements of this rotational barrier show it to be 17–18 kcal/mol. This value is typical for a TPP: Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 3660.
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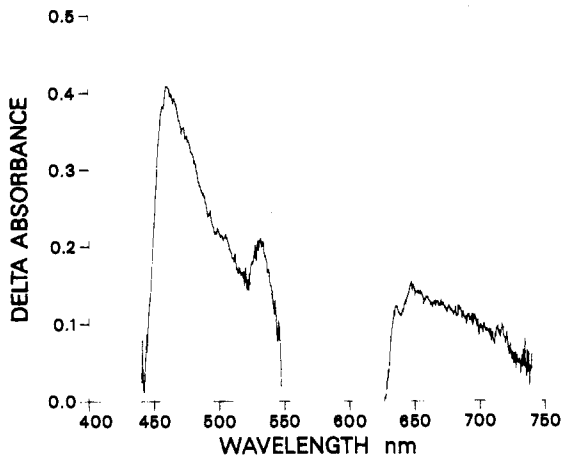

Figure 2. Changes in absorbance of a 2.6×10^{-4} M solution of ZnTPPNQ in toluene/2% pyridine at 100 ps following a 0.6-mJ, 2-ps, 600-nm laser flash. Cell pathlength, 2 mm. Filters that reject stray excitation light cut out the 550–620-nm wavelength region, while the sharp cutoff at 440 nm is due to the intense absorption of the porphyrin Soret band at 419 nm.

The transient absorption spectrum that is observed 100 ps after excitation of ZnTPPNQ in toluene with a 2-ps, 600-nm laser pulse is shown in Figure 2. This transient spectrum possesses single exponential, wavelength-independent rise and decay times of 25 and 370 ps, respectively. The <50-ps lifetime of S_1 in ZnTPPNQ leads us to conclude that the transient we are observing is not an S_1 to S_n absorbance. Measurements of ZnTPPNQ at times >5 ns exhibit no transient absorbance changes, which shows that no long-lived ZnTPP triplet state is formed.

We assign the transient absorption spectrum shown in Figure 2 to the $ZnTPP^+NQ^-$ radical ion pair, since it is very similar to the published spectrum of $ZnTPP^+$.[13] Specifically, the molar extinction coefficient for $ZnTPP^+$ is 3.3×10^4 at 460 nm and 10^4 at 650 nm,[13] while that of NQ^- is 3.2×10^3 at 460 nm and 800 at 650 nm.[14] Thus, the $ZnTPP^+$ spectrum strongly dominates Figure 2.[15] Our evidence is consistent with a simple model in which S_1 decays to a charge-separated state in 25 ps followed by nonradiative decay of this state to ground state in 370 ps.

The quantum yield of $ZnTPP^+NQ^-$ formation was measured. A 2.6×10^{-4} M solution of ZnTPPNQ in toluene was excited with 1.5×10^{15} photons over a sample of volume of 0.015 cm^3. The fraction of the photons absorbed by the sample was determined by measuring the energy of the excitation light incident on the sample and that which passed through the sample. Ignoring the few percent of the photons reflected by the 2-mm path length sample cell, 46% of the photons were absorbed by the sample. Thus, 7.0×10^{14} molecules were excited. The absorbance change in Figure 2 and the molar extinction coefficient for $ZnTPP^+$ at 460 nm yield 5.5×10^{14} $ZnTPP^+NQ^-$ species produced per flash, or a 79% quantum efficiency.

Our results show that *π-stacked geometries are not necessary* for very rapid, efficient electron-transfer quenching of porphyrin singlet states. Moreover, for a given known set of donor–acceptor distances and relative geometries as exemplfied by the series of molecules presented here, photoinduced electron-transfer reactions remain sensitive to both the exothermicity of the electron transfer and the dielectric properties of the medium. A question yet to be addressed is the role of the hydrocarbon spacer as a possible transmission line for the electron transfer.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38.

Supplementary Material Available: NMR and visible spectroscopic data for TPPAQ, TPPNQ, and TPPBQ (2 pages). Ordering information is given on any current masthead page.

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(15) Since ϵ for ZnTPPNQ ground-state absorption is <1000 over the entire wavelength range depicted in Figure 2, the transient difference spectrum shown is a good approximation to the absorption spectrum of the observed transient state.

Book Reviews

Human Biochemistry. By Wilhelm R. Frisell (East Carolina University School of Medicine). Macmillan Publishing Co., Inc., New York. 1982. IX + 845 pp. $35.00.

This textbook has been written for the medical student engaged in his first course in biochemistry, a one-semester course dealing with the fundamentals of human biochemistry. To achieve his stated purpose, the author has made a unitary presentation of human biochemistry within the contexts of the background and of the intended career practices of the first-year medical student-eventually-physician. Since the chemical background of his student is limited while career application is extensive, the text is dominantly verbal, chemical theory and chemical structure being limited to essentials and mechanism non-existent. If the latter are faults, this reviewer does not so consider them in view of the book's purposes; they are to a certain extent remedied by the adequate problem and answer sections of the book.

To achieve a coherent presentation, the author follows a short introductory section entitled General Consideration (Unit I), Part I, Basic Biochemistry (Units II through VII), and Part II, Metabolic Basis of Human Biochemistry (Units VIII and IX). Units II through VII detail the elements of molecular and cellular biochemistry, proteins and their enzymatic function, bioenergetics, carbohydrate metabolism, lipid metabolism, nitrogen metabolism, replication, and expression of genetic information. Units VIII and IX are entitled Compartmentation of Metabolic Activities—Tissue and Organ Interrelationships and Regulation—Balance and Imbalance in Human Metabolism, respectively.

Each unit consists of several chapters, at least, allowing a relatively full exploration of the unit. Unit VIII contains nine chapters, ranging from Chapter 25, Compartmentation of Metabolic Systems and Transmembrane Transport, to Chapter 33, Biochemistry of Vision, with organ and tissue biochemistry in between. Unit IX contains four chapters with topics ranging from metabolic controls to elements of nutrition. Parts I and II are about equal in allotted pages. Part II is particularly well documented with schema, diagrams, structures, and illustrations.

The appendix contains useful physicochemical tables of units and abbreviations, a glossary, as well as a quite complete table, alphabetically arranged, of "normal" ranges of the constituents of body fluids. In addition the appendix contains an answer section to the problems found at the end of each chapter. The answers are informative and instructive and anchor the students' knowledge.

In a textbook of voluminous detail but not of exaggerated length, errors of osmission, in particular, and errors of commission are bound to occur. The reviewer noted several. The equation (page 19) for the oxidative decarboxylation of pyruvic acid lacks oxygen as a reactant; the international unit (IU) of enzyme activity is mentioned but not defined; the tail-to-tail fatty acid membrane model is not depicted; and the use (page 19) of proposed reaction intermediates to model biochemical reactions is questionable. The mitochondrion in its ultrastructure is not depicted except as part of a striated muscle fiber (page 506) and there the label is incorrectly positioned.

This reviewer considers the book within its stated purposes a formidable one, one to be recommended to the usually bright medical student