

another. A positive rotation brings the methyl carbon towards eclipse with N-H, while a negative rotation brings the methyl carbon toward a methylene carbon. All angles are fairly near  $0^\circ$ , except for two near  $120^\circ$  which represent another staggered conformation in which one methyl carbon projects axially from the methylene carbon in a direction opposite from that of the N-H bond. No previous studies of the conformations of  $\text{Et}_3\text{NH}^+$  ions have appeared, and we do not recommend them as ordered positive ions in the studies of structures of the negative ions, unless the location of H atoms is a critical part of the study.

**Acknowledgments.** We wish to thank Dr. M. F. Hawthorne for providing a sample of  $(\text{Et}_3\text{NH})_3\text{B}_{20}\text{H}_{18}\text{NO}$ , Dr. R. L. Lewin for determining the unit cell and space group of this compound, the Office of Naval Research and the Advanced Research Projects Agency for grants supporting this work, and the National Science Foundation for a predoctoral fellowship for C. H. S.

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### Detection of Cyclobutadienocyclopentadienyl Anion

Sir:

In principle, cyclic antiaromatic systems of four  $\pi$  electrons, such as cyclobutadiene, can be stabilized in two ways by fusion to other conjugated rings. Fusion to rings with six  $\pi$  electrons, as in biphenylene, is stabilizing because of diminished bond order in the cyclobutadiene ring even though the over-all system retains  $4n$   $\pi$  electrons.<sup>1</sup> On the other hand, fusion of two  $4n$   $\pi$  electron systems produces a composite with  $4n + 2$   $\pi$  electrons on the periphery; a number of examples are known<sup>2</sup> in which cyclooctatetraene is fused to another  $4n$   $\pi$  electron ring, but the energetic situation for such compounds is not yet completely clear.

The bicyclo[3.2.0]heptatrienyl system is particularly interesting in this regard. The cation Ia, a bridged tropylium ion, is the formal product of fusion of cyclobutadiene and cyclopentadienyl cation; the anion Ib is on its periphery a cycloheptatrienyl anion, but it is also a cyclopentadienyl anion. HMO calculations predict a total  $\pi$  energy of  $8.906\beta$  for both species, and a  $\Delta\text{DE}$  of  $1.918\beta$  for ionization of a covalent bicycloheptatriene (e.g., Ic) to either species. The HMO calculated  $\Delta\text{DE}$  for converting cyclopentadiene to its anion is only  $2.000\beta$ , so Ic should be comparably acidic. As an approach to Ia and Ib we have generated the hydrocarbon Ic. This strained triene is so labile that we have not yet been able to isolate it undimerized, but it has still been possible to demonstrate that the ionization of Ic to the anion Ib is a facile process.

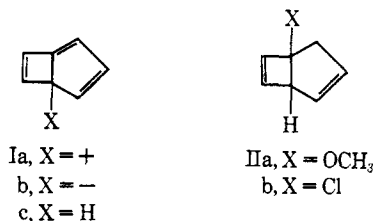
Treatment of 1-methoxybicyclo[3.2.0]hepta-3,6-diene (IIa)<sup>3</sup> with  $\text{BCl}_3$  at  $-75^\circ$  afforded the chlorodiene IIB<sup>4</sup>

(1) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

(2) R. Breslow, W. Vitale, and K. Wendel, *Tetrahedron Letters*, 365 (1965); R. Breslow, W. Horspool, H. Sugiyama, and W. Vitale, *J. Am. Chem. Soc.*, **88**, 3677 (1966); J. Elix, M. Sargent, and F. Sondheimer, *Chem. Commun.*, 509 (1966); G. Schröder and H. Röttele, *Angew. Chem. Intern. Ed. Engl.*, **7**, 635 (1968).

(3) O. L. Chapman and G. W. Border, *Proc. Chem. Soc.*, 221 (1963).

(4) Mass and nmr spectra consistent with the assigned structure.



in 63% yield. On standing for 3 hr at  $25^\circ$  with 0.2  $M$   $\text{KO}-t\text{-Bu}$  in tetrahydrofuran, IIB eliminates  $\text{HCl}$  to produce a dimer of the triene Ic,  $m/e$  180; the nmr data are consistent with a structure derived by 1,4 addition of the cyclopentadiene in Ic to the strained trisubstituted double bond of a second molecule of Ic. Triene Ic can also be trapped as an adduct with diphenylisobenzofuran, present during the base treatment of IIB. The adduct,  $m/e$  360, is from the nmr data a mixture of the two stereoisomers formed by addition across the new strained double bond in Ic.

The same dimer, as well as the adduct with diphenylisobenzofuran, can be prepared by reaction of IIB with  $N$ -bromosuccinimide and dehalogenation of the resulting bromo-IIB<sup>4</sup> with  $\text{Li}(\text{Hg})$  in ether.

Dimerization of Ic is fairly rapid: treatment of a  $5 \times 10^{-4} M$  solution of IIB with 0.1  $M$  potassium  $t$ -butoxide in tetrahydrofuran for 5 min at  $25^\circ$ , followed by neutralization, leads to partial development of a new chromophore,  $\lambda_{\text{max}}$  316 nm, which decays with second-order kinetics,  $t_{1/2} \sim 3$  hr. Assuming that this uv absorption is due to triene Ic, at preparative concentrations it would have a half-life of a few minutes at best. Nonetheless, when the elimination of  $\text{HCl}$  from IIB is performed by stirring with 0.2  $M$   $\text{KO}-t\text{-Bu}$  in 74 ml of tetrahydrofuran and 6 ml of  $t\text{-BuOD}$  for 4 hr at  $25^\circ$ , a 40% yield of the dimer was formed containing 65% of 2.0 D/dimer. The 60% of recovered IIB has no deuterium, and the dimer does not exchange under these conditions. When some dimethyl- $d_6$  sulfoxide is added to the dehydrochlorination mixture the product dimer has 100% of 2.0 D/dimer. The nmr spectrum of deuterated dimer is consistent with dimerization of I ( $X = \text{D}$ ). Apparently hydrocarbon Ic exchanges *via* anion Ib at a rate comparable to its rapid dimerization; while it is difficult to relate this observation to a precise  $\text{p}K_a$  for Ic, it does suggest that the HMO prediction of acidity in Ic is correct.

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### Cations and Cation Radicals of Porphyrins and Ethyl Chlorophyllide a

Sir:

The polarographic oxidation of a variety of porphyrins has been studied in butyronitrile<sup>1</sup> and in methylene chloride.<sup>2</sup> Oxidation proceeds *via* two well-defined one-

(1) A. Stanienda and G. Biebl, *Z. Physik. Chem. (Frankfurt)*, **52**, 254 (1967).

(2) S. W. Feldberg, private communication.

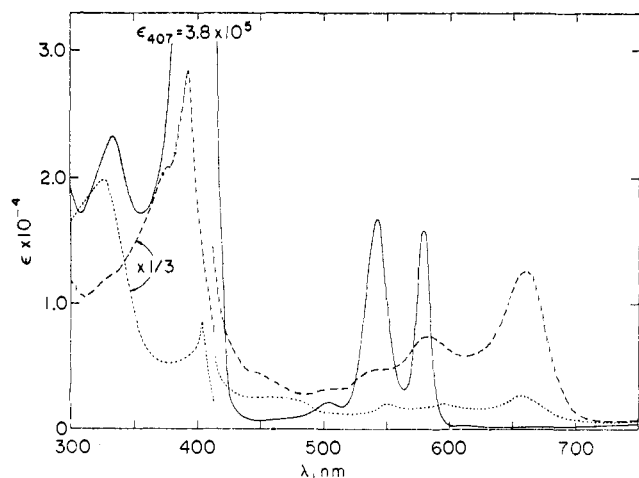


Figure 1. Absorption spectra of MgOEP (—), MgOEP<sup>+</sup> (---), MgOEP<sup>2+</sup> (·····) in CH<sub>2</sub>Cl<sub>2</sub>.

electron abstractions, and cyclic voltammetry showed these reactions to be reversible and the intermediates to be stable. We describe here the electrolytic and chemical preparation of cation radicals of various porphyrins and of ethyl chlorophyllide *a* as well as the formation of the dication of magnesium octaethylporphyrin.

Electrolysis<sup>3</sup> of magnesium octaethylporphyrin (MgOEP) in CH<sub>2</sub>Cl<sub>2</sub> at +0.7 V *vs.* sce (aqueous) yielded a blue-green solution, and the resulting species (principal absorption maxima at 378, 392, 585, and 660 nm; see Figure 1) was shown by coulometry<sup>4</sup> to be the product of a one-electron oxidation. Isosbestic points, observed as the oxidation was followed spectrophotometrically, were indicative of the smooth course of the reaction. ESR measurements on these solutions showed a single line,  $g = 2.0028$ , 2.5 G wide (peak to peak). MgOEP underwent a similar one-electron oxidation when treated with bromine in either methylene chloride or chloroform. The product of the chemical oxidation was spectroscopically similar to the cation radical obtained *via* electrolysis and was stable in these solvents. Our optical and magnetic data are consistent with those of the radical obtained by Fuhrhop and Mauzerall.<sup>5</sup> Because of its absorption spectrum and its stability, these authors have proposed that the MgOEP radical formed in alcohols is a phlorin derived from the solvent. However, the agreement between the calculated<sup>6</sup> and observed electronic absorption spectra of the cation radicals and our observation of their stability in alcohol-free solvents render this proposal unnecessary.

Additional evidence for a simple cation radical in which an electron has been abstracted from the porphy-

(3) Controlled potential electrolyses were performed *in situ*, at platinum electrodes, in either a Cary Model 14 spectrophotometer or a Varian V-4502 esr spectrometer. Methylene chloride solutions of porphyrins ( $\sim 10^{-4}$  M) and electrolyte (0.1 M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>) were purged with argon. Potential plateaus were obtained from ref 1. For esr measurements, the anodic potential was slowly raised until a signal appeared.

(4) Errors in the coulometric data do not exceed 10%.

(5) J. H. Fuhrhop and D. Mauzerall, *J. Am. Chem. Soc.*, **90**, 3875 (1968), have recently reported the one-electron oxidation of magnesium octaethylporphyrin by iodine in alcohols.

(6) Open-shell, restricted Hartree-Fock calculations<sup>7</sup> of the optical and esr spectra of the porphyrin cation radical were performed in the Pariser-Parr-Pople approximation. Calculated transitions are at 371, 398, 724, 740 nm. In the same order, dipole oscillator strengths are 0.032, 1.628, 1.014, 0.018.

(7) J. Fajer, B. H. J. Bielski, and R. H. Felton, *J. Phys. Chem.*, **72**, 1281 (1968).

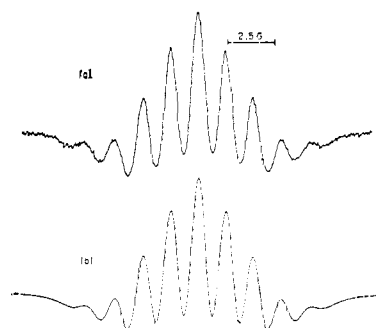


Figure 2. (a) Second-derivative esr spectrum of ZnTPP<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>. (b) Computer-simulated spectrum: 1.22-G line width, Lorentzian line shape, four equivalent nitrogens,  $a_N = 1.43$  G, and eight equivalent protons,  $a_H = 0.24$  G.

rin ring is found in the reversible one-electron oxidation of magnesium and zinc tetraphenylporphyrins (TPP). Thus the partially resolved nine-line esr spectrum of ZnTPP<sup>+</sup> (Figure 2, second derivative presentation) can readily be assigned to four equivalent nitrogens. Hyperfine splitting constants of  $a_N = 1.5$  and  $a_H = 0.25$  G (eight  $\beta$  protons of the pyrroles) were obtained by the SCF-MO calculations described below.<sup>8</sup> A computer-simulated spectrum (Figure 2), based on  $a_N = 1.43$  and  $a_H = 0.24$  G, adequately resembles the experimental data.<sup>8</sup>

Continued electrolysis of MgOEP<sup>+</sup> at +0.9 V *vs.* sce resulted in the removal of an additional electron, and the optical spectrum at this stage is shown in Figure 1. (The esr signal associated with MgOEP<sup>+</sup> decreased during the course of the electrolysis.) Two-electron reduction of this new species regenerated 95% of the initial MgOEP. Addition of MgOEP to the oxidized product re-formed the cation radical in accord with the reaction



Electrolysis of MgTPP<sup>+</sup> and ZnTPP<sup>+</sup> also proceeded to the dication stage. Oxidation of metalloporphyrins, by the methods described, is not limited to group II metals but may be extended to transition metals. Thus cobalt(II) octaethylporphyrin (Co<sup>II</sup>OEP), in chloroform, underwent two distinct one-electron oxidations when treated with bromine. The first step, which required  $0.51 \pm 0.02$  mol of bromine, brought about the oxidation of divalent to trivalent cobalt giving [Co<sup>III</sup>OEP]<sup>+</sup>Br<sup>-</sup>.<sup>9,10</sup> Further oxidation of the trivalent complex used  $0.51 \pm 0.02$  mol of bromine and yielded a green species (Figure 3) formulated as [Co<sup>III</sup>OEP]<sup>2+</sup>2Br<sup>-</sup>. This formulation is supported by the quantitative conversion of the dication according to



The two-electron oxidation stage could also be reached by electrolysis in CH<sub>2</sub>Cl<sub>2</sub>.

The interest shown in the redox products<sup>11</sup> of chloro-

(8) Although the assignments may not be unique because of the incomplete resolution, the experimental spectrum could not be matched without the proton splittings.

(9) [Co<sup>III</sup>OEP]<sup>+</sup>Br<sup>-</sup> was isolated, and recrystallized from methylene chloride-ligroin. Satisfactory elemental analyses and mass spectra were obtained.

(10) The analogous [(etioporphyrin I)cobalt(III)] bromide has previously been reported: A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 2979 (1960).

(11) (a) A. Stanienda, *Z. Physik. Chem.* (Leipzig), **229**, 257 (1965); (b) K. Seifert and H. T. Witt, *Naturwissenschaften*, **55**, 222 (1968).

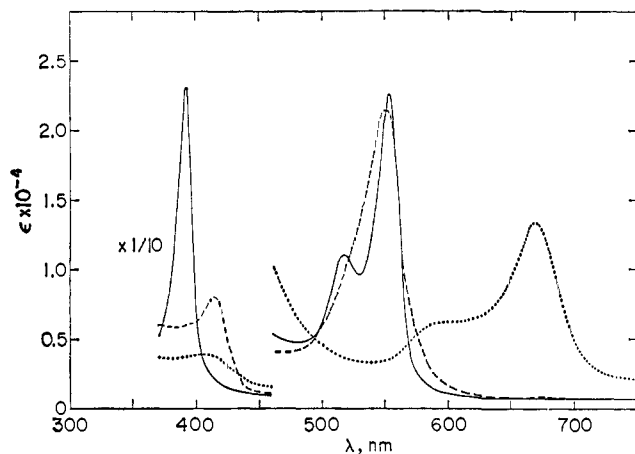


Figure 3. Absorption spectra of CoOEP (—),  $[\text{Co}^{111}\text{OEP}]^+\text{Br}^-$  (---), and  $[\text{Co}^{111}\text{OEP}]^{2+}2\text{Br}^-$  (.....) in  $\text{CHCl}_3$ .

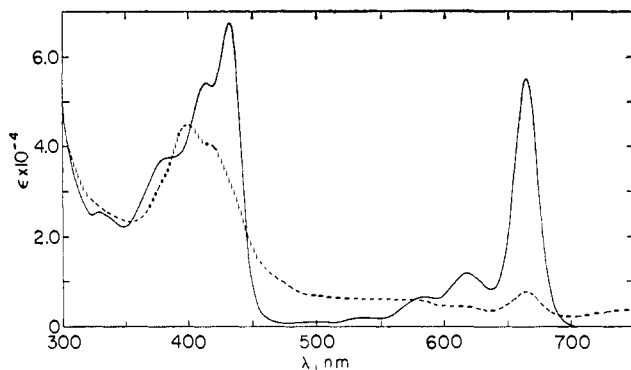


Figure 4. Absorption spectra of ethylchlorophyllide *a* (—) and its cation radical (-----) in  $\text{CH}_2\text{Cl}_2$ .

phylls prompted us to study the electrochemical oxidation of ethyl chlorophyllide *a*. One-electron oxidation at 0.6 V *vs.* sce yielded a yellow solution whose optical spectrum is shown in Figure 4. The product exhibited a singlet esr signal 9 G wide ( $g = 2.0028$ ). Attempted chemical oxidation by bromine led to allomerized material.

Stable oxidized products of CdTPP, CoTPP,  $\text{H}_2\text{TPP}$ , zinc tetraphenylchlorin, free base and zinc etioporphyrin I, and ZnOEP have also been prepared by the above techniques. These results will be discussed fully in a later publication.

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## A Large Deuterium Solvent Isotope Effect on a Photochemical Reaction<sup>1</sup>

Sir:

We wish to draw attention to a large acceleration, measured in methanol-*O-d*, of the photochemically induced double bond migration in  $\alpha,\beta$ -unsaturated esters.

In a previous publication<sup>2</sup> we reported that isomerization of ester **1** in methanol proceeded overwhelmingly with the abstraction of the tertiary allylic hydrogen leading to **2**, rather than to esters **3** or **4** which would result from the relocation of primary allylic and homoallylic hydrogens, respectively. We have now observed that irradiation in methanol-*O-d* brings about a remarkable change in the reaction course;<sup>3</sup> esters **2** and **3** are generated at comparable rates in this medium.

The results of the photolysis of **1a** in methanol-*O-d* and ordinary methanol are plotted in Figure 1.<sup>3,4</sup> The

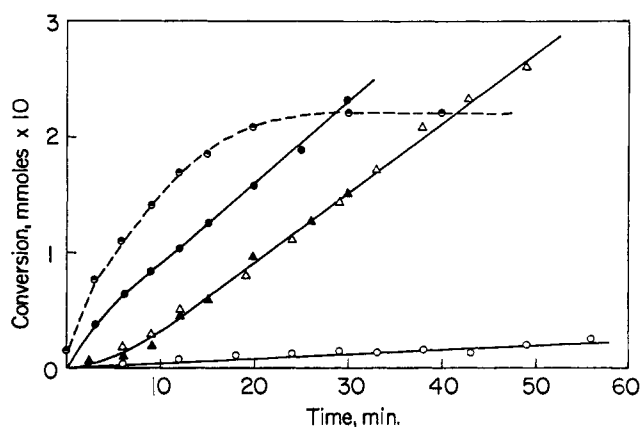


Figure 1. Irradiation of **1a** (0.4 mmol, 4% of **1b** present) in methanol and methanol-*O-d* (5.0 ml): photoequilibration of **1a**, depicted as mmol of total starting ester present as the *cis* isomer (**1b**) (broken line,  $\odot$ ); formation of ester **3**, in methanol ( $\circ$ ), in methanol-*O-d* ( $\bullet$ ); formation of ester **2**, in methanol ( $\Delta$ ), in methanol-*O-d* ( $\blacktriangle$ ).

rate of formation of **3** is much faster than that of **2** during the period over which the photostationary state is being approached, consonant with previous conclusions<sup>5,6</sup> that the photochemical deconjugation reactions occur stereospecifically from the geometrically isomeric states of the starting ester. The solvent isotope effect ( $k_{\text{CH}_3\text{OD}}/k_{\text{CH}_3\text{OH}}$ ) on the formation of ester **3**, while impossible to evaluate precisely,<sup>4</sup> is in the order of 15–50.

(1) Photochemistry of  $\alpha,\beta$ -Unsaturated Esters. VI.

(2) M. J. Jorgenson, *Chem. Commun.*, 137 (1965).

(3) Irradiations were conducted consecutively and on identical scales and concentrations, keeping the geometry of the irradiation set-up constant. A Hanovia 450-W lamp and Vycor filter were employed. Control experiments were carried out to exclude the possibility that the solvent effect of methanol-*O-d* was caused by the presence of impurities. Methanol-*O-d* prepared by three different routes gave identical results, and ordinary methanol prepared by one of these procedures did not differ in behavior from commercial samples. Added amounts of acid did not affect the reaction.

(4) Total yields of  $\beta,\gamma$  isomers in methanol-*O-d* was better than 95%; in the slower runs conducted in methanol the material balance remained not lower than 90% throughout the reaction course. Repeated runs in methanol-*O-d* gave similar results, **3** varying between 52 and 60%. Irradiations in ordinary methanol were more erratic; in a total of ten runs conducted under identical conditions the amount of **3** formed varied between 3 and 8%. Irradiation of **1a** in hexane gave results which were similar to those obtained in methanol, but the amount of **3** formed never exceeded 5%.

(5) M. J. Jorgenson and L. Gundel, *Tetrahedron Letters*, 4991 (1968).

(6) J. A. Barltrop and J. Wills, *ibid.*, 4987 (1968).