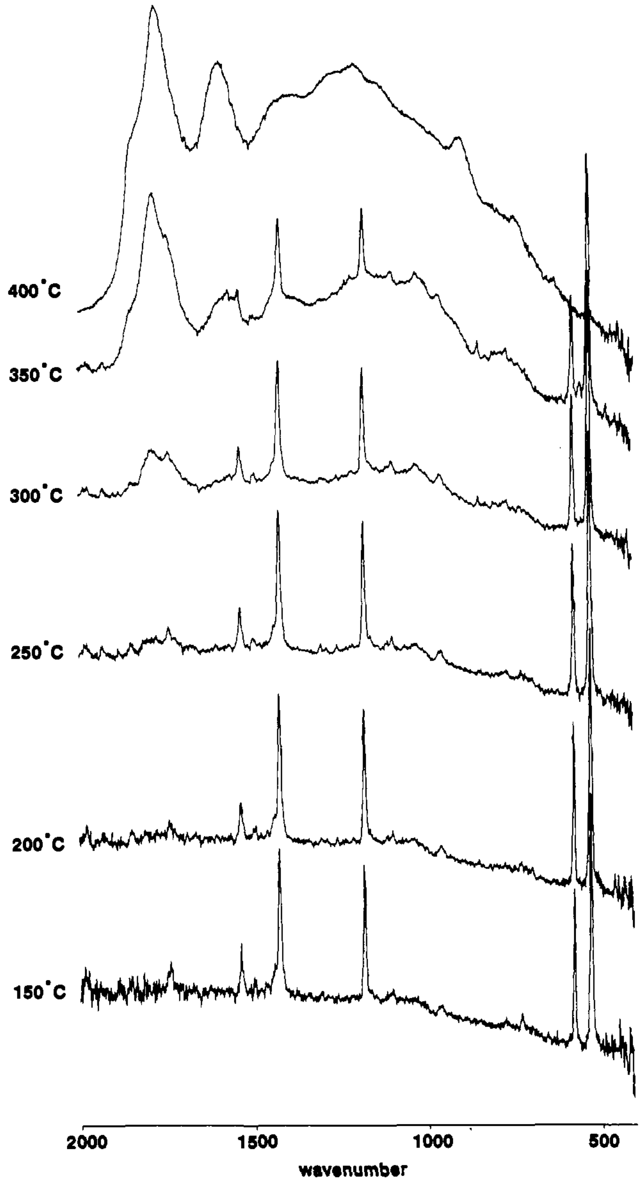


Figure 2. Infrared emission spectra of C$_{60}$ obtained under O$_2$/Ar (25% v/v) using conditions similar to those described in Figure 1.

At 600 °C, however, the signal intensity has decreased dramatically, indicating that the sample has substantially sublimed between 550 and 600 °C. Although subjected to no more than 60 s at each temperature, and a similar time period between each temperature hold point, it is evident that C$_{60}$ is thermally stable within this temperature range.

Oxidation experiments were carried out by introducing a mixture of oxygen in argon (25% v/v) into the sample chamber. The spectra obtained under this atmosphere are shown in Figure 2. There is no noticeable change in the spectra obtained at 100 and 150 °C, but the spectrum at 200 °C displays small additional broad emission peaks at 1743, 1102, 1037, and 958 cm^{-1}. Upon further heating to 250 °C, these bands increase in intensity up to 300 °C, when a strong broad band appears at 1786 cm^{-1}, in addition to the other bands. By 350 °C this band has developed a shoulder at 1844 and 1735 cm^{-1} and another broad band centered at ~1590 cm^{-1} has developed. More bands are also evident at 2323 (CO$_2$) and 2128 cm^{-1} (CO). A broad emission band has also formed between 700 and 1500 cm^{-1}. Above 350 °C the 1416- and 1174-cm^{-1} bands of C$_{60}$ are no longer clear although the two low-frequency peaks are still present at lower intensity. All evidence of C$_{60}$ has gone by 450 °C, and no signal from any species is seen above 550 °C (not shown). Similar experiments carried out at a constant temperature of 250 °C reveal that the emission bands of C$_{60}$ decrease steadily with time until approximately 90 min, after which no evidence of the C$_{60}$ molecule can be detected. The apparent discrepancy between the results obtained by Milliken et al.[20] and the results presented here are easily resolved. Milliken et al.[20] have used weight loss as an indicator of reactivity. It is clear from our results that oxidation is occurring at lower temperatures, however, our results also show, in agreement with Milliken et al.,[20] that by 500 °C a large fraction of the sample has oxidized to gas-phase products.

The destruction of the icosahedral symmetry by the addition of oxygen renders the IR spectrum much more complex; nevertheless, some interpretation is possible. The assignment of the strong band at 1780 cm^{-1} in the spectrum obtained at 350 °C is consistent with five-membered-ring lactones, but their formation in the absence of hydroxy groups would not be facile. Vibrational bands in the 1850–1750-cm^{-1} region of oxidized carbons and chars can, however, usually be assigned to cyclic anhydrides,[22,23] e.g., phthalic anhydride, and the ~60-cm^{-1} band separation (between 1844 and 1786 cm^{-1}) is typical of five-membered rings, although the presence of six-membered cyclic anhydrides condensed to aromatic systems is also a possibility. The main emission band centered at ~1600 cm^{-1} in the spectra obtained at 400 °C and above is very similar to that observed in coal and heat-treated carbonaceous material and has been assigned to an aromatic C–C stretch enhanced by polar functional groups.[24,25]

Although the mechanism of oxygen addition is as yet undetermined, it is clear that a complex product is the result and that anhydrides may be implicated in this mechanism.

Acknowledgment. The National Energy Research and Development Council of Australia is acknowledged for partial funding of the FTIR emission spectrometer. Mr. C. Dawson and Mr. T. McDonald of the CSIRO Division of Coal and Energy Technology are thanked for the construction of the arc generator.

---

(22) Meldrum, B. J.; Rochester, C. H. *Fuel* **1991**, *70*, 57–63.
(23) Zawadzki, J. *Chem. Phys. Carbon* **1989**, *21*, 147–380.
(24) Painter, P. C.; Starsinic, M.; Coleman, M. In *Fourier Transform Infrared Spectroscopy*; Ferraro, J. R., Basile, L. J., Eds.; Academic Press, Inc.: Orlando, 1985; Vol. 4, p 183.
(25) Akhter, M. S.; Keifer, J. R.; Chughtai, A. R.; Smith, D. M. *Carbon* **1985**, *23*, 589–591.
(26) Cole-Clarke, P. A.; Vassallo, A. M., submitted to *Fuel*.
(27) Vassallo, A. M.; Cole-Clarke, P. A.; Pang, L. S. K.; Palmisano, A. P. *Appl. Spectrosc.*, in press.

Polymeric Polyhalogenated Metalloporphyrin Catalysts for Hydroxylation of Alkanes and Epoxidation of Alkenes

Teddy G. Traylor,[*,†] Young S. Byun,[†] Patricia S. Traylor,[‡]
Pierrette Battioni,[§] and Daniel Mansuy[§]

Department of Chemistry, 0506
University of California, San Diego
Gilman Drive, La Jolla, California 92093-0506
Department of Chemistry, University of San Diego
San Diego, California 92110-2492
Université René Descartes
Laboratoire de Chimie et Biochimie
rue des Saints-Pères, Paris Cedex 06, France

Received January 22, 1991
Revised Manuscript Received July 8, 1991

The development of electronegatively substituted hemin catalysts[1-6] has provided rapid, high-yield, high-turnover oxidations

---

[†] University of California, San Diego.
[‡] University of San Diego.
[§] Université René Descartes.

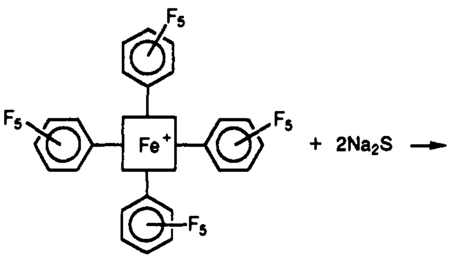
(1) Chang, C. K.; Kuo, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 3413–3415.
(2) Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279–280.
(3) Traylor, T. G.; Tsuchiya, S. *Inorg. Chem.* **1987**, *26*, 1338–1339.

of hydrocarbons in solution. It would be advantageous for continuous oxidation processes to immobilize these catalysts on high-surface polymers. This has been done with less stable porphyrins by copolymerizing vinyl-substituted porphyrins with styrenes.[7] Application of this method to polyhalogenated catalysts suffers two disadvantages. The polyhalogenated vinyl porphyrin must first be synthesized, and the polymer backbone is susceptible to oxidation.

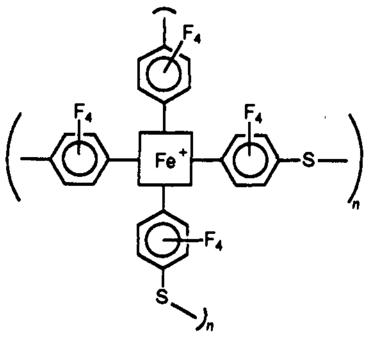
Because hexafluorobenzene and hexachlorobenzene undergo facile nucleophilic substitution,[8] the pentafluorophenyl or pentachlorophenyl groups on porphyrins should also undergo such substitution.[9,10] The use of bifunctional nucleophiles in this reaction makes the preparation of polymeric porphyrins from readily available, robust, halogenated metalloporphyrins feasible.[11] The availability of four substitutionally reactive phenyl groups makes cross-linking possible in these polymers.

(1)

We have reacted the iron(III) tetra(pentafluorophenyl)porphyrin chloride with 2 mol of sodium sulfide. The first reaction produces the nucleophilic thiophenylate anion which participates in the polymerization; the second mole assures cross-linking.



A

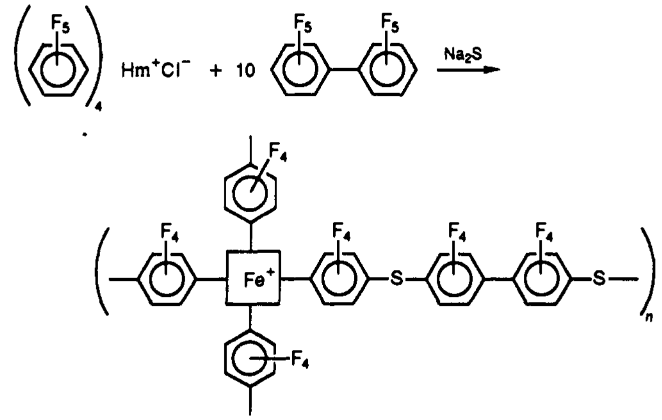


1

Stirring 40 mg (3.76 × 10^{-5} M) of the hemin chloride (A) with 18 mg (7.52 × 10^{-5} M) of sodium sulfide hydrate in 1 mL of dimethylformamide at 160 °C under argon for 4 h resulted in the precipitation of a black solid. Very little color remained in the solution. Cooling, filtering, washing successively with dimethylformamide, acetone, methanol, and methylene chloride, and drying afforded 38 mg of hard black solid that was insoluble and did not swell in any solvent tried. Such properties are indicative of highly cross-linked polymers. Iron(III) tetra(pentachlorophenyl)porphyrin chloride[2] gave similar results but required a higher temperature (220 °C) in sulfolane in keeping with the lower reactivity of chlorinated compared to fluorinated aromatics toward nucleophilic substitution.[8]

A solution of 1 M cyclohexane and 0.06 M pentafluoroiodosylbenzene (PFIB) in 0.5 mL of dichloromethane, trifluoroethanol, and water (80:18:2 by volume)[13] containing 4 mg of the solid hemin polymer (**1**) was stirred for 3 min and the supernatant liquid analyzed by gas–liquid chromatography. With use of the peak area for pentafluoroiodobenzene and the relative sensitivity factors, the yield (based on oxidant) was 70% cyclohexanol and about 1% cyclohexanone. Longer reaction times did not increase the yield. The recovered catalyst was reused in five successive, identical experiments without reduction in yield. After seven recyclings the polymer became lighter in color. Similar yields were obtained when the solvent used was dichloromethane containing 1% hexafluoroacetone trihydrate, a combination which also solubilizes PFIB. With norbornene as substrate, a quantitative yield of oxidized products, displaying an exo/endo epoxide ratio of 12/1, was obtained.

Copolymers were prepared by adding 10 mol of perfluorobiphenyl per mol of hemin in the method described. Other copolymers were prepared by adding perfluorotriphenylphosphine or di(perfluorophenyl) sulfide. In all cases, the catalytic properties resembled those of the homopolymers[14] but the polymeric material was somewhat less brittle.



2

Yields of cyclohexanol and cyclohexanone obtained with these catalytic polymers are shown in Table I.

The feasibility of using a continuous flow reactor was examined by making a small column (5-mm diameter by 2-cm length) of copolymer **2** (see Table I) and passing a solution of PFIB and cyclohexane through this column at a rate of about 0.3 mL/min. The eluate was analyzed by gas–liquid chromatography. Cyclohexanol containing about 1% cyclohexanone was obtained in 50% yield, based upon PFIB.

It is not clear why only 50–70% yields of cyclohexanol were obtained, in view of the quantitative epoxidation of norbornene. Competing solvent oxidation might be involved. The catalyst remains active as evidenced by its reusability. The catalyst (**1**) is finally partially destroyed after seven sequential reactions. However, the hemin used is known to be less stable toward oxidative destruction than are perhalogenated hemins whose polymers are currently under study.[4,6,15]

---

(4) Traylor, T. G. *Pure Appl. Chem.* **1991**, *63*, 265–274.

(5) Hoffmann, P.; Labat, G.; Robert, A.; Meunier, B. *Tetrahedron Lett.* **1990**, *31*, 1991–1994.

(6) Tsuchiya, S.; Seno, M. *Chem. Lett.* **1989**, 263–266.

(7) Kojima, T.; Urata, Y.; Yonekura, H. *J. Polym. Sci., Part C; Polym. Lett.* **1990**, *28*, 129–132.

(8) Miller, J. *Aromatic Nucleophilic Substitution*; Eaborn, C., Chapman, N. B., Eds.; Elsevier: Amsterdam, 1968; pp 124–132.

(9) This type of substitution was recently realized by boiling tetra(pentafluorophenyl)porphine and cobalt acetate in dimethylformamide. The resulting tetra(*p*-dimethylamino)cobalt derivative was presumably formed after decomposition of DMF to dimethylamine.[10]

(10) Kadish, K. M.; Araullo-McAdams, C.; Han, B. C.; Franzen, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 8364–8368.

(11) Polymers have been prepared from hexafluorobenzene using arenedithiols as bifunctional nucleophiles.[12]

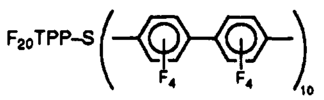
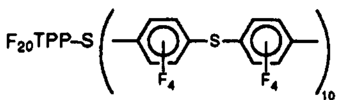
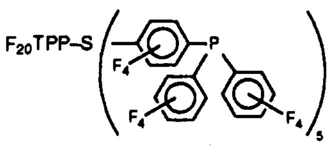
(12) Kellman, R.; McPheeters, J. C.; Gerbi, D. J.; Williams, R. F. *Polym. Prepr.* **1981**, *22*, 383.

(13) Traylor, T. G.; Marsters, J. C., Jr.; Nakano, T.; Dunlap, B. E. *J. Am. Chem. Soc.* **1985**, *107*, 5537–5539.

(14) Although this reaction is, in a sense, a copolymerization with sulfide ion, we refer to polymers like **2** as homopolymers having only one kind of haloaromatic monomer.

(15) Tsuchiya, S. Unpublished results.

Table I. Yield of Cyclohexanol in Polymer-Catalyzed Oxidations[a]

polymer[b]	% yield of cyclohexanol + cyclohexanone	alcohol/ ketone
1. F$_{20}$ TPP-S-	70	45
2. 	78	52
3. 	65	55
4. 	60	45
5. F$_{20}$Cl$_8$TPP-S-	33	90
6. Cl$_{20}$TPP-S-[c]	70	100

[a] Catalyst (4 mg), PFIB (9.4 mg), and cyclohexane (54 μL) in 0.5 mL of the mixed solvent were stirred 3 min and analyzed (see text). The formulas refer to the original metalloporphyrin used in the polymerization. [b] The fluorines are on the phenyl groups. [c] The chlorines are on the phenyl groups.[2]

Preparation of different copolymers and the use of other oxidants such as hydrogen peroxide and dioxygen are also being investigated.

Acknowledgment. We are grateful to the National Science Foundation for financial support (Grant CHE 87-21364), to both the NSF (Grant CHE 88-14866) and the National Institutes of Health (Grant PHS RR 04733) for instrument grant support, and to Professor Karl Kadish for helpful discussions.

Registry No. 1, 135645-47-5; **1** pentachloro derivative, 135645-48-6; **2**, 135645-49-7; cyclohexane, 110-82-7; cyclohexanol, 108-93-0; cyclohexanone, 108-94-1; norbornene, 498-66-8; norbornene epoxide, 278-74-0.

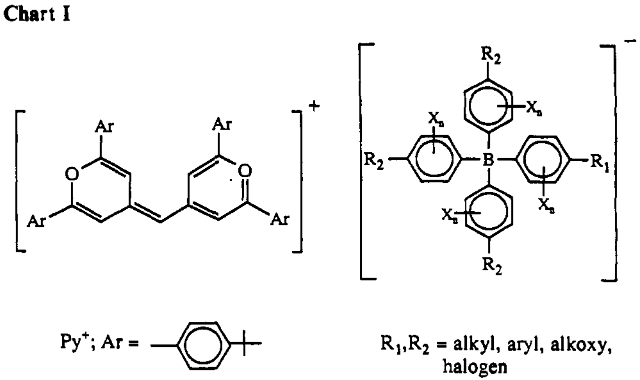
Electron Transfer and Back Electron Transfer in Photoexcited Ion Pairs: Forward and Back Directions Have Different Maximum Rates

Chaofeng Zou, Jeffrey B. Miers, Richard M. Ballew,
Dana D. Dlott,* and Gary B. Schuster*

Department of Chemistry, University of Illinois
Urbana, Illinois 61801

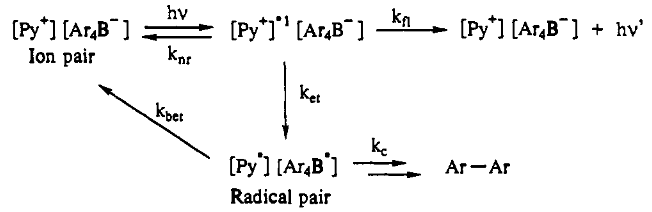
Received May 28, 1991
Revised Manuscript Received August 14, 1991

Chart I



R$_1$,R$_2$ = alkyl, aryl, alkoxy, halogen
X = H, F

Scheme I



The efficiency of photoinitiated electron transfer in natural[1] and artificial[2] systems is determined by the competition between reaction rates. In the forward direction, transfer of an electron to or from an electronically excited state (k_{et}) competes with radiative and nonradiative dissipation of the excitation energy. In the back direction (k_{bet}), transfer of an electron to regenerate ground-state reagents competes with separation and irreversible chemical reaction. Current theoretical models recognize three key rate-determining parameters:[4-6] the driving force for reaction (ΔG_{et}), the reorganization energy (λ), and a measure of the electron-exchange interaction between donor and acceptor (V_r).

Herein we report results from investigation of photoinitiated electron transfer reactions in pyrylium borate ion pairs ([Py$^+$][Ar$_4$B$^-$], Chart I).[7,8] Systematic structural variation of the borate anion permits precise control of ΔG_{et} in both the forward and the back electron transfer. Ultrafast time-resolved spectroscopic measurements of k_{et} and k_{bet} reveal that V_r depends on the direction of electron transfer.

In benzene solution the pyrylium borate salts exist essentially exclusively as ion pairs.[8,9] However, since there is no or very little

---

(1) (a) Boxer, S. G. *Biochim. Biophys. Acta* **1983**, *726*, 265. (b) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Yeates, T. O. *J. Mol. Biol.* **1984**, *180*, 385. (c) Chang, C. H.; Tiede, D.; Tang, J.; Smith, U.; Norris, J.; Schiffer, M. *FEBS Lett.* **1986**, *205*, 82. (d) *Photoinduced Electron Transfers*; Fox, M. A.; Channon, M., Eds.; Elsevier: Amsterdam, 1988. (e) *Covalently Linked Donor Acceptor Species for Mimicry of Photosynthetic Electron and Energy Transfer*. Gust, D.; Moore, T. A. Eds.; Tetrahedron Symposium-in-Print No. 39, 1989; Vol. 45.

(2) (a) Chibisov, A. K. *Russ. Chem. Rev.* (*Engl. Transl.*) **1981**, *50*, 615. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (c) Fox, M. A. *Adv. Photochem.* **1986**, *113*, 237. (d) *Electron Transfer Reactions in Organic Chemistry*; Eberson, L., Ed.; Springer-Verlag: Berlin, 1987. (e) *Topics in Current Chemistry. Photoinduced Electron Transfer I*; Mattay, J., Ed.; Springer-Verlag: New York, 1990. (f) Bochman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669. (g) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8305. (h) Kroon, J.; Oliver, A. M.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 4868. (i) Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719. (j) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.

(3) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 4966. (b) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962. (c) Kakitani, T.; Mataga, N. *Chem. Phys. Lett.* **1986**, *124*, 437. (d) Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1986**, *90*, 993. (e) Wolynes, P. G. *J. Chem. Phys.* **1987**, *86*, 5133. (f) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (g) Bader, J. S.; Chandler, D. *Chem. Phys. Lett.* **1989**, *157*, 501. (h) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1989**, *134*, 323. (i) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078. (j) Tachiya, M. *Chem. Phys. Lett.* **1989**, *159*, 505.

(4) (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

(5) (a) Kahlow, M. A.; Kang, T. J.; Barbara, P. F. *J. Phys. Chem.* **1987**, *91*, 6452. (b) Smit, K. J.; Warman, J. M.; De Hass, M. P.; Paddon-Row, M. N.; Oliver, A. M. *Chem. Phys. Lett.* **1986**, *152*, 177. (c) Suppan, P. *Chimia* **1988**, *42*, 320. (d) Schmidt, J. A.; Liu, J.-Y.; Bolton, J. R.; Archer, M. D.; Gadzekpo, V. P. Y. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1027. (e) Heitele, H.; Finckh, P.; Weeren, S.; Pöllinger, F.; Michele-Beyerle, M. E. *J. Phys. Chem.* **1989**, *93*, 5173. (f) Chen, J.-M.; Ho, T.-I.; Mou, C. H. *J. Phys. Chem.* **1990**, *94*, 2889. (g) O'Driscoll, E.; Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1990**, *112*, 7091. (h) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 3601.

(6) (a) Heitele, H. P.; Weeren, S.; Pöllinger, F.; Michele-Beyerle, M. E. *Chem. Phys. Lett.* **1990**, *168*, 598. (b) Rodriguez, J.; Kirmaier, C.; Johnson, M. R.; Friesner, R. A.; Holten, D.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 1652. (c) Perkins, T. A.; Hauser, B. T.; Eyler, J. R.; Schanze, K. S. *J. Phys. Chem.* **1990**, *94*, 8745.

(7) Wilt, J. R.; Reynolds, G. A.; Van Allan, J. A. *Tetrahedron* **1980**, *29*, 795. All new compounds give satisfactory elemental analyses.

(8) Chatterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, M. E.; Sauerwein, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329. Pyrylium Salts: Synthesis Reactions and Physical Properties. *Advances in Heterocyclic Chemistry*; Katrizky, A. R., Ed.; Academic Press: New York, 1982; Suppl. 2.

0002-7863/91/1513-7823$02.50/0