sponding *trans* isomers. The cis/trans epoxide ratio is 7 in the case of an aliphatic olefin and 4.3 in the case of a conjugated aromatic olefin like *cis*-stilbene. Terminal olefins are slowly epoxidized (7 turnover numbers for 1-octene).

The iron analogue, Fe(Br$_8$TMP)OAc, was also evaluated as a possible catalyst under the same reaction conditions, but without pyridine derivative (Table II). The iron octabromo-TMP derivative is less efficient than the manganese complex. The highest catalytic activities are always in the range of two to four cycles, with a maximum for *cis*-stilbene at 8–12 cycles. Since the binding constant of a second pyridine for iron porphyrin complexes is higher than the binding constant for ligation of the first one,[10] it is not possible to take advantage of the proximal effect of pyridine ligands to enhance the catalytic activity of this iron porphyrin. Yields are the same with or without addition of pyridine in the reaction mixture. In the case of manganese porphyrin complexes, the monopyridine adduct is the major species up to 50–200 equiv of nitrogen base with respect to the porphyrin complex. In the epoxidation of *cis*-stilbene, the isomer epoxide ratio is 4–5 in favor of the cis isomer. The same reactivity is observed with Fe(Br$_8$TMP)Cl, suggesting that the anionic axial ligand does not largely influence the selectivity of the catalytic reaction.

As a general comment on the selectivity of this metalloporphyrin-catalyzed ozone epoxidation, it can be mentioned that the key factor reducing the selectivity is the noncatalyzed direct ozonolysis of the olefin. For example, three products have been detected in the direct ozonolysis of *cis*-stilbene after its complete conversion: benzaldehyde (54% yield), benzoic acid (7%), and a nonidentified compound[11] (34%) (balance material: 95%). In the Mn(Br$_8$TMP)Cl-catalyzed oxidation of the same olefin, the following products have been detected at a conversion of 95%: *cis*-stilbene oxide (34% yield), *trans*-stilbene oxide (8%), benzaldehyde (22%), benzoic acid (12%), and traces of deoxybenzoin (<1%). In this case, the balance material was 76%. So, the epoxide formation is the main pathway of the catalytic reaction, whereas benzaldehyde and benzoic acid are the products of the direct ozonolysis reaction.

We are currently studying how to improve reaction yields of this rare example of ozone epoxidation catalyzed by metalloporphyrin complexes.

Experimental Section

Gas chromatographic analyses were performed as previously described.[5] Chemicals were purchased from Aldrich or Janssen; noncommercially available epoxides were obtained from the corresponding olefins with *m*-chloroperbenzoic acid (85% pure, Merck). Peroxides were removed from olefins by passing them through a short column of Florisil before use. Dichloromethane (99.95%) was used without purification. The porphyrin ligands TMPH$_2$, TDCPPH$_2$, and Br$_8$TMPH$_2$ and their corresponding manganese and iron derivatives were prepared using a modified Lindsey method.[6,7] *meso*-Tetramesityl-β-octabromoporphyrin, Br$_8$TMPH$_2$, was obtained by NBS bromination of the β-pyrrole positions of TMPH$_2$.[6] Ozone was generated in a stream of oxygen by an ozonizer Labo 76 type from Trailigaz (Garges-les-Gonesse, France) (oxygen stream: 200 L/h; current intensity 1.25 A; ozone concentration was 1.3 mM by iodometric titration).

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(10) (a) Walker, F. A.; Lo, M. W.; Ree, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 5552–5560. (b) Meunier, B.; de Carvalho, M. E.; Bortolini, O.; Momenteau, M. *Inorg. Chem.* **1988**, *27*, 161–164.

(11) Since this compound has the same GC retention time as styrene oxide, its yield was calculated by using the same response factor.

Photodimerization of 9-Vinylanthracene: X-ray Crystal Structure of the Dimer

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Photodimerization of anthracene is one of the oldest known photochemical reactions and a classical example of photoaddition. Several meso-substituted anthracenes have been known to undergo photodimerization via first excited singlet state.[1] However, in 9-vinylanthracene (VA) there could be other photochemical reaction pathways to compete with the photodimerization. For example, it could undergo photopolymerization or photohydration in the excited state, and both the reactions would involve the vinyl moiety as the reaction center. The present paper deals with the complete characterization of the photoproduct of VA.

VA was obtained from Aldrich Chemical Co. and was recrystallized from ethanol. Preparatory scale irradiations were performed in a Rayonet RPR-100 reactor. The wavelength for the irradiation was 254 or 300 nm. The solution was purged with nitrogen or argon for 20 min prior to irradiation.

Irradiation of a solution (either 50:50 (v/v) acetonitrile/water or pure acetonitrile) of VA results in complete disappearance of the anthracene-like absorption band (387, 368, 351 nm). This clearly indicates that photoexcitation directly effects the anthracene skeleton by removing the conjugation. Prolonged irradiation of a saturated solution in acetonitrile resulted in a white precipitate, which was isolated and subjected to spectroscopic analyses. The solid product was found to be a clean dimer by NMR spectroscopy, and no indication of any polymerization product was found to be associated with it. Furthermore, no other primary photoproduct was found to be present in solution in any significant amount. Though similar precipitation was detected by Ebeid et al.,[2] the complete characterization of the product has not been attempted until now. On the basis of the IR spectral analyses, Ebeid et al. proposed it to be a dimeric species.

UV absorption and ^{1}H and ^{13}C NMR spectra[8] have been presented in our earlier paper.[3] Present X-ray analysis[9] (see Figure 1) confirms this product to be a highly symmetrical dimer of VA. The vinyl groups are in a trans configuration with respect to the anthracene skeleton. No indication of cis isomer has been found. This indicates the photoaddition reaction is highly stereospecific in nature. The lack of reactivity of VA toward photohydration, unlike several other aromatic alkene and alkyne analogues[4], in aqueous acid solution has been explained as due to inefficient charge transfer in the excited singlet state.[4] This could be due to the fact that the vinyl group and the aromatic moiety are not in the same plane in the ground state due to steric reasons.

C(sp^3)–C(sp^3) bond lengths, i.e., C1–C4(I) in Figure 1, which connect the two half-molecules, are quite long (1.61 Å). This is similar to that found in the case of the dimer of 9-anthraldehyde.[5] Each half of the molecule is bent

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(1) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum Press: New York, 1976; Chapter 2.

(2) Ebeid, E. M.; El-Gamal, M. A.; Morsi, S. E. *Photochem. Photobiol.* **1986**, *44*, 547.

(3) Sinha, H. K.; Thomson, P. C. P.; Yates, K. *Can. J. Chem.* **1990**, *68*, 1507.

(4) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157.

0022-3263/91/1956-3727$02.50/0

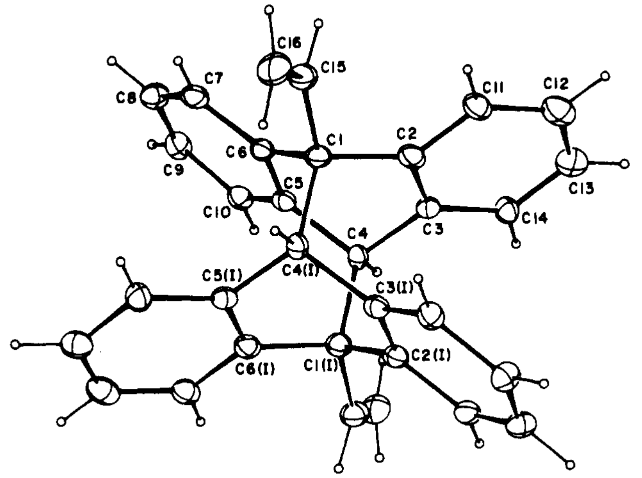

Figure 1. X-ray crystal structure of 9-vinylanthracene dimer. Hydrogen atoms are not labeled for clarity. The roman numeral I refers to the equivalent position 1-x, 1-y, 1-z relative to the reference molecule at x, y, z.

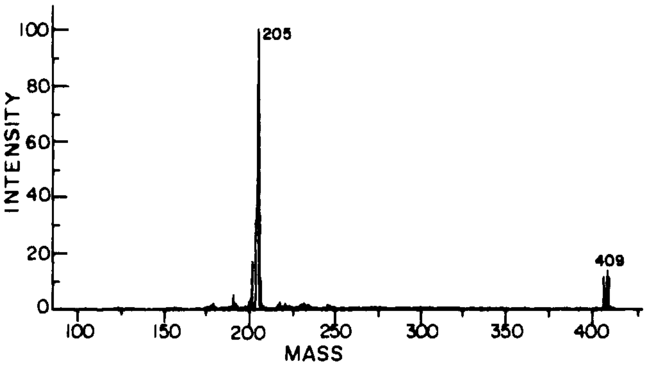

Figure 2. Mass spectrum (methane CI) of 9-vinylanthracene dimer (only H$^+$ (monomer) and H$^+$ (dimer) peaks are shown).

through an angle of 2 × 23°, again similar to the dimer of 9-anthraldehyde.[5] This dimer, like other dimers of anthracene, is unstable at higher temperatures (>150 °C) and is converted to the monomeric species upon heating. Therefore, during mass spectral analyses the signal corresponding to the monomeric mass is predominantly present. However, careful analysis and amplification of signals revealed a small peak at *m/e* 409 (see Figure 2) corresponding to the protonated dimeric mass.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

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(5) Ehrenberg, M. *Acta Crystallogr.* 1968, *B24*, 1123.

(6) Sheldrick, G. M. *SHELXS86, A program for crystal structure determination*; University of Gottingen: F.R.G., 1986.

(7) Sheldrick, G. M. *SHELX76, A program for crystal structure determination*; University of Cambridge: England, 1976.

(8) The dimer is insoluble in most solvents for UV analysis. ^{1}H NMR data in CDCl$_3$: (400 MHz) δ 4.86 (s, 2 H), 5.95 (d, J = 11.02 Hz, 2 H), 6.15 (d, J = 17.58 Hz, 2 H), 6.39 (q, J = 17.7 Hz, 2 H), 6.81 (m, 12 H), 6.99 (m, 4 H). ^{13}C NMR data δ 53.57, 58.56, 115.82, 125.27, 125.62, 126.04, 127.71, 142.36, 142.39, 145.61.

(9) Crystal data: C$_{32}$H$_{24}$, M = 408.5, monoclinic, space group $P2_1/c$, a = 8.085 (2) Å, b = 13.224 (3) Å, c = 10.533 (3) Å, β = 109.92 (2)°, U = 1058.8 Å^3, Z = 2, D_c = 1.29 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 0.68 cm^{-1}, F(000) = 432, room temperature, R = 0.042 (R_w = 0.038) for 862 reflections (measured on a CAD4 diffractometer) with $I > 3\sigma(I)$. The crystals were grown by slow evaporation of solvent from benzene solution. The structure was solved by direct methods[6] and reduced by full-matrix least squares.[7] Carbon atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the —CH═CH$_2$ group and the hydrogen bonded to the sp^3 hybridized carbon were refined with isotropic thermal parameters. All other hydrogen atoms were included in the refinement as riding atoms with d(C–H) of 0.95 Å and a general thermal parameter for these atoms refined to U = 0.045 (3) Å^2.

Preparation of Thiophenols from Unactivated Aryl Chlorides and Sodium Alkanethiolates in *N*-Methyl-2-pyrrolidone

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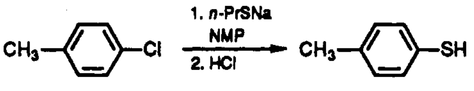
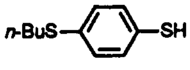
Thiophenols can be prepared in high yield by nucleophilic substitution reactions of unactivated and deactivated aryl chlorides with sodium alkanethiolates in *N*-methyl-2-pyrrolidone (NMP). The one-pot method involves the reactions shown in Scheme I.

These reactions have been previously carried out in hexamethylphosphoramide (HMPA)[1] and *N,N*-dimethylformamide (DMF)[2] with more reactive aryl chlorides. However, HMPA has the disadvantages of carcinogenic properties and high cost. Our work has shown that using DMF with deactivated aryl chlorides such as 4-chlorotoluene gave poor results. After being refluxed for 20 h in DMF, most of the 4-chlorotoluene was unreacted and the yield of 4-methylbenzenethiol was only 16%. It has been found that the yield of thiophenols can be dramatically improved if NMP is used as solvent. Reaction of 4-chlorotoluene with sodium propanethiolate or sodium butanethiolate (4 mol equiv) in NMP at reflux gave 4-methylbenzenethiol in 90–96% yield as determined by GC. Di-*n*-propyl sulfide or di-*n*-butyl sulfide was produced as a coproduct.



Reaction of 2-chlorotoluene with excess sodium butanethiolate under the same conditions gave a 96% yield of 2-methylbenzenethiol. Any steric hindrance in 2-chlorotoluene was apparently not a problem in the reactions. Application of this method to the more reactive chlorobenzene also resulted in a high yield (92%) of thiophenol. The reaction time and temperature were less for chlorobenzene than for 4-chloro- or 2-chlorotoluene.

Attempts to prepare 1,4-benzenedithiol from 1,4-dichlorobenzene failed. Instead, compound 1 was produced (94% yield) apparently because the sodium salt of this compound fails to undergo further reaction with excess *n*-BuSNa (6 mol equiv) in NMP.



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In the aforementioned reactions, sodium alkanethiolates derived from primary alkyl mercaptans were used. If sodium alkanethiolates from tertiary alkyl mercaptans were used, the second reaction in Scheme I was not possible due to steric factors, so aryl alkyl sulfides were obtained instead

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(1) Testaferri, L.; Tingoli, M.; Tiecco, M. *Tetrahedron Lett.* 1980, *21*, 3099–3100.

(2) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Synthesis* 1983, 751–755.

0022-3263/91/1956-3728$02.50/0