1623 (w), 1442 (m), 1025 (m), 970 (m), 873 (m) cm^{-1}; MS *m/e* (relative intensity) 170 (13), 168 (M^+, 35), 133 (41), 91 (100), 80 (42), 67 (51).

9-Homonoradamantan-9-ol (11a) was prepared in 84% yield by $LiAlH_4$ reduction of ketone **10**. **11a**: mp 219–220 °C; ^{1}H NMR ($CDCl_3$) δ 4.0 (dt, 1 H), 2.7–1.1 (m, 15 H); IR (KBr) 3310 (s), 2915 (s), 2825 (m), 1450 (m), 1048 (m), 1030 (m), 1000 (m) cm^{-1}; MS *m/e* (relative intensity) 152 (M^+, 14), 134 (100), 119 (24), 108 (25), 105 (25), 92 (46), 79 (67), 67 (56).

Reaction of 9-Homonoradamantan-9-ol (11a) with Sulfuric Acid.[20] To a mixture of concentrated sulfuric acid (3 mL) and pentane (15 mL) vigorously stirred at room temperature was added 304 mg (2 mmol) of **11a** all at once. After 30 min 10 mL of pentane was added and the resulting mixture was poured on 50 mL of ice–water. The layers were separated and the aqueous one was extracted with pentane (5 × 20 mL) followed by ether (5 × 20 mL). The combined pentane extracts were washed with water (2 × 20 mL) and dried. The solvent was carefully removed through a Vigreaux column and the residue sublimed in vacuo to give 152 mg (1.1 mmol, 55%) of adamantane (≥98% pure by GLC, SE-30, 90 °C). From the ether extracts only adamantane (ca. 10 mg) was isolated.

9-Homonoradamant-9-yl tosylate (11b) was prepared by the standard pyridine method.[31] The crude tosylate was recrystallized from 9:1 pentane–ether at −15 °C. Pure **11b** was obtained in 77% yield (mp 41–43 °C).

Kinetic Measurements. The solvolysis rate of **11b** was determined by continuous potentiometric titration by using a Radiometer Copenhagen SBR 2/TTT 11 pH-stat, maintaining the pH of the reaction solution at 6.8. The initial concentration of the tosylate was ca. 0.002 M (10 mg in 15 mL of solvent). The rate constant was calculated from the standard integrated first-order law and is an average value of five individual rate constants; k_{11b} (60% aqueous EtOH, 25 °C) = $(3.59 \pm 0.01) \times 10^{-4}$ s^{-1} (the uncertainty is one standard error).

Attempts of Bromination of 9-Homonoradamantane (1). A mixture of **1** (204 mg, 1.5 mmol) and bromine (5 mL, 91 mmol) was stirred for 5 h at room temperature and then dissolved in CCl_4 (20 mL) and poured onto ice–water (50 mL). The layers were separated and the aqueous one was extracted with carbon tetrachloride (3 × 20 mL). Combined carbon tetrachloride extracts were shaken with 50-mL portions of saturated aqueous sodium bisulfite until colorless, washed with water (2 × 20 mL), and dried over $CaCl_2$. The solvent was evaporated in vacuo and the residue (130 mg) analyzed by GLC (SE-30, 90 and 150 °C). Only unchanged **1** was detected. Sublimation in vacuo yielded pure **1** (110 mg). The reactions under gentle reflux of bromine for 2.5 h without catalyst and in the presence of boron tribromide (0.8 mL, 8.5 mmol) yielded also exclusively unchanged **1**. However, stirring of **1** (120 mg, 0.88 mmol) in carbon disulfide (6 mL) with bromine (3 mL, 58 mmol), in the presence of $AlBr_3$ (150 mg) for 4 h at room temperature, gave a complex mixture of products (170 mg) containing, in addition to **1**, material insoluble in $CHCl_3$ (78 mg) and two major products with GLC retention times close to that of 1-bromoadamantane.

Solvolysis Product Studies. A solution of **11b** (460 mg, 1.5 mmol) and 2,6-lutidine (177 mg, 1.65 mmol) in 5 mL of 66.7% aqueous dioxane was stirred for 2.5 h at 50 °C. The reaction mixture was allowed to cool down, water (20 mL) was added, and the resulting mixture was extracted with ether (55 × 20 mL). Combined ether extracts were washed with 1% aqueous HCl (20 mL) and 1% aqueous $NaHCO_3$ solution (20 mL) and dried. The solvent was carefully evaporated and the residue (ca. 200 mg) was analyzed by GLC (QF-1, 110 °C). The analysis revealed the presence of three products in the ratio of 0.5:2:1. The products were separated by preparative GLC (QF-1, 110 °C) and identified by IR, ^{1}H NMR, and mass spectra as well as by GLC comparison with authentic samples to be 9-homonoradamant-9-ene, 5-*endo*-protoadamantanol, 9-homonoradamantan-9-ol, respectively.

Essentially the same product ratio (0.5:2:1) was obtained after 2.5 and 8 h, indicating the products were stable under the reaction conditions used.

Acknowledgment. This work was supported by a grant from the Research Council of the Republic of Croatia (SIZ-II).

Registry No. **1**, 49700-60-9; **3**, 65989-65-3; **4**, 71382-25-7; **5**, 71382-26-8; **6**, 71382-27-9; **6** tosylhydrazone, 71382-28-0; **6** tosylhydrazone sodium salt, 71382-29-1; **7**, 31517-39-2; **8**, 71382-30-4; **9**, 23691-62-5; **9** ethylene ketal, 23691-63-6; **10**, 71382-31-5; **10** tosylhydrazone, 71382-32-6; **11a**, 63923-71-7; **11b**, 71382-33-7; **12**, 63923-70-6; **13**, 71382-34-8; sodium methoxide, 124-41-4; bicyclo[3.3.1]non-2-ene 9-ethylene ketal, 71382-35-9; *exo*-bicyclo[3.3.1]nonan-3-ol 9-ethylene ketal, 70260-42-3; *exo*-bicyclo[3.3.1]nonan-2-ol 9-ethylene detal, 40540-94-1; bicyclo[3.3.1]nonan-3-one 9-ethylene ketal, 54283-54-4; bicyclo[3.3.1]nonan-3-one 9-ethylene ketal tosylhydrazone, 71382-36-0; bicyclo[3.3.1]nonan-3-one 9-ethylene ketal tosylhydrazone sodium salt, 71382-37-1; adamantane, 281-23-2; phosphorus trichloride, 7719-12-2; phosphorus pentachloride, 10026-13-8; 5-*endo*-protoadamantol, 31503-22-7.

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[31] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, 1962, p 1180.

Ion Radicals. 45. Reactions of Zinc Tetraphenylporphyrin Cation Radical Perchlorate with Nucleophiles[1,2]

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Details are given of the reactions of zinc tetraphenylporphyrin cation radical perchlorate ($ZnTPP^{+\cdot}$, ClO_4^-) with pyridine, triphenylphosphine, triphenylarsine, nitrite ion, thiocyanate ion, methanol, water, ammonia, methylamine, and dimethylamine. Reaction with the first five of these nuclophiles gave ZnTPP and a β-substituted ZnTPP according to the usual stoichiometry of reactions of aromatic cation radicals with nucleophilies. From the reaction with nitrite ion a bilitriene was also obtained, identical with that reported earlier by Evans and Smith. The bilitriene was also obtained from reaction with water in tetrahydrofuran. Reaction with methanol gave a meso-substituted methoxyisoporphyrin, previously isolated by Dolphin et al. from reaction of $ZnTPP^{2+}$ with methanol. Reaction with ammonia and the amines gave large yields of ZnTPP. The way in which the bilitriene is formed, the problem of electron exchange with nitrite ion, and the reaction with methanol are discussed.

Four years ago we reported briefly that zinc tetraphenylporphyrin cation radical perchlorate ($ZnTPP^{+\cdot}$, ClO_4^-) reacted with pyridine in acetonitrile solution and gave the β-substituted pyridinium derivative (**1**).[3] The

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stoichiometry of the reaction appeared to be of the usual kind for the reaction of a cation radical with a nucleophile, i.e., as in eq 1. We reported also that analogous reactions

$$2ZnTPP^{+\cdot}, ClO_4^- + py \rightarrow ZnTPP + 1 + HClO_4 \quad (1)$$

occurred with nitrite and thiocyanate ions, methanol, triphenylphosphine, and triphenylarsine, but no details were given. At the time our work was in progress it was generally believed that metalloporphyrin π-cation radicals were unreactive toward nucleophiles, in contrast with the corresponding π-dications.[4] However, coincident with our work Barnett and Smith found that the oxidation of magnesium aetioporphyrin-I (MgAeP-I) and zinc octaethylchlorin (ZnOEC) by iodine and silver ion in the presence of nitrite ion led to the nitration of the metalloporphyrins.[5] These reactions were interpreted[5] as being between the π-cation radicals and nitrite ion in analogy with reactions of aromatic cation radicals.[6] Following the earlier publications,[3,5] a number of other reactions of metalloporphyrin π-cation radicals with nucleophiles have been reported, to which we shall refer in the text. We now wish to give details of our reactions and to comment particularly on those with nitrite ion and methanol.

Results and Discussion

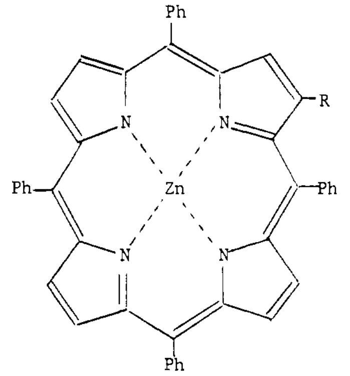
Reaction with Pyridine, Triphenylphosphine, and Triphenylarsine. When pyridine is added to a solution of $ZnTPP^{+\cdot}$, ClO_4^- in acetonitrile, reaction occurs quickly. A fleeting red color is seen, but the solution remains greenish thereafter. In the concentrations used (see Experimental Section) the reaction is over in 5 min. The major products of reaction are ZnTPP and the pyridinium perchlorate (**1**). The structure of **1** was deduced from elemental analysis and ^{1}H NMR, the latter being resolved with the aid of the corresponding 1-d_5 made from the reaction of $ZnTPP^{+\cdot}$, ClO_4^- with perdeuteriopyridine. Removal of the zinc atom from **1** with perchloric acid gave the corresponding pyridinium derivative (**6**) of tetraphenylporphyrin (TPP). Thus, the reaction of $ZnTPP^{+\cdot}$ was entirely analogous to the well-documented reactions of other aromatic and heteroaromatic cation radicals with pyridine[7] and left no doubt that in reacting with nucleophiles $ZnTPP^{+\cdot}$ appeared, in contrast with earlier belief,[4] to be no different from these other cation radicals. Later it was shown that zinc and magnesium octaethylporphyrin cation radicals ($ZnOEP^{+\cdot}$ and $MgOEP^{+\cdot}$) reacted with pyridine and some methylpyridines, giving the meso pyridinium derivatives.[8]

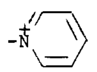
Reaction of $ZnTPP^{+\cdot}$ with triphenylphosphine and triphenylarsine gave the corresponding phosphonium and arsonium derivatives **2** and **3**, and the reactions appear to follow the stoichiometry of eq 1. Reaction of $ZnTPP^{+\cdot}$ with these nucleophiles was uncommon in that, to our knowledge, at the time of our work no reactions of other cation radicals with phosphines and arsines had been reported. Since then Evans and Smith have found that triphenylphosphine reacts with $ZnOEP^{+\cdot}$ at a meso position.[9]

Reaction with Thiocyanate Ion. Addition of sodium thiocyanate to a green solution of $ZnTPP^{+\cdot}$, ClO_4^- in acetonitrile caused the solution to become red immediately. Thus, reaction was fast and ZnTPP (red) was formed. The reaction, however, had the stoichiometry of eq 2. The

$$2ZnTPP^{+\cdot}, ClO_4^- + SCN^- \rightarrow ZnTPP + H^+/ZnTPP\text{-}SCN + 2ClO_4^- \quad (2)$$

product, ZnTPP-SCN (**4**), was identified by elemental analysis and ^{1}H NMR spectroscopy. Not many reactions of cation radicals with thiocyanate ion are known. Evans and Smith[9] have reported reaction with $ZnOEP^{+\cdot}$, and two of us have reported recently the reaction with *N*-phenylphenoxazine cation radical.[1] The oxidation potential of SCN^- is rather low.[10] Some reports of anodic thiocyanation of arylamines have been given in which it is proposed that the reactant is, in fact, the SCN radical or dithiocyanogen.[10] Therefore, it may be that the reaction of aromatic cation radicals with SCN^- is preceded by electron exchange. The 9,10-diphenylanthracene cation radical has, in fact, been reported to be reduced by SCN^-.[11] We have not pursued this problem, however, in the reaction of SCN^- with $ZnTPP^{+\cdot}$.



1, R =  , ClO_4^-; **2**, R = $-P(C_6H_5)_3^+$, ClO_4^-;

3, R = $-Sb(C_6H_5)_3^+$, ClO_4^-; **4**, R = $-SCN$; **5**, R = $-NO_2$

Reaction with Nitrite Ion. Reaction of $ZnTPP^{+\cdot}$ with nitrite ion gave ZnTPP, β-NO_2-ZnTPP (**5**), and the bilitriene (**7**). A small amount of TPP was also usually formed. The formation of ZnTPP and **5** appears to follow the usual pathway of a reaction of a nucleophile with a cation radical, that is according to eq 3. Nitrite ion is a

$$2ZnTPP^{+\cdot} + NO_2^- \rightarrow ZnTPP\text{-}NO_2 + ZnTPP + H^+ \quad (3)$$

"good" nucleophile in cation radical reactions, and several examples of the formation of nitro compounds via such reactions are now known.[7] Among reactions of metalloporphyrin cation radicals, that with nitrite ion was the first to be reported. That is, reaction of magnesium aetioporphyrin-I and zinc octaethylchlorin cation radicals with sodium nitrite gave, after removal of the metal ion, mononitroaetioporphyrin-I and γ-nitrooctaethylchlorin.[5] Also, zinc octaethylporphyrin cation radical gave, similarly, mononitrooctaethylporphyrin.[9]

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(1) Part 44: Shine, H. J.; Wu, S.-M. *J. Org. Chem.*, in press.

(2) Supported by Grant D-028 from the Robert A. Welch Foundation and Grants CHE 75-02794-A02 and CHE 78-00813 by the National Science Foundation.

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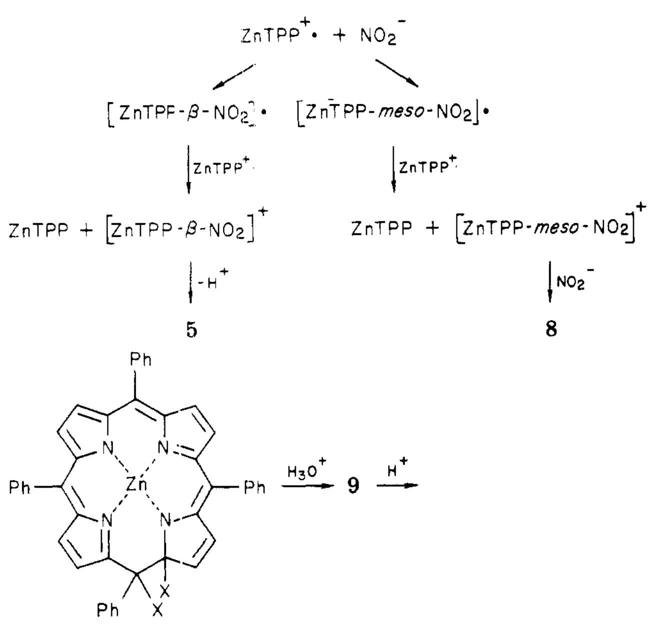
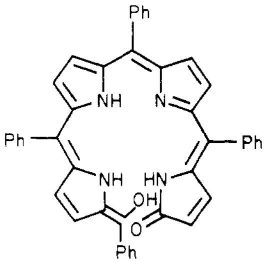
Scheme I



8, X = -ON=O
9, X = OH



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As for the bilitriene (7), this has been reported by Evans and Smith, who obtained it, contemporaneously with our own work, from reactions of thallium trifluoroacetate and thallium trinitrate with ZnTPP.[12] In the latter reaction some **5** was also obtained as a byproduct. It appears that nitrite ion, in giving ZnTPP, **5**, and **7**, may (like nitrate ion) attack ZnTPP$^{+}\cdot$ at both a meso and a β position. In each case a radical is formed which is then oxidized by ZnTPP$^{+}\cdot$ to the cation. Alternatively, the initial attack may be at only one of these positions (e.g., the meso) and be followed, after the second oxidation step, by rearrangement in the cation (e.g., to the β position). In any case, two cations are formed. One of these (the β-nitro) can lose a proton and give **5**; the other (the meso nitro) cannot lose a proton but, in reactions analogous to those proposed earlier,[12] can go on to the dinitrito compound **8** from which the bilitriene can be formed (Scheme I).

Although the formation of our products can be set out along the lines of Scheme I, we are not certain that the reactions are so straightforward. Johnson and Dolphin have proposed that the reaction of a metalloporphyrin cation radical with nitrite ion is preceded by electron exchange and that the product-forming reaction is in fact between cation radical and NO_2.[13] While we do not share the latter view, we feel that the problem of a redox reaction between a cation radical and nitrite ion does exist. One of us has commented on this earlier and has raised a similar question in reactions of cation radicals with halide ions.[14]

In some of our work with ZnTPP$^{+}\cdot$, reduction by nitrite ion was extensive. For example, when a solution of ZnTPP$^{+}\cdot$, ClO_4^- in THF was treated with water alone, slow reactions occurred, leading finally to TPP (18%), ZnTPP (66%), and the bilitriene (13%). In contrast, when aqueous sodium nitrite in sevenfold excess was used (to ensure having a soluble source of NO_2^-), 92% conversion into ZnTPP occurred along with 1% of **5** and 1% of **7**.

Attempts to carry out similar reactions in acetonitrile and methylene chloride have been thwarted to some extent by solubility problems. ZnTPP is not too soluble in acetonitrile. Addition of aqueous sodium nitrite to a green solution of ZnTPP$^{+}\cdot$, ClO_4^- in acetonitrile caused the immediate formation of a magenta precipitate of ZnTPP. Workup gave TPP (0.7%), ZnTPP (95%), **5** (1%), and **7** (1.5%). Here, therefore, extensive reduction by nitrite ion again occurred. Addition of either solid sodium nitrite or solid potassium nitrite to a solution of ZnTPP$^{+}\cdot$, ClO_4^- in acetonitrile caused a reddening of the solution but not the precipitation of ZnTPP. A suspension of solid sodium nitrite, for example, gave, in contrast with aqueous sodium nitrite, ZnTPP (41%), **5** (25%), and **7** (24%).

Both ZnTPP$^{+}\cdot$, ClO_4^- and ZnTPP are soluble in methylene chloride. When a green solution of ZnTPP$^{+}\cdot$, ClO_4^- in this solvent was stirred with solid sodium nitrite, the color changed slowly over a period of hours to reddish brown. Before workup the solution showed the peaks (846, 765 nm) either of an isoporphyrin or of **7**. Workup gave TPP (1.8%), ZnTPP (48%), **5** (32%), and **7** (19%).

It is possible, of course, that in the reactions which gave large amounts of **5** and **7** the ZnTPP$^{+}\cdot$ was first reduced to ZnTPP and that this then reacted with NO_2. We have found, in fact, that NO_2 reacts with ZnTPP in methylene chloride to give both **5** and **7**. What we are confronted with here is the reasonable possibility that electron exchange (eq 4) occurs, but it may not be too meaningful to ask

$$\mathrm{ZnTPP}^{+}\cdot + NO_2^- \rightleftarrows \mathrm{ZnTPP} + NO_2 \qquad (4)$$

which pair leads to the radical adduct. Electron exchange may occur and, particularly where ZnTPP is insoluble, lead only to ZnTPP. Electron exchange may occur in homogeneous solution also, but we cannot say with certainty how the final products (**5** and **7**) are formed. The extent of the exchange in eq 4 could be known from the appropriate oxidation potentials. Unfortunately, oxidation potentials for the reactants are not available for a common solvent. That is, the $E_{1/2}$ of ZnTPP in butyronitrile is 0.71 V (vs. SCE),[15] while $E_{1/2}$ of NO_2^- in nitromethane is 0.42 V (adjusted to SCE from Ag/AgCl).[16] The indications are that, assuming solvent and electrolyte effects to be modest, the electron exchange of eq 4 would be reasonable and lie on the ZnTPP side.

One might expect the differentiation between nitration by NO_2 and nitrite ion could be achieved by including urea in the reaction medium. This was achieved by Evans and Smith[9] who found that the presence of urea did not prevent reaction of ZnOEP$^{+}\cdot$ with nitrite ion in methanol solution.[17] We have also failed to prevent nitration of ZnTPP$^{+}\cdot$, but where our tests would have been most useful,

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(12) Evans, B.; Smith, K. M. *Tetrahedron Lett.* **1976**, 4863.

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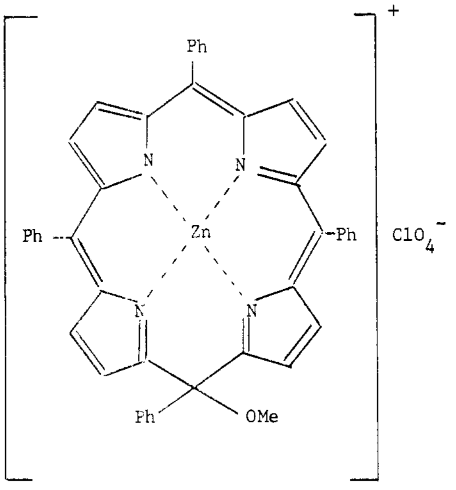
(17) One would expect that reduction of MgOEP$^{+}\cdot$ and MgAeP-I$^{+}\cdot$ by NO_2^- would be more difficult than reduction of ZnTPP$^{+}\cdot$. The relevant $E_{1/2}$ values are MgOEP (0.54 V)[18] and MgAeP-I (0.40 V).[15]

(18) Fuhrhop, J.-H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140; in butyronitrile vs. SCE, 0.1 M TBAP.

that is in nonaqueous methylene chloride and acetonitrile solutions, urea was insoluble. We found in fact that urea in suspension was not able to suppress the reaction of deliberately added NO_2 with ZnTPP in methylene chloride. Thus although electron exchange between ZnTPP$^{+\cdot}$ and nitrite ion can occur, we cannot say whether it has a role in the formation of **5** and **7**.

In connection with the formation of **7**, we have pointed out above that reaction of ZnTPP$^{+\cdot}$, ClO_4^- with water in THF also gave **7**. This is entirely in accord with Scheme I in which, this time, water is the nucleophile. Reaction of aromatic and heteroaromatic cation radicals with water is well documented.[7] The formation of **7** has some bearing on the reaction of methanol with ZnTPP$^{+\cdot}$, which we discuss below. That is, in analogy with methanol, toward which the literature would call for ZnTPP$^{+\cdot}$ to be inert, water has also reacted at a meso position.[19]

Reaction with Methanol. Reaction of ZnTPP$^{+\cdot}$ with methanol gave the methoxyisoporphyrin perchlorate **10** and ZnTPP. This reaction is uncharacteristic in that it occurred at a meso rather than a β position. The only analogues to it are the reaction with nitrite ion, which led not only to the β-substituted product but also to the ring-opened bilitriene, and the reaction with water, which gave the bilitriene. Formation of the bilitriene involves reaction at a meso position.



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The methoxyisoporphyrin was identical in its absorption and ^1H NMR spectra with that obtained by Dolphin and co-workers[20] from the reaction of ZnTPP^{2+} with methanol. The formation of both isoporphyrin and ZnTPP from the cation radical reaction indicates that the reaction was of the customary kind (eq 5). Our finding is unusual, however, in that much of the work in the literature reports ZnTPP$^{+\cdot}$ (and its analogues) to be stable in methanol and other alcohols. Thus, Fuhrhop and Mauzerall obtained stable solutions of cation radicals by oxidation of metallooctaethylporphyrins (Mg, Zn, Cu, Ni, and Pd) and bacteriochlorophyll in methanol and methanol–dichloromethane solutions with iodine or ferric perchlorate; oxidation of chlorophyll-*a* led to the cation radical but gave eventually a chlorin whose structure was different from that of the original chlorophyll.[21,22] Dolphin et al. have recorded the absorption and ESR spectra of MgOEP$^{+\cdot}$ after in situ anodic oxidation of MgOEP in methanol.[4,24] The ESR spectrum of ZnTPP$^{+\cdot}$ has also been recorded in methanol–dichloromethane[23] and in methanol alone.[25] Fuhrhop and co-workers have measured the dimerization equilibrium of ZnOEP$^{+\cdot}$ in methanol–chloroform (10:1).[26] Dolphin and Felton, in commenting on the inertness of metalloporphyrin cation radicals to the reaction with nucleophiles, note that the cation radicals may be crystallized routinely from nucleophilic solvents such as methanol.[24] Barnett and Smith, who were the first to show that a nucleophile (nitrite ion) will react with metalloporphyrin cation radicals in solution, did so in methanol solution. They remarked that it was on account of their unexpected stability in methanol that metalloporphyrin cation radicals had been, until that time, generally regarded as being resistant to attack by nucleophiles.[5] Further, Evans and Smith carried out, later, reactions of ZnOEP$^{+\cdot}$ (dissolved in tetrahydrofuran–methylene chloride) with a series of nucleophiles dissolved in methanol,[9] from which it is evident that the nucleophiles reacted with ZnOEP$^{+\cdot}$ but the methanol did not. Small concentrations of MgOEP$^{+\cdot}$ and analogous Mg tetraarylporphyrin cation radicals, made by in situ oxidation of the porphyrins with iodine, have been used by Sanders and Baxter in line-broadening NMR studies in methanol–chloroform solutions.[27] However, in these cases the cation radicals were not indefinitely stable in solution.[28]

$$2\mathrm{ZnTPP}^{+\cdot}, \mathrm{ClO_4}^- + \mathrm{MeOH} \rightarrow \mathrm{ZnTPP} + \mathrm{ZnTPP\text{-}OMe}^+, \mathrm{ClO_4}^- + \mathrm{HClO_4} \quad (5)$$

Solutions of chlorophyll-*a* (Chl-*a*) cation radical in water and methanol are also not stable.[29,30] The decomposition of this cation radical in solution has been attributed to reaction with the nucleophilic solvent.[30] The decay of Chl-*a*$^{+\cdot}$ in methanol has been interpreted as possibly involving Chl-*a*$^{2+}$, formed by disproportionation of Chl-*a*$^{+\cdot}$, rather than the direct reaction of Chl-*a*$^{+\cdot}$ itself.[31]

We have been unable to resolve the difference between our formation of a methoxyisoporphyrin from ZnTPP$^{+\cdot}$ (and MgTPP$^{+\cdot}$) and the stabilities of methanol solutions of porphyrin cation radicals recorded in the literature. There is no doubt from our analytical and spectroscopic work that the methoxyisoporphyrins were formed. At the same time we have on occasion obtained solutions of MgOEP$^{+\cdot}$ in methanol which did not decay perceptibly over a period of a few hours.[32] Reaction of these metalloporphyrin cation radicals with nucleophilic solvents should, we feel, not be unexpected, and the question of their lifetime in alcoholic solutions needs to be further resolved.

Reactions with Ammonia and Amines. In contrast with reactions with pyridine, reactions of ZnTPP$^{+\cdot}$, ClO_4^-

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[19] Reaction of ZnTPP^{2+} with water gave the hydroxyisoporphyrin.[20] In our reaction of ZnTPP$^{+\cdot}$ with water small amounts of products besides TPP, ZnTPP, and **7** were taken off the chromatography column but not identified.

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with ammonia and amines resulted in reduction to ZnTPP. The fate of the reducing agent is not known. This is not an uncommon observation in reactions of other cation radicals with amines.[7]

^{1}H NMR Spectra. The ^{1}H NMR spectrum of ZnTPP consists of a low-field singlet at 9.05 ppm for the eight equivalent β protons and two multiplets for the phenyl protons. One multiplet for ortho protons appears at 8.25 ppm and the other for meta and para protons at 7.83 ppm.[20] These relative chemical shifts are caused by the ring current of the porphyrin ring. Because meso substitution by the methoxy group in **10** causes interruption of the aromatic system of the porphyrin ring and loss of the deshielding effect of the ring current, the phenyl protons of **10** are shifted to higher field (7.06 ppm) as compared with those of ZnTPP. Furthermore, the β protons are now found at higher rather than lower field than those of the phenyl groups. In C_6D_6 the signals appeared, like those reported earlier,[20] as multiplets centered at 6.28 ($J \simeq 4.5$ Hz) and 6.56 ppm.

In contrast with the shifts in **10**, the signals from the β protons of **1**–**5** are to be found again at lower field than those of the phenyl protons, showing that, as in the parent ZnTPP, the porphyrin ring current is intact in these compounds. In each case also one of the β-proton signals appeared as a singlet at the lowest field and was thus identifiable as the proton adjacent to the substituent: 9.36 (**1**), 8.9 (**2**), 9.0 (**3**), and 9.1 ppm (**4** and **5**). The other β-proton signals appeared as two (**2**, **3**, and **5**) or three (**1**) multiplets, except for those of **4** which appeared as a singlet signal. The phenyl-proton signals of **4** and **5** were clearly separated as two multiplets of 12 meta and para protons in the region of 7.9–7.6 ppm and eight ortho protons in the region of 8.3–8.1 ppm. The signals for the phenyl protons of **1** were identifiable as ortho, meta, or para with the aid of the analogous pentadeuteriopyridine product (**1**-d_5). On the other hand, it was not possible to identify the two groups of phenyl rings and their particular protons in **2** and **3**. Details are given in the Experimental Section.

Experimental Section

Tetraphenylporphyrin (TPP) from the Strem Chemical Co. was purified (to remove the small amount of chlorin) as described by Smith[33] until it had spectroscopic properties agreeing with those in the literature.[34] Zinc tetraphenylporphyrin (ZnTPP) was prepared in the usual way by using zinc acetate.[35] Crystalline ZnTPP$^{+}\cdot$, ClO_4^- was prepared in two ways. In the first method, ZnTPP was oxidized with $I_2/AgClO_4$ in CH_2Cl_2, and after filtration from AgI the ZnTPP$^{+}\cdot$, ClO_4^- was precipitated with petroleum ether. For example, to 972 mg (1.43 mmol) of ZnTPP in 20 mL of methylene chloride was added a mixture of 203 mg (0.80 mmol) of iodine in 10 mL of methylene chloride and 332 mg (1.60 mmol) of silver perchlorate in 3 mL of acetonitrile. A green solution and grey precipitate formed immediately. After the mixture was stirred for 30 min and filtered, the filtrate was poured into 100 mL of petroleum ether. The suspension of ZnTPP$^{+}\cdot$, ClO_4^- was cooled for 4 h in the refrigerator, filtered, washed with petroleum ether, and dried under vacuum to give an almost quantitative yield of ZnTPP$^{+}\cdot$, ClO_4^- which assayed iodimetrically as 95% cation radical content. The visible spectrum (in methylene chloride) agreed with that in the literature.[23] In the second method, ZnTPP in methylene chloride was oxidized with a suspension of the cation radical perchlorate of dibenzodioxin (DBDO) prepared either by electrochemical means[36] or by oxidation with sodium dichromate and perchloric acid. For example, 600 mg (3.26 mmol) of DBDO in 25 mL of ethyl acetate was added to a solution of 180 mg of sodium dichromate in 10 mL of acetic anhydride. The mixture was cooled in ice for 20 min, and 1 mL of 70% perchloric acid was added. The blue precipitate of DBDO$^{+}\cdot$, ClO_4^- was filtered, washed, and dried, giving 840 mg (2.96 mmol, 91%) of product assaying at 91% cation radical content. To 1.45 g (2.14 mmol) of ZnTPP in 50 mL of methylene chloride was added 742 mg (2.62 mmol) of DBDO$^{+}\cdot$, ClO_4^-. The suspension was stirred for 20 min and filtered, and 200 mL of cold ether was added, causing the precipitation of 1.35 g (1.74 mmol, 81%) of ZnTPP$^{+}\cdot$, ClO_4^-, assayed at 88% cation radical content. The ZnTPP$^{+}\cdot$, ClO_4^- made in this way was used for preparing **1**–**6** and **10**, while the ZnTPP$^{+}\cdot$, ClO_4^- made with $I_2/AgClO_4$ was used for reactions with nitrite ion.

In all preparations of ZnTPP$^{+}\cdot$, ClO_4^- the solvents were distilled and dried prior to use, except for acetonitrile which was Eastman's anhydrous grade stored over molecular sieve and was used as purchased.

Reaction of ZnTPP$^{+}\cdot$, ClO_4^- with Pyridine. Formation of ZnTPP–Py$^+$, ClO_4^- (1). To a solution of 205 mg of ZnTPP$^{+}\cdot$, ClO_4^-, containing 0.227 mmol (86%) of ZnTPP$^{+}\cdot$ in 20 mL of acetonitrile, was added 1 mL of pyridine which had been dried and distilled over potassium hydroxide. As soon as the pyridine was added the acetonitrile became red but turned green in less than 1 min. After 5 min the solution gave a negative starch–iodide test. After being stirred for 30 min, the solution was evaporated on a rotary evaporator, the residue was dissolved in methylene chloride, and the solution was washed with water, dried over sodium carbonate, and evaporated to give a blue solid. This was chromatographed on a column of neutral alumina (activity III). Elution with chloroform (200 mL) gave 108 mg of crude ZnTPP. Continued elution (350 mL) gave 31 mg of a tan sticky solid which was discarded. Elution with acetone (600 mL) gave 87 mg (0.102 mmol, 45%)[37] of crude **1**. Crystallization from methylene chloride–pentane gave 64 mg (0.075 mmol, 33%) of greenish blue solid, mp >360 °C.

Anal. Calcd for $C_{49}H_{32}ZnN_5ClO_4$ (**1**): C, 68.8; H, 3.77; N, 8.18; Cl, 4.14. Found: C, 68.4; H, 3.78; N, 8.19; Cl, 4.20.[38]

^{1}H NMR [$(CD_3)_2C{=}O$] δ 9.30 (s, 1 H, β-H adjacent to py$^+$), 9.21 (d, 2 H, $J = 6$ Hz, py$^+$), 8.86–8.44 (m, 7 H, β-H and py$^+$), 8.26–8.10 (m, 6 H, *o*-H), 8.0–7.64 (m, 13 H, *m*- and *p*-H and py$^+$), 7.40–7.10 (m, 3 H, *m*- and *p*-H of phenyl nearest py$^+$).

Reaction of ZnTPP$^{+}\cdot$, ClO_4^- with Pyridine-d_5. This reaction followed, in principle, the one with pyridine; the reactants were 157 mg of ZnTPP$^{+}\cdot$, ClO_4^- containing 0.182 mmol (90%) of ZnTPP$^{+}\cdot$ and 0.2 mL of pyridine-d_5 in 10 mL of acetonitrile. Elution with 150 mL of chloroform gave 101 mg of crude ZnTPP, with 400 mL of chloroform gave 37 mg of a purple solid, and with 150 mL of chloroform gave 8 mg of a green solid having an isoporphyrin-like visible spectrum. These solids were not investigated further. Elution with acetone–methanol (4:1) gave 40 mg (0.047 mmol, 26%) of **1**-d_5, mp >360 °C.

During elutions with acetone some trouble was experienced with the formation of small amounts of mesityl oxide.

^{1}H NMR [$(CD_3)_2C{=}O$] δ 9.36 (s, 1 H, β-H adjacent to py$^+$), 8.88 (s, 2 H, β-H), 8.86 (s, 2 H, β-H), 8.78 (d, 1 H, $J = 5$ Hz, β-H), 8.59 (d, 1 H, $J = 5$ Hz, β-H), 8.32–8.16 (m, 6 H, *o*-H), 7.95 (dd, 2 H, $J = 2$, 7.5 Hz, *o*-H of phenyl nearest py$^+$), 7.86–7.76 (m, 9 H, *m*- and *p*-H), 7.50–7.36 (m, 3 H, *m*- and *p*-H of phenyl nearest py$^+$).

Preparation of TPP–py$^+$, ClO_4^- (6) from ZnTPP–py$^+$, ClO_4^-. To a solution of 201 mg (0.235 mmol) of ZnTPP–Py$^+$, ClO_4^- in 100 mL of methanol was added 25 mL of 35% perchloric acid. The dark green methanol solution became light green. Fifty milliliters of water and 150 mL of methylene chloride were added, and ammonia was bubbled into the mixture. The **6** was extracted into the methylene chloride layer by shaking. Extraction was continued with three additional portions of methylene chloride.

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(37) All yields are expressed for simplicity as percent of the starting amount of ZnTPP$^{+}\cdot$. Therefore, in many cases they do not correspond with stoichiometry of eq 1. Where products were formed according to this stoichiometry the yields should be doubled.

(38) Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

The combined methylene chloride solution was concentrated, and ammonia was again bubbled into it. After being washed with water, the methylene chloride solution was evaporated to leave 171 mg (0.216 mmol, 92%) of crude **6**. Crystallization from acetone–ether gave blue crystalline **6**, mp >360 °C.

Anal. Calcd for $C_{49}H_{34}N_5ClO_4$ (**6**): C, 74.3; H, 4.32; N, 8.84; Cl, 4.47. Found: C, 74.3; H, 4.49; N, 8.77; Cl, 4.40.

Reaction of $ZnTPP^{+\cdot}$, ClO_4^- with Triphenylphosphine. Formation of $ZnTPP–P(C_6H_5)_3^+$, ClO_4^- (2). To a solution of 662 mg of $ZnTPP^{+\cdot}$, ClO_4^- containing 0.716 mmol (84%) of $ZnTPP^{+\cdot}$ in 30 mL of acetonitrile was added 100 mg (0.38 mmol) of triphenylphosphine. After being stirred for 24 h, the green solution was concentrated and chromatographed on a column of silica gel. Elution with methylene chloride gave 297 mg of a mixture of ZnTPP and TPP. This mixture was separated on a column of alumina (activity I), giving 53 mg of TPP (benzene elution) and 230 mg of ZnTPP (acetone elution). Continued elution of the silica column with ether gave 30 mg of a yellow solid which was discarded. Elution with acetone gave 439 mg of crude $ZnTPP–P(C_6H_5)_3^+$, ClO_4^-. This was purified by dissolving in methanol and adding a mixture of ether and petroleum ether to cause deposition of 264 mg (0.254 mmol, 35%) of fine, dark blue crystals. These were found to lose 5.06% of their weight on drying at 100 °C, equivalent to $3H_2O$/mol. The dried solid was analyzed.

Anal. Calcd for $C_{62}H_{42}ZnN_4PClO_4$ (**2**): C, 71.7; H, 4.08; N, 5.39; P, 2.98; Cl, 3.41. Found: C, 71.5; H, 4.30; N, 5.11; P, 2.91; Cl, 3.70.

^1H NMR [$(CD_3)_2$ C=O] δ 9.10 (s, 1 H, β-H adjacent to PPh_3^+), 8.86 (m, 5 H, β-H), 8.66 (m, 1 H, β-H). The remaining signals were spread over a wide region from 8.30 to 6.6 ppm. There was a low-field multiplet for 2 H centered at δ 6.76. Analysis of the phenyl signals was not possible.

Reaction of $ZnTPP^{+\cdot}$, ClO_4^- with Triphenylarsine. Formation of $ZnTPP–As(C_6H_5)_3^+$,ClO_4^- (3). To a solution of 793 mg of $ZnTPP^{+\cdot}$,ClO_4^- containing 0.77 mmol (75%) of $ZnTPP^{+\cdot}$ in 40 mL of acetonitrile was added 156 mg (0.50 mmol) of triphenylarsine. After being stirred for 30 min, the green solution was concentrated and chromatographed on silica. Elution with chloroform gave a mixture of ZnTPP and TPP which was later separated on alumina into 36 mg of TPP and 260 mg of ZnTPP. Elution with ether gave 53 mg of solid which was discarded. Elution with acetone gave 506 mg of crude $ZnTPP–As(C_6H_5)_3^+$,ClO_4^-. Crystallization from acetone–ether gave 324 mg (0.299 mmol, 39%) of reddish blue product, mp 266–268 °C.

Anal. Calcd for $C_{62}H_{42}ZnN_4AsClO_4$ (**3**): C, 68.8; H, 3.91; N, 5.17; As, 6.92. Found: C, 68.6; H, 4.02; N, 5.27; As, 7.25.

^1H NMR [$(CD_3)_2$ C=O] δ 8.8 (s, 1 H, β-H adjacent to $AsPh_3^+$), 8.72 (m, 4 H, β-H), 8.48 (m, 2 H, β-H). The remaining signals were spread over a wide region from 8.20 to 6.50 ppm. Two low-field multiplets were observed at δ 7.2 (4 H) and 6.6 (2 H). Analysis of the phenyl signals was not possible.

Reaction of $ZnTPP^{+\cdot}$,ClO_4^- with Thiocyanate Ion. Formation of ZnTPP–SCN (4). To a solution of 641 mg of $ZnTPP^{+\cdot}$,ClO_4^- containing 0.726 mmol (88%) of $ZnTPP^{+\cdot}$ in 30 mL of acetonitrile was added 300 mg (4.7 mmol) of sodium thiocyanate. The solution immediately became red. After being stirred for 1 h, the concentrated solution was chromatographed on a column of alumina (activity I). Elution with benzene–chloroform (95:5) gave 74 mg of impure ZnTPP. Elution with chloroform gave 484 mg of a mixture of mainly ZnTPP and the desired product. This mixture was separated on a series of thick-layer plates with benzene–petroleum ether into three bands. The combined upper bands gave 176 mg of ZnTPP, while the combined lowest bands gave 27 mg of solid which was discarded. The combined center bands gave 189 mg (0.257 mmol, 35%) of **4**, which crystallized from methylene chloride–pentane as blue-black needles, mp 340–342 °C.

Anal. Calcd for $C_{45}H_{27}ZnN_5S$ (**4**): C, 73.5; H, 3.70; N, 9.54; S, 4.35. Found: C, 73.4; H, 3.90; N, 9.59; S, 4.01.

^1H NMR [$CDCl_3$] δ 9.10 (s, 1 H, β-H), 8.92 (s, 4 H, β-H), 8.89 (d, 1 H, β-H), 8.73 (d, 1 H, J = 5 Hz, β-H), 8.28–8.00 (m, 8 H, *o*-H), 7.89–7.64 (m, 12 H, *m*- and *p*-H).

Reaction of $ZnTPP^{+\cdot}$,ClO_4^- with Solid Sodium Nitrite in Acetonitrile. Formation of $ZnTPP–NO_2$ (5) and Bilitriene (7). A. To a solution of 416 mg (0.535 mmol) of $ZnTPP^{+\cdot}$,ClO_4^-, which had 98% cation radical content, in 30 mL of acetonitrile was added 41 mg (0.60 mmol) of solid sodium nitrite. After 40 h of being stirred, the solution had λ_{max} 849, 765, 626, 551, 550, 440, and 375 nm, indicating the presence of ZnTPP and either the bilitriene (**7**) or an isoporphyrin, and the absence of $ZnTPP^{+\cdot}$. After the residual sodium nitrite was filtered and washed with benzene, the combined solution was evaporated to dryness on a rotary evaporator at room temperature, giving 455 mg of blue solid. This was chromatographed on a 2.5 × 30 cm column of neutral alumina (Woelm, activity II). Elution with 330 mL of benzene gave 135 mg (0.199 mmol, 37%) of ZnTPP. A further 50 mL of benzene gave 2 mg of solid which was discarded. Elution with 500 mL of benzene–chloroform (80:20 by volume) gave 91.3 mg of blue-black solid shown to be $ZnTPP–NO_2$ (**5**) (λ_{max} 599, 556, 520, and 418 nm), while 350 mL of benzene–chloroform (50:50) gave a further 3.2 mg of **5**; the total yield was 0.131 mmol (25%). Elution with 400 mL of chloroform gave 5 mg of solid which was discarded. Elution with chloroform–methanol (95:5) was next carried out. The first 50 mL gave 15 mg of what was again found to be ZnTPP, giving a total ZnTPP yield of 0.222 mmol (41%). The next 20 mL gave 1.7 mg of tan solid which was discarded, and the following 50 mL gave 83 mg of purple solid which was shown to be **7** (0.128 mmol, 24%). Continued elution with chloroform–methanol (95:5 and 50:50) gave six fractions totaling 11.4 mg of solid, while elution with methanol gave 10 mg of solid. None of these fractions was identified.

B. To a solution of 530 mg of $ZnTPP^{+\cdot}$,ClO_4^- containing 0.58 mmol (86%) of $ZnTPP^{+\cdot}$ in 35 mL of acetonitrile was added 500 mg (5.9 mmol) of potassium nitrite, causing the solution to become red. The suspension was stirred for 30 min, filtered, concentrated, and chromatographed on a column of alumina (activity II). Elution with benzene gave 3.7 mg of TPP, with benzene–chloroform (90:10) gave 135 mg of ZnTPP, with chloroform gave 97 mg (0.134 mmol, 23%) of crude **5**, and with acetone gave 89 mg (0.138 mmol, 24%) of purple solid, assumed to be the bilitriene (**7**). Crystallization of crude **5** from ether–petroleum ether gave fine black crystals which did not melt below 360 °C.

Reaction of $ZnTPP^{+\cdot}$,ClO_4^- with Aqueous Sodium Nitrite in Acetonitrile. To a solution of 427 mg (0.55 mmol) of $ZnTPP^{+\cdot}$,ClO_4^- (98%) in 30 mL of acetonitrile was added a solution of 324 mg (4.7 mmol) of sodium nitrite in 2 mL of water. This caused the green solution to turn magneta immediately, and some magenta precipitate was formed. After the mixture was stirred for 45 h, the solvent was evaporated, and the solids were dissolved in methylene chloride which was then washed with water, dried, and evaporated to give 398 mg of blue solid. Column chromatography on 2.5 × 33 cm of neutral alumina (activity II) gave, with benzene, 2.4 mg of TPP (0.7%), 355 mg (0.524 mmol, 95%) of ZnTPP, and 4.5 mg (0.006 mmol, 1%) of **5**. Further elution with benzene, benzene–chloroform, and chloroform gave small amounts of solid which were not identified. Elution with chloroform–methanol gave 5.4 mg (0.008 mmol, 1.5%) of **7**.

Reaction of $ZnTPP^{+\cdot}$,ClO_4^- with Aqueous Sodium Nitrite and Urea in Acetonitrile. An experiment similar to the one above was carried out with 471 mg (0.606 mmol) of $ZnTPP^{+\cdot}$,ClO_4^- and a solution of 235 mg (3.41 mmol) of sodium nitrite and 293 mg (4.89 mmol) of urea in 2 mL of water. The color change and precipitation occurred again. Workup gave 367 mg (0.541 mmol, 89%) of ZnTPP, 10 mg (0.014 mmol, 2.3%) of **5**, and 13.8 mg (0.021 mmol, 3.5%) of **7**.

Reaction of $ZnTPP^{+\cdot}$,ClO_4^- with Water in Tetrahydrofuran (THF). A 2-mL sample (111 mmol) of water was added to a green solution of 420 mg (0.54 mmol) of $ZnTPP^{+\cdot}$,ClO_4^- in 30 mL of THF. The color was initially unchanged but became grey-brown after 1 h. After 48 h the visible spectrum of an aliquot in methylene chloride had λ_{max} 864, 780, 655, 593, 552, and 420 nm. Evaporation, extraction into methylene chloride, etc. gave 353 mg of blue solid. Column chromatography gave 60 mg (0.098 mmol, 18%) of TPP, 241 mg (0.356 mmol, 66%) of ZnTPP, and 47 mg (0.073 mmol, 13%) of **7**. Several small fractions were obtained and were not identified.

Reaction of $ZnTPP^{+\cdot}$,ClO_4^- with Aqueous Sodium Nitrite in THF. Repetition of the above experiment with 402 mg (0.517 mmol) of $ZnTPP^{+\cdot}$,ClO_4^- and 244 mg (3.54 mmol) of sodium nitrite in 2 mL of water caused an immediate change in color from green to red (ZnTPP). After 45 h an aliquot in methylene chloride had λ_{max} 547, 512, 483, 420, and 401 nm; the spectrum was like that of ZnTPP. Workup gave 323 mg (0.476 mmol, 92%) of ZnTPP, 3.7 mg (0.005 mmol, 1%) of **5**, and 4 mg (0.006 mmol, 1%) of **7**.

Reaction of ZnTPP$^{+\cdot}$,ClO$_4^-$ with Solid Sodium Nitrite in Methylene Chloride. A solution of 445 mg of ZnTPP$^{+\cdot}$,ClO$_4^-$ (95% pure, 0.544 mmol) in 30 mL of methylene chloride was stirred for 48 h with 291 mg (4.22 mmol) of solid sodium nitrite. The visible spectrum had λ_{max} 846, 765, 586, 549, 510, 421, and 400 nm, indicating the presence of ZnTPP and either **7** or an isoporphyrin. Workup gave 6 mg (0.0098 mmol, 1.8%) of TPP, 176 mg (0.26 mmol, 48%) of ZnTPP, 126 mg (0.174 mmol, 32%) of **5**, and 66 mg (0.102 mmol, 19%) of **7**.

Reaction of ZnTPP$^{+\cdot}$,ClO$_4^-$ with Solid Sodium Nitrite and Urea in Methylene Chloride. A reaction similar to that above was carried out with 550 mg of ZnTPP$^{+\cdot}$,ClO$_4^-$ (91% pure, 0.645 mmol), 247 mg (3.58 mmol) of sodium nitrite, and 2.14 g (35.7 mmol) of urea. The solution slowly turned grey-brown. After 40 h the visible spectrum showed weak bands characteristic of either **7** or an isoporphyrin. Workup gave 4.2 mg (0.0068 mmol, 1%) of TPP, 215 mg (0.318 mmol, 49%) of ZnTPP, 130 mg (0.180 mmol, 28%) of **5**, and 63 mg (1.01 mmol, 15%) of **7**.

Identification of ZnTPP–NO$_2$ (5) and the Bilitriene (7). Products from the reactions of sodium nitrite and water with ZnTPP$^{+\cdot}$ (i.e., TPP and ZnTPP) were identified by their visible and mass spectra and occasionally by TLC. ZnTPP–NO$_2$, mp >360 °C, was identified by mass spectrum (*m/e* found 721.147 55, calcd 721.1356), ^{1}H NMR, and elemental analysis.

Anal. Calcd for $C_{44}H_{27}ZnN_5O_2$ (**5**): C, 73.1; H, 3.76; N, 9.68. Found: C, 73.2; H, 3.90; N, 9.52.

^{1}H NMR [$(CD_3)_2C{=}O$] δ 9.10 (s, 1 H, β-H), 8.84 (s, 6 H, β-H), 8.30–8.10 (m, 8 H, *o*-H), 7.90–7.60 (m, 12 H, *m*- and *p*-H).

The bilitriene (**7**), mp 140–144 °C, was identified by mass spectrometry and by comparison of its ^{1}H NMR absorption spectra with those of a sample supplied by Professor K. M. Smith.[39] The spectra were identical in all aspects except for weak NMR signals attributable to small amounts of impurity.

Reaction of ZnTPP$^{+\cdot}$,ClO$_4^-$ with Methanol. Formation of ZnTPP–OMe$^+$, ClO$_4^-$ (10). To 35 mL of methanol which had been distilled from magnesium and iodine was added 787 mg of ZnTPP$^{+\cdot}$,ClO$_4^-$ containing 0.86 mmol (85%) of ZnTPP$^{+\cdot}$. After being stirred overnight, the red solution was concentrated and chromatographed on a column of silica. Elution with chloroform gave a mixture of TPP and ZnTPP which was separated later on a column of alumina (activity I) into 36 mg of TPP and 233 mg of ZnTPP. Elution with ether gave 57 mg of solids which were discarded. Elution with acetone gave 427 mg of brown solid, part of which was rechromatographed on silica to give 307 mg (0.379 mmol, 44%) of **10**. Three crystallizations of part of the brown solid from benzene–petroleum ether gave brown granular crystals which did not melt below 360 °C.

Anal. Calcd for $C_{45}H_{31}ZnN_4ClO_5$ (**10**): C, 66.8; H, 3.87; N, 6.93; Cl, 4.38. Found: C, 66.6, 66.7; H, 4.43, 4.16; N, 6.74; Cl, 4.03.

^{1}H NMR [C_6D_6] δ 7.06 (m, 20 H, phenyl protons), 6.56 (m, 6 H, β-H), 6.28 (d, 2 H, J = 4.5 Hz, β-H), 3.58 (br s, 3 H, Me).

Reaction of ZnTPP$^{+\cdot}$,ClO$_4^-$ with Ammonia and Amines. Formation of ZnTPP. In separate experiments, ammonia, methylamine, and dimethylamine were bubbled into solutions of ZnTPP$^{+\cdot}$,ClO$_4^-$ in acetonitrile. In each case the solution turned red. Workup and chromatography on alumina (activity III) gave ZnTPP in yields of 91% (ammonia), 100% (methylamine), and 86% (dimethylamine). Some small bands were also seen on the columns but were not collected.

Absorption Spectra. These were recorded with solutions in methylene chloride and are given in λ nm ($10^{-4}\epsilon$): **1**, 594 (1.28), 555 (1.67), 520 sh (0.572), 427 (27.0); **2**, 601 (1.61), 561 (1.43), 527 sh (0.484), 433 (36.9); **3**, 597 (1.59), 558 (1.74), 524 sh (0.483), 490 sh (0.212), 431 (43.1); **4**, 586 (0.567), 551 (2.45), 515 (0.383), 485 sh (0.183), 426 (48.4); **5**, 597 (1.02), 555 (1.55), 520 sh (0.391), 426 (21.7); **6**, 656 (1.16), 601 (0.514), 560 sh (0.413), 525 (1.71), 425 (24.9).[40]

Registry No. **1**, 60165-30-2; **1**-d_5, 71435-51-3; **2**, 71435-53-5; **3**, 71435-55-7; **4**, 71435-56-8; **5**, 71435-57-9; **6**, 60148-22-3; **7**, 63160-30-5; **10**, 25895-68-5; TPP, 917-23-7; ZnTPP, 14074-80-7; ZnTPP$^{+\cdot}$ClO$_4^-$, 34465-02-6; pyridine, 110-86-1; pyridine-d_5, 7291-22-7; triphenylphosphine, 603-35-0; triphenylarsine, 603-32-7; sodium thiocyanate, 540-72-7; sodium nitrite, 7632-00-0; potassium nitrite, 7758-09-0; methanol, 67-56-1; ammonia, 7664-41-7; methylamine, 74-89-5; dimethylamine, 124-40-3.

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(39) We thank Professor Smith for sending us copies of his spectra and a sample of his bilitriene and for comparing also in his laboratory a sample of our bilitriene with that isolated in Liverpool.

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Chromium(VI) Oxidations of Alkynes

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The distribution of products from the reaction of several chromium(XI) reagents with various alkynes was studied in order to determine the most efficient reagent for α-oxidation. Chromic acid, chromyl acetate, chromyl chloride, *tert*-butyl chromate, chromium trioxide–pyridine complex, and pyridinium chlorochromate were compared with regard to their ability to oxidize diphenylethyne, 1-phenyl-1-ethyne, 1-phenyl-1-ethyne, 2-decyne, 5-decyne, 4-octyne, and 7-tetradecyne. The chromium trioxide–pyridine complex and pyridinium chlorochromate were found to be the most efficient reagents for preparing conjugated ynones.

Chromium(VI) and manganese(VII) are two of the strongest and most commonly used oxidizing agents for organic compounds. These reagents, however, exhibit quite different selectivities. Chromium(VI) oxidizing agents have been used extensively in organic synthesis[1a–e] and in particular are useful for the conversion of primary alcohols to aldehydes[2a–g] and carboxylic acids and secondary alcohols to ketones. In addition, chromium(VI) reagents have been used to prepare α,β-unsaturated carbonyl compounds. While manganese(VII) rapidly reacts directly with the π

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