

Review Article

Photocatalytic Oxygenation by Water-Soluble Metalloporphyrins as a Pathway to Functionalized Polycycles

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Photocatalytic processes are present in natural biochemical pathways as well as in the organic synthetic ones. This minireview will cover the field of photocatalysis that uses both the free-base and specially metallated porphyrins as catalysts. While free-base porphyrins are valuable sensitizers to output singlet oxygen, metalloporphyrins are even more adjustable as photocatalysts because of their coordination capacity, generating a wider range of oxidation reactions. They can be applied in autooxidation reactions, hydroxylations, or direct oxygen transfer producing epoxides. This review will mainly focus on how manganese and some iron porphyrins can be utilized for the functionalization of compounds that have a polycyclic skeleton in their structure. These kinds of compounds are notoriously taxing to obtain and difficult to further functionalize by conventional organic synthetic methods. We have focused on photocatalytic oxygenation reactions in mild conditions with the use of water-soluble porphyrins, as this has been proven to be a good tool for these transformations. In the photocatalytic reactions of some polycyclic heteroaromatic compounds, new polycyclic epoxides, enediones, ketones, alcohols, and/or hydroperoxides are yielded, depending on the catalyst applied. The application of anionic and cationic Mn(III) porphyrins under different reaction parameters results in different reaction pathways generating a vast number of photocatalytic products. Recently, Co and Ni complexes have been also photophysically investigated and confirmed as potential photocatalysts for the functionalization of organic substrates.

1. Introduction

Photocatalytic processes have been demonstrated to be numerous in both natural and artificial surroundings, such as photosynthesis, which is the basis of the food chain on Earth [1], as well as oxidative degradation of manifold damaging organic pollutants [2] and surfactants [3]. These processes are also used in photodynamic therapy (PDT) and oxidation of organic compounds. Living organisms can also profit from the application of these processes where different sensitizers such as porphyrins can, by excitation, lead to in situ production of singlet oxygen and/or superoxide radical anion in the tissue of malignant tumors [4] as oxidative agents. Singlet oxygen can be employed for preparative reasons in organic synthetic chemistry, like for the synthesis of

oxygenated derivatives of organic compounds. When a nonmetallated porphyrin is the photoactive species in the reaction, the longer-lived triplet is the key state in the photo-induced reactions. The porphyrin acts as a sensitizer and produces singlet oxygen via triplet quenching by the dissolved ground-state oxygen molecules. While free-base porphyrins are useful sensitizers for the production of singlet oxygen [5–9], metalloporphyrins are much more versatile photocatalysts due to their coordination ability, promoting a wider range of oxidation reactions as was first represented by Hennig et al. [10–12] (Figure 1).

Metalloporphyrins can be applied in autooxidation, hydroxylation, or direct oxygen transfer giving epoxides [10, 11]. Cationic Mn(III) porphyrins are attested to be effective catalysts for oxygenation of α -pinene (Scheme 1).

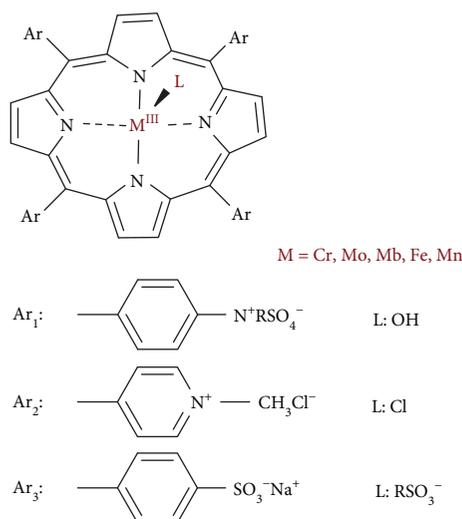


FIGURE 1: Structures of metalloporphyrins investigated by Hennig et al. [11].

The selective epoxidation giving compound **2** was detected in aqueous systems at an apropos low substrate/catalyst ratio ($S/C = 500$), until in aprotic organic solvents, such as benzene or toluene, allylic hydroxylation (**3–5**) and keto products (**6,7**) were formed [12]. Using various metalloporphyrins in acetonitrile, photocatalytic epoxidation of cyclooctene was also achieved [13]. Photocatalytic oxygenation of cycloalkenes [12–15] and other unsaturated heteroaromatics [5] was carried out by the application of both metallated and free-base porphyrins [5, 12–15], and it was confirmed that Fe- and Mn-porphyrin complexes give the most effective results as photocatalysts. Resemblances and differences in the photocatalytic oxygenation runways may shed light on the mechanisms of the diverse oxygenation processes, giving an indication for a convenient choice of a catalyst and efficient conversion with high selectivity. The ligand charge, affecting its Lewis basicity, may cause the catalytic activity of the complex through the metal center.

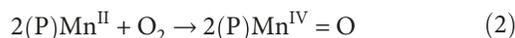
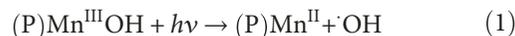
By photocatalytic oxygenation of various alkenes, with dioxygen and (5,10,15,20-tetraarylporphyrinato)iron(III) complexes, allylic oxygenation products and/or epoxides are obtained. The composition of the product mixture is influenced by the nature of the substrate and by the concentrations, but the axial ligands also play a role. Alkenes that have a strained double bond preferentially give epoxides, and allylic oxygenation is observed when unstrained alkenes are used. The proposed reaction mechanisms [16] give the oxoiron(IV) porphyrinate ((P)Fe^{IV}=O) as the catalytically active species. The selectivity of this species is related to the oxygenation of α -pinene with microsomal cytochromes P-450 and P-420 obtained from the yeast strain *Torulopsis apicola* [16]. Oxygenation products observed in both cases give evidence for the occurrence of an oxoiron(IV) heme species in microsomal cytochrome P-450-mediated reactions. The enantio-, regio-, and chemoselectivities of the photooxygenation with the iron(III) porphyrins and molecular oxygen are explained by the abstraction of the allylic hydrogen atom followed by catalyzed autoxidation and direct oxygen-

transfer reactions [16]. Oxoiron(IV) porphyrinate exhibits a broad spectrum of oxygenation reaction pathways as does the microsomal cytochrome P-450. It can be presumed that the (P)Fe^{IV}=O would be an attractive candidate for an alternative and/or a competing analogous iron heme complex in cytochrome P-450-mediated oxygenation reactions.

Besides the water solubility of the metalloporphyrins, their photostability is of great importance and in that way manganese porphyrins are much more stable than the analogous iron complexes [11]. Taking this enhanced photostability of the porphyrin complexes into consideration, the manganese(III) porphyrinates were precisely the ones used in the more recent investigations.

According to previous studies on the oxygenation of cycloalkenes, the mechanism of the photooxygenation reaction is quite complicated, involving at least 3–4 elementary steps [5, 6, 9]. In some of the earlier studies [12, 17–30], as well as in more recent ones [13, 15], it is explained that when Mn(III) porphyrins act as photocatalysts, (P)Mn^{IV}=O and (P)Mn^V=O intermediates play a key function in all of the in situ-produced reactive species in the oxygenation of cycloalkenes (Scheme 2).

The production of (P)Mn^V=O in the primary photoreactions was detected in acetonitrile. (P)Mn^{IV}=O was produced by photoinduced homolysis of the O-Cl or O-N bond of axially coordinated chlorate or nitrate, respectively, in acetonitrile [13, 15], or via a ligand-to-metal charge-transfer process (also a photoinduced homolysis but that of the metal-ligand bond) with chloride or hydroxide axial ligands in aqueous systems [11, 12]. In the latter case, the Mn(II) species was formed in the primary photochemical step (equation 1) followed by the coordination of oxygen (equation 2).

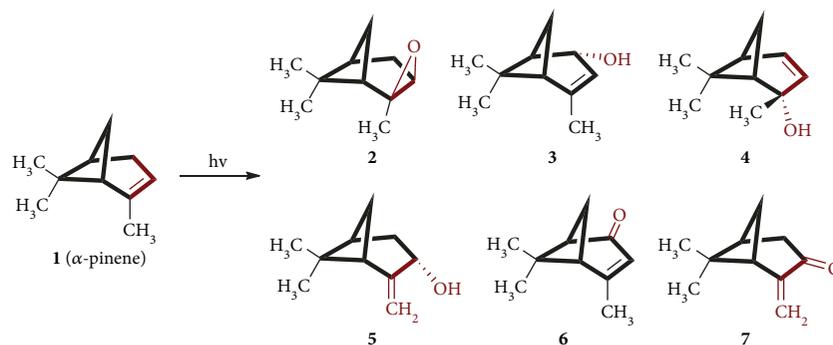
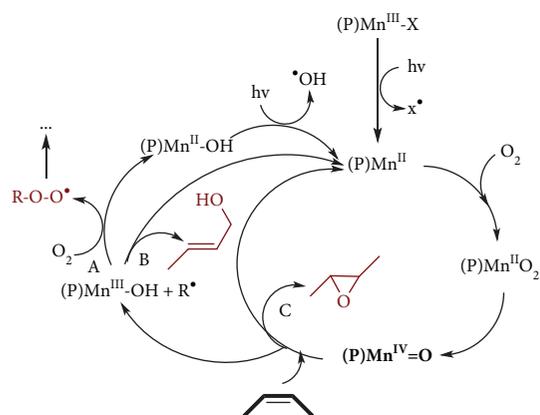


Equation 2 is an overall reaction comprising of several steps. When experiments are run in water-acetone as solvent mixtures, hydroxide or water is axially coordinated around the Mn(III) center. Hydroxyl radicals formed in the primary photochemical step most probably react with the organic solvent. The Mn(IV) complexes are readily disproportionated and give highly reactive manganese(V)-oxo species (equation 3) [13, 15].



Disproportionation is much faster than synproportionation in the equilibrium system. A polar solvent promotes the disproportionation process, and in this case, the process comes over with nearly a diffusion-controlled rate constant [31]. The rate constants for epoxidation of olefins are several orders of magnitude higher for Mn(V)-oxo porphyrins than for the convenient Mn(IV) species. It is considered that the (P)Mn^V=O species is the principal oxidant in the photocatalytic oxygenations in the investigated systems.

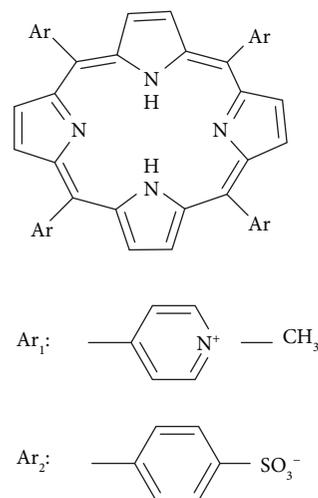
Starting with the idea that a polycyclic structure can be easily modified and functionalized by the utilization of a

SCHEME 1: Product distribution for photocatalytic oxygenation of α -pinene (1) [11, 17].

SCHEME 2: Photocatalytic oxygenation of alkenes in the presence of metal porphyrins [11] (A—autooxidation; B—oxygen rebound mechanism; and C—direct oxygen transfer).

photocatalytic approach, Kikaš et al. and Vuk et al. have made significant progress in this area. They have been proliferative in the field of photocatalytic oxygenation using water-soluble manganese porphyrins applied to bicycloalkenes [32–35]. From their viewpoint, it was very important to consider the structure of the natural terpene, α -pinene (Scheme 1), as a compound having the bicyclo(3.1.1)hexene structure, very similar to the structure of photoproducts obtained by a cycloaddition reaction in very good yields. Recently, these yields have even been improved by the utilization of the flow-photochemical methodology [36]. The manganese(III) complexes of the cationic 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin (Mn(III)TMPyP⁵⁺) and the anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (Mn(III)TSPP³⁻) along with the anionic free base were used in the experiments (Figure 2).

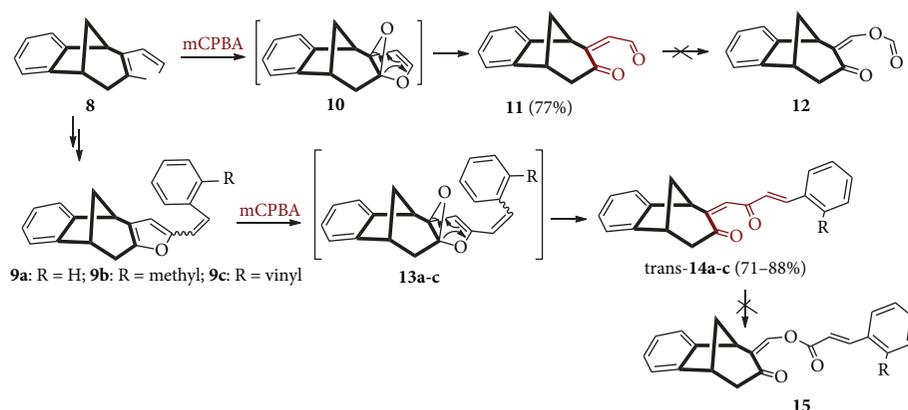
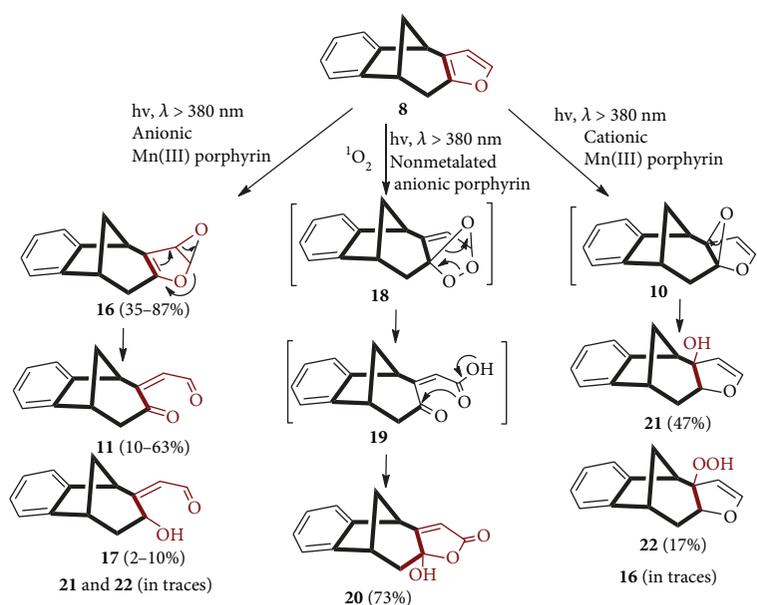
In the first published paper by these authors, an investigation was performed on the benzobicyclo(3.2.1)octadiene system **8** where the oxygenation runways of this furobicyclic skeleton in a thermal reaction involving mCPBA and photocatalytic processes mediated by nonmetallated and Mn(III) porphyrins are compared. In the thermal reaction of **8** and **9** using mCPBA (Scheme 3), the enedione **11** is obtained via the rearrangement of intermediate epoxide **10** produced primarily from **8**.

FIGURE 2: Structures of cationic porphyrin (Ar₁) and anionic porphyrin (Ar₂).

There are two epoxidation possibilities on the furan derivative **8**, but the authors corroborate with the literature and propose that the initial epoxidation comes over at the substituted cyclohexyl side of the furan ring as signified in the left sequence in Scheme 3. This is judicious on the basis of the idea that epoxidation should occur at the double bond holding the more electron-donating functional group. Further oxygenation to **12** does not take place. Compounds **9a-c** were also subjected to additional thermal transformations using mCPBA, producing all *trans*-**14a-c** (formed via intermediates **13a-c**). Further oxygenation to the product **15** was not observed.

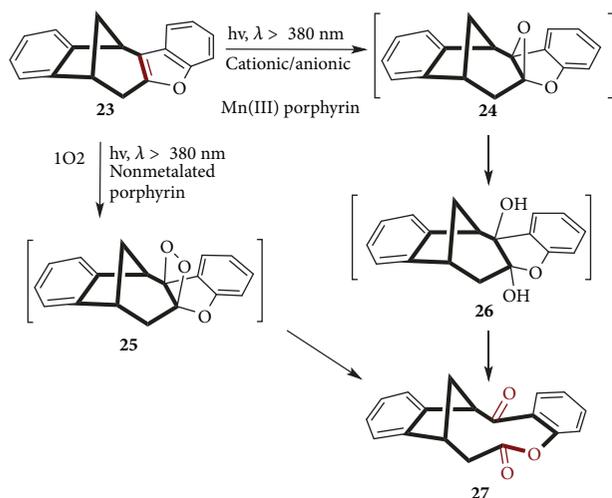
Light-initiated oxygenation of **8** was carried out using various porphyrins as photocatalysts (Scheme 4).

It was concluded that the longer-lived triplet state plays a role in the photoinduced reactions if a free-base porphyrin is the photoactive species used. This catalyst operates as a sensitizer thus producing singlet oxygen via triplet quenching. The product is the hydroxybutenolide **20** (Scheme 4), which is not detected in any other oxygenation process. This obviously demonstrates that this is the only case when singlet oxygen is the oxidative agent. Thus, due to previous studies on the oxygenation of cycloalkenes, the mechanism

SCHEME 3: Proposed reaction pathways for the thermal reactions of **8** and **9a-c**.SCHEME 4: Proposed reaction runways for the photocatalytic oxygenation of **8** (pH = 7, air saturation).

of this reaction is sufficiently complicated [5, 6, 9]. In the case when anionic Mn(III)TSP^{3-} was used, the epoxy-derivative **16** and furan ring-opened **11** and **17** products were observed (Scheme 4). When the Mn(III)TMPyP^{5+} porphyrin is used, hydroxy **21** and hydroperoxy **22** derivatives are the major products. The change in the sign of the charge of the ligand alters the assignment of the products. The lower Lewis basicity of the porphyrin ligand improves oxygenation on C=C bonds, and this was verified by flash photolysis experiments with Mn(III) porphyrins holding substituents of different electron demands [15, 31]. When the authors modified the experimental conditions (pH or oxygen concentration), there were variations in the ratio of the products, but this did not affect the establishment of further novel species. Enhancement of pH to 10 magnified the quantity of the epoxide **16**. They explain that higher pH disrupts further oxidation of this derivative, and this can be linked to the function protons play in the disproportionation producing an Mn(V) species. Bubbling oxygen instead of air

significantly enhanced the amounts of the compounds **16** and **17**. Studies [12, 13, 15] have pointed out that in the case of Mn(III) porphyrins as photocatalysts, $(\text{P})\text{Mn}^{\text{IV}}=\text{O}$ and $(\text{P})\text{Mn}^{\text{V}}=\text{O}$ intermediates play a key function in the oxygenation of cycloalkenes. The production of $(\text{P})\text{Mn}^{\text{V}}=\text{O}$ was observed in acetonitrile as a consequence of heterolytic cleavage of the O-Cl bond in the axially coordinated perchlorate counterion [15, 31]. $(\text{P})\text{Mn}^{\text{IV}}=\text{O}$ was produced by photoinduced homolysis of the O-Cl or O-N bond of axially coordinated chlorate or nitrate, respectively, in acetonitrile [15, 31] or via a ligand-to-metal charge-transfer process with chloride or hydroxide axial ligands in aqueous systems [11, 12]. The mechanism of this complex set of reactions is as described previously by Hennig et al. and already presented earlier in the minireview. As indicated in Scheme 4, the positively charged porphyrin ligand advances the electrophilic attack to the inside double bond of the furan ring. The anionic catalyst favors the outside double bond. Likened to the outside C=C bond, the accessibility of



SCHEME 5: Proposed reaction pathways for photocatalytic oxygenation of 23.

the inside double bond for the oxygen atom coordinated to the lumbering macrocyclic skeleton is sterically interfered with its bicyclic environment. From an electronic aspect, this bond is more favored for an electrophilic attack as an outcome of the electron-donating consequence of the nearby hydrocarbon (bicycloalkyl) parts of the molecule. Because of the lower Lewis basicity of the cationic complex, the corresponding Mn(V)-oxo intermediate has a much more electrophilic performance than the anionic one. For the lesser electrophilic anionic complex, steric disturbance is the predominant result, promoting the attack at the more accessible outside bond. To study the effect of the increased steric hindrance of the oxidative attack at the outer bond of the furan ring, photocatalytic oxygenation experiments using both the anionic and cationic manganese(III) porphyrins (Mn(III)TSPP³⁻ and Mn(III)TMPyP⁵⁺) and their corresponding free bases (H₂TSPP⁴⁻ and H₂TMPyP⁴⁺) were carried out with the annulated derivative 23 (Scheme 5) [33].

The major product was the same in every case, no matter which catalyst was used under diverse conditions [33]. Structure determination and characterization unambiguously showed that 10-membered ketolactone 27 was obtained. This result propounds that, beside a strong steric disturbance, a considerable electronic consequence was enforced by the annulation of a benzene ring to the outside of the furan ring.

In their later paper [34], the same authors investigate more polycyclic substrates containing oxygen and sulfur in their structures. When the structure that is studied has a (2,3-*b*-furo) moiety incorporated into the skeleton, the results with both cationic and anionic Mn(III) porphyrin catalysts differ (Scheme 6) from the previously studied (3,2-*b*-furo)-octadienes [32].

While in the case of 8, using the anionic Mn(III) porphyrin, epoxide and furan ring-opened derivatives were the main products, and photocatalytic oxygenation of 28 led to the formation of hydroxy 29 and hydroperoxy 30 derivatives. In the presence of the cationic Mn(III) porphyrin, only one product was formed (Scheme 6), the hydroxybutenolide derivative 31,

which is similar to that observed in the photocatalytic oxygenation of 8 (Scheme 4, formed when using the free-base catalyst where the photochemically generated singlet oxygen was the oxidative agent) [32]. The results in this study suggest that in the compound 28 the inner double bond is more preferred by the attack of the cationic Mn(III) porphyrin than by the anionic one. The replacement of oxygen by sulfur resulted in changes in photocatalytic reactivity (Schemes 7 and 8).

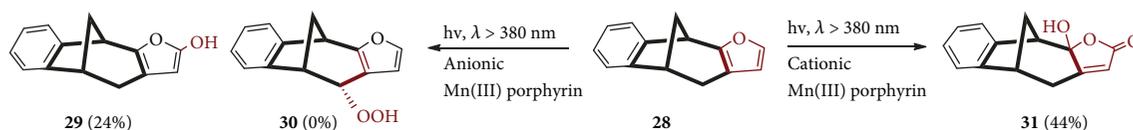
The reactivity of these thienyl substrates is much lower than that of the corresponding furan ones, and this is attributed to the much higher aromaticity of the thiophene ring. The products formed from 32 suggest that the attack by hydroxyl radicals (equation 1) play a more determining role in this system than the Mn(V)=O species do, and this is in accordance with the catalyst-independent yields.

Continuing this study of photocatalytic oxygenations of various bicyclic organic compounds, derivatives with an isolated/free double bond were investigated [35]. These compounds also contained a phenyl group (unsubstituted or substituted) close to the free double bond, which significantly affected the mechanism of manganese(III) porphyrin-based photocatalytic oxygenation and the products gained (Scheme 9).

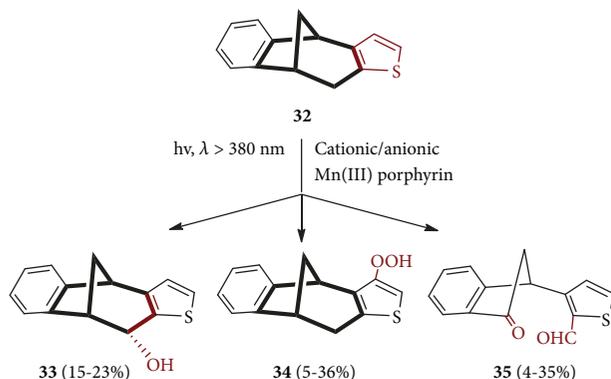
A considerable π -stacking interaction between that phenyl ring and the porphyrin catalyst promoted the functionalization of the carbon atom resulting in the formation of the suitable hydroperoxy derivatives of 38a and b. No effect of the porphyrin charge was observed in these cases, and the main oxygenation reaction of the methoxy derivative 38c was efficient only with the cationic complex; this is probably due to its interaction with the electron-rich free double bond. These results further corroborate that both steric and electronic effects govern the mechanisms of the photocatalytic oxygenations of these compounds.

All the presented successful results confirm that the use of the photocatalytic activity of water-soluble Mn(III) porphyrins for the oxygenation of benzobicyclo(3.2.1)octadienes 8, 23, 28, 32, 36, and 38 was justified, especially as they possess a basic core very similar to those previously analyzed and naturally coming over cycloalkenes, which are bioactive and significant substances isolated from nature [37].

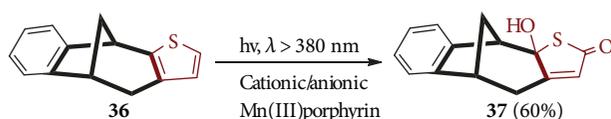
Recently, Co and Ni complexes have also been photophysically investigated by Horváth et al. as potential photocatalysts as well as for the functionalization of organic substrates by photocatalytic oxygenation in comparison to Mn(III) porphyrins [38–40]. The obtained results well demonstrated how the size of the metal center determines the structure and, thus, the photoinduced behavior of the porphyrin complexes, along with the substituents on the ligand. Co(III) porphyrin complexes showed similar photophysical characteristics as the depicted Mn(III) porphyrins, while Ni complexes display somewhat different photophysical behavior and function as special sensitizers, which immediately transmit their excitation energy to the electron donor, promoting the direct charge transfer toward the acceptor. All those results well demonstrate that both Co(III) and Ni(II) porphyrin complexes may be applicable for solar energy utilization in the visible range and probably as oxidative



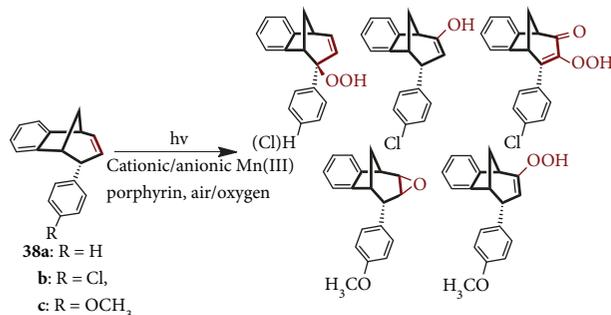
SCHEME 6: Proposed reaction pathways for the photocatalytic oxygenation reactions of **28** (pH = 7, oxygen saturation) [34].



SCHEME 7: Reaction pathway for the photocatalytic oxygenation reactions of **32** (pH = 7, oxygen saturation) [34].



SCHEME 8: Photocatalytic oxygenation of **36** to photoproduct **37** (pH = 7, oxygen saturation) [34].



SCHEME 9: Photocatalytic oxygenation of **38** (pH = 7, air/oxygen saturation) [35].

reagents for photocatalytic oxygenation of the described unsubstituted photoproducts to give new functionalized polycycles very similar to the structures of some terpenes from nature.

2. Conclusions

It is shown that free-base and metallated porphyrins are extremely useful in photocatalysis. This minireview has focused on the utilization of these porphyrins for the functionalization of compounds that have a polycyclic skeleton in

their structure. These kinds of compounds are notoriously taxing to obtain and difficult to further functionalize using conventional organic synthetic methods, so photocatalytic oxygenation is a good tool for these transformations. In these photocatalytic processes, novel polycyclic epoxides, enediones, ketones, alcohols, and/or hydroperoxides are formed, subordinate to the catalyst used. The application of anionic and cationic Mn(III) porphyrins under different reaction parameters resulted in different reaction pathways thus generating a vast number of photocatalytic products. As a future development in the field, Co and Ni complexes have also been recently photophysically investigated and confirmed as good potential photocatalysts for further functionalization of organic substrates.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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