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A new and efficient aerobic oxidation of aldehydes to carboxylic acids with singlet oxygen in the presence of porphyrin sensitizers and visible light

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ABSTRACT

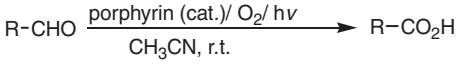
A new aerobic route is introduced for the oxidation of a variety of aromatic and aliphatic aldehydes to the corresponding carboxylic acid derivatives using molecular oxygen in the presence of tetraphenylporphyrin (H_2TPP), tetramesitylporphyrin (H_2TMP), tetrakisdichlorophenylporphyrin (H_2TDCPP), ZnTPP, and ZnTMP as sensitizers using visible light in an organic solvent. The method has a wide range of applications, does not involve cumbersome work-up, exhibits chemoselectivity, and proceeds under mild reaction conditions. The products are obtained with good conversions and in reasonable reaction times.

Oxidation is a fundamental reaction in synthetic organic chemistry and a variety of oxidants have been developed. The oxidation of aldehydes to carboxylic acids has been of long-standing interest in synthetic organic chemistry.[1] The popular conventional method involves the use of the Jones' reagent.[2] This is a stoichiometric reaction using highly acidic conditions which may not be tolerated by acid-sensitive functionalities in the substrate. Moreover, the generation of Cr-based side products may be viewed as a potential environmental hazard. Other efficient reagents that have been reported in the literature to achieve such transformations include Oxone,[3] calcium hypochlorite,[4] and 2-hydroperoxyhexafluoro-2-propanol.[5] Some interesting methods involving metal-mediated transformations of aldehydes into carboxylic acids have also been reported.[6]

Porphyrins and metalloporphyrin complexes (MP) have received significant attention due to their relevance to numerous biological systems.[7] Metalloporphyrins have been found to be efficient biomimetic catalysts for hydrocarbon oxidation using molecular oxygen and various oxygen transfer reagents.[8] However, finding a catalytic system for hydrocarbon oxidation by O_2 under mild conditions is still a challenging issue. Iron porphyrins have been used as catalysts for alkane hydroxylation by O_2 whilst consuming a stoichiometric amount of the reducing agent.[9] The oxidation of alkanes to alcohols and ketones was achieved at 80 °C under a 10 atm pressure of oxygen.[10] A few examples of photochemical photooxidation using O_2 and an MP catalyst have been reported.[11,8] In previous studies, oxidation of hydrocarbons by metalloporphyrins that have a strong affinity for the generation of metal-oxo species (M=O) was investigated with chemical oxidants such as *meta*-chloroperbenzoic acid (*m*-CPBA).[12] Recently, Noyori and co-workers used Na_2WO_4 for the oxidation of a variety of aromatic and aliphatic aldehydes to the corresponding carboxylic acid derivatives.[6m]

The photosensitized production of singlet oxygen has significance in the areas of photooxidation of organic compounds, DNA damage, and photodynamic therapy.[13,14] Therefore, a variety of photosensitizers have been developed and their photochemical and photophysical properties have been extensively studied.[15] Among these, tetrapyrrolic compounds such as porphyrins and phthalocyanines are promising candidates as photosensitizers due to their unique photophysical properties.[16–20] The syntheses of porphyrin isomers have opened routes for the development of new photosensitizers.[21–23] In this work we investigated the photocatalytic oxidation of aldehydes and describe the effects of solvent, time, metal, and the structure of the sensitizers on these reactions.

In continuation of our studies on porphyrins and aerobic oxidation of organic compounds,[24] we describe the photocatalytic oxidation of aldehydes to carboxylic acids by molecular oxygen under irradiation with visible light in the presence of porphyrins as sensitizers (sens) (Scheme 1). Scheme 2 shows the structures of



Scheme 1. Oxidation of aldehydes to carboxylic acids.

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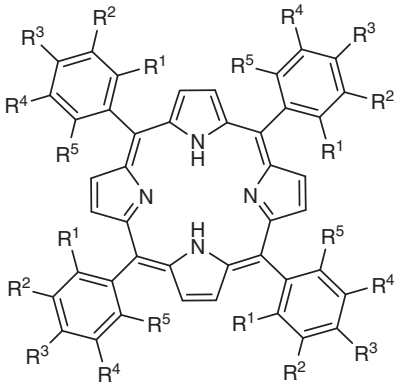


H_2TPP: $R^1=R^2=R^3=R^4=R^5=H$
H_2TMP: $R^1=R^3=R^5=CH_3$, $R^2=R^4=H$
H_2TDCPP: $R^1=R^5=Cl$, $R^2=R^3=R^4=H$

Scheme 2. Non-metallated (H_2TMP, H_2TPP, and H_2TDCPP) porphyrins used as catalysts.

the sensitizers employed in the photooxidations. Photooxygenation was performed in oxygenated solutions of CH_3CN under visible light, in the presence of sensitizers (porphyrins) under 1 atm pressure of oxygen at room temperature.

Initial attempts to optimize the reaction conditions for the oxidation of aldehydes to the corresponding carboxylic acids were performed with 4-bromobenzaldehyde as the substrate. As indicated in Table 1, we used non-metallated (H_2TMP) and metallated (Fe, Mn, and Zn) porphyrins as catalysts to study the effects of metal and ligands on the photooxidation yield.

The conversions for paramagnetic metal (Fe and Mn) systems were negligible. Zinc porphyrins were relatively reactive (59% and 62% conversions), but the best catalyst was the free base porphyrin which converted the aldehyde quantitatively into the corresponding acid. Paramagnetic metals are claimed to quench singlet oxygen by an energy transfer mechanism from oxygen to the low-lying d electron levels and have very short triplet lifetimes.[25] Zn-porphyrin is known to quench singlet oxygen by a charge transfer mechanism.[25] However, it has a much larger triplet lifetime compared to the paramagnetic metalloporphyrins.[26] It seems that metalloporphyrins in the presence of O_2 and visible light do not have the potential to generate a reactive intermediate (P°+MO^{IV}),[27] whereas light of higher energy can do so and delivers a new mechanism for olefin oxidation in high conversions.[24a] Table 2 shows the conversions for the formation of 4-bromobenzoic acid in various solvents. The results show that CH_3CN was the best solvent for the generation of carboxylic acids.

According to the literature, DMSO, H_2O, and DMF are singlet oxygen quenchers.[28,29] For the *m*-THPC (5,10,15,20-tetra(*m*-hydroxyphenyl)chlorin) sensitizer, the singlet oxygen lifetime in DMSO is 19 μs compared to 65 μs in acetonitrile.[30] The main mechanism

Table 1
Effect of various porphyrins on the photooxidation of 4-bromobenzaldehyde[a]

Entry	Catalyst	Conversion into 4-bromobenzoic acid (%)
1	ClMnTMP	Trace
2	ClMnTPP	Trace
3	ClFeTMP	Trace
4	ZnTPP	59
5	ZnTMP	62
6	H_2TMP	100

[a] 1×10^{-6} mol porphyrins, 1×10^{-3} mol 4-bromobenzaldehyde, 16 h.

Table 2
Effect of solvent on the photooxidation of 4-bromobenzaldehyde[a]

Entry	Solvent	Conversion into 4-bromobenzoic acid (%)
1	CH_3CN	100
2	DMF	Trace
3	DMSO	Trace
4	$NaN_3/Na_2SO_3/CH_3CN$	20
5	H_2O	Trace

[a] 1×10^{-6} mol H_2TMP, 1×10^{-3} mol 4-bromobenzaldehyde, 16 h.

occurring under our reaction conditions may be the generation of singlet oxygen and its reaction with the substrates according to the data in Table 1, since all the porphyrins gave higher conversions in comparison with metalloporphyrins. Krasnovskii et al. determined the values of singlet oxygen physical quenching,[25] and our conversions correlate with these values. Further evidence for an $^1O_2$ mechanism was obtained by performing the photooxygenation in the presence of N_3^- which is a known singlet oxygen scavenger.[31] Entry 4 in Table 2 shows that the yield of product was considerably reduced under these conditions. In the presence of N_3^-, degradation of the porphyrin sensitizers was also inhibited.

Table 3 shows the conversions of 4-bromobenzoic acid on variation of the free base porphyrins. The conversion into 4-bromobenzoic acid decreases in the order H_2TMP > H_2TPP > H_2TDCPP. It is important to note that oxidation of substrate did not continue in the absence of porphyrin or when the irradiation was interrupted (the conversion of 4-bromobenzoic acid was negligible). Therefore, the presence of a porphyrin, light, and O_2 is essential for the conversion of 4-bromobenzaldehyde into 4-bromobenzoic acid.

Figure 1 shows the percentage of 4-bromobenzoic acid formation versus time in an oxygenated solution in CH_3CN under visible light irradiation in the presence of H_2TMP. The Soret band of H_2TMP was monitored at 418.5 nm using a UV–vis method. This method showed that sensitizer bleaching for H_2TMP was complete in 16 h under our conditions. After disappearance of the porphyrin Soret band, the formation of the oxidation products stopped and the reaction conversion remained constant. Therefore, the optimum reaction time was 16 h for these reactions.

Table 3
Effect of porphyrins on the photooxidation of 4-bromobenzaldehyde[a]

Entry	Porphyrin	Conversion into 4-bromobenzoic acid (%)
1	H_2TMP	100
2	H_2TPP	90
3	H_2TDCPP	72

[a] 1×10^{-6} mol porphyrin, 1×10^{-3} mol 4-bromobenzaldehyde, 16 h.

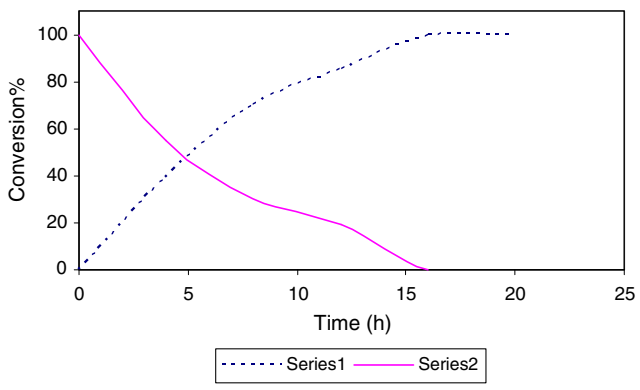
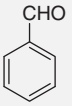
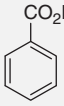
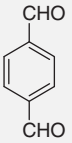
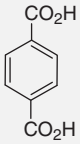
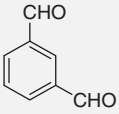
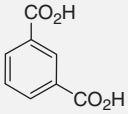
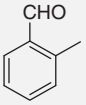
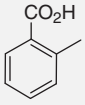
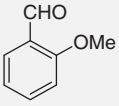
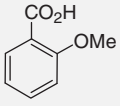
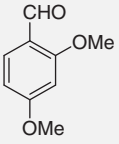
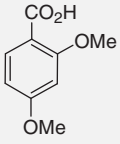
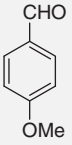
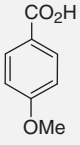
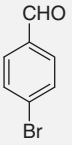
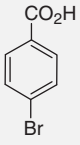
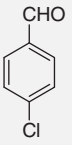
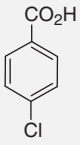
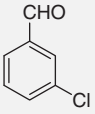
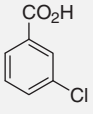
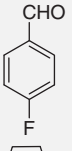
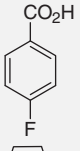
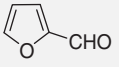
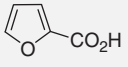
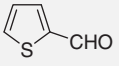
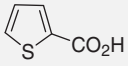
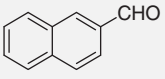
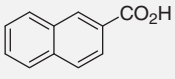


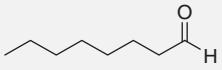
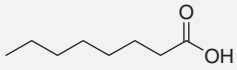
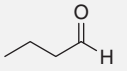
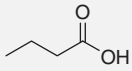
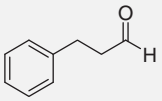
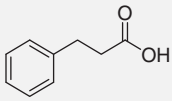
Figure 1. Conversion versus time of irradiation for H_2TMP in acetonitrile (Series 1). Percent of remaining H_2TMP versus time (Series 2).

Table 4
Oxidation of aldehydes to carboxylic acids in the presence of H_2TMP[a]

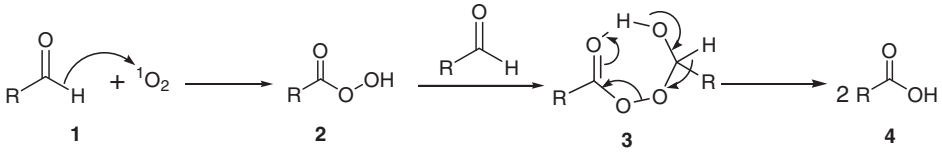
Entry	Aldehyde	Acid	Time (h)	Conversion[b] (%)	TON[c]
1			72	87	870
2			16	100	2000
3			16	100	2000
4			72	93	930
5			72	71	710
6			72	21	210
7			48	95	950
8			16	100	1000
9			72	89	890
10			72	70	700
11			48	74	740
12			48	100	1000
13			48	55	550
14			48	100	1000

(*continued on next page*)

Table 4 (*continued*)

Entry	Aldehyde	Acid	Time (h)	Conversion[b] (%)	TON[c]
15			48	96	960
16			48	100	1000
17			72	96	960

[a] 1×10^{-6} mol H_2TMP and 1×10^{-3} mol aldehydes as substrates.
[b] %Selectivity was >99% in all cases.
[c] Turnover number of the catalyst.



Scheme 3. A possible mechanism for the formation of the carboxylic acids.

To check the generality of this method, the oxidation of a variety of aromatic and aliphatic substrates was studied. As shown in Table 4, this catalytic system was applicable to a wide range of aromatic and aliphatic substrates. The aldehydes were converted into the corresponding carboxylic acids in good isolated conversions in reasonable times with a high turnover number. Aromatic aldehydes possessing electron-withdrawing groups on the phenyl ring (Table 4, entries 2, 3, and 9–12) were more reactive than those with electron-donating substituents (Table 4, entries 4–8). Porphyrin degradation was accelerated in the presence of less reactive substrates. This observation shows that there is competition between the porphyrins and the substrates for $^1O_2$.

We have explored a new porphyrin catalyst for the aerobic oxidation of aldehydes.[32–35] Our method requires low catalyst concentrations, gave the highest turnover numbers (TON), has low cost, safety, and avoids using a heavy metal. The catalyst showed good activity in the aerobic oxidation of aldehydes.[36]

A possible mechanism for the formation of the products is shown in Scheme 3. Thus, in the presence of singlet oxygen, there may be a new photochemical pathway that involves the overall insertion of molecular oxygen into the C–H bond of aldehyde **1** to form a peracid **2**.[37] In the final stage of the reaction, aldehyde **1** and peracid **2** generate the adduct **3**. Compound **3** then decomposes to give the final product **4**.[38]

In conclusion, we have developed a new approach for the aerobic oxidation of aldehydes to the corresponding carboxylic acids using a catalytic amount of a porphyrin in the presence of visible light and O_2 in acetonitrile under very mild conditions. This procedure is very simple and works efficiently at room temperature affording good to excellent conversions.

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36. *General procedure for the synthesis of carboxylic acids*: The aldehyde (1 mmol) and a 1 mL CH_2Cl_2 solution of the porphyrin (1×10^{-3} mmol) were dissolved in 14 mL of CH_3CN in a quartz tube. Oxygen was bubbled throughout the solution and the sample was irradiated using visible light (Fluorescent Circular Lamp, 22 W and 230 V) and (λ >350 nm) for 16–72 h. The solvent was removed under vacuum, and the residue was separated by column chromatography (silica gel, *n*-hexane/EtOAc, 13:1) to give the corresponding carboxylic acid (Table 4). The conversion and selectivity of products were determined by GC. The structure of the products from entries **2** and **3** Table 4 was confirmed from the melting points and ^{1}H and ^{13}C NMR spectra. *Terephthalic acid* (**2**): Colorless crystals; mp >260 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ: 8.00–8.15 (4H, m, H Ar), 13.31 (2H, br s, CO_2H). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ: 129.9, 130.4, 134.9, 139.3, 167.1. *Isophthalic acid* (**3**): Colorless crystals; mp >260 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6) 7.61 (1H, t, J = 7.3 Hz, H Ar), 7.15 (2H, d, J = 7.4 Hz, H Ar), 8.48 (1H, br s, H Ar), 13.23 (2H, br s, CO_2H). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ: 129.5, 129.7, 130.4, 131.6, 133.8, 167.0.
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