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Oxidations with Hydrogen Peroxide Catalysed by the [WZnMn(II)₂(ZnW₉O₃₄)₂]¹²⁻ Polyoxometalate

Ronny Neumann* and David Juwiler

Casali Institute of Applied Chemistry, Graduate School of Applied Science, The Hebrew University, Jerusalem, Israel, 91904

Abstract: Polyoxometalates can be used as catalysts for the activation of molecular oxygen and 30% aqueous hydrogen peroxide for the selective transformation of various organic substrates. In this paper results are presented for the oxidation of alkenes, dienes, alkenols, and sulfides using 30% aqueous H_2O_2 as oxidant and $[WZnMn(II)_2(ZnW_9O_{34})_2]^{12-}$ as catalyst. In certain but not all cases high reactivity, chemoselectivity and sterospecificity has been observed especially in the epoxidation of alkenols with primary hydroxyl units. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The oxidation chemistry developed during the past century for the transformation of commodity hydrocarbons derived directly from petroleum exclusively uses molecular oxygen as the oxygen donor. Two types of catalytic reactions have been used. The first are homogeneous liquid phase reactions based on formation of hydrocarbon free radicals derived from alkanes and autooxidation mechanisms as for example in the oxidation of *p*-xylene to terephthalic acid.[1] The second are heterogeneous gas phase reactions generally proceeding by the Mars-van Krevalan mechanism as in the oxidation of propene to acrylic acid.[2] On the other hand emphasis in synthetic organic chemistry common to the academic laboratory and the fine chemical industry has mostly been on stoichiometric oxidants where an enormous range of reagents generally based on metal-oxo compounds and conditions allow almost all types of oxidations of many functional groups often with respectable selectivity.[3] However, commonly, use of these reagents leads to formation of prodigious amounts of waste, which is also often toxic.[4] Environmental and economic concerns now make it essential that new alternatives be sought out. One direction is to use newer more benign stoichiometric oxidants, for example urea hydroperoxide,[5] dimethydioxirane,[6] sodium perborate or sodium percarbonate.[7] These oxidants may lead to highly selective functionalization, however, there still remain the problems of at least stoichiometric amounts of spent oxidant and relatively high costs of the oxidants. A more pleasing approach from an environmental and economic point of view would be to use cheap, available and non-polluting oxidants. Excellent candidates in this sense are hydrogen peroxide and molecular oxygen <u>provided</u> that catalysts and catalytic conditions can be found whereby reactions proceed with high activity and selectivity. Both have high oxygen content and only water as additional product after oxygen donation. The major problem in the use of hydrogen peroxide, a weak oxidant, is that often activation by metal catalysts partially leads to undesired homolytic cleavage. Thus, there is both non-productive decomposition of the oxidant and formation of hydroperoxy and hydroxy radicals which in turn yield undesired side products.[8] The use of molecular oxygen in the liquid phase synthesis of organic compounds is limited because its triplet ground state precludes reaction with singlet organic compounds.

Therefore, oxidation by molecular oxygen entails use of non-selective free radical autoxidations. Alternative approaches include metal activation in the presence of at least stoichiometric quantities of reducing agent, often high valued aldehydes.[9] While such research is of great theoretical importance, the use of the co-reductant mitigates the practical advantage gained in using dioxygen. Alternatively, dioxygen has been used as a secondary oxidant not directly involved in the functionalization of the organic compound; most prominently palladium catalysed Wacker type ketonizations of alkenes.[10]

In this paper, we describe our efforts in developing catalytic procedures for oxidation of organic substrates using hydrogen peroxide as oxidant and polyoxometalates as catalysts. In many cases, the oxidation reactions proceed with very high catalytic turnover, yield and selectivity. Polyoxometalates are inorganic compounds having a general formula $[X_xM_mO_y]^{q-}$ $x \leq m$ where X is the heteroatom and M = Mo and/or W, are the addenda. Over the past decade these compounds have awoken interest for catalytic oxidations[11] as they are inherently stable to oxidation. As concerns oxidation with hydrogen peroxide, most of the research described[12] has been using the Keggin compounds $PW_{12}O_{40}^{3-}$ or $PMo_{12}O_{40}^{3-}$, figure 1a, as catalysts. There is, however, now ample evidence[13], that in almost all cases these polyoxometalates are reduced to simpler peroxophosphometalates, $\{PO_4[MO(O_2)_2]_4\}^{3-}$, figure 1b, which are in fact the active catalysts.
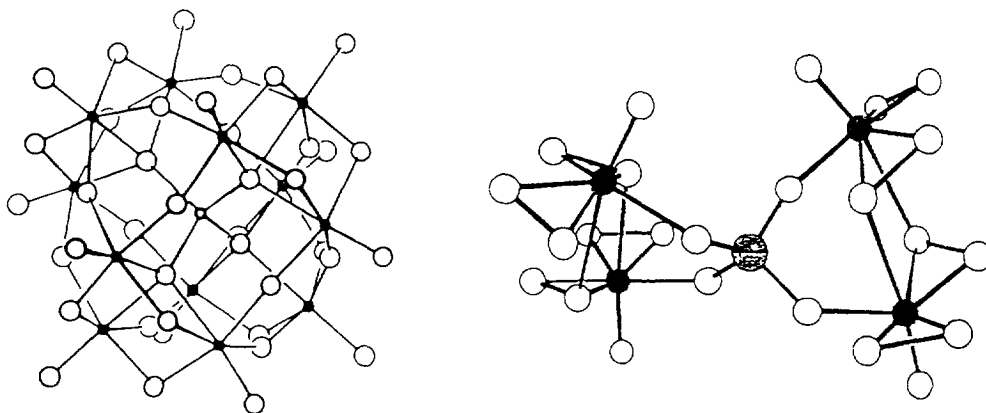

Figure 1. Representation of (a) $PM_{12}O_{40}^{3-}$ and (b) $\{PO_4[MO(O_2)_2]_4\}^{3-}$ polyoxometalates.

An especially interesting subclass of polyoxometalates are compounds where one or perhaps more of the addenda are substituted by lower valent transition metals. These so called transition metal substituted polyoxometalates, TMSP, are uniquely synthetically attractive as well as interesting as oxidation catalysts because one may visualize these compounds as having reactive low valent transition metal centers complexed by inorganic oxometalate ligands which also have high capacity for electrons. In the past, these types of compounds have not been amenable to catalysis with aqueous hydrogen peroxide because they solvolytically decompose in the presence of this oxidant. Recently, however, compounds pictured as having a "ring" of transition metals "sandwiched" between two trivacant forms of a parent Keggin structure,[14] figure 2, have been shown to be highly stable to aqueous hydrogen peroxide. Thus, $[Fe(II)_4(PW_9O_{34})_2]^{10-}$ has been shown to activate H_2O_2 (few turnovers) for alkene epoxidation in monophasic systems,[15] whereas $[WZnMn(II)_2(ZnW_9O_{34})_2]^{12-}$ was found to be highly active (thousands of turnovers) in biphasic alkene epoxidation and alcohol oxidation with H_2O_2.[16]
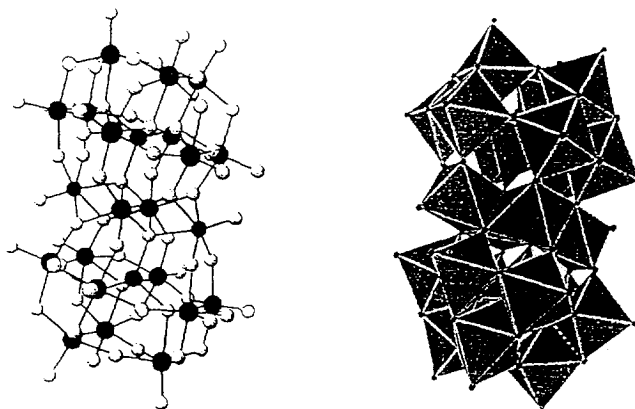
Figure 2. Ball and stick, and polyhedral models of the "sandwich" type TMSP.

We will decribe below our results on the use of the manganese substituted polyoxometalate, $[WZnMn(II)_2(ZnW_9O_{34})_2]^{12-}$, as catalyst for the oxidation of various organic compounds with different functional groups, including alkenes and dienes, alkenols and sulfides using aqueous 30% H_2O_2 as oxidant in biphasic (1,2-dichloroethane-water) reaction media.

RESULTS AND DISCUSSION

The original research[16] employing $[WZnMn(II)_2(ZnW_9O_{34})_2]^{12-}$ (WZnMn) as catalyst was carried out by transferring the anionic polyoxometalate into an organic 1,2-dichloroethane (DCE) via metathesis of the potassium salt with tricaprylmethylammonium chloride (Aliquot 336). At substrate/H_2O_2/catalyst ratios of 1/2/0.0005 epoxidation of alkenes was highly selective with no allylic oxidation at ambient or lower temperatures. Catalytic activity was a function of the degree of substitution at the double bond carbons so that reactivity was 2,3-dimethyl-2-butene > 2-methyl-2-heptene > 1-methyl-2-heptene > 2-octene > 1-octene. In addition cyclic alkenes were more active than acyclic analogs *eg* cyclooctene >> 2-octene; also cyclooctene was more reactive than cyclohexene. In general, although turnover numbers were very high but often yields were low. In order to increase yields up to essentially quantitative, the most effective procedure is to perform reactions in continuous cycles. That is, first one performs the reaction at a molar ratio H_2O_2/substrate of 2/1 with anywhere between 0.1 - 0.01 mol % catalyst. After the hydrogen peroxide has been used up, the aqueous phase is removed and another portion of hydrogen peroxide is added. This procedure may be continued until the substrate is completely reacted; the number of required cycles is inversely proportional to the reactivity of the substrate. Addition of a larger excess of oxidant in a one cycle reaction is generally much less effective.

Our first aim in the continuing investigation of catalytic oxidation by (WZnMn) was to further study the epoxidation of mono-alkenes, figure 3. Comparison of the reactivity of terminal alkenes (one cycle) shows that there is little difference between the reactivity (epoxidation and bond cleavage) of styrene, 4-nitrostyrene, 4-methoxystyrene and 1-octene. This indicates that the interaction between the aromatic ring and double bond has little influence on the reaction pathway.
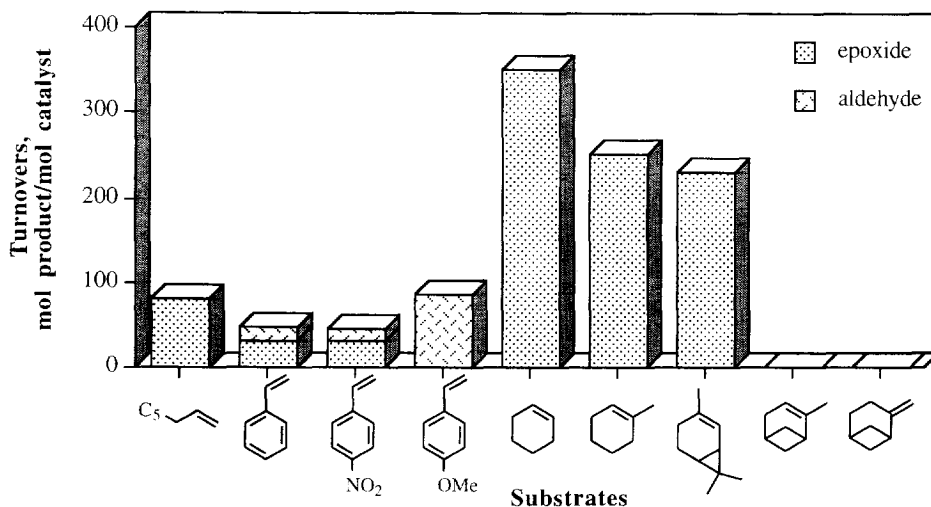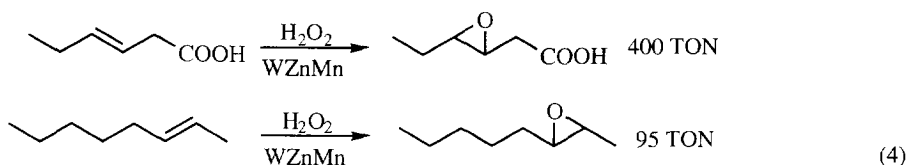
Figure 3. Oxidation of various monoalkenes.

The presence of the aromatic ring does, however, increase the likelihood of carbon-carbon double cleavage to the appropriate benzaldehyde. This reaction is not catalysed by the polyoxometalate as is easily observed by comparative reactions of the intermediate epoxides with and without catalyst, eq 2.

$$\text{(2)}$$

45% with catalyst
42% without catalyst
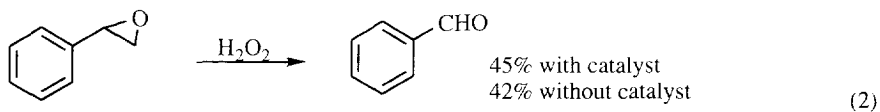
Other reactions with cyclohexene derivatives showed some interesting and unexpected results. Importantly, all compounds showed selectivities to epoxide products that were greater than 98%. Reactivity trends were curious in that increased substitution at the double bond did not lead to increased reactivity but the opposite was found *ie* cyclohexene > 1-methylcyclohexene ~ 2-carene >> α-pinene. The relative reactivities especially the inertness of both α- and β-pinene seems to point to steric factors, taking in to account also the large bulk of the polyoxometalate, as being responsible for the reactivity trends observed. Another view on the reactivity of alkenes, substitution *vs* steric effects, can be gained by investigating the regioselectivity found in the oxidation of dienes. Thus, 4-vinylcyclohexene reacted exclusively at the ring double bond whereas in limonene reactivity was similar for both double bonds, eq 3. It might be added that this result is not typical for manganese-oxo type reactions (as is the low reactivity of styrene derivatives) where typically 7:1 endo *vs* exo epoxidations are observed[17] and tends to support a peroxotungstate reaction intermediate as has been previously discussed.[16]

$$\text{(3)}$$
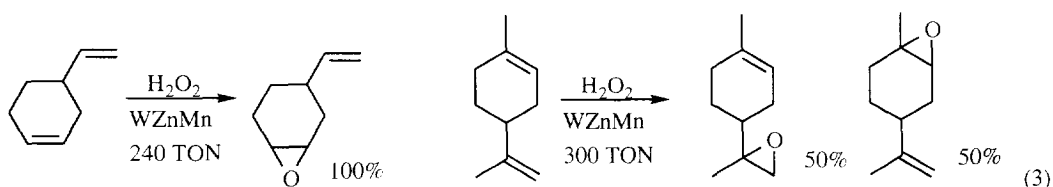
The next stage in the research was to look into alkenes with additional functional units in the molecule. Thus, α,β-unsaturated acids, esters and anhydrides such as *trans*-2-hexenoic acid, butylmethacrylate and maleic anhydride among others were inert. The strongly electron withdrawing substitutents reduce the nucleophilicity of the substrate and prevent reaction. A β,γ-unsaturated acid such as *trans*-3-hexenoic acid was however, significantly more reactive than a simple alkene such as *trans*-2-octene, eq 4. This and other results below indicate that the epoxidation may be ligand assisted.

$$\text{(structures)} \quad \xrightarrow[\text{WZnMn}]{\text{H}_2\text{O}_2} \quad \text{(structures)} \quad 400 \text{ TON}$$

$$\text{(structures)} \quad \xrightarrow[\text{WZnMn}]{\text{H}_2\text{O}_2} \quad \text{(structures)} \quad 95 \text{ TON} \qquad (4)$$

Further investigations into oxidation of functionalized alkenes were made by studying the oxidation of alkenols. In this case, of course, the question of chemoselectivity is also of importance. Comparison of the reactivity of alkenols with primary hydroxyl units, figure 4, shows a reactivity trend of allyl alcohols > homoallyl alcohols ~ ω-alkenols and *cis* > *trans*. The epoxides were all formed with 100% stereospecificity *ie cis*-epoxides from *cis*-alkenols. Interestingly, the more reactive allyl alcohols, 2-hexen-1-ol and cinnamyl alcohol, showed less chemoselectivity; with ~5-10% oxidation of the alcohol to aldehyde. The oxidation at the primary alcohol was somewhat unexpected since simple alcohols such as 1-octanol are inert.[16] On the other hand homoallyl alcohols and ω-alkenols were 100% chemoselective to epoxidation. The higher reactivity of *cis*- versus *trans*-substrates is typical for epoxidation reactions. Alkenols with secondary hydroxyl groups reacted in a significantly different manner so that both epoxy-ones and en-ones were formed in large quantities; chemoselectivity is low. Thus, both cyclohexen-2-ol and isopulegol gave mostly the ketone as product, whereas 1-octene-3-ol and 1-hexen-3-ol gave equivalent amounts of ketone and epoxide.
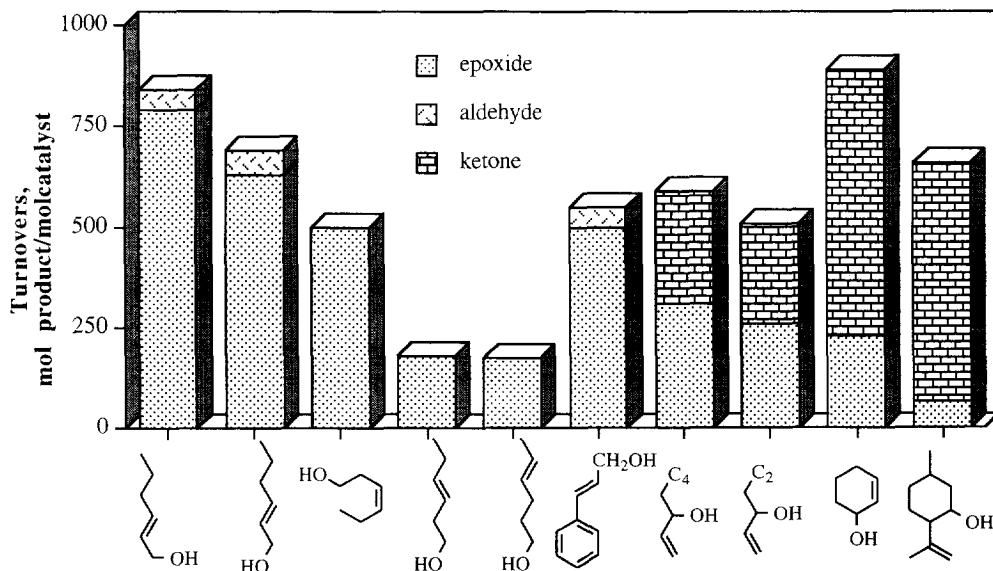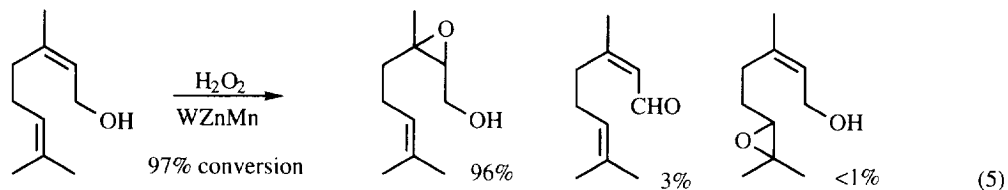

Figure 4. Oxidation of alkenols.

The following stage in the research was to investigate the reactivity of functionalized dienes. Geraniol was oxidized in high chemoselectivity to the allylic epoxide at 97% yield, eq 5. This result is in line with the efficient oxidation of 2-hexen-1-ol *vs* the sluggish reaction of simple alkenes.

$$\text{(5)}$$

On the other hand the oxidations of linalool and carveol, eq 6 and eq 7 were not selective. This result is also compatible for what was found in the reaction of cyclohexen-2-ol, limonene and 1-octen-3-ol.

$$\text{(6)}$$

$$\text{(7)}$$
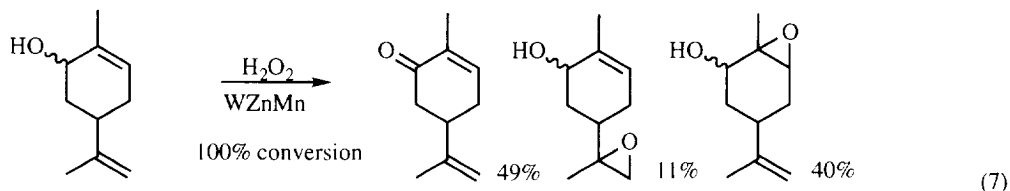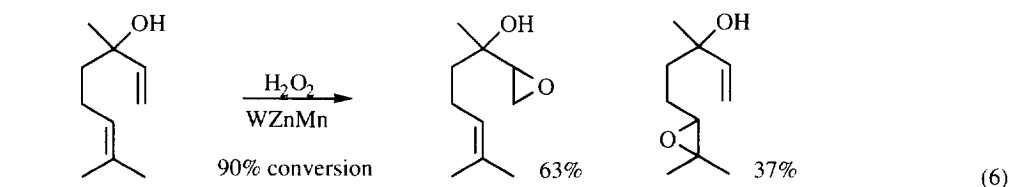
The final portion of this paper is devoted to the oxidation of sulfides whereby the object of the investigation was to see if sulfides could be oxidized selectively to sulfoxides with minimal overoxidation to sulfones. From the results as summarized in figure 5, one must divide substrates into classes; aromatic and aliphatic sulfides. For both thianthrene and diphenylsulfide, there is little reaction without catalyst. Catalytic reactions and substrate/oxidant ratios of 1/1 yield sulfoxide as major product with selectivities of 85 -90 %. For aliphatic substrates there is significant oxidation also in the absence of WZnMn. However, there is some improvement in the selectivity to sulfoxide is observed in the catalytic reaction. As may be expected for thioanisole intermediate results may be observed.

One may conclude in saying that the use of the manganese substituted polyoxometalate, $[\text{WZnMn(II)}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, as catalyst for activation of aqueous hydrogen peroxide to oxidation has been presented for a variety of substrates. For non-functionalized alkenes, reactivity is based on a combination of two effects, the nucleophilicity of the carbon-carbon double bond as a function of substitution at the bond and steric effects. Combination of different double bonds in a single molecule can lead to high regioselectivity depending on the relative reactivity at each alkene unit. Epoxidation may be ligand assisted. Alkenols with primary hydroxy groups may be epoxidized with very high chemoselectivity and stereospecificity. However, alkenols with secondary hydroxy groups are oxidized with poor chemoselectivity. In the oxidation of sulfides, moderate selectivity to oxidation to sulfoxide could be achieved with strong catalytic effects in the oxidation of aromatic sulfides and weak effects with aliphatic sulfides.
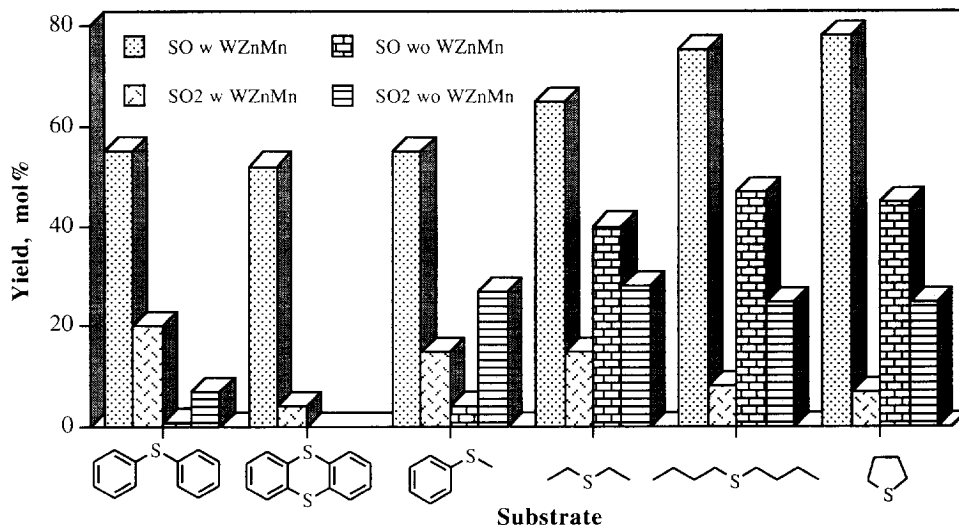
Figure 5. Oxidation of sulfides

EXPERIMENTAL PART

The polyoxometalate, $K_{12}[WZnMn(II)_2(ZnW_9O_{34})_2]\cdot 23H_2O$ was prepared and purified by the literature procedure.[14] The amount of water was determined by thermogravimetric analysis. Elementary analysis was performed by alkaline digestion of the polyoxometalate followed by atomic absorption measurements (GBC 903 single beam spectrometer) with a acetylene-air or acetylene-nitrous oxide flame oven for Na, K, Zn, and Mn, whereas W was determined gravimetrically[18]. The compound was thus found to be a hydrate with 23 water molecules (7.18% by TG). Experimental (theoretical) K - 8.09 (8.13); W - 60.87 (60.53); Zn - 3.30 (3.40); Mn - 2.03 (1.90). . The analysis was not significantly different than those found for the original synthesis. Solvents used were of analytical grade and used without further purification. The substrates were of the highest purity commercially available from Aldrich or Fluka and used without further purification. H_2O_2 was used a 30% aqueous solution (Merck). The amount of hydrogen peroxide was measured by use of the common iodometric titration. Reaction products were characterized and quantified using reference compounds when available by use of GLC (Hewlett-Packard 5890 gas chromatograph) with a flame ionization detector and a 15 m x 0.32 mm methylsilicone (0.25μm coating) capillary column and helium carrier gas. Products whose initial identity was questionable were unambiguously identified using a gas chromatograph equipped with a mass selective detector (GC-MS Hewlett-Packard 5970A) equipped with the same column described above. The procedure for all catalytic oxidations was as follows. Stock solutions of 1.0 mM $[WZnMn(II)_2(ZnW_9O_{34})_2]^{12-}$ were prepared by mixing 0.10 mmol $K_{12}[WZnMn(II)_2(ZnW_9O_{34})_2]\cdot 23H_2O$ with 2.5 mmol methyltricaprylammonium chloride in 100 ml 1,2-dichloroethane and filtering off the precipitated KCl. Reactions were carried out in 3 ml vials equipped with stirring bars. In a typical reaction, substrate (1 mmol) was dissolved in 1 ml of the stock solution and the reaction brought to the desired temperature. The reaction was initiated by addition of 2 mmol 30% hydrogen peroxide to the stock solution under atmospheric conditions and stirred in what forms a biphasic reaction system. The reaction was monitored by withdrawing aliquots from the organic phase of the reaction medium and directly injecting the sample into the gas chromatograph.

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