

Catalytic Oxidation of Saturated C—H Bonds by Tetrabutylammonium Periodate and Manganese Porphyrins†

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Arylalkanes and cycloalkanes are oxidized to their corresponding alcohols and ketones with tetra-*n*-butylammonium periodate in the presence of manganese(III) porphyrin catalysts and imidazole in CH₂Cl₂, with low to high yields and moderate to high selectivities at ambient temperature.

Efficient oxyfunctionalization of saturated hydrocarbons under mild conditions is one of the most challenging reactions in synthetic chemistry.¹ Biomimetic processes, based on oxygenation by cytochrome P-450 enzymes, using synthetic metalloporphyrins and various oxygen sources seem to offer a promising route to this goal.² Recent studies have shown that the Mn(TPP)Cl³-Im-periodate system can be used for efficient epoxidation of alkenes.⁴ These findings turned our attention to the important problem of alkane oxidation. We describe here the catalytic oxygenation of arylalkanes and cycloalkanes with Bu₄NIO₄ by various manganese(III) porphyrin complexes in the presence of imidazole under mild conditions. Results of these investigations are listed in Table 1.

In a typical experiment, to a solution of Mn catalyst (0.006 mmol) in dichloromethane (2 ml) imidazole (0.06 mmol), substrate (0.5 mmol) and Bu₄NIO₄ (1 mmol) were added successively. The resulting solution was stirred continuously under air for 24 h. The reaction products were identified by comparison of their spectroscopic (¹H NMR, IR) and chromatographic (GC) properties with those of authentic samples.

Inspection of the results given in Table 1 indicates that Mn(TPP)OAc, Mn(TNP)OAc and Mn(TMP)OAc complexes as a group are highly effective catalysts for oxidation of benzylic C=H bonds. The high catalytic efficacy shown by the simple catalyst Mn(TPP)OAc in the oxidation of the more reactive substrates is particularly noteworthy. It leads to a conversion of 62% of tetralin and 43% of indane to their oxidized forms within less than 5 h at room temperature. The Mn(TPFPP)OAc and Mn(TDCPP)OAc complexes, with electron withdrawing substituents on the phenyl rings, are not very efficient catalysts for benzylic C=H bond oxidation, and achieve much lower yields especially at shorter reaction times. However, oxidation of all the substrates proceeds with 100% selectivity to the formation of the corresponding alcohols and ketones.

In the oxidation of the less reactive secondary C=H bonds of cycloalkanes, stability of catalysts toward oxidative destruction plays an important role. Although Mn(TPP)OAc is a relatively active catalyst at the beginning of the oxidation reactions of cycloalkanes, it leads approximately to half or less than half the conversions achieved by the stable Mn(TPFPP)OAc after 24 h. Oxidation of cyclooctane by Mn(TNP)OAc, Mn(TMP)OAc and Mn(TPFPP)OAc catalysts proceeds with relatively high conversions (72–88%) to a mixture of cyclooctanol and cyclooctanone within 24 h, whereas oxidation of cyclohexane with all the catalysts ends with much lower yields in the same period. The total selectivities for the formation of

alcohols and ketones in the oxidation of cycloalkanes ranges between 78 and 92%. The low catalytic activities shown by the very robust Mn(TDCPP)OAc complex is due to its intrinsic steric and electronic properties. The greater catalytic ability of Mn(TPFPP)OAc in comparison with Mn(TDCPP)OAc in the oxidation of cycloalkanes seems particularly to reflect the significance of steric factors in the latter.

The mechanism of some of the oxidation reactions by these catalytic systems will be discussed elsewhere. However, preliminary spectral studies provide an interesting clue as to the identity of the active oxidizing intermediate in these

Table 1 Oxidation of arylalkanes and cycloalkanes with Bu₄NIO₄ in the presence of various manganese(III) porphyrins and imidazole^a

| Catalyst ^b | Conversion (%) ^d | Ketone ^c yield (%) ^d | Alcohol ^e yield (%) | t/h ^e |
|--------------------------|-----------------------------|--|--------------------------------|------------------|
| Substrate = tetralin | | | | |
| (A) | 73(62) | 65(52) | 8(10) | (5) |
| (B) | 72(57) | 63(47) | 9(10) | (7) |
| (C) | 70(39) | 58(31) | 12(8) | (7) |
| (D) | 21(10) | 18(8) | 3(2) | (7) |
| (E) | 20(5) | 17(4) | 3(1) | (7) |
| Substrate = indane | | | | |
| (A) | 63(43) | 51(28) | 12(15) | (5) |
| (B) | 70(45) | 56(33) | 14(12) | (7) |
| (C) | 70(40) | 52(27) | 18(13) | (7) |
| (D) | 18(8) | 13(6) | 5(2) | (7) |
| (E) | 16(4) | 13(3) | 3(1) | (7) |
| Substrate = ethylbenzene | | | | |
| (A) | 24(14) | 20(10) | 4(4) | (5) |
| (B) | 33(17) | 27(13) | 6(4) | (7) |
| (C) | 28(15) | 22(11) | 6(4) | (7) |
| (D) | 10(3) | 8(2) | 2(1) | (6) |
| (E) | 8(2) | 7(1) | 1(1) | (6) |
| Substrate = cyclooctane | | | | |
| (A) | 42(20) | 20(9) | 16(9) | (5) |
| (B) | 72(62) | 36(29) | 30(25) | (7) |
| (C) | 86(48) | 33(17) | 43(25) | (6) |
| (D) | 88(10) | 39(5) | 32(5) | (4) |
| (E) | 41(16) | 15(6) | 17(9) | (7) |
| Substrate = cyclohexane | | | | |
| (A) | 12(7) | 4(2) | 6(4) | (5) |
| (B) | 21(7) | 9(2) | 10(4) | (7) |
| (C) | 28(12) | 11(4) | 14(6) | (6) |
| (D) | 24(10) | 10(3) | 12(6) | (5) |
| (E) | 15(7) | 7(3) | 6(3) | (5) |

^aReactions are carried out in air at room temperature (25 ± 3 °C). Molar ratios for substrate:oxidant:Mn-porphyrin:imidazole are 83.3:166.6:1:10. ^bCatalysts are: (A) Mn(TPP)OAc; (B) Mn(TNP)OAc; (C) Mn(TMP)OAc; (D) Mn(TPFPP)OAc; (E) Mn(TDCPP)OAc. ^cKetones: 1-tetralone from tetralin, indan-1-one from indane, acetophenone from ethylbenzene, cyclooctanone from cyclooctane, and cyclohexanone from cyclohexane. Alcohols: 1-tetralol from tetralin, indan-1-ol from indane, 1-phenylethanol from ethylbenzene, cyclooctanol from cyclooctane, and cyclohexanol from cyclohexane. ^dGLC conversions and yields are based on the starting substrates. ^eAll the reaction times are 24 h. The times given are related to the conversions and yields in parentheses.

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reactions. When the green solution of Mn(TPP)OAc in CH₂Cl₂, with a Soret band at 478 nm, was treated with an excess of Bu₄NIO₄ in the presence of imidazole at either room or low temperature (−63 °C) no change in the Soret band, due to the formation of a high-valent manganese-oxo species, was noticed. This result contrasts sharply with the observation of an oxo(tetraphenylporphyrinato)manganese species, with a characteristic Soret band (at 401 nm),⁵ when NaIO₄ was reacted with Mn(TPP)OAc in a two-phase (CH₂Cl₂–H₂O) medium. These experiments imply that the primary oxidizing species in the ImMn(TPP)OAc–Bu₄NIO₄ system is likely to be a complex formed by the coordination of periodate and [ImMn(TPP)]⁺. To test this view, we examined the interaction of a CH₂Cl₂ solution of Mn(TPP)F with an excess of Bu₄NIO₄. A gradual shift of the Mn(TPP)F Soret band from 454 to 478 nm, which is close to λ_{max} (Soret) expected for an anionic oxygen donor ligand, provides acceptable evidence for the replacement of F[−] by periodate species in the solutions.⁶

In conclusion the simple Mn(TPP)OAc, Mn(TNP)OAc and Mn(TMP)OAc complexes are effective catalysts for the oxidation of benzylic C–H bonds and cycloalkanes by Bu₄NIO₄ in the presence of imidazole. Mn(TPFPP)OAc shows a particularly high efficacy for catalytic oxidation of cyclooctane. Oxidation of benzylic C–H bonds leads to much higher yields of ketones rather than alcohols, whereas in the oxidation of cycloalkanes comparable amounts of ketones and alcohols are obtained.

Further work is underway to learn more about the factors that influence these catalytic systems.

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- Abbreviations used include Bu₄NIO₄, tetra-*n*-butylammonium periodate; Im, imidazole; TPP, *meso*-tetraphenylporphyrin dianion; TNP, *meso*-tetrakis(1-naphthyl)porphyrin dianion; TMP, *meso*-tetramesitylporphyrin dianion; TPFPP, *meso*-tetrakis(pentafluorophenyl)porphyrin dianion; TDCPP, *meso*-tetrakis(2,6-dichlorophenyl)porphyrin dianion.
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