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HYDROXYLATION OF SATURATED HYDROCARBONS BY MAGNESIUM MONOPEROXYPHTHALATE CATALYSED BY MANGANESE PORPHYRINS

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Summary: magnesium monoperoxyphthalate is a very efficient oxygen donor for the hydroxylation of saturated hydrocarbons: with tetra(2,6-dichlorophenyl)porphinatomanganese acetate as a catalyst, alcohols and ketones are obtained in 40-65% yields with turnover rates up to 80 cycles/min.

The selective functionalization of saturated hydrocarbons is still a challenge to the synthetic organic chemist. However, the introduction, during the last ten years, of metallo-porphinates as oxygenation catalysts has represented an important breakthrough in this field.[1] A number of different oxygen donors has been evaluated (e.g.: iodosylarenes, sodium hypohalites, dioxygen, potassium hydrogen persulfate, hydrogen peroxide)[1,2] and, although the alcohols obtained are also usually oxidised under the reaction conditions, monooxygenated products have been obtained in good yields[2] with turnover rates up to 22 cycles/min (with cyclohexane as the substrate;[3] as a comparison, P-450/NADPH/O_2, the enzymatic system responsable for the alkane hydroxylation in living organisms, catalyses cyclohexane oxidation at a rate of 8.8 cycles/min[4]).

Here we report that significantly higher rates are obtained using, as the oxidant, the magnesium monoperoxyphthalate (MMPP), recently shown to be a very efficient oxygen donor for manganese porphinates catalysed reactions, such as the epoxidation of alkenes[5] and the oxidative cleavage of DNA.[6] With MMPP the oxidation of unactivated alkanes is easily performed, at room temperature and under phase-transfer conditions, in the presence of both 5,10,15,20-tetra(2,6-dichlorophenyl)porphinatomanganese (III) acetate (TDCPP-Mn) and a heterocyclic nitrogen base: with 0.5% of catalyst and saturated hydrocarbons as substrates, alcohols and ketones are obtained in acceptable yields (40-65%) within 2-10 minutes.

In a typical experiment a 20% aqueous solution of MMPP (1 mmol) was carefully deaerated. Then dichloromethane (2.5 ml), TDCPP-Mn (5 µmol), 4-tert-butylpyridine (5 µmol), benzyldimethylhexadecylammonium chloride (10 µmol) and adamantane (1 mmol) were added under nitrogen and the resulting mixture was vigorously stirred at 20 °C. After 2 minutes n-tetradecane was added as an internal standard and the aqueous and the organic layers were separated. The g.l.c. analysis of the latter showed an 84% conversion of adamantane and 42, 10 and 2% yields of adamantan-1-ol, adamantan-2-ol and adamantan-2-one, respectively. No other products were detected in the organic phase, thus suggesting that water-soluble polyhydroxylated compounds were also formed. As a matter of fact, selectivities were sistematically higher at lower conversions, when polyhydroxylation was less likely to occur. Moreover, in a blank experiment, adamantan-1-ol, employed as the substrate, reacted nearly as quickly as the adamantane itself and without forming any detectable product in the organic phase.

The procedure has been applied to substrates other than adamantane: some significant results are summarized in Table 1. No formation of oxygenated products occurred when the reactions were repeated in the absence of the metal porphinate. The nitrogen base, on the other hand, although useful, was not essential. Noteworthy, according to a recent report,[7] using a lipophilic ligand such as 4-tert-butylpyridine, good results were obtained with just one mole of base per mole of TDCPP-Mn. The reaction efficiency was also affected by the presence of molecular oxygen: somewhat lower conversions were always obtained under aerobic conditions or, even worse, under an oxygen atmosphere, a similar behaviour having been yet observed in a closely related catalytic system (see Table 1 of ref. 2a).

A marked preference for the oxidation of tertiary C-H versus secondary C-H bonds was observed in the oxidation of adamantane (C_3/C_2 ratio 10.5-13 after statistical correction). However the reaction appeared to be rather sensitive to geometric constraints and some secondary C-H bonds reacted faster than the tertiary ones of more sterically demanding substrates. Thus ethylbenzene was oxidised more quickly than cumene or triphenylmethane (73, 66 and 43% conversion respectively, within 10 minutes under standard conditions). As regards CH_3 reactivity, both ethylbenzene and cumene gave only very little amounts, if any, of products arising from methyl oxidation.

In all cases, the oxidation of benzylic C-H gave quite poor yields of the expected products (see Table 1). No tars formation or carbon dioxide evolution having been observed, further work is in progress to check the fate of aromatic substrates.

In the oxidation of adamantane, turnover rates (moles of products/moles of TDCPP-Mn x min) up to 80 cycles/min have been easily obtained (conditions as previously described but 0.5 mmol of MMPP; 1 minute; 51% conversion of adamantane; 31, 8 and 1% yields of adamantan-1-ol, adamantan-2-ol and adamantan-2-one, respectively). These findings confirm the very high

Table 1. Hydroxylation of alkanes by magnesium monoperoxyphthalate catalysed by TDCPP-Mn.[a]

Alkane	Nitrogen base, base/Mn ratio	Time (min)	Conversion (%)	Yields (%)[b]					
Adamantane	none, 0	5	28	adamantan-1-ol	21	adamantan-2-ol	5	adamantan-2-one	0
"	pyridine, 40	5	80	"	41	"	8	"	2
"	4-picoline, 40	5	82	"	50	"	12	"	2
"	4-tert-butylpyridine, 1	2	84	"	42	"	10	"	2
"	" , 1[c]	2	75	"	40	"	9	"	2
Cyclohexane	" , 1	6	72	cyclohexanol	22			cyclohexanone	20
Cyclooctane	" , 1	3	76	cyclooctanol	29			cyclooctanone	15
Ethylbenzene	" , 1	10	73	1-phenylethanol	12			acetophenone	41
Cumene	" , 1	10	68	2-phenyl-2-propanol	17				
Diphenylmethane	" , 1	10	52	benzhydrol	6			benzophenone	9
Triphenylmethane	" , 1	10	43	triphenylmethanol	7				

[a] Conditions as described in the text. [b] Yields (based on starting alkene) were determined by g.l.c. using n-dodecane (n-tetradecane for adamantane, cumene and diphenylmethane) as an internal standard. [c] Under oxygen atmosphere.

efficiency of MMPP as oxygen donor in metallo-porphinates catalysed oxidations and make the MMPP/TDCPP-Mn/nitrogen base system one of the most efficient tools for the homogeneous catalytic hydroxylation of saturated hydrocarbons.

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