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ALLYLIC AMINATION OF ALKENES BY TOSYLIMINOIODOBENZENE : MANGANESE PORPHYRINS AS SUITABLE CATALYSTS

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Abstract : Manganese-porphyrins and particularly Mn(TPP)(ClO_4) were found to be much better catalysts than iron-porphyrins for allylic N-tosylamination of alkenes by tosyliminoiodobenzene. With the former catalysts, cyclohexene was selectively transformed into 3-tosylaminocyclohexene with yields up to 70% and cis- and trans-hex-2-ene into allylic N-tosylamines with yields around 40%, whereas cyclooctene led to the corresponding allylic and homoallylic N-tosylamines.

Iron- and manganese-tetraphenylporphyrins catalyze the insertion of the N-tosyl moiety of tosyliminoiodobenzene, PhI=NTs, into a C-H bond of cyclohexane with low yields (3 and 8% respectively) (1). Iron-porphyrins are efficient catalysts for the N-tosylaziridination of alkenes by PhI=NTs with good yields (2,3). In particular, the N-tosylaziridination of 1,2-dialkylethylenes catalyzed by Fe(TDCPP(4))(ClO_4) is almost stereospecific (3). This paper shows that the reaction of PhI=NTs with alkenes, in the presence of a manganese-porphyrin, exhibits a different chemoselectivity and mainly leads to allylic N-tosylamination of alkenes.

In a typical experiment, a solution of Mn(TCDPP)(ClO_4) (5) 2.5mM and cis-hex-2-ene 5M in anhydrous CH_2Cl_2 was added to solid PhI=NTs (6) (20 eq. relative to the catalyst) under argon at 20°C, in the presence of molecular sieves (2,3). As shown by gas chromatography iodobenzene was formed almost quantitatively within less than 30 min. The other products were separated by thin-layer chromatography on SiO_2 (CH_2Cl_2 as eluent). p.Toluenesulfonamide ($TsNH_2$) and the N-tosylaziridines 1 and 2 were identified by comparison with authentic samples (3), and four allylic N-tosylamines, 3, 4, 5 and 6, were identified from elemental analysis (C,H,N,S), mass spectrometry and ^1H NMR data (7) (eq.1).

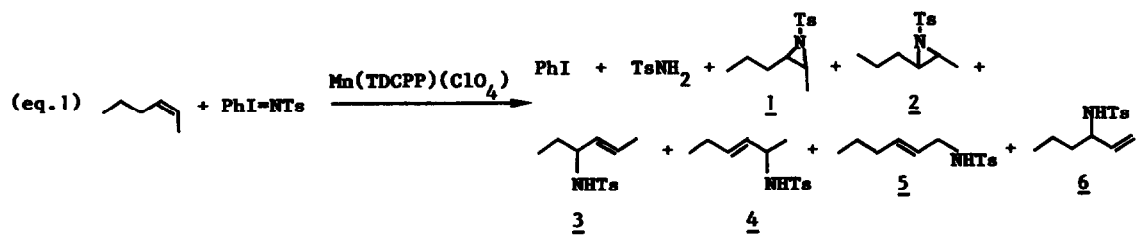


Table 1 compares the yields of N-tosylaziridines (1 + 2) and allylic N-tosylamines (3+4+5+6) formed upon reaction of cis- and trans-hex-2-ene with PhI=NTs in the presence of various Fe- or Mn-porphyrin catalysts.

Table 1 : Allylic amination versus N-tosylaziridination in reactions of PhI=NTs with cis- and trans-hex-2-ene catalyzed by Fe- and Mn-porphyrins.

Alkene	Products	Yields (%)[a] as a function of the catalyst nature			
		Fe(TPP(4))(ClO_4)	Fe(TDCPP)(ClO_4)	Mn(TPP)(ClO_4)	Mn(TDCPP)(ClO_4)
Cis-hex-2-ene	N-tosylaziridines (AZ)	12	35	<2	11
	Allylic tosylamines (AA)	20	13	37	26
	R = AA/AZ	1.7	0.4	>18	2.4
Trans-hex-2-ene	N-tosylaziridines	27	33	<2	4
	Allylic tosylamines	30	23	41	35
	R = AA/AZ	1.1	0.7	>20	8.7

(a) Yields of $TsNH_2$, N-tosylaziridines and allylic N-tosylamines, based on starting PhI=NTs,were determined by gas chromatography using N-cyclohexyl-p-toluenesulfonamide as an internal standard.

In all cases, the total yields of $TsNH_2$, which came presumably from hydrolysis of PhI=NTs or of an intermediate metal=NTs complex (2,3), and of the products derived from transfer of NTs to the alkene (aziridines + allylic N-tosylamines) were close to 100%. The total yields of NTs transfer were similar with Fe- or Mn-porphyrins (between 32 and 57% or 37 and 43% respectively) (Table 1), but the allylic N-tosylamines : N-tosylaziridines ratio(R) varied very much with the nature of the catalyst. For the two porphyrin ligands used, replacement of Fe by Mn led to a large increase in this ratio by a factor of 6 to 20. In particular, Mn(TPP)(ClO_4) appeared to be the best catalyst for allylic N-tosylamination. In its presence, cis and trans-hex-2-ene were converted into allylic N-tosylamines in 40% yield with almost no formation of N-tosylaziridines.

Table 2 shows the results obtained for the reactions of several alkenes with PhI=NTs in the presence of Mn(TPP)(ClO_4) or Mn(TDCPP)(ClO_4) catalysts under conditions identical to those used previously. With both catalysts, the reaction of cyclohexene was completely chemoselective and led only to 3-tosylaminocyclohexene **8**. A 70% yield was obtained with Mn(TDCPP)(ClO_4) as the catalyst. This reaction was used to convert cyclohexene since its addition to 3 equiv. of PhI=NTs in the presence of Mn(TDCPP)(ClO_4) led to its almost complete transformation and a yield of 75% in **8**. In the case of cyclooctene the reaction was less selective as the N-tosylaziridine **9** was obtained along with the expected allylic N-tosylamine **10**. Surprisingly, the third product formed, **11**, was formally dérived from insertion of the NTs moiety into a homoallylic C-H bond. Whereas trans-alk-2-enes are known to be much less reactive than their cis-isomers towards oxygen transfer from PhI=O in the presence of Fe- or Mn porphyrins (8), as mentioned above, the amount of NTs transfer was similar with either trans-hex-2-ene or its cis-isomer. Two major allylic N-tosylamines **3** and **4** were formed from both alkenes along with two minor isomers **5** and **6**. These two latter allylic N-tosylamines were also formed upon reaction of PhI=NTs with hex-1-ene. However, in

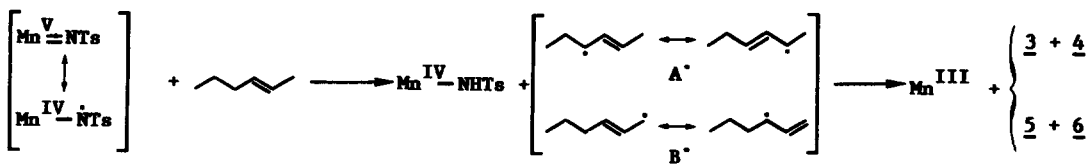
the particular case of this terminal alkene, N-tosylaziridination was more important than allylic N-tosylamination even with Mn-porphyrins as catalysts. It is noteworthy that even in this case Fe(TPP)(ClO_4) and Fe(TDCPP)(ClO_4) led to lower allylic N-tosylamines : N-tosylaziridines ratios (3) than their manganese analogues.

Table 2 : Reactions of various alkenes with PhI=NTs catalyzed by Mn-porphyrins.

Alkene	Products	Yields (%)[a] as a function of the catalyst nature	
		Mn(TPP)(ClO_4)	Mn(TDCPP)(ClO_4)
Cyclohexene	3-tosylaminocyclohexene **8**[b]	40	70
Cyclooctene	Cyclooctyl-N-tosylaziridine **9**[b]	9	11
	3-tosylaminocyclooctene **10**[b]	17	15
	4-tosylaminocyclooctene **11**[b]	16	13
Cis-hex-2-ene	**1** + **2**	< 2	11[c]
	3	17	10
	4	14	9
	5	5	3
	6	< 1	4
Trans-hex-2-ene	**1** + **2**	< 2	< 4
	3	22	17
	4	16	11
	5	2	7
	6	< 1	< 1
Hex-1-ene	2-butyl-N-tosylaziridine **7**[b]	20	23
	5	6	4
	6	3	4

(a) Based on starting PhI=NTs, determined by gas chromatography using N-cyclohexyl-p-toluenesulfonamide as in internal standard. (b) N-tosylaziridines **7** and **9** (3), and 3-tosylaminocyclohexene (9) were identified by comparison with authentic samples. The structure of N-tosylamines **10** and **11** was established from elemental analysis (C,H,N,S) and ^1H NMR and mass spectroscopy (7). (c) Only the cis isomer was formed.

The most likely mechanism for alkane hydroxylation and alkene allylic hydroxylation by PhI=O, the oxygen analogue of PhI=NTs, in the presence of Fe- or Mn-porphyrins, involves hydrogen atom abstraction from the hydrocarbon by a high-valent metal-oxo complex having a free radical like reactivity ($M^{IV}-O^{\bullet}$) (8,10). Our results could be explained by a similar mechanism (scheme 1) with hydrogen atom abstraction by a high-valent Mn-nitrene



Scheme I

intermediate (formally a Mn^{IV} - NTs species (3)). Such a mechanism would take into account (i) the nature of the four allylic N-tosylamines obtained from hex-2-enes which would derive from a transfer of the NHTs ligand of Mn^{IV} to the mesomeric forms of the allylic radicals A˙ and B˙ (ii) the preferential formation of 3 and 4, from the more stable secondary radical A˙, in the case of hex-2-enes (iii) the formation of 11 from cyclooctene via an homoallylic radical.

The present work confirms that the chemoselectivity of NTs transfer from PhI=NTs to alkenes varies greatly with the nature of the catalyst. It was previously shown that among the various iron-porphyrins studied, Fe(TDCPP)(ClO_4) was the best catalyst for stereospecific N-tosylaziridination of alkenes (3). This paper shows that Mn(TPP)(ClO_4) is the best catalyst for the insertion of the NTs moiety into allylic C-H bonds and provides an easy access to allylic N-tosylamines, since PhI=NTs is prepared from PhI in two steps (6). The origin of this different chemoselectivity of high-valent Fe- and Mn-nitrene complexes which are possible intermediates in these reactions remains to be determined.

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3. Mahy, J.P. ; Bedi, G. ; Battioni, P. ; Mansuy, D., J. Chem. Soc., Perkin Trans II, in press.
4. TDCPP and TPP stand respectively for the dianions of meso-tetra-orthodichlorophenyl-porphyrin and meso-tetraphenylporphyrin.
5. The perchlorato-Mn(III)-porphyrins were prepared as follows : a solution of 5.10^{-6} mol of Mn(TPP)(Cl) (3.5mg) or Mn(TDCPP)(Cl) (4.8 mg) in 1 ml of anhydrous CH_2Cl_2 is added under argon to 5.2 mg of solid $AgClO_4$ ($2.5\ 10^{-5}$ mol). The mixture is stirred until the perchlorato-Mn(III)-porphyrin is formed as shown by UV-visible spectroscopy (λmax = 390, 474, 525, 570, 605 nm for Mn(TPP)(ClO_4) and λmax = 382, 472, 580, 690 mn for Mn(TDCPP)(ClO_4)). The solution is then filtered to eliminate the excess of solid $AgClO_4$.
6. Yamamada, Y. ; Yamamoto, T. ; Okawara, M., Chem. Lett. 1975, 361.
7. Mass (E.I.) and ^1H NMR ($CDCl_3$, 20°C, δ (ppm/Me_4Si)) characteristics of the allylic N-tosylamines.
   3 : m/z=91(100%) ; 155(50%) ; 224(82%) ; 253(1%) ; δ=0.82(t,3H, J=7.5Hz) ; 1-1.5(m,2H) ; 1.92(d,3H,J=7.5Hz) ; 2.40(s,3H) ; 3.58(m,1H) ; 4.35(d,1H,J=9.5Hz) ; 5.04(m,1H) ; 5.35(m,1H) ; 7.28(d,2H,J=7.5Hz) ; 7.72(d,2H,J=7.5Hz) ;
   4 : m/z=91(100%) ; 155(25%) ; 238(22%) ; 253(1%) ; δ=0.82(t,3H, J=7.5Hz) ; 1-1.5(m,2H) ; 1.92(dt,2H) ; 2.40(s,3H) ; 3.86(m,1H) ; 4.31(d,1H,J=9.5Hz) ; 5.13(m,1H) ; 5.42(m,1H) ; 7.28(d,2H,J=7.5Hz) ; 7.70(d,2H,J=7.5Hz).
   5 : m/z=91(100%) ; 98(44%) ; 155(33%) ; 184(10%) : 210(8%) ; 224 (10%) ; 253(3%) ; δ=0.82(t,3H,J=7.5Hz) ;1-1.08(m,2H) ; 1.92(dt, 2H) ; 2.40(s,3H) ; 3.5(dd,1H) ; 4.24(t,1H,J=10Hz) ; 5.00(dd,1H) ; 5.30(dt,1H) ; 7.31(d,2H,J=7.5Hz) ; 7.72(d,2H,J=7.5Hz).
   Because of its low yields, 6 was only identified by G.C-mass spectrometry (m/z=91 (100%) ; 155(68%) ; 210(75%) 253(1%)) and by ^1H NMR spectroscopy (signal due to the proton in α to the NHTs group at 3.95 ppm (m,1H)). 3, 4 and 5 were found as trans-isomers as shown by a 15Hz value for the coupling constant between the vinylic protons.
   10 : m/z=91(100%) ; 124(17%) ; 155(40%) ; 210(26%) ; 279(8%) ; δ=1-2(m,8H) ; 2.40(dt,2H) ; 2.42(s,3H) ; 4.18(m,1H) ; 4.34(d,1H,J=9.6Hz) ; 5.1(m,1H) ; 5.58(m,1H) ; 7.26(d,2H,J=7.5Hz) ; 7.74(d,2H,J=7.5Hz).
   11 : m/z=91(100%) ; 124(35%) ; 155(23%) ; 184(25%) ; 210(15%) ; 236(21%) ; 279(25%) ; δ=1-2(m,8H) ; 2.08(dd,2H) ; 2.41(s,3H) ; 3.44(m,1H) ; 4.35(d,1H,J=10Hz) ; 5.48(m,1H) ; 5.76(m,1H) ; 7.29(d,2H,J=7.5Hz) ; 7.75(d,2H,J=7.5Hz).
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