Iron- and Manganese-porphyrin Catalysed Aziridination of Alkenes by Tosyl- and Acyl-iminoiodobenzene

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N-Substituted aziridines are formed by Fe- or Mn-porphyrin catalysed reactions of PhI=NR compounds (R = tosyl or $COCF_3$) with alkenes; the stereochemical characteristics of these reactions are very different from those of the analogous epoxidation of alkenes by PhI=O.

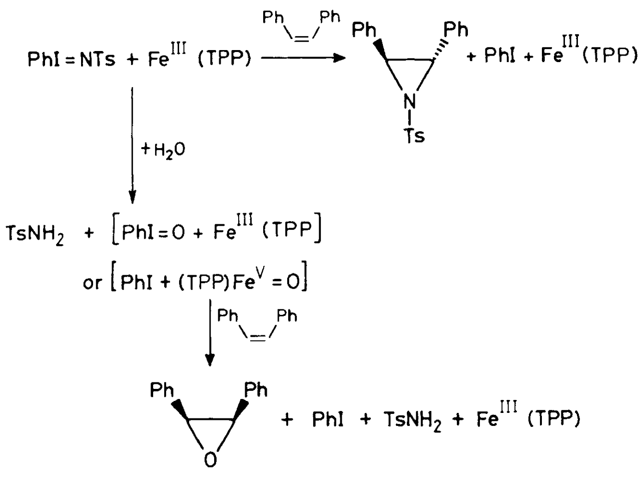
Cytochrome P-450[1] as well as Fe-[2,3] and Mn-porphyrins[4,5] catalyse the transfer of the oxygen atom of iodosylbenzene to several substrates including alkanes and alkenes. High-valent metal–oxo complexes, $Fe^V{=}O$[6] and $Mn^V{=}O$,[4,5] seem to be the active intermediates in these reactions. High-valent metal–nitrene complexes are the nitrogen analogues of these oxo complexes. Recently, such complexes, namely porphyrin–iron–nitrene complexes, $Fe^{II} \leftarrow N{-}NR_2 \longleftrightarrow Fe^{IV}{=}N{-}NR_2$[7] and a porphyrin–manganese–nitrene complex, $Mn^V{=}N{-}COCF_3$,[8] which could transfer its nitrene moiety to cyclooctene, have been described.

The nitrogen analogue of oxygen atom transfer from PhI=O

Table 1. Products[a] formed from the reaction of PhI=NTs with alkenes catalysed by Fe(TPP)(Cl) or Mn(TPP)(Cl).

		% Yield	
Alkene	Products	Fe(TPP)(Cl)	Mn(TPP)(Cl)
Styrene	*N*-Tosyl-2-phenylaziridine	55	80
	$TsNH_2$	40	20
cis-Stilbene	*trans*-*N*-Tosyl-2,3-diphenylaziridine	37	20
	$TsNH_2$	63	80
trans-Stilbene	*trans*-*N*-Tosyl-2,3-diphenylaziridine	32	16
	$TsNH_2$	65	80
1,1-Diphenylethylene	*N*-Tosyl-2,2-diphenylaziridine	21	56
	$TsNH_2$	75	40

[a] The structures of the *N*-tosylaziridines were established by comparison with authentic samples prepared by a technique described previously (ref. 12).



Scheme 1

to substrates would be nitrene NR transfer from PhI=NR. Two examples of such reactions, the tosylamidation of cyclohexane by PhI=N–Ts (Ts = tosyl) with catalytic amounts of Fe(TPP) (TPP = tetraphenylporphyrin) or Mn(TPP)(Cl)[9] and the intramolecular insertion of the nitrene moiety of 2,5-di-isopropylbenzenesulphonyliminoiodobenzene into a benzylic C–H bond,[10] have recently been described.

We are interested in the transfer of NR from PhI=NR to alkenes catalysed by metalloporphyrins, and in the comparison of the characteristics of this reaction with those of oxygen transfer from PhI=O under similar conditions.

Fe(TPP)(Cl) (2.5 mM) [or Mn(TPP)(Cl)] and the alkene (5 M) in anhydrous CH_2Cl_2, were added to solid PhI=NTs[11] [20 equiv. relative to Fe(TPP)(Cl)] under argon at 20 °C, and the reaction was followed by g.l.c. With all the alkenes used (Table 1), PhI=NTs was completely consumed within less than 15 min, iodobenzene being formed in almost quantitative yield. Two major products were separated by column chromatography: toluene-*p*-sulphonamide ($TsNH_2$) and the *N*-tosylaziridine derived from addition of the N–Ts moiety to the double bond of the alkene (Table 1). The total yields of the observed products (*N*-tosylaziridine + $TsNH_2$) based on starting PhI=NTs are close to 100%, and no *N*-tosylaziridines were formed in the absence of the Fe(TPP)(Cl) or Mn(TPP)(Cl).

We found the following results concerning the formation of $TsNH_2$, the major side reaction. (i) PhI=NTs is slowly hydrolysed into PhI=O and $TsNH_2$ in $(CD_3)_2SO$ upon addition of H_2O (25 equiv.), and the formation of $TsNH_2$ is very fast in the presence of catalytic amounts of Fe(TPP)(Cl) under these conditions. (ii) *N*-Tosylaziridination of *cis*-stilbene under the conditions described above, gave *cis*-stilbene oxide (45% based on PhI=NTs or 69% based on $TsNH_2$) in addition to *N*-tosylaziridine and $TsNH_2$, when Fe(TPP)(Cl) was used as the catalyst, and *cis*- and *trans*-stilbene oxides (30 and 38% based on PhI=NTs or 38 and 48% based on $TsNH_2$, respectively) with Mn(TPP)(Cl). Since reactions of PhI=O with *cis*-stilbene have been found to give high yields of *cis*-stilbene oxide with Fe(TPP)(Cl) as catalyst[2b] and a mixture of *trans*- and *cis*-stilbene oxides in a ratio of *ca.* 1.6 : 1 with Mn(TPP)(Cl),[5] it appears that the major secondary reaction observed during *N*-tosylaziridination of alkenes by PhI=NTs results either from the fast hydrolysis of PhI=NTs into PhI=O and $TsNH_2$ catalysed by Fe- or Mn-(TPP)(Cl) (Scheme 1) or from the fast exchange of the N–Ts moiety of a possible Fe^V=NTs intermediate complex with the oxygen atom from water.†

Accordingly, we found that the *N*-tosylaziridine : $TsNH_2$ ratio can be markedly increased by using anhydrous solvents and by performing the reactions in the presence of molecular sieves. The yields indicated in Table 1 were obtained under such conditions but have not been optimized.

The stereochemical characteristics of these *N*-tosylaziridinations catalysed by Fe(TPP)(Cl) are very different from those of the corresponding alkene epoxidation by PhI=O.[2—5] First, epoxidation of *cis*- and *trans*-stilbene catalysed by Fe(TPP)(Cl) is stereospecific[2,3] whereas *N*-tosylaziridination is only stereoselective since it gives exclusively the more stable *trans*-*N*-tosyl-2,3-diphenylaziridine from either *cis*- or *trans*-stilbene. Moreover, epoxidation of *cis*-stilbene catalysed by Mn(TPP)(Cl) gives a mixture of *cis*- and *trans*-epoxides whereas *N*-tosylaziridination also gives only the *trans*-aziridine. It is noteworthy that *cis*-*N*-tosyl-2,3-diphenylaziridine is stable under the reaction conditions. Secondly, the yields of *N*-tosylaziridine from either *cis*- or *trans*-stilbene are very similar, in contrast to those of the epoxides which are very high for *cis*-stilbene and close to zero for *trans*-stilbene.[2b,3]

In order to see whether groups other than N–Ts could be transferred to alkenes by a similar method, we have prepared a new PhI=NR derivative (R = $COCF_3$), by the reaction of CF_3CONH_2 with $PhI(OCOMe)_2$ and KOH in MeOH at −40 °C, under conditions similar to those reported for PhI=NTs.[11]

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† Similar high-valent tosylimino–iron complexes have been postulated as intermediates in the reactions of alkenes and alkanes with chloramine-T in the presence of $FeCl_2$ (ref. 13).

The solid compound, PhI=NCOCF$_3$ (explosive decomp. *ca.* 100 °C, $\nu_{C=O}$ 1665 cm^{-1}), obtained was found to be very sensitive to water and could not be completely purified. However, its reaction with styrene in the presence of Fe(TPP)(Cl) under conditions identical to those described above afforded *N*-trifluoroacetyl-2-phenylaziridine (*ca.* 50% yield) whose structure has been established by comparison with an authentic sample.[14] This preliminary result suggests that the synthesis of *N*-substituted aziridines from alkenes and certain PhI=NR derivatives could be general.

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