

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 $\text{PhI}=\text{NR}$ compounds ($\text{R} = \text{tosyl}$ or COCF_3) with alkenes; the stereochemical characteristics of these reactions are very different from those of the analogous epoxidation of alkenes by $\text{PhI}=\text{O}$.

Cytochrome P-450¹ 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, $\text{Fe}^{\text{V}}=\text{O}$ ⁶ and $\text{Mn}^{\text{V}}=\text{O}$,^{4,5} seem to be the active intermediates in these reactions. High-valent metal-nitrene complexes are the nitrogen analogues of these oxo

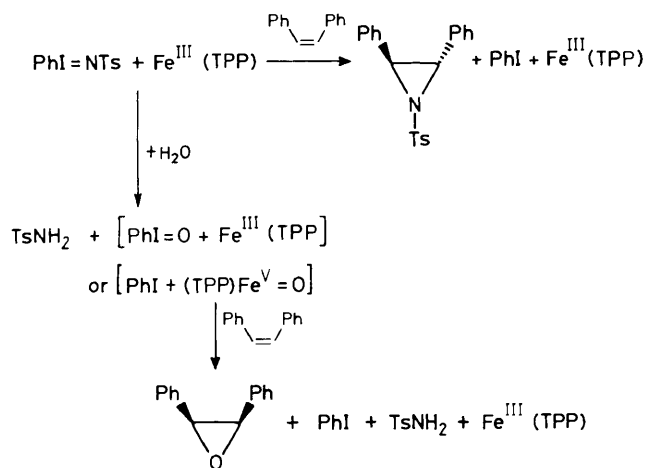
complexes. Recently, such complexes, namely porphyrin-iron-nitrene complexes, $\text{Fe}^{\text{II}} \leftarrow \text{N}-\text{NR}_2 \longleftrightarrow \text{Fe}^{\text{IV}}=\text{N}-\text{NR}_2$ ⁷ and a porphyrin-manganese-nitrene complex, $\text{Mn}^{\text{V}}=\text{N}-\text{COCF}_3$,⁸ which could transfer its nitrene moiety to cyclooctene, have been described.

The nitrogen analogue of oxygen atom transfer from $\text{PhI}=\text{O}$

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

Alkene	Products	% Yield	
		Fe(TPP)(Cl)	Mn(TPP)(Cl)
Styrene	<i>N</i> -Tosyl-2-phenylaziridine	55	80
	TsNH ₂	40	20
<i>cis</i> -Stilbene	<i>trans</i> - <i>N</i> -Tosyl-2,3-diphenylaziridine	37	20
	TsNH ₂	63	80
<i>trans</i> -Stilbene	<i>trans</i> - <i>N</i> -Tosyl-2,3-diphenylaziridine	32	16
	TsNH ₂	65	80
1,1-Diphenylethylene	<i>N</i> -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-diisopropylbenzenesulphonyliminoiodobenzene 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 CH₂Cl₂, were added to solid PhI=NTs¹¹ [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 (TsNH₂) 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 + TsNH₂) 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 TsNH₂, the major side reaction. (i) PhI=NTs is slowly hydrolysed into PhI=O and TsNH₂ in (CD₃)₂SO upon addition

of H₂O (25 equiv.), and the formation of TsNH₂ 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 TsNH₂) in addition to *N*-tosylaziridine and TsNH₂, 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 TsNH₂, 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 TsNH₂ 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:TsNH₂ 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 = COCF₃), by the reaction of CF₃CONH₂ with PhI(OCOMe)₂ and KOH in MeOH at -40 °C, under conditions similar to those reported for PhI=NTs.¹¹

† 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 FeCl₂ (ref. 13).

The solid compound, $\text{PhI}=\text{NCOCF}_3$ (explosive decomp. ca. 100 °C, $\nu_{\text{C=O}}$ 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 $\text{Fe}(\text{TPP})$ (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 $\text{PhI}=\text{NR}$ derivatives could be general.

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