

## 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  $\text{COCF}_3$ ) 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-450<sup>1</sup> as well as Fe-<sup>2,3</sup> and Mn-porphyrins<sup>4,5</sup> catalyse the transfer of the oxygen atom of iodosylbenzene to several substrates including alkanes and alkenes. High-valent metal-oxo complexes,  $\text{Fe}^{\text{V}}=\text{O}$ <sup>6</sup> and  $\text{Mn}^{\text{V}}=\text{O}$ ,<sup>4,5</sup> seem to be the active intermediates in these reactions. High-valent metal-nitrene complexes are the nitrogen analogues of these oxo

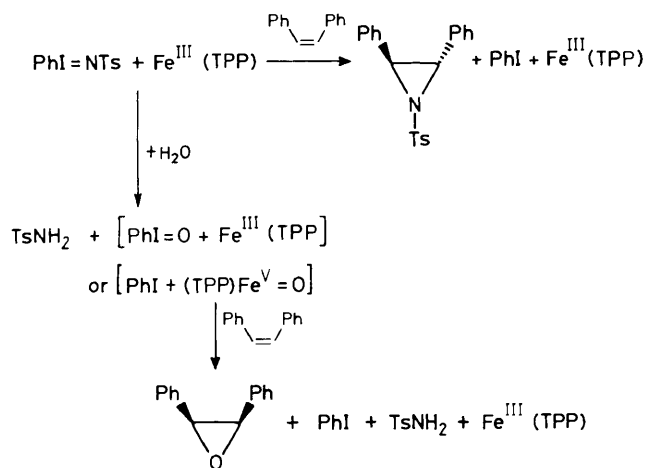
complexes. Recently, such complexes, namely porphyrin-iron-nitrene complexes,  $\text{Fe}^{\text{II}} \leftarrow \text{N}-\text{NR}_2 \longleftrightarrow \text{Fe}^{\text{IV}}=\text{N}-\text{NR}_2$ <sup>7</sup> and a porphyrin-manganese-nitrene complex,  $\text{Mn}^{\text{V}}=\text{N}-\text{COCF}_3$ ,<sup>8</sup> 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<sup>a</sup> 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 <sub>2</sub>	40	20
<i>cis</i> -Stilbene	<i>trans</i> - <i>N</i> -Tosyl-2,3-diphenylaziridine	37	20
	TsNH <sub>2</sub>	63	80
<i>trans</i> -Stilbene	<i>trans</i> - <i>N</i> -Tosyl-2,3-diphenylaziridine	32	16
	TsNH <sub>2</sub>	65	80
1,1-Diphenylethylene	<i>N</i> -Tosyl-2,2-diphenylaziridine	21	56
	TsNH <sub>2</sub>	75	40

<sup>a</sup> 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)<sup>9</sup> and the intramolecular insertion of the nitrene moiety of 2,5-diisopropylbenzenesulphonyliminoiodobenzene into a benzylic C-H bond,<sup>10</sup> 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<sub>2</sub>Cl<sub>2</sub>, were added to solid PhI=NTs<sup>11</sup> [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<sub>2</sub>) 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<sub>2</sub>) 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<sub>2</sub>, the major side reaction. (i) PhI=NTs is slowly hydrolysed into PhI=O and TsNH<sub>2</sub> in (CD<sub>3</sub>)<sub>2</sub>SO upon addition

of H<sub>2</sub>O (25 equiv.), and the formation of TsNH<sub>2</sub> 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<sub>2</sub>) in addition to *N*-tosylaziridine and TsNH<sub>2</sub>, 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<sub>2</sub>, 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<sup>2b</sup> and a mixture of *trans*- and *cis*-stilbene oxides in a ratio of ca. 1.6:1 with Mn(TPP)(Cl),<sup>5</sup> 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<sub>2</sub> catalysed by Fe- or Mn-(TPP)(Cl) (Scheme 1) or from the fast exchange of the N-Ts moiety of a possible Fe<sup>V</sup>=NTs intermediate complex with the oxygen atom from water.†

Accordingly, we found that the *N*-tosylaziridine:TsNH<sub>2</sub> 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.<sup>2-5</sup> First, epoxidation of *cis*- and *trans*-stilbene catalysed by Fe(TPP)(Cl) is stereospecific<sup>2,3</sup> 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.<sup>2b,3</sup>

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<sub>3</sub>), by the reaction of CF<sub>3</sub>CONH<sub>2</sub> with PhI(OCOME)<sub>2</sub> and KOH in MeOH at -40 °C, under conditions similar to those reported for PhI=NTs.<sup>11</sup>

† 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<sub>2</sub> (ref. 13).

The solid compound,  $\text{PhI}=\text{NCOCF}_3$  (explosive decomp. ca. 100 °C,  $\nu_{\text{C=O}}$  1665  $\text{cm}^{-1}$ ), obtained was found to be very sensitive to water and could not be completely purified. However, its reaction with styrene in the presence of  $\text{Fe}(\text{TPP})$  ( $\text{Cl}$ ) 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.<sup>14</sup> 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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