Aziridination of Alkenes catalysed by Porphyrinirons: Selection of Catalysts for Optimal Efficiency and Stereospecificity

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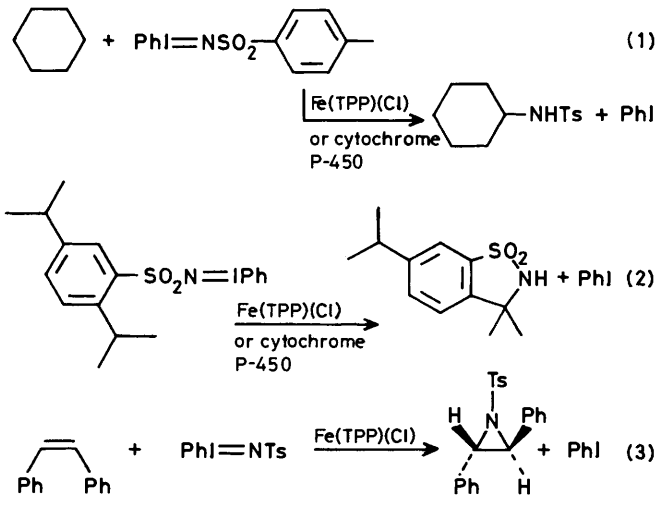
meso-Tetra-arylporphyriniron(III) derivatives catalyse the *N*-tosylaziridination of aryl-substituted styrenes by tosylimidoiodobenzene, PhINTs, a nitrogen analogue of iodosylbenzene. Three secondary reactions were found to limit the yield of *N*-tosylaziridination: (i) the formation of toluene-*p*-sulphonamide, $TsNH_2$, which is presumably derived from hydrolysis of a possible iron-nitrene, Fe=NTs, intermediate, (ii) the conversion of the Fe(TPP)(Cl) (TPP = tetraphenylporphyrin) catalyst into an iron(III) complex where the NTs moiety is inserted into an iron–nitrogen bond of Fe(TPP)(Cl), (iii) an oxidative degradation of the porphyrin catalyst. These secondary reactions were avoided to a great extent by using anhydrous conditions and Fe(TDCPP)(ClO_4) (TDCPP = tetrakis-2,6-dichlorophenylporphyrin) as a catalyst instead of Fe(TPP)(Cl) and Fe(TPP)(ClO_4). Under these conditions, *N*-tosylaziridination of styrene, *cis*- and *trans*-stilbene, and 1,1-diphenylethylene was performed with yields between 40 and 90%. Fe(TDCPP)(ClO_4) was also found to be the best catalyst for *N*-tosylaziridination of aliphatic alkenes such as hex-1-ene, cyclo-octene, and *cis*- and *trans*-hex-2-enes. Although *N*-tosylaziridination of the two latter alkenes catalysed by Fe(TPP)(Cl) was not stereospecific, this reaction became stereospecific with Fe(TDCPP)(ClO_4) as catalyst. These results show that by a proper choice of the porphyriniron catalyst, relatively good yields of *N*-tosylaziridination of alkenes by PhINTs can be obtained. As for 1,2-disubstituted aliphatic alkenes, *syn* addition of the NTs moiety to the double bond takes place. A possible mechanism is presented.

Cytochrome P-450[1] and model iron-[2] or manganese-porphyrins[3] catalyse the transfer of the oxygen atom of iodosylbenzene to hydrocarbons. The model mono-oxygenation reactions involve high-valent intermediate iron-oxo or manganese-oxo complexes as active species for oxygen-atom transfer into substrates.[2–4] Simple iron- and manganese-porphyrins are also able to catalyse the transfer of the *N*-tosylnitrene moiety of tosylimidoiodobenzene, PhI=NTs, a nitrogen analogue of PhIO, into hydrocarbons. Fe(TPP)(Cl) and Mn(TPP)(Cl) (TPP = tetraphenylporphyrin) have thus been found to catalyse the intermolecular tosylamination of cyclohexane by PhINTs with yields between 3 and 8% under mild conditions[5] [equation (1)] as well as the intramolecular insertion of the nitrene moiety of 2,5-di-isopropylphenylsulphonylimidoiodobenzene into a benzylic C–H bond with high yield[6] [equation (2)]. These catalysts have also been reported to catalyse the aziridination of styrene, stilbenes, and 1,1-diphenylethylene by PhINTs with yields between 16 and 80%.[7] Contrary to the epoxidation of stilbenes by PhIO in the presence of Fe(TPP)(Cl) which is stereospecific,[2a,d,g] aziridination of either *cis*- or *trans*-stilbene by PhINTs leads exclusively to the *trans*-aziridine[7] [equation (3)].



Recent results have shown that cytochrome P-450 isoenzymes purified from rabbit liver microsomes also catalysed the intramolecular transfer of the nitrogen atom of 2,5-di-isopropylphenylsulphonylimidoiodobenzene into a benzylic C–H bond of the molecule [equation (2)], as well as tosylamination of cyclohexane by PhINTs[8] [equation (1)]. The relatively low rates observed (1 and 0.31 nmol formed per nmol cytochrome P-450 per min for the intramolecular and intermolecular amination respectively) should be due to the fast hydrolysis of a possible transient iron-nitrene complex into the corresponding iron-oxo complex. This secondary reaction has been observed both in cytochrome P-450-[9] and in metalloporphyrin-catalysed reactions of PhINTs.[7]

This report is concerned with a study of the reactions of various alkenes with PhINTs catalysed by different porphyriniron(III) derivatives. It describes the various reactions which are occurring besides the expected aziridination of alkenes and shows that, by a proper choice of the porphyrin catalyst, it is possible to avoid or to limit secondary reactions and to perform stereospecific aziridination of aliphatic alkenes.

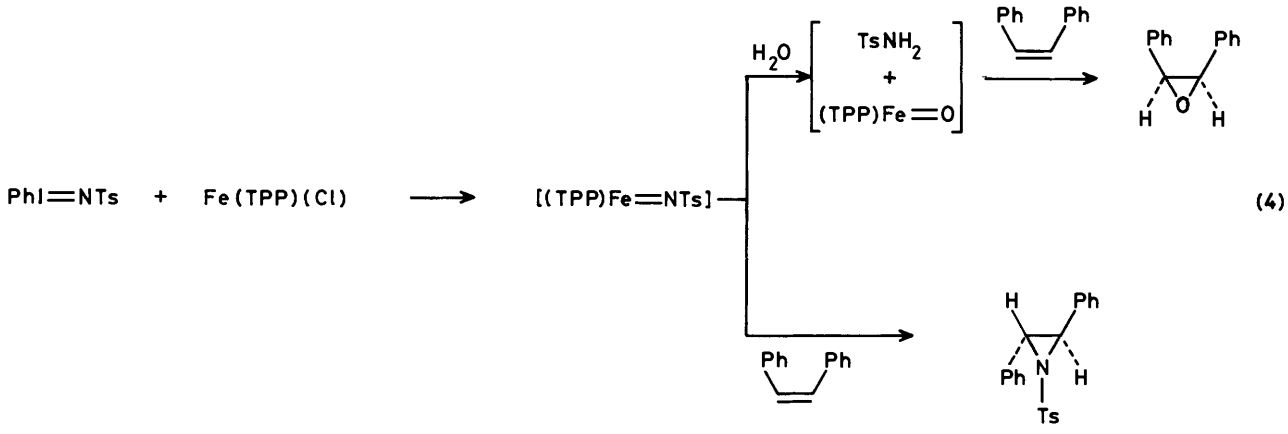
Results

Reaction of cis-*Stilbene with* PhINTs *catalysed by Porphyrinirons.*—Reaction of PhINTs[10] with *cis*-stilbene in excess (1:100 ratio) in CH_2Cl_2 containing catalytic amounts of Fe(TPP)(Cl) (0.05 equiv. relative to PhINTs) under argon at 20 °C leads to complete consumption of PhINTs within 30

min. Analysis of the reaction mixture by g.c. shows the formation of iodobenzene, *trans*-*N*-tosyl-2,3-diphenylaziridine, *cis*-stilbene epoxide, and toluene-*p*-sulphonamide (tosylamine) (yields in Table 1). When the same reaction is performed with Mn(TPP)(Cl) as catalyst, analogous results are obtained except for the formation of a mixture of the *cis*- and *trans*-epoxides of stilbene (Table 1).

mediate, formed upon transfer of the NTs moiety of PhINTs to the metal, reacts either with stilbene leading to the observed aziridines or with traces of water leading to the corresponding high-valent Fe=O or Mn=O epoxidizing complexes and $TsNH_2$ [equation (4)].

In the reactions of PhINTs catalysed by Fe(TPP)(Cl), the catalyst was found to be almost completely transformed at the



(4)

It is noteworthy that in both cases the total yields of $TsNH_2$ and aziridine are close to 100%, indicating that no other important reaction involving the NTs moiety has occurred. Moreover, the nature and ratios of the epoxides (Table 1) are almost identical to those previously reported for epoxidation of *cis*-stilbene by PhIO catalysed either by Fe(TPP)(Cl)[2a] or Mn(TPP)(Cl)[3b] which should involve Fe^{V}=O or Mn^{V}=O intermediates.

These results are easily understandable if one admits, as indicated previously,[7–9] that a possible high-valent metal-nitrene complex, formally a Fe^{V}=NTs or Mn^{V}=NTs inter-

end of the reaction. As described previously, the corresponding final iron complex was isolated and completely characterized.[11] It derives formally from the insertion of the NTs moiety into an Fe–N bond of Fe(TPP)(Cl).

All experiments were performed under conditions as anhydrous as possible (anhydrous solvents and substrates distilled before use, drying of PhINTs under vacuum, and reactions performed in the presence of molecular sieves) in order to limit the hydrolysis of possible intermediate metal-nitrene complexes. Moreover, different iron-porphyrins were studied as catalysts in order to increase the aziridination yields and to keep the catalyst intact during the reaction.

Reaction of PhINTs *with Aromatic Alkenes catalysed by Porphyrinirons.*—Under the aforementioned anhydrous conditions, the yield of aziridination of *cis*-stilbene increases from *ca.* 20 to 37% with Fe(TPP)(Cl) as catalyst (compare Tables 1 and 2). Table 2 compares the aziridine yields obtained upon reaction of various alkenes of the styrene type, with no allylic hydrogens, with PhINTs in the presence of different catalysts. In addition to Fe(TPP)(Cl) the cationic complex Fe(TPP)(ClO_4) was studied because of a possible easier access and greater reactivity of the metal towards PhINTs. Fe(TDCPP)(ClO_4) (TDCPP = tetrakis-2,6-dichlorophenylporphyrin) was also studied because of its greater catalytic activity and stability

Table 1. Reaction of *cis*-stilbene with PhINTs catalysed by Fe(TPP)(Cl) or Mn(TPP)(Cl)[a]

	Products (yield %)[b]		
Catalyst	$TsNH_2$	Aziridine[c]	Stilbene oxide
Fe(TPP)(Cl)	80	20	45 (*cis*)
Mn(TPP)(Cl)	84	16	30 (*cis*) + 38 (*trans*)

[a] Conditions indicated in the Experimental section. Proportions of the reactants: catalyst:PhINTs:stilbene 1:20:2 000 in CH_2Cl_2. No particular precautions were taken to avoid traces of water. [b] Yields based on starting PhINTs. [c] *trans*-*N*-Tosyl-2,3-diphenylaziridine. No *cis* isomer could be detected.

Table 2. Aziridination of aromatic olefins by PhINTs catalysed by various porphyrinirons[a]

		Yields (%) as a function of the catalyst nature[b]		
	Products	Fe(TPP)(Cl)	Fe(TPP)(ClO_4)	Fe(TDCPP)(ClO_4)
Styrene	*N*-Tosyl-2-phenylaziridine	55	57	74
	$TsNH_2$	40	35	20
cis-Stilbene	*trans*-*N*-Tosyl-2,3-diphenylaziridine	37	36	43
	$TsNH_2$	63	60	55
trans-Stilbene	*trans*-*N*-Tosyl-2,3-diphenylaziridine	32	24	36
	$TsNH_2$	65	75	63
1,1-Diphenylethylene	*N*-Tosyl-2,2-diphenylaziridine	21	40	90
	$TsNH_2$	75	58	5

[a] Conditions indicated in the Experimental section. Proportions of reactants as in Table 1. Conditions as anhydrous as possible. [b] Based on starting PhINTs (%).

Table 3. Reactions of aliphatic alkenes with PhINTs catalysed by porphyrinirons[a]

Alkene	Products	Yields (%) as a function of the catalyst nature[b] Fe(TPP)(Cl)	Fe(TPP)(ClO_4)	Fe(TDCPP)(ClO_4)
Cyclo-octene	2,3-Hexamethylene-*N*-tosylaziridine	13	28	33
	Allylic amines[c]	4	5	12
	$TsNH_2$	80	68	55
Hex-1-ene	*N*-Tosyl-2-n-butylaziridine	13	20	22
	Allylic amines[c]	n.d.	⩽2	<1
	$TsNH_2$	81	77	74
cis-Hex-2-ene	*cis*-*N*-Tosyl-2-methyl-3-n-propylaziridine	1	12	35
	trans-*N*-Tosyl-2-methyl-3-n-propylaziridine	2	<1	<1
	Allylic amines[c]	3	20	13
	$TsNH_2$	77	65	50
trans-Hex-2-ene	*cis*-*N*-Tosyl-2-methyl-3-n-propylaziridine	1	2	3
	trans-*N*-Tosyl-2-methyl-3-n-propylaziridine	2	25	30
	Allylic amines[c]	6	30	23
	$TsNH_2$	65	42	40

[a] Conditions as in Table 2. [b] Based on starting PhINTs. [c] Yields estimated from the integration of the signals of the allylic protons α relative to NTs in ^1H n.m.r.

towards oxidants used in oxygen-transfer reactions.[2i,12] With all these catalysts, *cis*- and *trans*-stilbene gave only *trans*-*N*-tosyl-2,3-diphenylaziridine. The corresponding *cis*-aziridine was prepared by previously described methods[13] but could not be detected in our reactions using PhINTs. For almost all the alkenes studied, styrene, *cis*- and *trans*-stilbene, and 1,1-diphenylethylene, the aziridination yields increased when passing from Fe(TPP)(Cl) to Fe(TPP)(ClO_4) and to Fe(TDCPP)(ClO_4) (Table 2). This is particularly obvious for 1,1-diphenylethylene for which a 21% yield was obtained with Fe(TPP)(Cl) and a 90% yield with Fe(TDCPP)(ClO_4). By correct choice of the catalyst, it is thus possible to obtain the *N*-tosylaziridine of styrene, stilbene, and 1,1-diphenylethylene with yields of 74, 43, and 90%, respectively.

Another important feature of these aziridinations is the state of the catalyst at the end of the reaction. With styrene as well as *cis*- and *trans*-stilbene, Fe(TPP)(ClO_4) was found to be almost completely destroyed at the end of the reactions. This was shown by the almost complete disappearance of the u.v.–visible peaks of the starting catalyst with no clear appearance of new peaks betwen 400 and 700 nm. After reactions of stilbenes catalysed by Fe(TPP)(Cl), the catalyst was only partly destroyed but mainly transformed into the Fe(TPP)(NTs)(Cl) bridged complex.[11] This transformation was not observed upon styrene aziridination catalysed by Fe(TPP)(Cl) presumably because of the higher reactivity of styrene towards the postulated iron-nitrene intermediate [equation (4)]. More interestingly, Fe(TDCPP)(ClO_4) which gave the best aziridination yields was always found to be unchanged at the end of reactions, under the conditions used (catalyst:PhINTs:olefin 1:20:2 000; 2 h at 20 °C under argon). Identification of the various *N*-tosylaziridines was done by comparison with authentic samples prepared by a previously described method.[13]

Reaction of Various Alkenes with PhINTs *catalysed by Porphyrinirons.*—Reaction of *cis*-hex-2-ene with PhINTs catalysed by Fe(TPP)(Cl), under conditions identical with those used for aromatic alkenes, leads to a complex mixture of *cis*- and *trans*-*N*-tosylaziridines and of allylic tosylamines. The two main products exhibited g.c. and ^1H n.m.r. characteristics identical with those of *cis*- and *trans*-*N*-tosyl-2-methyl-3-n-propylaziridines which have been prepared by a previously described method.[13] The two isomers are easily distinguished in ^1H n.m.r. spectroscopy by the signals of the hydrogen α to the methyl group which appear, respectively, at δ 2.84 and 2.7 (in $CDCl_3$) in the spectra of the *cis*- and *trans*-*N*-tosylaziridines. It was thus possible to quantify their proportions by a study of the ^1H n.m.r. spectrum of the crude reaction mixture.

Besides *cis*- and *trans*-aziridines, the reaction mixture contained compounds which were not completely purified because of their relatively low yields. However, their mass spectra (after g.c. separation) indicated that they are isomers of the *N*-tosylaziridines. A study of the ^1H n.m.r. spectrum of their crude mixture clearly showed that they were isomeric *N*-tosylamines derived presumably from the insertion of the NTs group into allylic C–H bonds of *cis*-hex-2-ene. A study of these secondary products is under way. As shown in Table 3, the reaction of PhINTs with *cis*-hex-2-ene catalysed by Fe(TPP)(Cl) is not regioselective since it leads to a mixture of *N*-tosylaziridines and of allylic *N*-tosylamines. With Fe(TPP)(ClO_4), the yields increase considerably with the almost exclusive formation of the *cis*-*N*-tosylaziridine in contrast to reactions catalysed by Fe(TPP)(Cl) which lead to a 2:1 mixture of *trans*- and *cis*-*N*-tosylaziridines. However, the reaction remains non-regioselective with significant formation of allylic *N*-tosylamines. Use of the Fe(TDCPP)(ClO_4) catalyst leads to a clear improvement in the regioselectivity. With this catalyst, the *cis*-*N*-tosylaziridine is formed in 35% yield (Table 3) (Scheme).

The reactions of cyclo-octene, *trans*-hex-2-ene, and hex-1-ene were studied in a similar manner. The *N*-tosylaziridines formed in these reactions were identified by comparison with authentic samples.[13] Secondary products were also formed. From a study of the crude mixture by g.c. coupled with mass spectrometry and by ^1H n.m.r., these products are isomeric allylic *N*-tosylamines.

For the four aliphatic alkenes studied (Table 3), Fe(TPP)(Cl) leads to low yields of products derived from the transfer of the NTs moiety into the substrate and to non-selective reactions. For instance, in the case of *cis*- and *trans*-hex-2-enes, mixtures of *cis*- and *trans*-*N*-tosylaziridines are obtained together with equivalent amounts of allylic *N*-tosylamines. The use of Fe(TPP)(ClO_4) leads to a clear increase in the total yield of NTs transfer, from a factor of 1.5 for hex-1-ene to a factor of 6.3 for *trans*-hex-2-ene. Another major improvement when passing from Fe(TPP)(Cl) to Fe(TPP)(ClO_4) is a marked increase of the stereospecifity of the aziridination reaction. *N*-Tosylaziridination of hex-2-enes by PhINTs catalysed by Fe(TPP)(ClO_4) is at least 90% stereospecific and is a *syn* addition of the NTs moiety to the double bond (Scheme). However, the best catalyst for the *N*-tosylaziridination of aliphatic alkenes

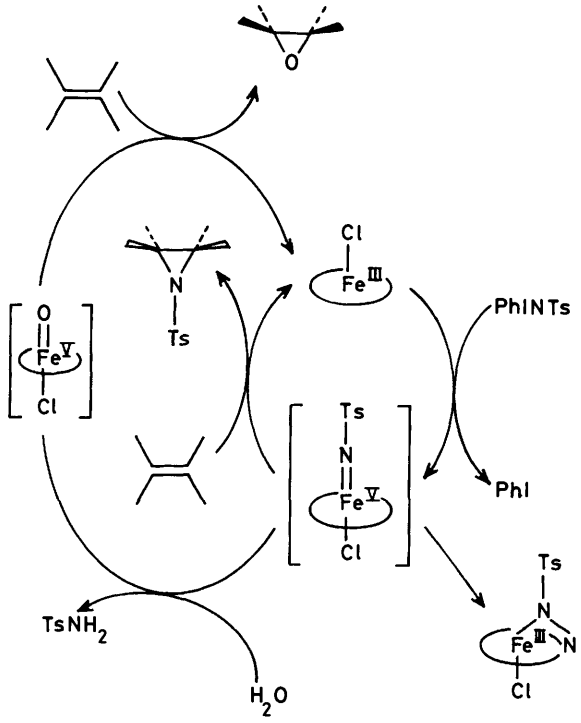


Figure 1. Different reactions observed upon interaction of PhINTs with alkenes in the presence of porphyrinirons

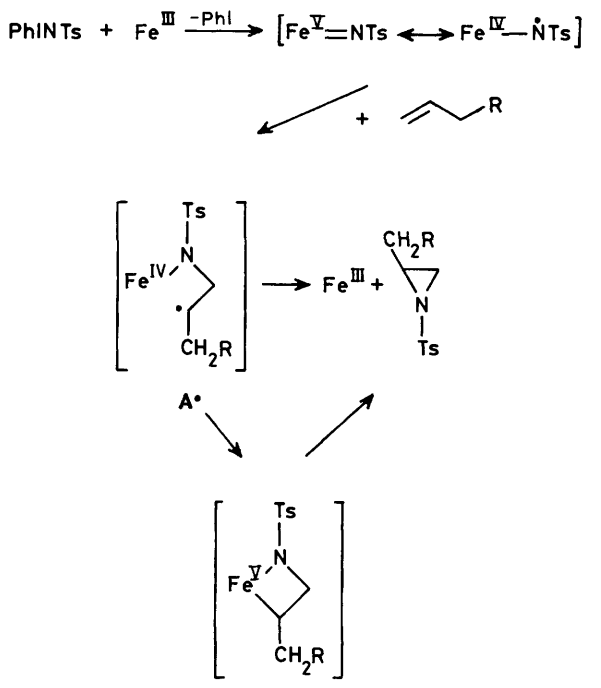


Figure 2. Possible mechanism for *N*-tosylaziridination of alkenes by PhINTs catalysed by porphyriniron(III) derivatives

is Fe(TDCPP)(ClO_4). When compared with Fe(TPP)(Cl) and Fe(TPP)(ClO_4), it exhibits four main advantages (Table 3): (i) it leads to the highest total yield of NTs transfer to the alkene; (ii) it remains intact at the end of the reactions; (iii) it leads to a stereospecific *syn*-*N*-tosylaziridination of hex-2-enes; and (iv) it leads to the most regioselective reactions favouring *N*-tosylaziridination over allylic *N*-tosylamination.

Therefore, when passing from Fe(TPP)(Cl) to Fe(TDCPP)(ClO_4), the yield of *syn*-*N*-tosylaziridination of cyclooctene, hex-1-ene, *cis*-, and *trans*-hex-2-ene increases respectively by a factor of 2.5, 1.7, 35, and 15.

Discussion

Different Reactions observed upon Interaction of PhINTs *with Alkenes in the Presence of Porphyrinirons.*—Porphyrinirons are able to catalyse the transfer of the NTs moiety of PhINTs as well as of the oxygen atom of PhIO into alkenes. The aforementioned results and previous preliminary reports[7,11] show that the transfer of the NTs moiety of PhINTs into alkenes is limited by three main secondary reactions (Figure 1): (a) the hydrolysis of a possible metal-nitrene intermediate by water traces which could be present in the reaction mixture (see also refs. 8 and 9 for this point); (b) an irreversible modification of Fe(TPP)(Cl) with formation of a bridged Fe^{III}–NTs–N porphyrin complex;[11] and (c) progressive oxidative destruction of Fe(TPP)(Cl) and Fe(TPP)(ClO_4).

Reactions (b) and (c) do not occur with Fe(TDCPP)(ClO_4) under the conditions used in this study. Therefore, reactions performed with this catalyst under conditions as anhydrous as possible led generally to good yields of *N*-tosylaziridines. For instance, aziridination of aromatic alkenes having no allylic hydrogen atoms catalysed by Fe(TDCPP)(ClO_4) resulted in yields between 36 and 90%. In the case of aliphatic alkenes containing allylic C–H bonds, allylic *N*-tosylamines are formed besides *N*-tosylaziridines. Thus, the reactions of PhINTs with alkenes resemble those of PhIO with alkenes which are well known to give epoxides and allylic alcohols.[2] A possible mechanism for *N*-tosylaziridination could be proposed by analogy with a mechanism proposed for epoxidations by PhIO.[2d,g,j,k] It could involve the intermediate formation of a high-valent iron-nitrene complex[7–9,14] having a free radical-like reactivity as its iron-oxo analogue.[2,15] This intermediate, formally an Fe^{IV}–$\dot{N}$Ts species, may add to the alkene double bond. *N*-Tosylaziridines could be formed from the free radical derived from this addition either *via* direct oxidative transfer of the NTs ligand to the intermediate carbon-centred radical or *via* a four-membered Fe–C–C–N metallocycle (Figure 2).

Stereochemistry of N-*Tosylaziridination Reactions: Effects of Catalyst Structure.*—Whatever the nature of the catalysts used in this study, *N*-tosylaziridination of stilbenes is never stereospecific. In all reactions with either *cis*- or *trans*-stilbene, the more stable *trans*-aziridine is formed exclusively. On the other hand, the stereospecificity of the aziridination of aliphatic alkenes, *e.g.* hex-2-enes, greatly depends on the nature of the catalyst. *N*-Tosylaziridination of hex-2-enes is not stereospecific with Fe(TPP)(Cl) but becomes stereospecific with porphyriniron perchlorates (Table 3). We have verified that no *cis*–*trans* isomerization of the starting alkenes or of the *N*-tosylaziridines occurred under the reaction conditions.

Comparison between Oxygen Transfer from PhIO *and* NTs *Transfer from* PhINTs *catalysed by Porphyrinirons.*—As shown in Table 4, aziridination of alkenes by PhINTs is generally less

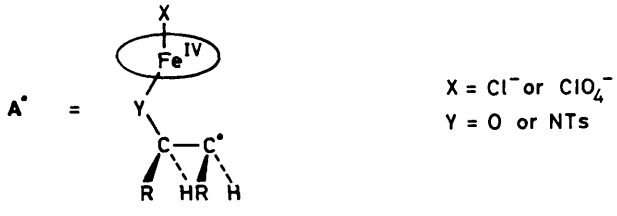
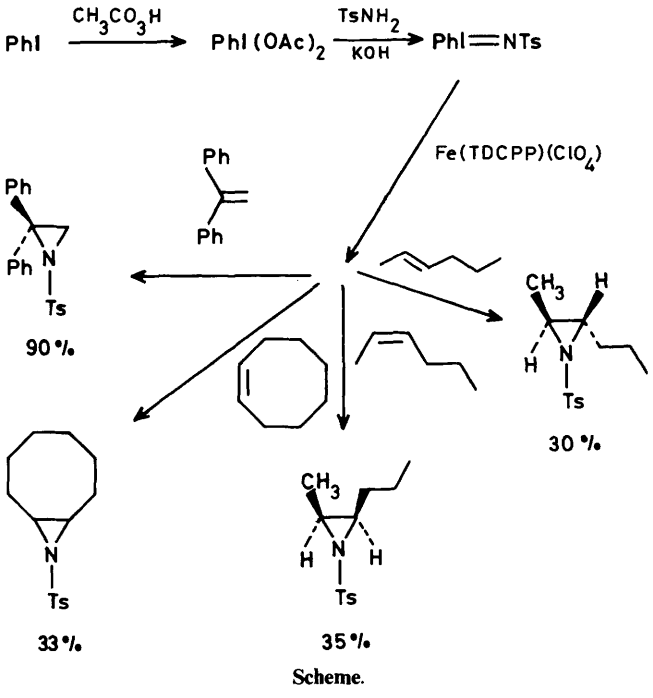


Table 4. Stereospecificity of alkene epoxidation or *N*-tosylaziridination catalysed by porphyrinirons

			Yields (%) of epoxide or *N*-tosylaziridine[a] obtained from			
			PhIO		PhINTs	
Catalyst	Alkene		*cis*-epoxide	*trans*-epoxide	*cis*-*N*-tosylaziridine	*trans*-*N*-tosylaziridine
Fe(TPP)(Cl)	Stilbene	*cis*	82	n.d.[b] [2a]	n.d.	37
		trans	n.d.	2 [2d]	n.d.	32 (this work)
Fe(TDCPP)(ClO_4)	Stilbene	*cis*			n.d.	43
		trans			n.d.	36 (this work)
Fe(TPP)(Cl)	Hex-2-ene	*cis*	51	n.d.	35	2
		trans	n.d.[c]	13 [2d]	3	2 (this work)
Fe(TDCPP)(ClO_4)	Hex-2-ene	*cis*			1	1
		trans			1	30 (this work)

[a] Based on starting PhIO or PhINTs. [b] n.d. = not detected. [c] Results obtained from epoxidation of *cis*- and *trans*-4-methylpent-2-ene.



Scheme.

stereospecific than their epoxidation by PhIO.[2a,d,g] It has been proposed that the stereospecificity of alkene epoxidation by PhIO catalysed by porphyrinirons could be due to a very fast oxidation of the possible intermediate carbon-centred free radical Å, derived from the addition of the active-oxygen Fe^{IV}–Ȯ species to the double bond, by the Fe^{IV} centre.[2k] Because of this fast reaction, the intermediate free radical Å (X = O) has not enough time to undergo rotation around its C–C bond.*

If an analogous mechanism is involved in *N*-tosylaziridination, one could explain the lack of stereospecificity observed in many cases by a slower intramolecular oxidation of the free radical by iron(IV) when Y = *N*-tosyl than when Y = O. The relatively stable benzylic radical derived from stilbenes would always have enough time to undergo rotation around its C–C bond and would lead exclusively to the more thermodynamically stable *trans*-*N*-tosylaziridine whatever the nature of the iron catalyst. In the case of hex-2-enes and Fe(TPP)(Cl) as catalyst, even the more reactive intermediate alkyl radical seems to have enough time to undergo rotation around its C–C bond before its oxidation and leads to a mixture of *cis*- and *trans*-aziridines. With the cationic porphyrinirons, $[Fe(TPP \text{ or } TDCPP)]^+ClO_4^-$, the absence of the strong Cl^- ligand in the *trans* position relative to the $NTsCHR^1$–ĊHR^2 ligand in intermediates of type Å might allow an easier movement of the iron towards the carbon-centred radical and more efficient control of this radical (Table 4).

There is another major difference between the characteristics of the reactions of alkenes with either PhIO or PhINTs. It has been clearly shown that *cis*-1,2-disubstituted alkenes were epoxidized by PhIO in the presence of tetra-arylporphyrinirons with very good yields whereas the corresponding *trans*-alkenes were far less reactive and gave low epoxidation yields.[2a,d]. On the other hand, *N*-tosylaziridination of *cis*- and *trans*-stilbene or of *cis*-and *trans*-hex-2-ene (Tables 2 and 3) occurs with very similar yields.

Much work is needed to understand the important differences between reactions performed by PhIO and PhINTs. Anyway, whatever its mechanism may be, the anhydrous PhINTs–Fe(TDCPP)(ClO_4) system is interesting for its production of *N*-tosylaziridines under mild conditions and especially for its stereospecific *N*-tosylaziridination of alk-2-enes. In that regard, it is noteworthy that this system is not only able to lead to good yields of aziridination based on starting PhINTs when alkenes are used in excess (Tables 2 and 3), but also to convert alkenes into *N*-tosylaziridines when a 1:4 alkene:PhINTs ratio is used (80% yield based on starting alkene in the case of styrene under these conditions, data not shown). Since PhINTs is prepared from PhI in two steps,[10] this provides a new method of access to aziridines of given stereochemistry from alkenes (Scheme).

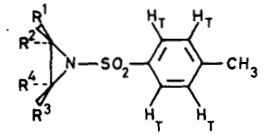
Experimental

Physical Measurements.—U.v.–visible spectra were recorded on an Aminco DW2 spectrophotometer. Mass spectra were obtained on a Ribermag apparatus (Ecole Normale Supérieure, Paris). Capillary g.c. was done on a Packard 437 instrument equipped with a flame ionization detector. Peak areas were measured by electronic integration using a Shimadzu CRIB integrator. ^1H N.m.r. spectra were recorded on a Bruker EM 250 spectrometer operating at 250 MHz. Elemental analyses were performed at the Service Central de Microanalyse, C.N.R.S. (Gif sur Yvette).

Materials.—Dichloromethane was purified by distillation from phosphorus pentaoxide and kept over molecular sieves.

* Cationic intermediates Fe^{III}–Y–CHR–$\dot{C}$HR have also been proposed [2m–o] in such alkene oxidations catalysed by porphyrinirons. As discussed in the text for the corresponding radical intermediates, the reaction stereospecificity should depend on the time that they have to undergo rotation around their C–C bond before intramolecular transfer of Y.

Table 5. Elemental analysis and ^{1}H n.m.r. and mass spectral characteristics of *N*-tosylaziridines



	δ(CDCl$_3$; Me$_4$Si)[a]							
	R^1	R^2	R^3	R^4	H_T	CH_3		Mass spectra[b] *m/z* (%)[b]
N-Tosyl-2,2-diphenylaziridine ($R^1 = R^2$ = Ph, $R^3 = R^4$ = H)	7—7.5 (m, 10 H)		6.70 (d, *J* 12.5 Hz, 1 H)	6.20 (d, *J* 12.5 Hz, 1 H)	7.70 (d, *J* 7.5 Hz, 2 H) 7.30 (d, *J* 7.5 Hz, 2 H)	2.38 (s, 3 H)	Calc.: C, 72.2; H, 5.4; N, 4.0; S, 9.2 Found: C, 72.4; H, 5.5; N, 3.8; S, 9.3%	91 (100), 155 (16), 194 (95), 349 (13)
2,3-Hexamethylene-*N*-tosylaziridine ($R^1 R^3 = C_6H_{12}$; $R^2 = R^4$ = H)	1—2 (m, 12 H, $R^1 R^3$)	2.74 (m, 2 H, $R^2 + R^4$)			7.76 (d, *J* 7.5 Hz, 2 H) 7.27 (d, *J* 7.5 Hz, 2 H)	2.36 (s, 3 H)	Calc.: C, 64.5; H, 7.6; N, 5.0 Found: C, 64.2; H, 7.8; N, 5.0%	91 (34), 124 (100), 155 (7), 279 (2)
N-Tosyl-2-n-butylaziridine (R^1 = n-C_4H_9, $R^2 = R^3 = R^4$ = H)	1—1.5 (m, 6 H) 0.80 (t, *J* 7.5 Hz, 3 H)	2.64 (m, 1 H)	1.95 (d, *J* 7.5 Hz, 1 H)	2.55 (d, *J* 10 Hz, 1 H)	7.80 (d, *J* 7.5 Hz, 2 H) 7.30 (d, *J* 7.5 Hz, 2 H)	2.33 (s, 3 H)	Calc.: C, 61.6; H, 7.6; N, 5.5; S, 12.65 Found: C, 61.9; H, 7.6; N, 5.4; S, 12.8%	91 (27), 98 (100), 155 (16), 253 (1)
cis-*N*-Tosyl-2-methyl-3-n-propylaziridine (R^1 = n-C_3H_7, R^2 = H, R^3 = CH_3, R^4 = H)	1—1.5 (m, 4 H) 0.82 (t, *J* 7.5 Hz, 3 H)	2.68 (dt, J_{24} 8, J_{21} 7.5 Hz, 1 H)	1.04 (d, *J* 7.5 Hz, 3 H)	2.84 (dq, J_{34} 7.5, J_{24} 8 Hz, 1 H)	7.78 (d, *J* 7.5 Hz, 2 H) 7.28 (d, *J* 7.5 Hz, 2 H)	2.36 (s, 3 H)	Calc.: C, 61.6; H, 7.6; N, 5.5; S, 12.65 Found: C, 61.1; H, 7.6; N, 5.5; S, 13.4%	91 (18), 98 (100), 155 (6), 253 (3)
trans-*N*-Tosyl-2-methyl-3-n-propylaziridine (R^1 = n-C_3H_7, $R^2 = R^3$ = H, R^4 = CH_3)	1—1.5 (m, 4 H) 0.85 (t, *J* 7.5 Hz, 3 H)	2.70 (m, 1 H)	1.29 (m, 1 H)	1.54 (d, J_{43} 7.5 Hz, 3 H)	7.82 (d, *J* 7.5 Hz, 2 H) 7.28 (d, *J* 7.5 Hz, 2 H)	2.36 (s, 3 H)	Calc.: C, 61.6; H, 7.6; N, 5.5 Found: C, 61.6; H, 7.7; N, 5.4%	91 (24), 98 (100), 155 (6), 253 (3)

[a] s = Singlet; d = doublet; t = triplet; m = multiplet; dt = doublet of triplets; dq = doublet of quadruplets. [b] Obtained by direct introduction at 200 °C (70 eV), electron impact.

cis- and *trans*-Stilbene and cyclo-octene were purchased from Janssen, 1,1-diphenylethylene from Ega-Chemie, and *cis*- and *trans*-hex-2-ene and hex-1-ene from Fluka. All alkenes were stored at 0 °C under argon.

Preparation of Tosylimidoiodobenzene.—PhI=NTs was synthesized according to an already described procedure.[10b] (Diacetoxyiodo)benzene (3.2 g, 10 mmol) was added at 5 °C under argon to a stirred mixture of toluene-*p*-sulphonamide (1.71 g, 10 mmol) and potassium hydroxide (1.4 g, 25 mmol) in methanol (40 ml). The resulting yellow, homogeneous solution was then stirred for 30 min at 5 °C and 30 min at room temperature. The mixture was then concentrated under argon (20 ml) and poured on ice (100 g). The precipitated pale yellow solid was then filtered off and washed with anhydrous ether (50 ml) to afford crystals of PhINTs (2.2 g, 60%; characteristics identical to those already published [10]). PhINTs was then dried under vacuum and stored at 0 °C in the dark under argon to avoid decomposition.

Porphyrin Catalysts.—*meso*-Tetraphenylporphyrin (TPP) was prepared according to Adler *et al.*[16] and *meso*-tetrakis-2,6-dichlorophenylporphyrin (TDCPP) was prepared according to Barnet *et al.*[17] The corresponding chloroporphyriniron(III) derivatives were prepared by a method already described by Fleischer *et al.*[18] The porphyriniron(III) perchlorates were prepared as follows: a solution of Fe^{III}(TPP)(Cl) (5×10^{-6} mol, 3.5 mg) or Fe^{III}(TDCPP)(Cl) (5×10^{-6} mol^{-1}, 4.8 mg) in CH_2Cl_2 (1 ml) is added under argon to solid $AgClO_4$ (2.5×10^{-5} mol, 5.2 mg) under argon. The mixture is stirred until the porphyriniron(III) perchlorate is completely formed (30 min), as shown by its u.v.–visible spectrum, identical with that previously described for Fe(TPP)(ClO_4).[19] The solution is then filtered under argon in order to eliminate the excess of $AgClO_4$, insoluble in CH_2Cl_2.

Synthesis of Authentic Samples of N-*Tosylaziridines.*—*N*-Tosyl-2-phenylaziridine and *cis*- and *trans*-*N*-tosyl-2,3-diphenylaziridines were synthesized according to the method already described by Seden *et al.* and their characteristics were found to be identical to those published previously.[13] The *N*-tosylaziridines derived from 1,1-diphenylethylene, cyclo-octene, *cis*-and *trans*-hex-2-ene, and hex-1-ene were prepared by the same method. Their ^{1}H n.m.r. and mass spectrum characteristics and elemental analysis are compared in Table 5.

N-*Tosyl*-2,2-*diphenylaziridine.* A solution of 1,1-diphenylethylene (0.6 g, 3.33×10^{-3} mol) in chloroform (6 ml) was added rapidly to a solution of *NN*-dichlorotoluene-*p*-sulphonamide ($TsNCl_2$) (0.8 g, 3.3×10^{-3} mol) in chloroform (10 ml) under argon. After a short induction time, an exothermic reaction ensued. The mixture was stirred at room temperature for 30 min and then heated under reflux for 2 h. After cooling down, the solution was shaken with an excess of sodium disulphite solution (15%) and evaporated. The residue was dissolved in toluene (70 ml) and a solution of sodium hydroxide (0.24 g) in water (16 ml) was added. This mixture was stirred vigorously at room temperature for at least 5 h. The organic phase was then evaporated and *N*-tosyl-2,2-diphenylaziridine was obtained as crystals (80%, 0.93 g) after recrystallization from ethanol, m.p. 171 °C.

2,3-*Hexamethylene*-N-*tosylaziridine.* 2,3-Hexamethylene-*N*-tosylaziridine was prepared as described above, starting from cyclo-octene (0.366 g, 3.33×10^{-3} mol) and $TsNCl_2$ (0.8 g) and obtained after purification on a silica gel column (CH_2Cl_2 as eluant) as crystals (50%, 0.46 g), m.p. 124 °C.

N-*Tosyl*-2-*n*-*butylaziridine.* *N*-Tosyl-2-n-butylaziridine was prepared from hex-1-ene (0.28 g, 3.33×10^{-3} mol) and $TsNCl_2$ (0.8 g, 3.33×10^{-3} mol) and obtained as a pale yellow oil (0.10 g, 12%) after purification on a silica gel column using CH_2Cl_2 as eluant.

cis- *and* trans-N-*Tosyl*-2-*methyl*-3-*n*-*propylaziridines.* The reaction of *trans*-hex-2-ene (0.28 g) with $TsNCl_2$ (0.8 g) afforded *trans*-*N*-tosyl-2-methyl-3-n-propylaziridine as a pale yellow oil (0.17 g, 20%) after purification on a silica gel column (CH_2Cl_2 as eluant). The reaction of *cis*-hex-2-ene (0.28 g) with $TsNCl_2$ (0.8 g) by the same procedure led to a mixture (0.3 g) of *cis*- and *trans*-*N*-tosyl-2-methyl-3-n-propylaziridine. These two products could be separated on a silica gel column using hexane–CH_2Cl_2 (40:60) as eluant. The *trans*-aziridine was obtained in 15% yield and the *cis*-aziridine as a pale yellow oil in 10% yield.

Reactions of Alkenes with Tosylimidoiodobenzene catalysed by Porphyriniron(III).—*Typical procedure in the case of styrene.* A solution of Fe(TPP)(Cl), Fe(TDCPP)(ClO_4), or Fe(TPP)(ClO_4) (5×10^{-6} mol) prepared as previously described in anhydrous CH_2Cl_2 (1 ml) was added under argon to styrene (1 ml). The resulting solution was transferred under argon in a flask containing tosylimidoiodobenzene (37.5 mg, 10^{-4} mol) and molecular sieves. The mixture was then stirred with a magnetic stirrer at room temperature.

Portions of the solution (20 μl) were taken and diluted 10 times in anhydrous CH_2Cl_2 and then analysed by u.v.–visible spectroscopy to follow the evolution of the catalyst. The same samples were analysed by g.c. *N*-Tosyl-2-phenylaziridine was identified by comparison with the authentic sample and quantified using *N*-cyclohexyltoluene-*p*-sulphonamide as internal standard. PhINTs was completely consumed within 30 min. The mixture was then filtered and the solvent and excess of styrene were removed under reduced pressure. The resulting solid was dissolved in $CDCl_3$. $TsNH_2$ and *N*-tosyl-2-phenylaziridine were identified by their characteristic signals in ^{1}H n.m.r. spectroscopy (see Table 5) and their yields were measured by using 1,1,2,2-tetrachloroethane as internal standard. The yields observed for the different reactions are indicated in Table 2. Moreover, $TsNH_2$ and *N*-tosyl-2-phenylaziridine were isolated by t.l.c. and identified by their mass and ^{1}H n.m.r. characteristics identical to those of authentic samples (Table 5).

Other alkenes. An identical procedure was used for the other volatile liquid alkenes (cyclo-octene, hex-1-ene, *cis*- and *trans*-hex-2-enes). The yields for these reactions are indicated in Table 3.

In the case of *trans*-stilbene which is a solid at room temperature, we used anhydrous CH_2Cl_2 (1 ml) saturated with *trans*-stilbene (720 mg, 4×10^{-3} mol) instead of styrene (1 ml).

In the case of the three less volatile alkenes, *cis*- and *trans*-stilbene and 1,1-diphenylethylene, the typical procedure was modified in one point. At the end of the reaction, only the solvent could be evaporated under reduced pressure so that the final mixture analysed by ^{1}H n.m.r. spectroscopy contained, in addition to $TsNH_2$ and the *N*-tosylaziridine, an excess of *cis*- or *trans*-stilbene or 1,1-diphenylethylene. Thus, the *trans*-*N*-tosyl-2,3-diphenylaziridine could only be identified by the singlet at δ 4.26 corresponding to its benzylic protons, the signals corresponding to the aromatic protons of its *N*-tosyl and phenyl groups being superimposed on those of the aromatic protons of *cis*- or *trans*-stilbene. For the same reason, *N*-tosyl-2,2-diphenylaziridine could only be identified by the signals at δ 6.24 and 6.74 corresponding to its CH_2 protons. Both *N*-tosylaziridines were quantified using 1,1,2,2-tetrachloroethane as internal standard. The yields obtained for these aromatic olefins are indicated in Table 2.

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