Tuning of Reactivity in Epoxidation of Alkenes by Iron and Ruthenium Complexes associated to Non-porphyrinic Ligands

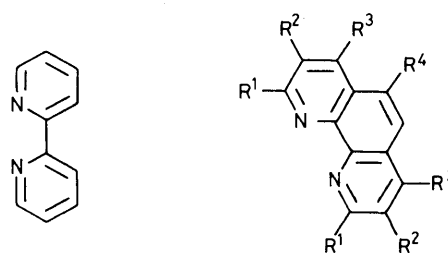**Christian Eskénazi, Gilbert Balavoine,* Florent Meunier, and Henriette Rivière**

Laboratoire de Chimie Organique des Eléments de Transition, UA-CNRS n·255, Institut de Chimie Moleculaire d'Orsay, Bat. 420 91405 Orsay Cedex, France

$RuCl_3 \cdot n(H_2O)$ or $FeSO_4$ associated with bipyridyl or substituted phenanthrolines, catalyse the epoxidation of stilbenes by IO_4^- or ClO^-; using phenanthrolines bearing electron donating or withdrawing groups, it is possible to modulate the reactivity of these systems.
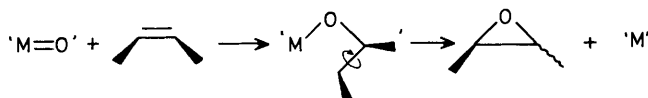
Selective oxidation of hydrocarbons has been the focus of considerable recent attention.[1] As part of our interest in oxygen transfer processes from a readily available oxidant to a substrate using a transition metal complex, we recently described a new system for the stereospecific epoxidation of olefins.[2]

In all previously reported oxidations of olefins with RuO_4 or with the '$RuCl_3 \cdot n(H_2O)$/hypochlorite or periodate' system the double bonds undergo the well-known oxidative cleavage to ketones or carboxylic acids.[1,3] We have observed that, in some cases, this reaction is accompanied by the formation of a very small amount of epoxide ($\leqslant 1$ %). We expected that a choice of ligands would allow us to control oxidation state changes at the metal and, if the ligand is electron donating, to moderate the electrophilic behaviour of the active species so as to favour the epoxidation at the expense of the oxidative cleavage.

cis- and *trans-*Stilbenes were selected for these investiga-

(1)

(2)

a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = Me$; $R^2 = R^3 = R^4 = H$
c; $R^2 = R^3 = Me$; $R^1 = R^4 = H$
d; $R^3 = Ph$; $R^1 = R^2 = R^4 = H$
e; $R^4 = NO_2$
f; $R^4 = Br$ $\quad R^1 = R^2 = R^3 = H$
g; $R^4 = Me$

Scheme 1

tions since the corresponding epoxides are quite stable under the reaction conditions. Thus, *cis-* or *trans-*stilbene (1.4 mmol) in 4 ml of CH_2Cl_2, along with icosane as an internal gas chromatography standard, were added all at once to a vigorously stirred solution containing ruthenium trichloride trihydrate (0.025 mmol), the ligand (0.15 mmol), and sodium metaperiodate (2.8 mmol) in 4 ml of water at room temperature. The reaction mixture was continuously stirred and periodically monitored by g.l.c. analysis of aliquots (100 µl) which were taken from the organic layer.

Results for *trans-*stilbene epoxidation are summarized in Table 1. Reaction times correspond to the consumption of all the starting olefin. Only yields of epoxide are indicated, the balance to 100% corresponds to products from the oxidative cleavage of the double bond. In all cases the reaction was stereospecific and gave the *trans-*epoxide.

The reduction potential of metal complexes $(Ru^{III}L_3)^{3+}/(Ru^{III}L_3)^{2+}$ exemplifies the electronic influence of the ligands and allows us to classify these ligands according to their electron donating or withdrawing ability.[4,5] Inspection of Table 1 reveals that electron rich ligands slow down the rate of the reaction and improve the selectivity and yield of the epoxide. Thus, with phenanthrolines bearing an electron donating group such as 3,4,7,8-tetramethylphenanthroline (2c), the oxidative cleavage of the double bond was almost completely avoided and a very high selectivity for epoxidation was observed. When substituents are in the 2 and 9 position of the phenanthroline, (2b), the steric congestion in the proximity of the nitrogens retards the complexation and the ligand-free active species lead exclusively to the cleavage of the stilbene. With ligands (1), (2c), and (2e) the results for *cis-*stilbene were very similar and oxidation occurred at about the same rate. The reaction was also stereospecific and gave the *cis-*epoxide.

In contrast to ruthenium chloride, the ability of closely related iron species to act as catalysts in the oxidation of organic substrates in the presence of hypochlorite or periodate has not been described (see Table 2, run 1: *n.b.* under these conditions high valent iron oxo species could be generated).[6] These observations suggest that iron species are either thermodynamically unstable, and/or not sufficiently reactive as these species are generally more electron rich than their ruthenium analogues.[7]

Iron metalloenzymes are known to catalyse oxygen transfer into organic substrates.[8] Iron porphyrin oxo complexes have been extensively studied as models of oxidases and shown to be active catalysts for epoxidation or hydroxylation of organic substrates in the presence of an oxygen atom source.[9] The role of the porphyrin could be explained by the fact that these ligands are a very good compromise between the stabilisation of high valent iron oxo species and the enhancement of their reactivity.

We found that when phenanthroline or bipyridyl ligands, which are able to stabilize high valent iron oxo species, are associated with $FeSO_4$, epoxidation of *trans-*stilbene in the presence of periodate was observed but, compared to ruthenium reactions, with lower rates and higher selectivity (Table 2, runs 2—5). At this point it might be expected that 'electrophilicity' and reactivity of an iron oxo intermediate could be markedly enhanced by using diimine ligands bearing electron withdrawing groups.

Table 1. Oxidation of *trans-*stilbene with $NaIO_4$ in the presence of $RuCl_3 \cdot nH_2O$ and ligand (6 equiv.).

Run	Ligand	Reaction time (h)[a]	% Epoxide	E° (V)[b]
1	Without	0.5	0[c]	
2	(1)	4.5	70[d]	1.25[e,f]
3	(2a)	4	26	1.26[e]
4	(2b)	0.5	0	—
5	(2c)	5	90	1.01[e,f]
6	(2d)	1	8	1.20[e]
7	(2e)	2	14	1.46[e]
8	(2f)	3.5	18	1.37[e]
9	(2g)	7	70	1.23[e]

[a] At room temperature. [b] E° of $(RuL_3)^{3+}/(RuL_3)^{2+}$. [c] With NaOCl instead of $NaIO_4$, the yield of epoxide is about 1%. [d] At 5 °C the yield of epoxide increases up to 83% after 15 h. [e] Ref. 4. [f] Ref. 5.

Table 2. Oxidation of *trans-*stilbene with $NaIO_4$ in the presence of $FeSO_4$ and ligand (6 equiv.).

Run	Ligand	Reaction time (h)	Temperature (°C)	Conversion into epoxide (%)
1	Without	120	20	0
2	(1)	70	20	20
3	(1)	48	40	55
4	(2a)	70	20	20
5	(2a)	48	40	80
6	(2b)	24	20	0
7	(2c)	90	20	20
8	(2d)	90	20	73
9	(2e)	20	20	100
10	(2f)	196	20	100

The results obtained with various ligands are summarized in Table 2 and provide strong support for our hypothesis. The reaction was carried out using conditions identical with those described above with ruthenium; the *trans-*stilbene epoxide was exclusively formed and the yield corresponded to the total conversion of the starting material. The reaction with *cis-*stilbene was found to proceed non-stereospecifically with lower rates and yields. Moreover we also observed that *cis-*stilbene was partially isomerised under the reaction conditions. Thus with 5-NO_2-phenanthroline, while *trans-*stilbene led to *trans-*epoxide (100%, 20 h), *cis-*stilbene gave after 100 h a mixture of *trans-*epoxide (12%), *cis-*epoxide (8%), *trans-*stilbene (8%), *cis-*stilbene (67%), and minor amounts of benzaldehyde and benzoic acid (5%). The lack of stereospecificity with this substrate was also recently observed with other systems.[10,11]

The observation that electron withdrawing groups on the diimine complexes increase the rate and the yield of the oxygen transfer to the organic substrate suggested that the rate determining step is the oxidation of the olefin by the iron oxo species. As we previously suggested for ruthenium, the mechanism of this process could involve an oxo metallacycle intermediate.[2] In the case of the *cis-*stilbene with the iron system, reversible process with rotation prior to ring closure could explain the lack of stereospecificity, Scheme 1.

This is in agreement with the epoxidation of both *cis-* and *trans-*stilbenes using the very reactive ruthenium system where the control of stereospecificity could be explained by the very short half-life of the intermediate resulting from the addition of the oxo species to the double bond.

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Replacing $NaIO_4$ by NaOCl gave results which were very similar except that chloride by-products were sometimes obtained in important amounts.

In summary, the results presented herein provide a demonstration that it is possible to modulate the reactivity of ruthenium and iron–oxygen complexes. We have been able to design good catalytic systems for the epoxidation of olefins either by moderating the ruthenium reactivity or by enhancing the iron reactivity. We are currently working on the generalisation of this concept of a tunable catalytic system, by variation of the nature of the metal, the ligand, and the oxidant according to the nature of the organic substrate.

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