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LETTERS

Iron(IV) corroles are potent catalysts for aziridination of olefins by Chloramine-T

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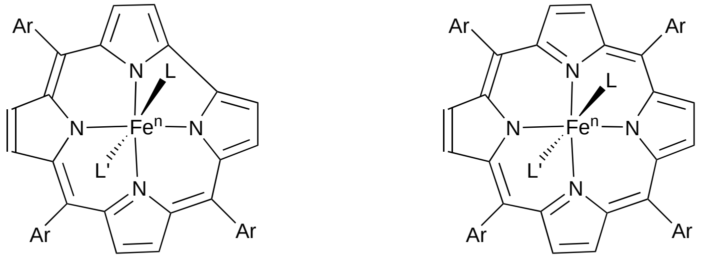
Abstract—Iron(III) corroles were found to be more selective catalysts than analogous porphyrins for the aziridination of olefins by PhI=NTs, and, most important, the iron(IV) corrole **1** displays the unique ability of utilizing Chloramine-T as nitrogen atom source. © 2001 Elsevier Science Ltd. All rights reserved.

In 1998, Sharpless and co-workers discovered a very interesting aziridination system, based on the reaction of Chloramine-T (TsN-ClNa) with olefins in the presence of 10 mol% of Br_3^-.[1] The same authors also reported in that publication that they had searched sporadically (and unsuccessfully) over two decades for a transition-metal-catalyzed aziridination process using Chloramine-T. This challenge had been met earlier that year by Komatsu and co-workers, who demonstrated that CuCl was able to serve as catalyst for that reaction, providing *N*-tosyl aziridines in yields of 18–75% with 5–10 mol% of catalyst.[2] To our knowledge, this and related work (all with copper) remain the only examples up to date about the utilization of Chloramine-T for aziridination of olefins.[3] Some mechanistic aspects of the copper-catalyzed aziridinations are still not well established.[3d] The more classical aziridination reagent is PhI=NTs (Ts = tosylate), which was introduced in the early 1980s by the groups of Breslow and Mansuy. They showed that heme enzymes and synthetic metalloporphyrins are efficient catalysts for transferring the NTs moiety of PhI=NTs into C–H and C=C bonds.[4] This methodology was subsequently extended to many other metal complexes, which has also included the asymmetric versions thereof.[5] The reactive intermediate in this reaction is considered to be a high valent metal=NTs complex, a conclusion that also holds for the related manganese porphyrin system.[6] However, there are drawbacks to the use of PhI=NTs: it is an expensive and inconvenient nitrogen source, iodobenzene is formed in equimolar amounts, and oxygenated hydrocarbons are dominant by-products.[7] This



1: n = IV, L = Cl (no L')
2: n = III, L = L' = OEt_2
3: n = III, L = NO (no L')
4: n = III, L = L' = OEt_2

1, **2**, **3**, **5**: Ar = C_6F_5
4, **6**: Ar = o-$Cl_2C_6H_3$

5: n = III, L = Cl (no L')
6: n = III, L = Cl (no L')

Figure 1. The catalyst utilized in this study.

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is in sharp contrast to Chloramine-T, which is commercially available, cheap and produces only NaCl as byproduct.

We have recently introduced easily accessible corroles and their metal complexes,[8,9] and shown that they are much more active catalysts than analogous porphyrin complexes in the cyclopropanation of olefins by carbenoids.[10] Since many complexes that catalyze cyclopropanation reactions are also effective aziridination catalysts,[11] we have decided to examine several iron corroles for the latter purpose. The results show that the iron(III) corroles are more potent catalysts than analogous porphyrin complexes for aziridination by PhI=NTs and disclose the unique ability of the iron(IV) corrole to utilize Chloramine-T as the nitrogen source.

First, the reaction of styrene with PhI=NTs was examined with the corrole-based catalysts **1**–**4** and the iron porphyrins **5** and **6** (Fig. 1). In all cases, the desired aziridine was obtained together with significant amounts of styrene oxide and phenylacetaldehyde. The optimal results in terms of yield and selectivity for aziridination versus oxygenation were obtained in benzene in the presence of molecular sieves: omitting the molecular sieves or using CH_2Cl_2 as solvent caused a significant increase in the yield of the undesired oxygenated products. Comparison between the various complexes (Table 1) shows that the corrole-based catalysts (entries 1–3) were more selective than the analogous iron porphyrin (entry 5). Interestingly, while the change of *meso*-aryl substitution from pentafluorophenyl in **1** and **5** to 2,6-dichlorophenyl in **4** and **6** was slightly advantageous for the porphyrin (entries 5 and 6), it resulted in a very large decrease in catalytic activity for the corrole (entries 1 and 4). In any case, the best catalyst is the iron(III) corrole **2**: it provides 84% of aziridine together with the largest selectivity (entry 2). However, the known limitation in metalloporphyrin catalyzed aziridination of olefins is still present: lowering the olefin/PhI=NTs ratio from 100:1 to 10:1 and 1:1 results in a very large drop of yield, from 84 to 31 and 0% aziridine (entries 2, 7–9), respectively.

All these results strongly indicate that the reactions proceed via an iron–nitrene intermediate, that reacts either with the olefin to produce the aziridine or hydrolyses to the (oxo)iron complex that subsequently oxidizes the olefin. This is shown in Scheme 1, which is

Table 1. Aziridination of styrene by PhI=NTs, under catalysis by 1 mol% iron corroles and porphyrins[a]

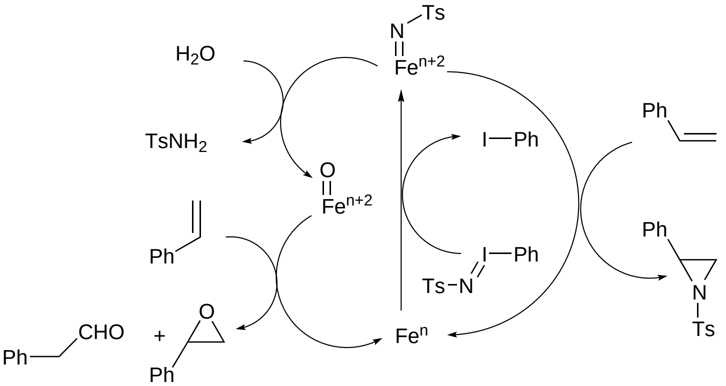
Entry	Catalyst	Product yield (%)			Selectivity
		Ph-I	Epoxide+aldehyde	Aziridine	
1	**1**	96	8.4+0	71.0	8.5
2	**2**	99	4.2+3.2	84.0	11.4
3	**3**	98	5.1+3.9	78.9	8.8
4	**4**	53	21+5.6	13.0	0.5
5	**5**	98	7.7+4.7	75.2	6.1
6	**6**	99	6.3+6.3	76.1	6.0
7	**2**[b]	90	7.1+4.0	30.9	2.8
8	**2**[c]	9	2.5+0.6	0	0
9	**2**[d]	71	4.4+3.3	0	0

[a] 30–56 mg (0.08–0.15 mmol) of PhI=NTs was added to dry benzene solutions that were 0.28–0.3 mM in catalyst (0.7–1.3 mg, 0.8–1.5 μmol) and contained 0.9–1.7 mL (8–15 mmol) styrene, 7 μL (68.5 μmol) nitrobenzene and activated molecular sieves. The chemical yields were determined by GC after filtration of the reaction mixtures, relative to nitrobenzene.

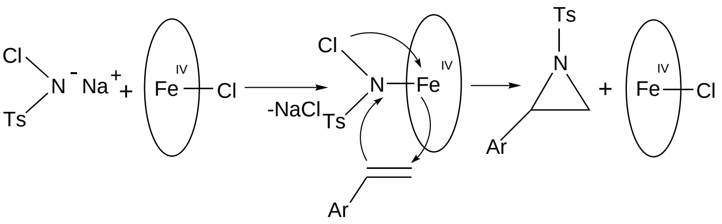
[b] Catalyst:PhI=NTs:styrene = 1:100:1000

[c] Catalyst:PhI=NTs:styrene = 1:1000:1000

[d] Catalyst:PhI=NTs:styrene = 1:100:100.



Scheme 1. Proposed catalytic cycles for iron complexes catalyzed reaction of styrene with PhI=NTs.



Scheme 2. Proposed activation of Chloramine-T by **1**.

the generally accepted mechanism with metalloporphyrin catalysts.[4c] Both the sensitivity to humidity and the need for large excess of olefin are considered to be different manifestations of the same phenomenon—the low hydrolytic stability of the metal–nitrene intermediate. The larger selectivity of corrole versus porphyrin iron complexes fits within this proposal, as corroles stabilize high valent metals significantly better than porphyrins.

Having demonstrated the potential of the iron corroles as aziridination catalysts, we turned our attention to Chloramine-T. All six complexes were investigated, under various reaction conditions (CH_3CN, CH_2Cl_2, benzene, aerobic and under N_2, with and without molecular sieves, different styrene/TsN-ClNa ratio). These examinations exposed the iron(IV) corrole **1** as the only active catalyst. The best results were obtained in CH_2Cl_2, either under Ar or in aerobic solution in the presence of molecular sieves. Interestingly, the disadvantageous characteristics of the reactions with PhI=NTs are not found in the **1**-catalyzed reactions of the styrene derivatives with Chloramine-T: there are no oxygenated by-products and the demand for large excess of olefin is much smaller. Accordingly, the Chloramine-T based system is *much* more practical than the one based on PhI=NTs. This is demonstrated in Table 2, which lists the results obtained with five styrene derivatives.

Note that in all these cases; the reported yields are of *isolated* products, Chloramine-T trihydrate was used without prior dehydration (by the potentially hazardous procedure),[1] and only 1 mol% of catalyst was used. The same substrates were also used for the construction of a Hammett plot via competition reactions of couples of substrates with Chloramine-T under low-conversion conditions ($\rho^+ = -0.5$).

Table 2. Aziridination of phenyl-substituted styrenes by Chloramine-T, under catalysis by 1 mol% **1**[a]

Substrate	Reaction conditions	Yield[b] (%)
Styrene	Ar	56
Styrene	Air	32
Styrene	Air + molecular sieves	56
4-Methylstyrene	Ar	57
3-Methylstyrene	Air + molecular sieves	60
4-Fluorostyrene	Air + molecular sieves	50
4-Chlorostyrene	Air + molecular sieves	48

[a] About 6 mg (6.8 μmol) of **1** and 1000 mol% substrate were dissolved in 10 mL of dichloromethane, and 100 mol% (0.2–0.21 g, 0.71–0.75 mmol) of Chloramine-T was added.

[b] Isolated by flash chromatography after 24 h, identified by ^1H NMR, purity determined by GC (>97% in all cases).

These observations are very different from those obtained in the aziridination by PhI=NTs with metal complexes of porphyrins and other ligands. Therein, competitive oxygenation is a serious problem and the Hammett's ρ values are much larger.[12] In addition, suggesting the mechanism of Scheme 1 for catalysis by the iron(IV) corrole **1** would require an unreasonable iron(VI) intermediate.

Based on the acquired data, we propose the mechanism shown in Scheme 2 for the activation of Chloramine-T by **1**. The polarity of the initial ionic and nucleophilic N–Na bond is inverted upon coordination to the iron(IV) corrole, allowing it to act as an electrophile for the reaction with olefins. The low ρ value is in accord with significant radical contribution, expected for such a four-centered mechanism.[3d] The mechanism also accounts for the absolute requirement for the strongly polarizing high valent metal. In conclusion, the properties of the iron(IV) corrole give rise to a novel and practical catalyst for aziridination of olefins by Chloramine-T.

Acknowledgements

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