

Nitrene transfer reaction catalyzed by substituted metallophthalocyanines

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Abstract

Metallophthalocyanines bearing substituents are found to be efficient catalysts for nitrene transfer reactions. Under optimized reaction conditions, aziridination of alkenes and amidation of C–H bonds with $\text{PhI} = \text{NTs}$ by using 3-trifluoromethylphenoxy-substituted phthalocyanine-iron complex led to the highest yields of 90% and 85% for 4-methylstyrene and 4-ethyltoluene, respectively.

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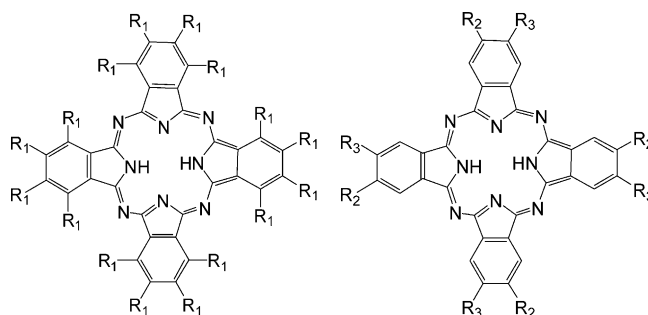
Keywords: Nitrene transfer; Aziridination; Amidation; Catalytic; Metallophthalocyanine

1. Introduction

Metal-mediated nitrene transfer to hydrocarbons is of particular importance in biomimetic investigation and is potentially useful in organic synthesis [1]. Among the wide variety of catalytic systems [2], metalloporphyrin has attracted considerable interest because of special high selectivity and catalyst turnover number obtained in recent years [3]. In the early 1980s, Mansuy et al. [4] and Breslow and Gellman [5] reported the first examples of aziridination of alkenes and amidation of C–H bonds catalyzed by Fe(III) and Mn(III)-TPP complexes with $\text{PhI} = \text{NTs}$, respectively. Since then, a number of nonchiral [6] and chiral metalloporphyrins [7] have been developed for this reaction.

For many years, phthalocyanines have been extensively studied due to their macrocyclic 18π -electron conjugated ring system [8], which are structurally similar to metalloporphyrins. Compared with porphyrin analogues, they are easier accessible, more stable to degradation [9]. However, low solubility of corresponding non-substituted phthalocyanine complexes in common organic solvents retarded their application in homogeneous catalysis [10]. In continuation to our studies on transition metal catalyzed synthetic transformation and recent progress in oxidation and cyclopropanation catalyzed by metallophthalocyanines [11], herein is reported the aziridination and amidation of hydrocarbons by using modified metallophthalocyanines.

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1: $R_1 = \text{H}$

2: $R_1 = \text{Cl}$

3: $R_1 = \text{F}$

4: $R_2 = \text{H}$ or $m\text{-O-C}_6\text{H}_4\text{-CF}_3$

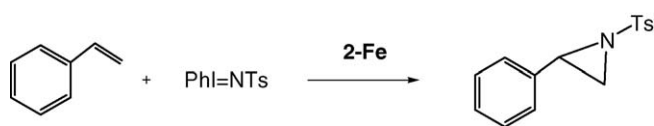
$R_3 = m\text{-O-C}_6\text{H}_4\text{-CF}_3$ or H

2. Experimental

2.1. Materials and instruments

All chemicals were purchased from Aldrich or Fluka and used as received unless otherwise noted. $\text{PhI} = \text{NTs}$ was prepared according to the literature procedure [12]. All the phthalocyanine complexes were prepared according to the methods described in the literatures [11b,13–17]. All the substrates were purified by standard procedures before use.

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Scheme 1.

^1H NMR spectra were measured on a Bruker DPX300 spectrometer by using tetramethylsilane (TMS) as an internal standard, the chemical shifts are relative to TMS. Infrared spectra (KBr) were recorded on NEXUS-670 FT-IR spectrometer. Elemental analyses were performed on a Carlo Erba 1106 instrument. Mass spectra were recorded on a Finnigan MAT 95 Mass spectrometer.

2.2. General procedure for the nitrene transfer reactions

In a typical procedure of catalysis, substrate (0.5 mmol) was added by means of syringe to a well-stirred suspension of 4 Å molecular sieves (50 mg) in dry dichloromethane (5 mL) containing catalyst (5×10^{-3} mmol) at room temperature under argon. After 10 min, PhI=NTs (0.75 mmol) was added. The reaction was maintained at 25 °C for 12 h. The molecular sieves were filtered off and washed with CH_2Cl_2 . The filtrate and washings were evaporated to dryness and the organic product purified by column chromatography was identified by ^1H NMR.

3. Results and discussion

3.1. Optimization of reaction conditions

The influences of reaction conditions such as temperature, solvents and amount of catalyst used were optimized by using 2-Fe as catalyst shown in Scheme 1, and the results were listed in Table 1:

In general, the reactions proceeded smoothly and were associated with the formation of *p*-toluenesulphonamide as main by-product, which is as usual to be from the hydrolyzation of imido intermediate formed by Pc complex and PhI=NTs as described for porphyrin analogue [18]. Indeed, the yield of aziri-

Table 1
Influences of reaction conditions^a

Entry	Condition	Yield (%) ^b
1	CH_2Cl_2 , 25 °C	78
2	CH_2Cl_2	42 ^c
3	CH_3CN	60
4	CH_3OH	12
5	Toluene	50
6	DMF	21
7	CH_3NO_2	57
8	CH_2Cl_2 , 0 °C	32
9	40 °C	80

^a Reactions were performed with a cat:styrene:PhI=NTs molar ration of 1:100:150.

^b Isolated yield based on styrene used.

^c Without adding molecular sieves.

dine decreased dramatically from 78% to 42% without adding 4 Å molecular sieves (entries 1 and 2).

To study the effects of solvent, catalytic aziridination of styrene were performed in various solvents including toluene, dichloromethane, acetonitrile, DMF, nitromethane and methanol at room temperature. Evidently, dichloromethane indicated to be the choice, which resulted in the highest yield of 78%, while only 12% yield for methanol (entries 1 and 4).

Investigation of the effects of temperature showed that higher temperature benefited to the results, thus, the yield increased from 32% to 78% when reaction temperature changed from 0 °C to 25 °C. When it increased further to 40 °C, slight increment in yield could be obtained (entry 9).

The study of the amount of catalyst loading were carried out by using 0.5%, 1%, 2%, 5% catalyst, and the aziridine could be obtained in the yields of 65%, 78%, 78% and 80% respectively. Increment of the loading more than 1% seemed to be not necessary due to the almost unchanged yields.

From the results obtained, the reaction conditions were optimized to be dry dichloromethane as solvent, 25 °C as reaction temperature and 1% catalyst was used with 4 Å molecular sieves as adduct.

3.2. Aziridination of styrene catalyzed by different metallophthalocyanines

To evaluate the influences of different central metal and substituents of ligand, 18 different phthalocyanine complexes were applied in the aziridination of styrene with PhI=NTs under the optimized reaction conditions summarized above. The results are listed in Table 2.

Table 2
Aziridination of styrene with PhI=NTs using different metallophthalocyanines catalysts^a

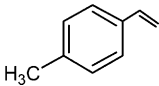
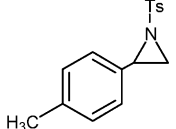
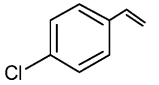
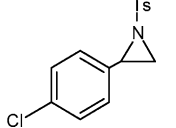
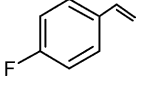
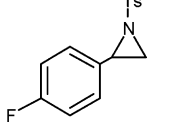
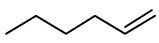
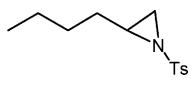
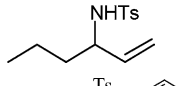
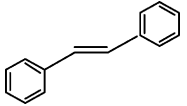
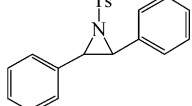
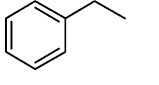
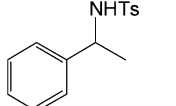
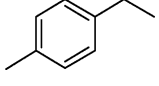
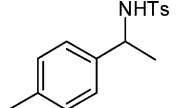
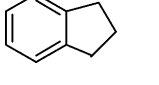
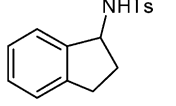

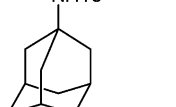
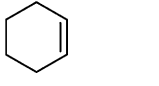
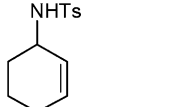
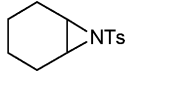
Entry	Catalyst	Yield (%) ^b
1	1-Fe(III)Cl	75
2	1-Mn(II)	41
3	1-Ni(II)	25
4	1-Cu(II)	73
5	1-Co(II)	33
6	2-Fe(II)	78
7	2-Mn(II)	47
8	2-Ni(II)	22
9	2-Cu(II)	71
10	2-Co(II)	38
11	3-Cu(II)	75
12	3-Ru(II)	86
13	3-Fe(III)Cl	79
14	4-Fe(III)Cl	88
15	4-Cu(II)	64
16	4-Mn(II)	41
17	4-Ni(II)	45
18	4-Co(II)	48

^a Reactions were performed with a cat:styrene:PhI=NTs molar ration of 1:100:150.

^b Isolated yield based on styrene used.

In general, the catalysts with Fe, Cu and Ru as central metals exhibited much higher catalytic abilities than others when the same ligand was used. It is reported that the solubility of the Pc complex was an important factor during

Table 3
Catalytic aziridination and amidation by **4**-FeCl^a

Entry	Substrate	Product	Yield (%) ^b
1			90
2			68
3			63
4			48
			6
5			40
6			72
7			85
8			74
9			71
10			75
			17

^a Reactions were performed with a cat:substrate:PhI=NTs molar ratio of 1:100:150.

^b Isolated yield based on substrates used.

catalysis [19]. The presence of eight *m*-CF₃-phenoxy groups at the periphery of the Pc macrocycle, in combination with suitable central metals, was also effective for the solubilization of phthalocyanines. Actually, substituted metallophthalocyanines contributed better results than the non-substituted ones, leading to the highest yields as 88% and 86% with **4**-FeCl and **3**-Ru (entries 12 and 14), which were higher than the corresponding non-substituted complexes. Meanwhile, the results also suggested the higher catalytic abilities of substituted metallophthalocyanines than those of Fe(TDCPP)(ClO₄) or [Ru(TPP)] porphyrinato complexes of 74% and 75% yields [3a,20].

Thus, the excellent yields indicated **4**-FeCl to be highly robust toward catalytic aziridination reactions. **4**-FeCl was thus selected for further catalytic nitrene transfer reactions.

3.3. Catalytic aziridination and amidation of other substrates

Catalytic aziridination and amidation of other substrates were examined with **4**-FeCl as catalyst under the optimized reaction conditions. The results were listed in Table 3.

As shown in Table 3, Aziridination of olefins substrates afforded the corresponding aziridines in the yields ranging from 48% to 90%, while amidation of C–H bonds in the yields ranging from 71% to 85%.

Similar to the reported [Ru(TPP)] complex, which benefited to the electron rich 4-methylstyrene in 78% yield while only 71% for electron deficient 4-Cl-styrene, **4**-FeCl catalyzed aziridination of 4-methylstyrene in 90% yield while only 68% for 4-Cl-styrene (entries 1–3) [3a]. The same phenomenon could be found during the amidation of ethyl benzenes with 85% yield for 4-ethyltoluene and 72% for ethylbenzene. It is worthy to note that both aziridine and amide product could be detected with 1-hexene and cyclohexene as substrates. As reported, aziridination predominated over C–H insertion with olefinic substrates, except in the case of cyclohexene [1c,2a]. In our experiments, aziridine was dominant product for the former, while amide for the latter.

4. Conclusion

In summary, substituted metallophthalocyanines showed to be efficient catalysts for aziridination and amidation of hydrocarbons with PhI=NTs as nitrene precursors. Under optimized reaction conditions, the aziridination/amidation of a variety of hydrocarbons by using 3-trifluoromethylphenoxy-substituted iron-phthalocyanine complex resulted in up to 90% and 85% aziridine/amide yields, respectively. The mechanism study and encapsulation of catalyst are in progress.

Acknowledgements

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