

Metallophthalocyanines as potent catalysts for aziridination of olefins

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Abstract

Copper, manganese and iron phthalocyanines were found to be highly efficient catalysts for aziridination of olefins using [*N*-(*p*-tolylsulphonyl) imino] phenyliodinane, Chloramine-T and Bromamine-T as nitrene precursors. [*N*-(*p*-Tolylsulphonyl) imino] phenyliodinane was found to be better nitrene donor as compared to the Chloramine-T and Bromamine-T and aromatic substituted olefins were found to be more reactive as compared to the aliphatic alkenes under these conditions.

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1. Introduction

Aziridination of olefins is an important synthetic transformation as aziridines find broad utility as electrophiles [1,2] and synthetic intermediates in the preparation of pharmaceuticals and agrochemicals [3,4]. Although the formation of aziridines from the addition of thermally or photochemically generated nitrenes to olefins is a well-known reaction, its utility is limited due to low yields and competing hydrogen abstraction and insertion reactions [5–7]. The metal catalyzed reactions of in situ generated nitrenes with olefins is an efficient and practical method for the preparation of aziridines and has received increasing attention in the recent years. In this context [*N*-(*p*-tolylsulphonyl) imino] phenyliodinane, PhI = NTs [8] has been widely used as nitrene precursor [9–13]. Recently transition metal catalyzed azirid-

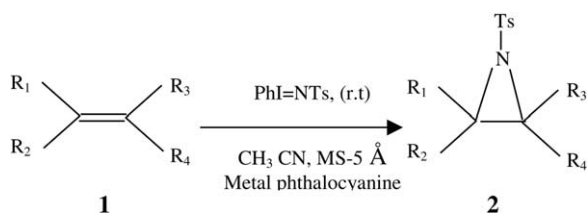
ination of olefins using Chloramine-T (TsN·NaCl) [14–20] and Bromamine-T (TsN·NaBr) [21–23] as nitrene precursors have been studied with a view to develop less expensive and more convenient substitute to PhI = NTs.

Transition metal triflates (Cu, Mn, Fe, Co, Ni) [24–27], salts [28], metallophorphyrins [29,30] and iron (IV) corroles [14] have been used as homogeneous catalysts for aziridination of olefins using PhI = NTs, Chloramine-T and Bromamine-T as nitrene precursors. Comparative study of the catalytic activity of various transition metals and their complexes, for aziridination by Evans et al. [12] have shown that the metal as well as nature of complexing agent determine the catalytic activity. The use of heterogeneous or heterogenized homogeneous catalysts for synthetic transformations is an area of current interest owing to ease of separation and recycling of the catalyst. In this context metal ion exchanged zeolites Y (containing Cr, Mn, Fe, Co, Ni, Cu, Zn) have been studied as the heterogeneous catalysts for aziridination of styrene using PhI = NTs and Chloramine-T as

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nitrene precursors [31–33]. However, these metal ion exchanged zeolites Y have severe limitations due to metal leaching and limited pore size which prohibits the aziridination of large olefins like *trans*-stilbene [31,32].

Metallophthalocyanine complexes (MPc) structurally similar to metal porphyrins, are easily accessible, more stable to degradation than porphyrins, have been extensively used to catalyze a variety of organic reactions [34–40]. Metallophthalocyanines being insoluble in common organic solvents can be easily separated from the reaction mixture for reuse and there are no pore size problems associated with their use. In continuation to our studies on transition metal catalyzed synthetic transformations [41–43], herein we report for the first time aziridination of olefins using metallophthalocyanines as catalysts and PhI = NTs, Chloramine-T and Bromamine-T as nitrene precursors (Scheme 1).

2. Experimental

Copper concentration in these solutions was determined by using Leeman Labs inductively coupled plasma-atomic emission spectrometer (ICP-AES, PS-3000UV).

2.1. Materials

Copper, iron, manganese, nickel and cobaltphthalocyanines were prepared according to the literature procedures. All olefins used were commercially available and distilled before use. [*N*-(*p*-Tolylsulphonyl)imino] phenyliodine [8] and Bromamine-T [21] were prepared according to the literature procedures. Chloramine-T trihydrate was purchased from Aldrich and dehydrated in vacuum at 100 °C. Acetonitrile

was dried by refluxing over CaH₂ and stored on 4 Å molecular sieves.

2.2. Typical procedure for aziridination of olefins

To a stirred suspension of 4-methylstyrene (3.3 mmol), PhI = NTs (0.67 mmol) and 5 Å molecular sieve (100 mg) in dry acetonitrile (5 ml) was added Cu(II) phthalocyanine (0.03 mmol, 5 mol%) under nitrogen atmosphere at room temperature. Stirring was continued for 0.5 h (completion of the reaction as indicated by complete dissolution of PhI = NTs) and then the Cu(II)Pc and molecular sieves were removed by filtration. The filtrate obtained was evaporated under vacuum to give an oil which was purified by passing through the silica gel column using (hexane/ethylacetate, 4:1) as eluent. Evaporation of the solvent yielded *N*-(*p*-tolylsulphonyl)-2-(*p*-methylphenyl)aziridine, m.p. 136 °C, (yield 90%). Similarly other aziridines were prepared.

3. Results and discussion

To evaluate the catalytic efficiency of various metallophthalocyanines, the reaction of 4-methylstyrene with PhI = NTs was studied using different metallophthalocyanines as catalysts and acetonitrile as solvent, with substrate/PhI = NTs molar ratio 5:1 in the presence of molecular sieves. These results are summarized in Table 1 and show that Cu(II) phthalocyanine is the most active catalyst followed by Mn(II) and Fe(II)-phthalocyanines. Ni(II)- and Co(II)

Table 1
Aziridination of 4-methylstyrene by PhI = NTs using different metal phthalocyanines as catalysts^a

Entry	Substrate	Catalyst (mol%)	Yield (%) ^b
1	4-Methylstyrene	Cu(II)Pc	90
2	4-Methylstyrene	Mn(II)Pc	35
3	4-Methylstyrene	Fe(II)Pc	40
4	4-Methylstyrene	Ni(II)Pc	20
5	4-Methylstyrene	Co(II)Pc	10

^a Metal phthalocyanine (5 mol%), 4-methylstyrene (390 mg, 3.3 mmol), PhI = NTs (250 mg, 0.67 mmol) in 5 ml of acetonitrile in the presence of 5 Å molecular sieves under N₂ atmosphere at room temperature.

^b Isolated yields.

Table 2
Cu(II) phthalocyanine catalyzed aziridination of olefins with PhI = NTs^a

Entry	Olefin	Reaction time (h)	Yield (%) ^b
1	Styrene	1.5	80
2	4-Methylstyrene	0.5	90
3	3-Methylstyrene	1.0	85
4	α -Methylstyrene	0.75	92
5	Methylmethacrylate	2.5	70
6	Cycloheptene	3.0	55
7	Vinylcyclohexane	2.5	48
8	Norbornylene	3.5	72
9	4-Chlorostyrene	2.0	70
10	<i>Trans</i> -stilbene	3.0	50

^a Metal phthalocyanine (5 mol%), 4-methylstyrene (390 mg 3.3 mmol), PhI = NTs (250 mg, 0.67 mmol) acetonitrile (5 ml) in the presence of 5 Å molecular sieves under N₂ atmosphere at room temperature.

^b Isolated yield.

phthalocyanines were found to be very less active for this reaction. To examine the versatility of Cu(II) phthalocyanine (CuPc) catalyst, a variety of olefins were reacted with the nitrene generated from PhI = NTs. These results are presented in Table 2 and clearly indicate that Cu(II)Pc is very active heterogeneous catalyst for these reactions and the obtained yields of aziridines remained comparable to very active copper catalysts like Cu(OTf)₂ and Cu(acac)₂. The results obtained also show that aromatic substituted alkenes afforded better yields of aziridines as compared to aliphatic alkenes. Further, aromatic substituted alkenes bearing electron-donating groups on benzene ring were found to be more reactive (Table 2, entry 2, 3, 4). It was interesting that *trans*-stilbene which did not yield any aziridination product when Cu exchanged zeolites Y was used as catalyst and PhI = NTs as nitrene precursor, could yield corresponding aziridine using Cu(II)Pc as catalyst. (Table 2, entry 10).

To evaluate the efficiency of the metallophthalocyanines as catalysts with other nitrene precursors, aziridination of 4-methylstyrene was studied with Chloramine-T, and Bromamine-T in presence of Cu(II)Pc as catalyst. These results are presented in Table 3. The results obtained show that although the use PhI = NTs as the nitrene precursor gave the highest yield of aziridine, Chloramine-T and Bromamine-T also yielded aziridines in regionably good yields with

Table 3
Aziridination of 4-methylstyrene with different nitrene donors using copper phthalocyanine as catalyst^a

Entry	Substrate	Nitrene donor	Yield (%) ^b
1	4-Methylstyrene	Ph = NTs	90
2	4-Methylstyrene	Chloramine-T	50
3	4-Methylstyrene	Bromamine-T	65

^a Copper phthalocyanine (5 mol%), 4-methylstyrene/nitrene donor (5:1), acetonitrile (5 ml) in presence of 5 Å molecular sieves under N₂ atmosphere at room temperature.

^b Isolated yield.

Cu(II)Pc as catalyst. All these reactions were associated with the formation of *p*-toluenesulphonamide as the by-product along with aziridine and reactions conducted without the use of 5 Å molecular sieves showed significant increase in *p*-toluenesulphonamide formation. The aziridination of 4-methylstyrene was also performed in different solvents with PhI = NTs using Cu(II) phthalocyanine as catalyst. These results are presented in Table 4. Among the solvents studied acetonitrile and nitromethane were found to be good solvents for this reaction. Copper and other metallophthalocyanine catalysts used in these aziridination reactions could be easily recovered by filtration and reused several times without any significant loss in their activity. To study the metal leaching in these reactions the filtrates obtained after completion of copper (II) catalyzed aziridination of olefins (styrene, 4-methylstyrene, 3-methylstyrene and α -methylstyrene) with PhI = NTs, were subjected to copper estimation using ICP-AES. The filtrates analyzed did not show presence of copper

Table 4
Cu(II) phthalocyanine catalyzed aziridination of 4-methylstyrene by PhI = NTs using different solvents^a

Entry	Substrate	Solvent	Yield (%) ^b
1	4-Methylstyrene	Acetonitrile	90
2	4-Methylstyrene	Dichloromethane	82
3	4-Methylstyrene	Nitromethane	89
4	4-Methylstyrene	Toluene	55
5	4-Methylstyrene	Benzene	50
6	4-Methylstyrene	Dichloroethane	80

^a Copper phthalocyanine (5 mol%) 4-methylstyrene/PhI = NTs (5:1) acetonitrile (5 ml) in presence of 5 Å molecular sieves under N₂ atmosphere at room temperature.

^b Isolated yield.

eliminating the possibility of metal leaching in these reactions.

4. Conclusions

In summary we have demonstrated for the first time copper, manganese, and iron phthalocyanines to be highly efficient heterogeneous catalysts for aziridination of olefins using PhI = NTs Chloramine-T and Bromamine-T as nitrene precursors. Unlike the transition metal exchanged zeolites Y heterogeneous catalysts there are no metal leaching and pore size limitations with the metallophthalocyanines. The simple preparation, easy separation of the catalyst, simple workup, comparable yields of aziridines and wide applicability with different nitrene precursors make these metallophthalocyanines as ideal heterogeneous catalysts for aziridination of olefins.

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