

CHAPTER - VI

Conclusions

Heterocyclic N-containing compounds like pyrazines and piperazines are the useful intermediates in the synthesis of various drugs, anthelmintics, perfumes, herbicides, germicides, dyes, vulcanization accelerators, electrographic developers, light resistant fluorescent polymers and also are starting materials in several pharmaceutical & agrochemical industries. The importance of these compounds and due to new environmental legislation and drive towards "Clean Technology" which has provided the new impetus to develop more convenient and eco-friendly procedures. In this programme of work, the industrially important compounds like dihydropyrazine (DHP), trans-bicyclo-[4.4.0]-1,4,6,9-tetraazadecane (TAD or perhydropyrazino (2,3-b) pyrazine), 2-methyl quinoxaline, quinoxaline, 2-methyl piperazine and piperazine have been synthesized with TiO₂/zeolite composite catalysts. The results embodied in the present work covers cyclization and oxidation reactions over semiconductor photocatalysts supported over zeolites.

As per the observations 2wt% TiO₂/H β is found to be more active forming high yield of dihydropyrazine of 20.4% and also 2wt% TiO₂ / HZSM-5 show more or less same catalytic activity for dihydropyrazine synthesis.

The evaluation of the TiO₂/zeolite composite catalysts for the cyclization of ethanol and ethylenediamine show alterations in the yields of perhydropyrazino(2,3-b)pyrazine over the three zeolites of study and the light energy source used. The structure of the H β -zeolite also may be helping to attain

the maximum yield of perhydropyrazino(2,3-b)pyrazine of 35.0% and 25.6% using artificial and solar light respectively. Also, the high yield of perhydropyrazino(2,3-b)pyrazine obtained with artificial light source in comparison to solar light may be attributed due to the high intensity of the UV component in artificial light.

The evaluation of TiO₂/zeolite catalysts for the cyclization of *o*-phenylenediamine and propyleneglycol show that 5 wt% TiO₂/Hβ(30) has shown high yields. The formation of 2-methyl quinoxaline (22.5%) and quinoxaline (12.6%) during the cyclization of *o*-phenylenediamine and propyleneglycol at ambient temperature is reported herewith over 5 wt% TiO₂ / Hβ(30) photocatalyst for the first time.

The photocatalytic reaction by all the semiconductor/zeolite catalysts gave 2-methyl piperazine and a demethylated product piperazine. On the otherhand, bare semiconductor photocatalyzed reaction did not yield any product The yields of 2-methyl piperazine and piperazine depended on the nature and type of the zeolite supports. All the semiconductor/zeolites were found to promote the reaction and the product formation is always moved to the direction to favor 2-methyl piperazine. Increase in the amount of semiconductor (TiO₂, ZnO and CdS) loading on zeolites (> 5) did not show better results. In this study, one of the best photocatalyst for the production of 2-methyl piperazine (major product) was found to be 5 wt% TiO₂/Hβ.

The photocatalytic synthesis of piperazine from N-(2,3-dihydroxypropyl)ethylenediamine was carried out over semiconductors (TiO_2 , ZnO, CdS and WO_3) supported on zeolites. Here, we have succeeded in one step synthesis of piperazine with a maximum yield of 37.9 % from N-(2,3-dihydroxypropyl)ethylenediamine at the ambient temperature photocatalysis. This is the first report, to the best of our knowledge, for the synthesis of piperazine via zeolite mediated semiconductor photocatalysis.

Regioselective photooxidative demethylation of methyl substituted – N-containing heterocyclic compounds such as 2-methyl pyridine, 3-methyl pyridine, 4-methyl pyridine, 2-methyl pyrazine, 2,4-dimethyl pyridine, 2,6-dimethyl pyridine, 2,4,6-trimethyl pyridine, 2-methyl indole and 2-methyl quinoline have been carried out over TiO_2 suspended acetonitrile solution in the presence of molecular oxygen upon irradiation at room temperature conditions. Molecular orbital calculations by AM 1 method has been performed for the electron densities of N-atoms of heterocyclics.

The results indicate that oxidation of 2-methyl pyridine, 2-methyl pyrazine, 2,4-dimethyl pyridine, 2,6-dimethyl pyridine, 2,4,6-trimethyl pyridine, 2-methyl indole and 2-methyl quinoline compounds gave their respective demethylated products in major quantity, whereas 2-methyl pyridine, has shown the corresponding aldehyde and acid in minor quantities. In contrast, substrates like

3-methyl pyridine and 4-methyl pyridine did not respond to the oxidation even after prolonged irradiation compared to the other substrates.

The yields of the major products obtained in the present study are time dependent and also steric hindrances are strongly influencing the reactions. It was observed from the results that 2-methylpyridine and 2-methylpyrazine substrates could yield the demethylated products in 6 hours duration whereas substrates 2,4-dimethylpyridine and 2,6-dimethylpyridine substrates took 8 hours of irradiation to yield the demethylated products. The aspect of steric hindrance is clearly seen in the oxidation of substrate 2,4,6-trimethylpyridine, which required longer irradiation period than the mono and dimethylpyridines. Similarly substrates like 2-methylquinoline and 2-methylindole have yielded their respective products during 8 hours of irradiation. The results obtained reveal that regioselective photocatalytic oxidation of N-heterocyclic compounds to the corresponding demethylated products is attainable in moderate yields.

The salient features of the results obtained in the present investigation are summarized in Table 6.1

Table 6.1 Salient features of photocatalytic cyclization and oxidation reactions carried out for the synthesis of N-heterocyclic compounds.

Sl.No	Reactants	Products	Catalyst	Yield (%)	Remarks (if any)
1	Ethylenediamine + Propyleneglycol	Dihydropyrazine	2 wt% TiO ₂ /H β	20.4	Chem. Comm 2000, 1533
2	Ethylenediamine + Ethanol	Perhydropyrazino(2,3-b)pyrazine	5 wt% TiO ₂ /H β	35.0	Chem. Lett (In Press)
3	o-Phenylenediamine + Propyleneglycol	2-methyl quinoxaline + quinoxaline	5 wt% TiO ₂ /H β	22.5, 12.6	Chem. Lett (In Press)
4	N-(2,3-dihydroxypropyl) ethylenediamine	Piperazine	5 wt% TiO ₂ /H β	37.9	J.Catalysis (Communicated)
5	N-(β -hydroxypropyl) ethylenediamine	2-methyl piperazine + piperazine	5 wt% TiO ₂ /H β	31.9, 14.8	Tet.Lett (Communicated)
6	Alkyl Heterocyclics	Substituted Regioselective products	dealkylated TiO ₂	> 30	J. Chemtech & Biotech (In Press)