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Final Report

UGC Minor Research Proposal

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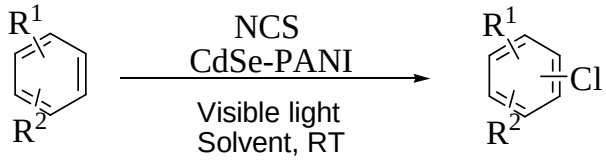
Photochemical halogenation of organic substrates is a fundamental reaction in organic chemistry. Organic substrates absorb visible light, and generate free radicals. These free radicals are responsible for chemical conversions/transformations. In photo-halogenation reactions of aromatic substrates, halogen radicals are generated which gives substitution reactions Literature survey for photo-bromination using conventional reagents and UV light gives 100% conversion within 20 min. However, sometimes with more reaction time effective conversion is not observed. Visible light is also beneficial and greener for chemical transformations. $KBrO_3$, NBS/PTSA, NBS/NaOHetc. are used for photobromination.Apart from these reagents nanomaterials, nanocomposites also possesses good photocatalytic properties.

CdSe-bimetallic semiconductors are important because of their many applications (1-3) polyaniline (PANI) has electrical conductivity and environmental stability. PANI can be synthesized by different methods. PANI has wide range of applications in the area of sensors, light emitting diode, electrochemical capacitor, rechargeable battery etc. A composite consisting of semiconductor nanomaterial and an organic polymer have many applications in the field of photovoltaic device.(3-6) Therefore, for this purpose, inorganic compounds are often doped with the polymers at an appropriate concentration in order to promote the formation of percolation pathways for charge transport . So we have developed a composite material with semiconducting nanoparticles and PANI that can efficiently harvest visible light and subsequently brings about organic transformations. (7-9)

We have prepared CdSe-PANI semiconducting nanocomposite and investigated its photocatalytic activity under visible light irradiation for the chlorination of aromatic compounds. These composites were characterized by XRD and TEM. Uniform dispersion of CdSe within PANI matrix was confirmed with TEM images.

Initially,photochlorination of phenol was carried out with N-chlorosuccinimide (NCS) using CdSe/PANI semiconducting nanocomposites with tungsten lamp (35W, $\lambda > 400$ nm) at ambient temperature.The chlorinated product/substrates were monitored by GC-MS analysis Reaction conditions were optimized for photochlorination of phenol and observed that acetonitrile was found to be the better solvent, 5% CdSe-PANI nanocomposite was suitable catalyst, one equiv NCS and 1 hr reaction time were optimum conditions for monochlorination.

Scheme 1: Photochlorination of different aromatic substrates under sunlight irradiation



R^1 = NH_2, NHAc, NHCOPh, OH, OCH_3, CH_3, Cl
R^2 = H, NO_2, OH

Reusability Study:

The efficiency of CdSe-PANI NC's was further evaluated for its repeated usage without sacrificing the catalytic activity. For this purpose, photochlorination of aniline and 2-naphthol were carried out with recovered catalyst under identical experimental conditions. These results suggest that the catalyst remains highly active up to six cycles with excellent conversion and 100% selectivity towards mono-chlorination for every cycle.

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