

Environmentally friendly efficient synthesis and mechanism of triazenes derived from cyclic amines on clays, HZSM-5 and sulfated zirconia

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Abstract

Diazotization and diazocoupling reactions of *para*-aminobenzene-1-sulfonyl azide and *para*-aminobenzene-1-sulfonyl amide with cyclic amines of various ring sizes (pyrrolidine, piperidine, 4-methylpiperidine, *N*-methylpiperazine, morpholine and hexamethyleneimine over eco-friendly clay catalysts, HZSM-5 and sulphated zirconia are described. These inexpensive, noncorrosive and reusable catalysts appear to exhibit bifunctional catalytic properties for these reactions. No considerable decreases in the efficiency of the catalysts were observed after four cycles of operation. The new method totally avoids the use of acid, alkali or toxic solvents in diazotization and diazocoupling reactions.

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Keywords: Environmental compatibility; Heterocyclic amines; Diazotization; Diazocoupling; Triazenes; Clays; HZSM-5; Sulfated zirconia

1. Introduction

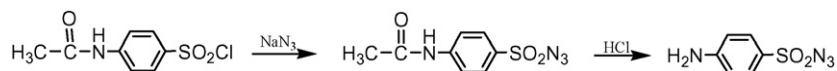
The formation of diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions, and azo coupling carried out at low temperature in the presence of nucleophilic coupling components, the reactivity of a nucleophilic substrate increases with increasing basicity phenolates and amines [1]. These conventional acid-based catalyzed processes are effective for the near quantitative formation of the desired products. But the main limitation of such synthetic processes is their environmental incompatibility. The acidic and basic effluents from the laboratory and industry produce permanent damage to the environment and disturb the ecological balance [2]. Clays have long been used as acidic catalysts and existence of both Lewis and Bronsted acid sites. These clays are low-cost, widely available materials, and synthetic organic chemists have largely used them in a variety of acid-catalysed reactions [3]. Montmorillonite clay functions as an efficient solid acid catalyst in organic transformations with excellent product, regio- and stereo-selectivity [4]. Nowadays, more and more heterogeneous

Bronsted acids, e.g., zeolites are preferred from an economical perspective as well as from an ecological viewpoint. Their excellent catalytic abilities are due to the presence of Bronsted and Lewis acid centers in the zeolite structure [5]. Due to its high protonic acidity and unique shape-selective behavior, HZSM-5, HY, and H-beta have been shown to be a highly active and stable catalyst for reactions [6]. Zirconia is attracting considerable interest on account of its potential use as a catalyst support, zirconia is active and its activity is due to acidic, basic, oxidizing and reducing surface properties [7].

Recently, we synthesized a new group of azo dyes containing azide group [8]. Triazenes, a very useful and diverse class of compounds, was synthesized by diazotization of an aromatic primary amine, followed by coupling of the diazonium salt to a secondary amine to provide the desired triazene [9]. Aromatic triazenes are of considerable interest for their reported biological activities, which include anti-tumour [10], anti-inflammatory [11]. They are a useful protecting group in organic synthesis [12], in polymer synthesis and more [13]. The importance of triazenes as a versatile tool in organic synthesis has also been reviewed recently [14]. As part of ongoing research program for exploring the bifunctional catalytic properties [15–17], herein we describe a new process for diazotization and diazocoupling reactions using clay based

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Scheme 1. Synthesis of 4-aminobenzene-1-sulfonyl azide.

layered silicates, HZSM-5 and sulfated zirconia (SZ) as a catalyst toward the synthesis of triazenes.

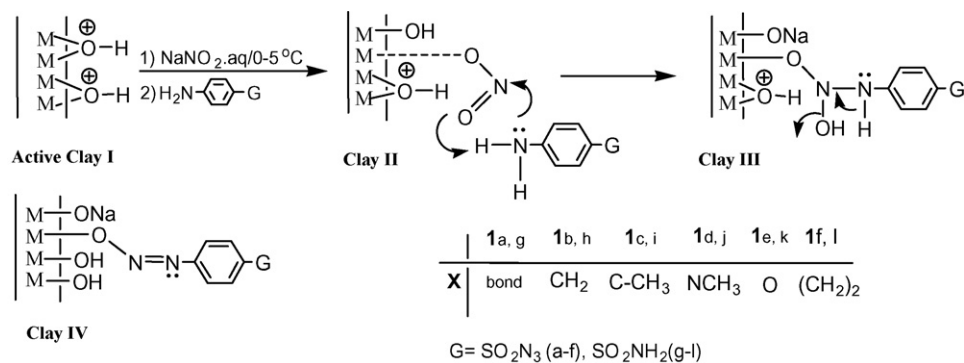
2. Results and discussion

This paper describes the facile and modified synthesis of triazenes without using conventional acid or base, namely in the presence of clays, HZSM-5 and sulfated zirconia. The 4-aminobenzene-1-sulfonyl azide was synthesized from the reaction of 4-acetamidobenzene-1-sulfonyl chloride with sodium azide followed by acid hydrolysis (Scheme 1).

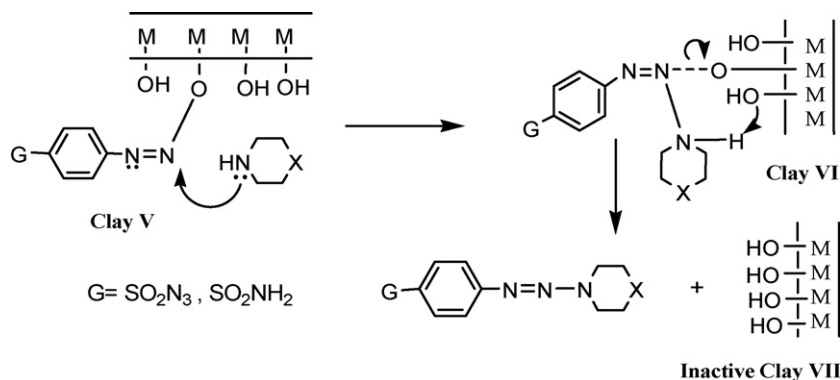
4-Aminobenzene-1-sulfonyl azide or 4-aminobenzene-1-sulfonyl amide, dilute NaNO₂ solution and active clay catalyst were mixed to a paste and then cooled down to 0–5 °C (Scheme 2). The diazonium-clay complex formed was subsequently coupled with cyclic amines (Scheme 3). The triazenes from 4-aminobenzene-1-sulfonyl azide or 4-aminobenzene-1-sulfonyl amide was separated from the catalyst by extracting from acetone or ethanol, respectively. The excess solvent was removed under vacuum. The generality of the process is proved by performing the reaction with all the three catalysts, with 4-aminobenzene-1-sulfonyl azide or 4-aminobenzene-1-sulfonyl amide and with coupling agents. After the formation of the

diazonium–clay complex, the edge hydroxyls of the clay platelets is believed to get converted into –ONa species by consuming the Na ions from NaNO₂ solution used for diazotization. This –ONa species helps to maintain the pH of the medium neutral or slightly alkaline for a quantitative coupling of the diazonium ion with the coupling agent. In almost all the cases, the isolated yields of the pure products were found to be near quantitative as outlined in Tables 1 and 2. Control reactions were carried out with the same reagents in the presence of mineral acids like HCl and bases by following the conventional procedure for comparing the yields. All yields for 4-aminobenzene-1-sulfonyl azide in the range of 50–75%, and for 4-aminobenzene-1-sulfonyl amide in the range of 40–60% are found to be slightly lower than the values obtained using mineral acid.

The clay catalysts were washed free of anions, dried at 110 °C for 2 h, and calcined at 430 °C for 2 h. This enriched the catalyst with acid sites and removed any organic or carbonate impurities (which were not catalytically active). Clay catalysts could function as Bronsted and/or Lewis acids. The Lewis acidity is due to Al³⁺ and Fe³⁺ at the crystal edges, and Bronsted acid character of the clays arises mainly due to the dissociation of the intercalated water molecules coordinated to cations. On



Scheme 2. Mechanism of diazotization.



Scheme 3. Mechanism of diazocoupling.

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