Catalysis Communications 43 (2014) 79–83

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

One pot catalytic NO_2 reduction, ring hydrogenation, and *N*-alkylation from nitroarenes to generate alicyclic amines using Ru/C-$NaNO_2$

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ARTICLE INFO

Article history:
Received 20 July 2013
Received in revised form 11 September 2013
Accepted 12 September 2013
Available online 20 September 2013

Keywords:
Hydrogenation
Nitrobenzene
Cyclohexylamine
Ruthenium catalyst

ABSTRACT

A report to produce alicyclic amines and subsequent *N*-alkylation with alcohols using Ru/C-$NaNO_2$ catalyzed facile transformation of nitrobenzene was investigated. Effects of solvent, temperature, pressure, reaction time, and molar-ratio of substrate/catalyst on product composition were also studied. These mechanistic studies explain that nitrobenzene undergoes hydrogenation reaction in the following order; $-NO_2$ reduction to $-NH_2$, aromatic ring-hydrogenation to alicyclic, and from the reaction of alcohol to give *N*-alkylated amines. This investigation shed lights on possible application to polyurethane chemistry since these amines are used as important precursors for diisocyanates.

1. Introduction

The efficient synthetic pathway for producing amines has been extensively investigated due to the fact that they are widely used as significant intermediate as well as final product in various chemical industries [1,2]. Especially, the cyclohexylamine (CHA) finds various applications in pharmacology or as agrochemicals in terms of its being raw material for carbamates and isocyanates. Among these, alicyclic diamines also more substantially used feedstock for the synthesis of non-yellowing polyurethanes.

Conventionally, the CHA has been produced from the following two step; i) reduction of nitrobenzene (NB) to aniline [3–9], ii) ring hydrogenation of aniline to CHA [1,2,10–13], which makes the process complicated. Therefore, development of a facile one step synthetic pathway to alicyclic amines from nitroarenes is of great importance with respect to process efficacy.

As to the industrial processes to manufacture aniline through NB hydrogenation, the process generally employs above 240 °C with copper-catalysts in two-stage bed reactor [14]. Recently, Langer et al. reported a low-pressure process for the hydrogenation of aniline to produce CHA with high selectivity using rhodium catalysts [11]. The literature indicates that ruthenium is the most used catalyst for ring-hydrogenation of aromatic amines due to its high activity, selectivity, and reproducibility [10–13]. The *N*-alkylation of amines using non-halide reagent is also an important process because conventional halogenated substances may generate harmful by-products such as HCl [15–17]. To overcome disadvantages, alcohols can be employed as direct alkylating agent for the *N*-alkylation of amines [18–21]. Since there has been no report on one-pot synthesis of CHA or *N*-alkylated amines from the reaction of NB with H_2 and alcohols, this approach might provide much greener pathway from the view point of process efficiency as well as cost saving.

In this context, a direct synthesis of alicyclic amines and their subsequent production of *N*-alkylated amines from the reaction of nitroarenes with H_2 and alcohols in the presence of a catalyst system comprising carbon supported Ru and $NaNO_2$ are presented.

2. Experimental

All the chemicals and catalyst were purchased from Aldrich (South Korea) and used without further purification.

2.1. Hydrogenation reaction

All the hydrogenation reactions were carried out in a 100 ml pressurized reactor with a magnetic stirrer and an electrical heater (Fig. 1). Detailed procedure of hydrogenation reactions is given in supporting information.

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http://dx.doi.org/10.1016/j.catcom.2013.09.012

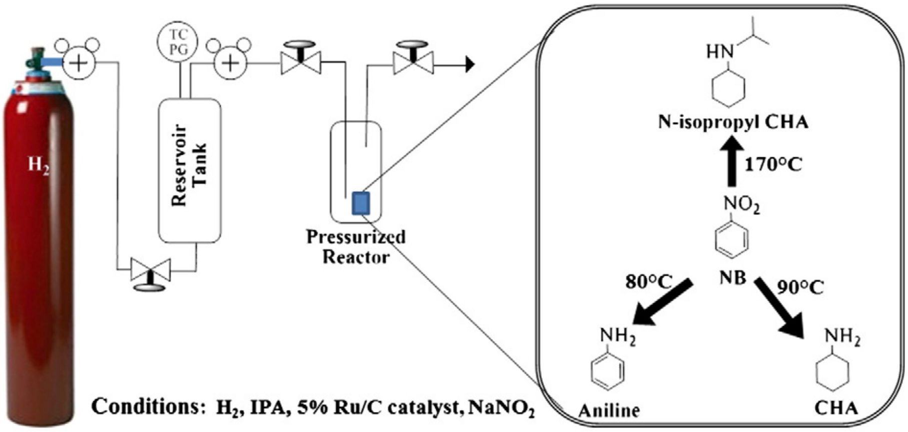

Fig. 1. Process diagram for alicyclic amines from NB.

3. Results and discussions

3.1. Effect of polar aprotic and protic solvents

Catalytic reduction of –NO$_2$ group and ring hydrogenation reaction of NB were carried out over Ru/C catalyst in the presence of various polar aprotic and alcoholic solvents at 170 °C. This temperature was used to figure out all the possible products from these harsh reaction conditions. The results summarized in Fig. 2 show that NB conversion was observed as 100% (data not shown) regardless of solvent used probably due to the high temperature. Among polar aprotic solvents, only NMP showed 100% selectivity toward CHA (entry 1, Fig. 2). On the other hand, DMF and acetonitrile delivered aniline as major product, which suggests that reaction is retarded in these solvents thus reaction did not continue further (entries 2–3, Fig. 2). It is generally accepted that the reaction rate of the reduction of –NO$_2$ group is regarded as faster than that of ring hydrogenation and it is somewhat supported from the results of very small amount of CHA in the reaction mixtures (entries 2–3, Fig. 2). In contrast, THF, diethyl ether, and diisopropyl ether produced considerable amount of CHA and dicyclohexylamine (DCHA) without the existance of aniline (entries 4–6, Fig. 2), giving a clue that they facilitate the reaction to undergo ring hydrogenation as well as –NO$_2$ reduction. From these results, NMP was found to be the most favorable polar aprotic solvent at 170 °C in terms of production of CHA and the rate of hydrogenation reaction is much influenced according to the solvent used.

However, when we employed polar protic solvents, the products were identified as CHA, DCHA, and *N*-alkyl CHA whilst the aniline was not detected, suggesting that due to high solubility of hydrogen gas in alcohols, these solvents accelerate both the ring hydrogenation and –NO$_2$ reduction. Among those solvents, it is interesting to note that IPA showed best result for obtaining ring-hydrogenated product, *N*-isopropyl CHA (IP-CHA) almost quantitatively at 170 °C (entry 9, Fig. 2). The facile synthesis of *N*-alkyl CHA is also significant since they are used as important intermediates in the fine chemical industry, especially when obtained directly from nitroarenes.

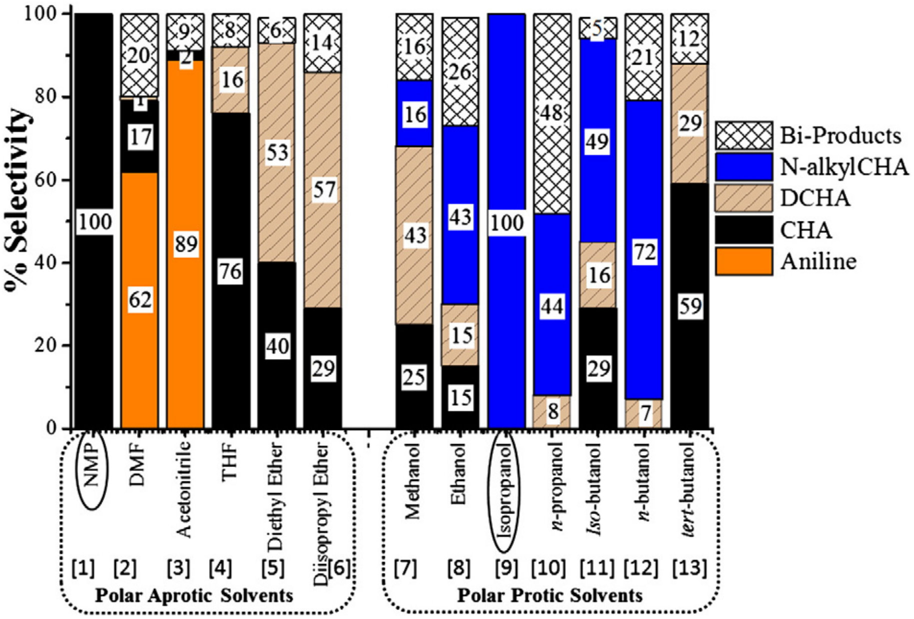

Fig. 2. Effect of various solvents on product composition: NB (7.5 mmol), 5 wt.% Ru/C (0.19 mmol of Ru), solvent (15 ml), $T = 170$ °C, $P = 8.3$ MPa, $t = 4$ h.