



Bio-based aliphatic primary amines from alcohols through the ‘Nitrile route’ towards non-isocyanate polyurethanes

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ABSTRACT

Bio-based primary amines obtained from the corresponding alcohols *via* nitrile intermediates and their subsequent polymerizations with cyclic carbonates are described. Nitrile compounds were synthesized under mild aerobic oxidation of primary aliphatic alcohols. CuI, bipyridine and TEMPO were used as a catalytic system, in the presence of aqueous ammonia and O₂. A series of bio-sourced alcohols were successfully oxidized into nitriles using this catalytic system. The so-formed bio-based dinitriles were subsequently reduced into primary diamines under H₂ in the presence of Ni Raney. The latter were polymerized with fatty acid-based bis-cyclic carbonates for the design of fully bio-based poly(hydroxyurethane)s.

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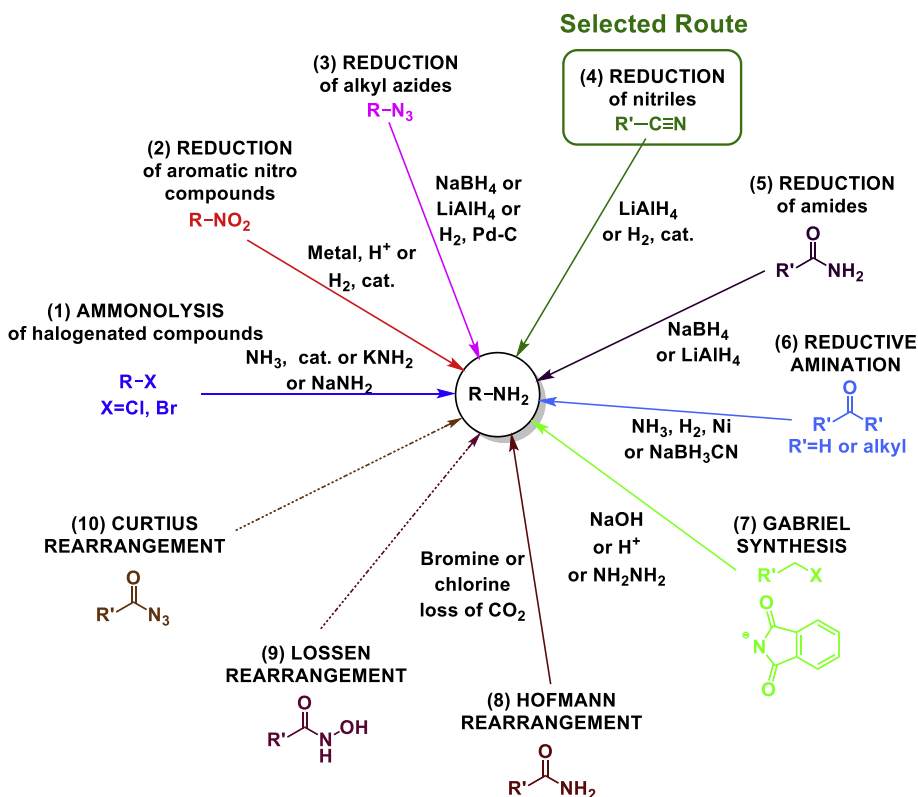
1. Introduction

Nowadays, amines and more specifically primary amines are extensively employed in the preparation of polymers and specially poly(hydroxyurethane)s (PHUs). The synthesis of poly(hydroxyurethane)s via the bis-cyclic carbonate/diamine route, allowing the replacement of toxic phosgene and isocyanates employed for the synthesis of classical polyurethanes is rising [1–4]. Due to the finite feedstock of fossil resources and to environmental issues, there is a growing need to develop sustainable chemical pathways and substrates [5–7]. In this purpose, multiple bis-cyclic carbonates have been developed from renewable resources and specially vegetable oils [8–10] but the development of ‘green’ amines and diamines appears to be crucial and need to be developed [11–16]. Numerous approaches are available in organic chemistry to prepare primary amines [17] (see Scheme 1). The latter can be either prepared by the ammonolysis of halogenated compounds (1) or by the reduction of nitro compounds (2), alkyl azides (3), nitriles (4) and amides (5) as well as by the reductive amination of ketones or aldehydes (6). Primary amines can also be obtained by Gabriel synthesis (7) and through Hofmann rearrangement (8); Lossen and Curtius (9–10) rearrangements can also indirectly lead to amines in the presence of water.

Various drawbacks can be pointed out from those reaction methods. First, the use of gaseous ammonia for ammonolysis (1) and reductive amination (6) is not safe and harsh conditions are usually requested. Moreover, the problems coming across with the alkylation of ammonia are the multiple alkylation reactions, which lead to a mixture of primary, secondary

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Scheme 1. Main approaches for the synthesis of amines.

and tertiary amines together with quaternary ammonium salts. Among the main methods, the reduction of alkyl azide intermediates (3) involves a large number of steps and a nucleophilic addition with azide-based intermediates, such as NaN_3 , which are explosive and toxic substances. For the reduction of amides (5), toxic acyl chloride precursors need to be prepared. Finally, following the Gabriel procedure (7), the atom efficiency is not acceptable due to the generation of phthalimide derivatives and, in the case of Hofmann rearrangement (8), a decrease in the carbon chain length is observed due to CO_2 removal.

Among these routes, the reduction of nitriles (4) represents an attractive approach to prepare bio-based amines in mild conditions. While most of the procedures to synthesize nitrile compounds employ also toxic reagents or produce wastes [18–20], the direct oxidation of primary alcohols with ammonia appears to be an attractive alternative approach for the preparation of nitriles [21].

Mizuno and coll. reported the direct oxidation of alcohol into nitrile using a heterogeneous $Ru(OH)_x/Al_2O_3$ catalyst and an excess of aqueous ammonia under air pressure (6 atm.) at $120\text{ }^\circ\text{C}$ [22]. Haruta et al. described a procedure using MnO_2 under pressurized oxygen (0.85 MPa) and NH_3 gas at $100\text{ }^\circ\text{C}$ [23]. These two approaches are quite efficient but are carried out at high temperature in autoclave. Besides, Cu/TEMPO system has been studied as a catalytic system for the oxidation of alcohols into aldehydes [24–27] with oxygen as the oxidant. Based on the work of Sheldon's group [24], Tao et al. [28] have developed a procedure to oxidize benzylic alcohols into nitrile in the presence of $Cu(NO_3)_3/TEMPO$ as a catalytic system and aqueous ammonia under 1 atm of oxygen at $80\text{ }^\circ\text{C}$. Aryl nitriles were synthesized in high yield but aliphatic alcohols could not be converted following these conditions. In the meantime, Yin et al. [29] described an aerobic oxidation of benzylic and few aliphatic alcohols under mild conditions using $CuI/TEMPO/bipyridine$ as a catalyst and an excess of aqueous ammonia under oxygen at room temperature. It should be mentioned that use of air instead of pure O_2 as oxidant is also reported. Yadav et al. [30] described an oxidation under air at $135\text{ }^\circ\text{C}$ of primary alcohols using $CuCl_2 \cdot 2H_2O$ as a catalyst, in the presence of K_2CO_3 and ammonium formate as nitrogen source. This procedure does not permit the conversion of aliphatic alcohols that would require working at high temperature. To avoid the use of O_2 as oxidant, Dornan et al. [31] utilized another procedure under air at $50\text{ }^\circ\text{C}$ with $Cu(OTf)_2/TEMPO/bipyridine$ and aqueous ammonia to oxidize aldehydes or alcohols into nitriles. Aliphatic alcohols could not be converted in nitriles with this method but the authors could convert aliphatic alcohols by replacing the catalytic system with $[Cu(MeCN)_4][OTf]/TEMPO/bipyridine$. This last catalytic system was applied on a petroleum-based aliphatic alcohol but was not fully optimized.

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