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Research Paper

Synthesis of primary amines *via* linkage of hydroaminomethylation of olefins and splitting of secondary amines

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ABSTRACT

An elegant method capable of synthesising primary amines from olefins is presented by a new orthogonal tandem amination reaction. Rh/Ru-catalysed *bis*-hydroaminomethylation of dienes towards secondary amines **10** and primary amines **13** is implemented. The obtained secondary amines **10** intermediates are then converted in a second reaction step to primary amines **13** *via* splitting of amines through subsequent addition of ammonia. Influences on the orthogonal catalytic system towards the formation of primary amines are discussed and point towards a novel *N*-dealkylation and alkylation mechanism. For the model substrate dicyclopentadiene (tricyclo [5.2.1.0^{2,6}]deca-3,8-diene, dcpd **1**) yields of up to 29% of the primary diamine (3(4),8(9)-*bis*(aminomethyl) tricycle-[**5.2.1.0** ^{2,6}]decane, TCD-diamine **13**) were achieved under optimized conditions, with a primary amine **13** to secondary amine **10** ratio of 5.8. The reverse reaction towards secondary amines was revealed as the limiting factor in the selective reaction towards primary amines **13** caused by the equilibrium of the reaction. In this equilibrium, however, a slight tendency towards the primary amine **13** was identified.

1. Introduction

Amines are valuable intermediates for the chemical industry and find various applications in organic synthesis, food additives, functional materials, dyes, agrochemicals and pharmaceuticals. Thus, the development of novel synthesis routes of amines continues to be of great interest to both industry and academia. Especially primary amines are important intermediates for both the bulk and fine chemicals industry. No selective and efficient method is describe in the literature to obtain primary amines directly from olefins [1,2].

Hydroaminomethylation (HAM) is one method to synthesise amines from olefins. In this efficient, atom-economic three-step tandem reaction amines can be gained from olefins [3–7]. A range of syntheses for various organic compounds are described for the HAM reaction [8,9], including the synthesis of natural products [10] or fatty amines from unsaturated fatty acid esters [11] and the synthesis of drugs [12] or monomers for plastics [13]. Nonetheless, the major drawback of the HAM reaction is the limitation to primary or secondary amines as substrates to gain both high yields and high selectivities. The use of ammonia as nitrogen source has been proven to be difficult regarding the selectivity towards primary amines, as often overalkylation occurs yielding a mix of amines (Scheme 1) [6,14–16].

The challenge is that *in situ* produced primary amines are more nucleophilic compared to ammonia and thus react as an alternative amine source. The initial produced primary amines react further, preferentially to form secondary or tertiary amines [17,18]. Both the unsatisfying chemo- and regioselectivity and the numerous side reactions remain the unsolved problems of the HAM with ammonia. Additionally, applicable catalyst species are deactivated from large excesses of ammonia resulting in reduced catalytic activity [6,16]. Regardless of all the challenges, Beller [16–20], Knifton [21], Eilbracht [22,23], and Behr [24] have applied ammonia as substrate in the HAM and the most general examples are shown in Table 1.

Notably, the previously used olefins such as 1-hexene, styrene, propene, 1-octene and limonene formed primary amines with low chemo- and regioselectivity. The selective formation of primary amines in the HAM with ammonia is very restricted. Especially the application of bifunctional substrates to obtain diamines has not been shown so far. The HAM reaction of various olefins is well known [13,24–27], however for the *bis*-HAM only a few examples have been reported [26,28–31]. Recently, we described the *bis*-HAM of dienes towards secondary diamines using primary amines such as *n*-butyl amine and obtained both high yields and high selectivities of secondary amines [32]. Due to difficulties in gaining primary amines from olefins *via*

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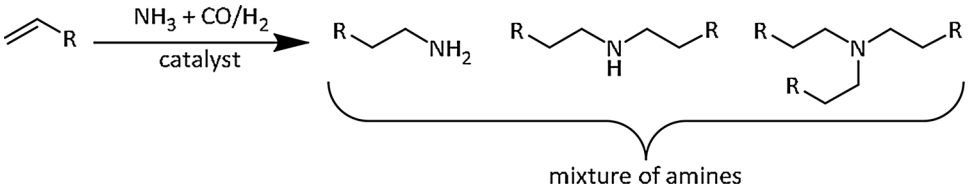
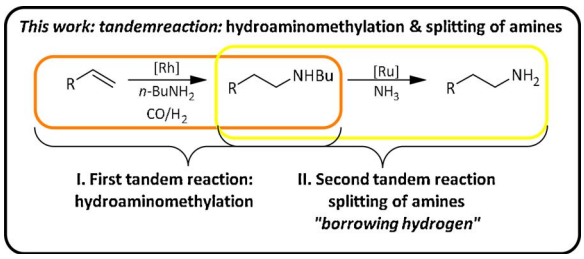


Scheme 1. Hydroaminomethylation of olefins with ammonia.

Table 1
Hydroaminomethylation of olefins with ammonia.

Olefine[Ref]	Catalyst systems	Prim. Amines, yield
1-hexene [21]	$Co_2(CO)_8$ + PPh_3	32%
styrene [22]	$[Rh(cod)Cl]_2$	< 1%
propene [17]	$[Rh(cod)Cl]_2$/$[Ir(cod)Cl]_2$ TPPTS	58%
1-octene [16]	$Ru(CO)_{12}$ 2-phosphino-substituted imidazole	< 8%
limonene [24]	$[Rh(cod)Cl]_2$	25%



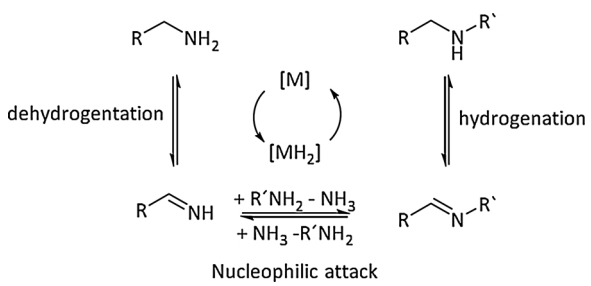
Scheme 3. Alternative strategy to gain primary amines.

HAM reaction with ammonia with high selectivity, other promising strategies to synthesise primary were developed using secondary amines as starting material [33].

Another amination reaction is the splitting of amines. In analogy to the amination of alcohols, this transfer reaction is expected to follow the “hydrogen shuttling concept” or the “borrowing hydrogen methodology” also known as “hydrogen-autotransfer” but in the presence of amines instead of alcohols. In most cases secondary or tertiary amines were activated and used in the alkylation of aliphatic and aromatic amines, however, the conversion of primary amines to secondary amines is also possible [34–39]. The conversion of primary amines to secondary amines and *vice versa* is described (Scheme 2).

Generally, imines are formed through dehydrogenation of the amines. To obtain secondary imines, primary imines react with primary amines under the elimination of ammonia. Contrarily, primary amines are gained through the reaction of secondary amines with ammonia and the elimination of a primary amine. In the re-hydrogenation step the corresponding imines are hydrogenated to amines. Williams et al. described the amine cross-coupling using iridium-catalysed “borrowing hydrogen” methodology with two secondary amine components which are capable of undergoing an oxidation to an imine [39]. Contrarily, Beller [33] and Vogt [38] described catalytic splitting of secondary or tertiary amines with ammonia to primary amines. The Shvo-catalyst was used to synthesise primary amines in good yields and with excellent selectivity [33]. According to the “borrowing hydrogen methodology” the splitting of amines begins with an amine as starting substrate to obtain primary amines with ammonia selectively.

The overall goal of this work was to implement tandem catalysis to produce primary amines. Tandem catalysis is the combination of two or more different catalysed reactions in one reaction vessel with no workup of intermediates. The advantage is that resources such as time, energy, solvents and costs are saved [4,9,40–42]. Thus, the



Scheme 2. Mechanism for the *N*-alkylation of amines with amines known as splitting of amines.

combination of hydroaminomethylation and splitting of amines to a new consecutive tandem amination reaction offers an alternative strategy to apply the advantages of both methods to achieve a direct route to primary amine from the plain olefin (Scheme 3). The linkage of these two well-known reactions bears the advantage that secondary amines are gained *in situ* selectively as intermediates. These secondary amine intermediates are then converted *in situ* to primary amines by reverse reaction and thus suppressing overalkylation. In addition, isolation of secondary amine intermediates is omitted.

Herein we report the first consecutive tandem amination reaction from olefins towards primary amines combining two reactions: hydroaminomethylation and splitting of amines. To the best of our knowledge the linkage of both methods has not been described yet.

To start, the HAM of dcpd and ammonia is investigated. As expected high formation of oligomers and side products are obtained. Investigating the Rh-catalysed HAM reaction in the presence of the Shvo-catalyst, revealed the synthesis of primary amines. The *N*-dealkylation mechanism for this new tandem amination reaction is investigated.

The splitting of amine reaction can cause an equilibrium of primary and secondary amines [33]. Various parameters are studied to countervail the equilibrium of the reaction. Whilst studying the tandem amination reaction, its feasibility not only towards primary amines but also the reverse reaction towards secondary amines is identified. However, slightly higher selectivities towards primary amines are obtained.

2. Results and discussion

We choose a reaction setup, where not only the starting material but also the desired amine product is easy accessible. Both dcpd **1** and TCD-diamine **13** (3(4),8(9)-*bis*(aminomethyl)-tricyclodecane) meet this criterion. Additionally, the industrial relevant TCD-diamines **13** are used as monomers for surface coating systems, such as specialty adhesives and high-performance epoxy resin hardeners. All isomers of TCD-diamine **13** are offered as isomer mix, thus the isomers were reported as the sum isomers.

Starting conditions for our investigation of the consecutive tandem amination reaction were chosen based on our previous experience in *bis*-hydroaminomethylation [32] and hydrohydroxy-methylation of dcpd **1** to TCD-diol [43]. Scheme 4 displays the tandem reaction path and thus the desired primary diamine **13** and corresponding intermediates.

The first consecutive tandem reaction *bis*-hydroaminomethylation is shown with green arrows (I. path) and is underlaid by an orange area [44]. To obtain the intermediate secondary diamines **10,** the