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Ru/C catalyzed cyclization of linear α,ω-diamines to cyclic amines in water

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ABSTRACT

A facile and convenient way to prepare cyclic amines in water was achieved by the catalyst system composed of Ru/C and Al powder. The α,ω-diaminoalkanes, 1,4-diaminobutane, 1,5-diaminopentane, and 1,6-diamino-heptane were converted to corresponding cyclic amines in good yields. The use of D_2O provided a novel route to obtain deuterated cyclic amines in good yields.

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1. Introduction

Alkylations of primary and secondary amines to obtain secondary- or tertiary amines are of considerable importance in organic synthesis. Conventionally such compounds have been prepared by reductive amination of the condensation products from amino compounds and carbonyl compounds or by amino dehalogenation from amines and halo-alkanes.[1] It is also known that amines themselves can be used as alkylating reagents to prepare secondary- or tertiary amines from primary amines. Murahashi and his co-workers reported an inter- and intramolecular coupling reaction of alkyl amines and diamines to secondary-, tertiary-, and cyclic amines using heterogeneous Pd black as a catalyst.[2] In a similar manner, α,ω-aminoalcohols can also be used to prepare heterocyclic amines.[3] Some related reports on the transition metal catalyzed synthesis of cyclic amines from aliphatic α,ω-diamines can be found in the literature. Raney nickel catalyzed intramolecular cyclization of aliphatic α,ω-diamines have been investigated in preparations of pyrrolidine and piperidine.[4] Kagiya, Ohtani, and his co-workers reported that TiO_2/Pt catalysts in water can transform α,ω-diamines to cyclic amines upon prolonged UV irradiation.[5] Some studies of the same have been carried out in the gas phase at high temperatures using zeolites as catalysts for the cyclic amine conversion.[6] Also, homogeneous late transition metal catalyst can also catalyze the intramolecular cyclization of α,ω-diamines in organic solvents.[7] Hydroamination can be considered as a further approach to prepare cyclic amines from alkyl amines bearing alkenyl- or alkynyl group at the terminal position of the starting materials. However, achieving control on the selectivity may be difficult as the addition to the C–C double or triple bonds usually favors the Markovnikov rule.[8] Additionally, there are a number of other ways to prepare nitrogen containing heterocycles such as intramolecular ring-closure of *N*-(ω-haloalkyl)imines, δ- and γ-alkenylimines, aminoalkanes, and *N*-chloroalkylamines.[9] Thus, most of the above reactions are carried out at high temperatures for prolonged reaction times, utilize organic solvents, and usually convert with less favorable selectivities, despite the use of transition metals catalyst.

Recently, we reported a novel, environmentally more benign way to convert primary amines to secondary amines.[10] A change of reaction conditions transforms amines on secondary alkyl groups to corresponding ketones. Herein, we would like to report the extension of this synthetic method for the conversion of aliphatic α,ω-diamines to corresponding cyclic amines. Contrary to previous investigations, our method uses heterogeneous catalysts and water is employed as a solvent and reagent. The use of water allows a different reaction pathway, which results in faster, more selective transformations.

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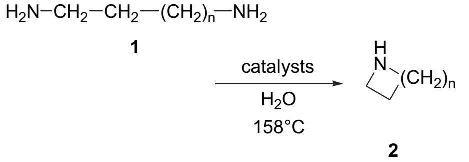
2. Results and discussion

We tested four different metal catalysts (Ru/C, Rh/C, Pd/C, and Pt/C) for the intramolecular catalytic cyclization of α,ω-diaminoalkanes, 1,4-diaminobutane and 1,6-daiaminohexane, to their corresponding cyclic amines, pyrrolidine and azepane, in water at 158 °C (Table 1). These reactions gave the desired cyclic amines along with side products. In the reactions with 1,4-diaminobutane, the cyclic imine, 1-pyrroline, was observed as a major side product together with small amounts of pyrrole and linear oligomeric products (entries 1–5). Adiponitrile, on the other hand, was observed in the reactions with 1,6-diaminohexane (entries 6–10). The formations of side products were confirmed by GC and GC–MS analysis. The results of these preliminary experiments suggested that Ru/C and Pd/C were effective catalysts for the reaction in terms of conversion and both showed better selectivity (entries 1, 2, 4, 6, 7, and 9) in comparison to Rh/C (entries 3 and 8). The Pt/C catalyst gave similar conversions compared to Ru/C and Pd/C, however selectivity of **2** was poor in 1,4-diaminobutane reaction (entry 5). Comparing Ru/C and Pd/C, the Ru/C catalyst showed higher selectivity than Pd/C in 1,6-diaminohexane cyclization. From above results we finally chose Ru/C as a suitable catalyst for the cyclization of α,ω-diaminoalkanes under the condition.

Table 1
Catalytic cyclization of α,ω-diaminoalkane



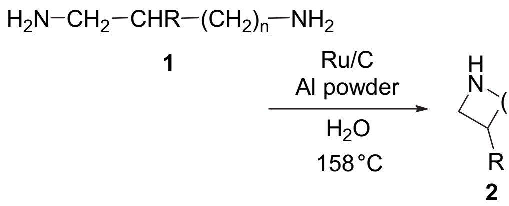
Entry	Diamine **1** n	Catalysts (mol %)	Time (h)	Conv.[a] (%)	Selectivity[a] **2** (%)
1	2	Ru/C (2.7)	1	7	39
2	2	Ru/C (2.7)	4	18	90
3	2	Rh/C (2.6)	1	7	—
4	2	Pd/C (2.6)	1	11	47
5	2	Pt/C (1.4)	1	8	—
6	4	Ru/C (2.9)	1	31	89
7	4	Ru/C (2.9)	4	43	95
8	4	Rh/C (2.8)	4	2	44
9	4	Pd/C (2.8)	4	39	72
10	4	Pt/C (1.5)	4	37	84

Reaction conditions; α,ω-diaminoalkane (100 mg), catalyst (50 mg), and water (2 mL) were placed in a 10 mL pressure resistant glass vessel.

[a] Conversions and selectivities were determined by GC and GC–MS analysis.

As the conversion and the selectivity of the reaction was relatively poor, aluminum powder was added to the reaction mixture. Previously, the addition of aluminum powder to the reactions where primary amines were converted to secondary amines has been found to drastically accelerate the reaction and enhance the selectivity of the secondary amine formation.[10b] Therefore we studied the Ru/C catalyzed cyclizations of 1,4-diaminobutane, 1,5-diaminopentane, 2-methyl-1,5-diaminopentane, and 1,6-diamino-heptane in the presence of aluminum powder. The addition of aluminum powder was found to dramatically facilitate the reaction and improve selectivity of the cyclization reaction. The starting diamines were almost completely consumed within 2 h and cyclic amine selectivities were over 88% in all cases (Table 2). While Pd/C gave similar results as Ru/C in the absence of Al, addition of it significantly slowed the reaction. Low conversions, less than 3%, of the starting material of 1,4-diaminobutane and 1,6-diaminohexane, respectively, were recorded.

Table 2
Ru/C catalyzed cyclization of α,ω-diaminoalkane in the presence of aluminum powder



Entry	Diamine **1**		Time (h)	Conv.[a] (%)	Selectivity[a] **2** (%)
	R	n			
1	H	2	0.5	42	95
2	H	2	2	99	88
3	H	3	0.5	46	86
4	H	3	1	99	98
5	Me	3	1.5	98	95
6	H	4	0.5	75	96
7	H	4	1	99	95

Reaction conditions; α,ω-diaminoalkane (100 mg), catalyst (50 mg, 2.6–2.9 mol % Ru), water (2 mL), and Al powder (30 mg) were placed in a 10 mL pressure resistant glass vessel.

[a] Conversions and selectivities were determined by GC and GC–MS analysis.

The conversion of 1,4-diaminobutane and 1,4-diaminohexane, plotted as a function of reaction time are shown in Figure 1. It is evident that the *in-situ* generated H_2 from the reaction of aluminum with water facilitates the hydrogenation of the imine intermediates to amines.[11] Similarly, dehydrogenation of imine intermediates were found to have significantly decreased as formation of side products such as adiponitrile were strongly suppressed. No reaction was seen when the reaction was carried out with aluminum in the absence of catalyst on carbon.

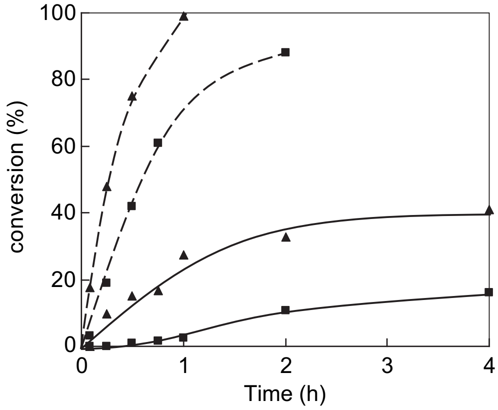
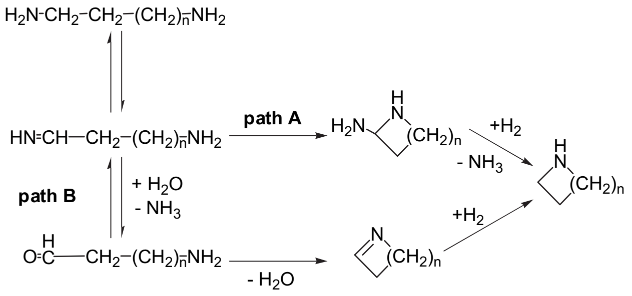


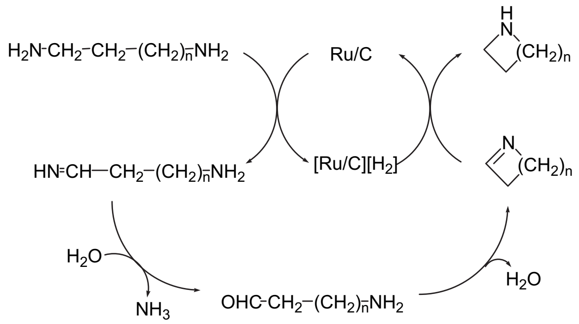
Figure 1. Plots of conversion of 1,4-diaminobutane (■) and 1,6-diaminohexane (▲) with (- - -) and without aluminum (—) vs reaction time. Conditions are the same as described in Table 1 and Table 2.

Some reports indicate that the ease of cyclization in the formation cyclic amines follows the order of ring size 5>3>6>7>4.[8,12] The results obtained for α,ω-diaminobutane, -pentane and -hexane cyclization in this study seems to disagree with earlier findings. The results obtained suggest that the reaction follow the order 7>6>5 in ring size. Although the detailed reaction pathway is not clear, the results suggests that the intramolecular cyclization of α,ω-diaminoalkane in water run through a different reaction intermediate. In previous studies of the cyclization of diamines, which have been carried out under dry conditions, aminal intermediates have been proposed. Such intermediates are formed by nucleophilic attack by an amine on an imine (Scheme 1, path A), which in turn are derived from the starting amines by metal catalyzed dehydrogenation. On the other hand, when water is employed as the reaction media, an imine is immediately hydrolyzed to form an aldehyde (Path B). The subsequent dehydration condensation reaction between aldehydes and amines is instantaneous and affords the unsaturated cyclic imine. The hydrogenation of it gives desired cyclic amines. Based on the above and the results, it seems that the ring strain of unsaturated cyclic imines affect the ease of ring closure. The intermediates in the present study have unsaturated cyclic imine structures, which have altered ring strain compared to their saturated analogs. Hence, in the formation process of the unsaturated cyclic imine structure, the formation of a less strained seven-membered ring appears to be more facile than its equivalent of decreasing ring size.



Scheme 1. Reaction pathways of the formation of cyclic amine.

Based on our previous report concerning to the intermolecular coupling of primary amines to secondary amines,[10b] we propose that the present, unique intramolecular coupling occurs through a similar mechanism. Scheme 2 depicts a plausible catalytic cycle of the reaction. The catalytic cycle begins with oxidative removal of dihydrogen from the starting diamine to give an alkyleneimine. This imine undergoes hydrolysis to give an aldehyde bearing an amine functionality. The formation of this intermediate is considered the key to the improved reaction outcome, compared to previous investigations. ^1H NMR studies have shown that such transient intermediates possessing the amine and aldehyde functionality, undergo rapid intramolecular condensation under basic conditions to give a cyclic alkyleneimine.[13] The catalytic cycle is completed by reduction of the cyclic imine to give its corresponding cyclic amine. It has been shown that hydrogen pressure is essential in conversion of 1-pyrroline to pyrrolidine,[14] which explains the beneficial effect of aluminum powder. The generation of H_2 from the reaction of water and aluminum powder enhances the reduction of the cyclic imine, resulting in faster and more selective reactions. A related, observation on the benefit of combination of water and aluminum to produce H_2 has been made during its use in the reduction of acetophenones.[15]

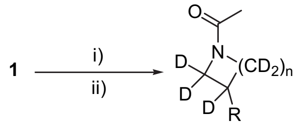


Scheme 2. Plausible catalytic cycle of cyclic amine formation.

The dilute conditions and short reaction times, combined with proper choice of catalyst, largely eliminate the formation of oligomeric amines as well as tertiary amines. This interpretation is based on the absence of signals in ^{13}C NMR spectra resulting from α-carbons to the nitrogen in linear secondary and tertiary amines. For example, in the case of 1,4-diaminobutane, the α-carbons in linear secondary and tertiary amines would be easily distinguished from their pyrrolidine and starting diamine counterparts. However, these signals are not observed.

The reaction using 1,3-diaminopropane did not give the expected azetidine under our reaction conditions. Instead, 1-aminopropane was obtained as a major product. Similar findings of 1-aminopropane formation have been reported earlier. This indicates insertion of catalyst into the carbon–nitrogen bond and subsequent β-elimination to give allylamine.[16] In fact, *n*-butylamine and *n*-hexylamine were observed in small amounts in GC-traces of several reactions. The insertion of metal catalysts to the carbon–nitrogen bond was confirmed by treating pyrrolidine (100 mg) with Pt/C (50 mg) and Al (30 mg) at 158 °C for 2 h. A product distribution of pyrrolidine (42%), butylamine (31%), dibutylamine (14%), and oligomeric products (13%) was observed. 1,7-diaminoheptane and 1,8-diaminooctane did not give the expected eight- and nine-membered cyclic amines under the described reaction conditions. Oligomers formed in intermolecular reactions were obtained along with recovered starting diamines. From the above results, the resultant ring-strain in the cyclic amine seems to be an important factor. Heterocycles with high deuterium contents can be obtained when D_2O is used instead of water under the described reaction conditions. The results are summarized in Table 3. Deuterium contents calculated from mass spectra of N-acetylated cyclic amines were 91, 82, 65, and 70 at % for pyrrolidine, piperidine, 3-methylpiperidine, and azepane, respectively. Determination of deuterium contents without acetylation was not possible due to significant M^+-1 peaks that lower the calculated deuterium content. Acetylation of the reaction products also permit calculation of deuterium content by ^1H NMR peak integration of the acetyl singlet peak vs non-deuterated protons in the heterocycles. The ^1H NMR spectrum of acetylated pyrrolidines prepared are depicted in Figure 2. Deuterium contents by MS were close to those calculated by NMR peak integration. NMR analysis based on integration of the methylene protons relative to H/D-exchanged protons further permitted calculation of the deuteration degree of each carbon on heterocycles.

Table 3
Ru/C catalyzed cyclization of α,ω-diaminoalkane in deuterium oxide



i) Ru/C, Al, D_2O, 158 °C ii) Ac_2O

Entry	R	n	Yield[a] (%)	D content[b] (atom%)			
				Overall	α−	β−	γ−
1	D	2	67	92(91)	94	89	—
2	D	3	82	83(82)	92	77 (β+γ)	
3	Me	3	66	58(65)	96	88	39
4	D	4	71	73(70)	95	64 (β+γ)	

[a] Isolated yields are shown.

[b] Deuterium contents were determined by ^1H NMR measurement and the values in parenthesis were derived from GC–MS analysis.

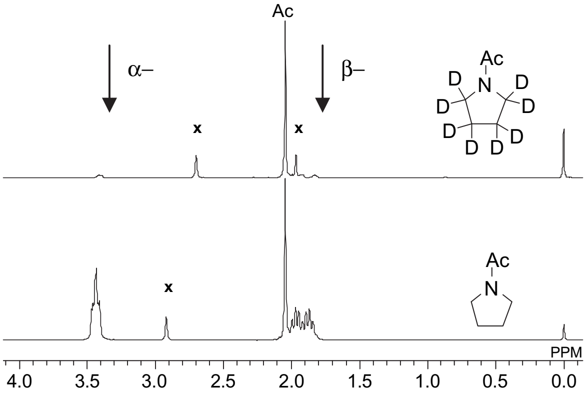


Figure 2. ^{1}H NMR of acetylated deuterated and non-deuterated pyrrolidines. Impurity peaks are denoted (x).

As expected, α-protons displayed highest deuterium contents (92–96 at %) while β-protons were determined to have undergone H/D-exchange to a slightly lower degree (88–89 at %). Overall deuterium contents of piperidine, and azepane were somewhat lower compared to pyrrolidine as the exchange of the γ-protons does not occur readily. Similarly, the methyl group in 3-methylpiperidine essentially does not undergo H/D-exchange readily (11 at % by NMR). The overall deuterium content of 3-methylpiperidine was calculated to be 58 at % assuming that the methyl group at 3-position does not undergo H/D-exchange. This is close to the value calculated for piperidine, thus providing further confirmation for calculated results. Lockley and his co-workers reported H/D-exchange reactions of various piperidines and dialkylamines using homogenous ruthenium catalysts with D_2O as a deuterium source, which gave products labeled with deuteriums at the α- and β- positions.[17] The results obtained with pyrrolidine suggest that the α- and β- positions are labeled almost to an equal degree, similar that reported by Lockley. However, the data obtained in this study cannot exclude H/D-exchange at γ- and other positions as noted above. The mechanism for deuteration at these positions is not fully evident. Unreacted diamines of non-acetylated samples were observed to display increased mass by GC–MS analysis. The observation of such partially deuterated diamines suggests that H/D-exchange reaction takes place with the starting diamines, reactive intermediates, and products. Indeed the reaction of piperidine under the same condition described in Table 3 gave deuterated piperidine, which showed almost same number of incorporated deuterium and molecular mass distribution of deuterated products.

While the concept of rapid cyclization of aliphatic α,ω-diamines has been proved with small scale reactions and high catalyst amounts, reactions carried out in larger scale confirm the results. Reactions with 2-methyl-1,5-diaminopentane were scaled up 20 and 50 times, gram scale preparation, to confirm GC observations and to assess possibilities for scale-up. In both cases, pure fractions with over 74% yields of 3-methylpiperidine as its HCl salt could be isolated.[18] The reaction at 20 time scale was carried out in a microwave reaction using identical chemical quantities as used in the small scale preparations. Of particular interest was the reaction carried out in 50 time scale using reduced catalyst (1 mol % of Ru) and aluminum amounts, suggests that the procedure described herein may be of significant practical importance.

3. Conclusion

In summary, we have developed a convenient and simple preparative way to five-, seven- and seven-membered cyclic amines from α,ω-diaminoalkanes and their deuterium labeled cyclic amines in good yields with moderate to high deuterium content. This protocol is environmentally friendly chemical process to obtain cyclic amines because of the use of water (deuterium oxide) as a solvent and hydrogen (deuterium) source.

4. Experimental

4.1. General synthetic procedure

A Teflon® covered magnetic stir bar, catalyst on active carbon support (50 mg, 5 wt % of metal), aluminum powder (30 mg, particle size ~425 μm), diamine (100 mg), and 2 mL water (deionized, <0.1 μS) were placed in a 10 mL pressure resistant glass tube. The tube was then sealed and immersed in a preheated oil bath at 158 °C for a predetermined time. After the reaction, K_2CO_3 was added until the solution was saturated and the aqueous solution was then extracted once with 2.5 mL diethyl ether. The organic layer was analyzed with GC and GC–MS. Conversions and relative yields were calculated from peak areas in the GC chromatograms.

4.1.1. General outline for determination of the degree of deuteration. A Teflon® covered magnetic stir bar, 50 mg of Ru/C (5 wt % of metal), aluminum powder (30 mg, particle size ~425 μm), diamine (100 mg), and 2 mL D_2O were placed in a 10 mL pressure resistant glass tube. The tube was then sealed and immersed in a preheated oil bath at 158 °C for predetermined time period. After the reaction, K_2CO_3 was added and the saturated aqueous solution was extracted once with 1 mL $CDCl_3$. Acetic anhydride (10% molar excess) was added to the $CDCl_3$ solution and the mixture was stirred for 15 min. Water and K_2CO_3 was added to remove unreacted anhydride and to extract the formed acetic acid. The $CDCl_3$ layer collected was analyzed by NMR and GC–MS.

4.1.2. Scaled-up preparation of 3-methylpiperidine using microwave reactor. A Teflon® covered magnetic stir bar, 1.0 g of Ru/C (5 wt % of metal), aluminum powder (400 mg, particle size ~425 μm), 2-methyl-1,5-pentamethyldiamine (2 g), and 40 mL H_2O were placed in a 80 mL pressure resistant glass vessel. The glass vessel was sealed and placed in a Discovery microwave oven (CEM Corp.) The reaction was carried out at 150 °C for 2.5 h. After the reaction, solids were separated by filtration, washed with water and CH_2Cl_2. K_2CO_3 was added to the filtrate to saturate the solution, the organic layer was removed and the satd aq K_2CO_3 was washed three times with CH_2Cl_2. The combined organic layers were dried over anhyd. $MgSO_4$ and filtered. Dry HCl gas was bubbled through the CH_2Cl_2 solution for 0.5–1 h or until the organic layer did not display volatile products by GC. The solvent was removed under reduced pressure. The residual solid was *re*-precipitated from MeOH with excess ether to give 1.9 g (78%) of a white solid mp 174–175 °C (lit. 173 °C).[18]

4.1.3. Scaled-up preparation of 3-methylpiperidine using autoclave. To a glass autoclave with a stir bar, 1.75 g of 5 wt % Ru/C (1.0 mol % based on substrate), 11.5 mL (86.2 mmol) of 2-methyl-1,5-diaminopentane, 30 mL of water, and 0.75 g of aluminum powder (particle size ~425 μm) were added successively. The equipment was sealed and heated at 158 °C for 14 h. After the reaction mixture had cooled down to room temperature, the solid materials were filtered and washed with water and CH_2Cl_2. K_2CO_3 was added to the aq solution until saturation and then it was extracted with CH_2Cl_2 three times. The organic layers were combined and dried over $MgSO_4$. (GC analysis shows that the conversion is 100%.) After filtration, the CH_2Cl_2 solution was bubbled through with dry HCl gas for 3 h. Then the solvent was removed under vacuum to give white solid as a crude product. The crude product was then *re*-dissolved in MeOH and *re*-precipitated with excess ether. Yield: 8.63 g (74%). Mp: 175–176 °C, ^{1}H NMR (D_2O): δ ppm 0.98 (d, J=8 Hz, 3H, CH_3); 1.17–1.26 (m, 1H, CH); 1.65–1.77 (m, 1H, $CHCH_2CH_2$); 1.80–1.96 (m, 3H, $CHCH_2CH_2$); 2.63 (t, J=12 Hz, 1H, CH_2CH_2NH); 2.91 (td, J=4, 12 Hz, 1H, CH_2CH_2NH); 3.31–3.40 (m, 2H, $CHCH_2NH$).

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