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ARTICLE

A new route to α,ω-diamines from hydrogenation of dicarboxylic acids and their derivatives in the presence of amines

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A new and selective route for the synthesis of polymer precursors, primary diamines or *N*-substituted diamines, from dicarboxylic acids, diesters, diamides and diols using a Ru/ triphos catalyst is reported. Excellent conversions and yields are obtained under optimised reaction conditions. The reactions worked very well using 1,4-dioxane as solvent, but the greener solvent, 2-methyl tetrahydrofuran, also gave very similar results. This method provides a potential route to converting waste biomass to value added materials. The reaction is proposed to go through both amide and aldehyde pathways.

Introduction

Amines are an important group of chemicals, which are useful intermediates for a wide range of applications such as the manufacture of drugs, azo-dyes or nylons. Amines are industrially synthesized by alkylation of ammonia using alcohols.[1] The same amines can be obtained by the reaction between haloalkanes and ammonia or amines, however, the degree of alkylation is hard to control.[2] Amines can also be obtained by reduction of nitriles,[3] alkylazides[4], amides[5] and nitrocompounds[6] catalytically or stoichiometrically. Reductive amination of aldehydes[7] and ketones[8] can also produce amines, however, it requires more steps for the synthesis of the starting materials, and carboxylic acids and esters are more easily obtained from nature.

N-alkylation of amines with alcohols has been studied by different groups using different metals.[9–15] However, there are fewer examples for the *N*-alkylation of amines with carboxylic acids and esters which could save the step of alcohol synthesis. In 2007, some of us developed the first homogeneous catalytic method for *N*-alkylation using molecular hydrogen as reductant. Nonanoic acid was converted to nonylamine in 50 % yield using a ruthenium catalyst containing the 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) ligand.[16] This study was followed up later with an extended substrate scope using a Lewis acid promoter.[17] Heterogeneous Re/TiO_2 can also be used for the conversion of carboxylic acids or esters to amines with dimethylamine, a reaction that is believed to proceed by hydrogenation of the acid or ester to the alcohol followed by amination of the alcohol.[18] Karstedt's catalyst was also found to be active for this *N*-alkylation reaction using carboxylic acids. However, a stoichiometric amount of silane was used as the hydride source. Reactions only proceeded well with carboxylic acids as the reagents, while, starting with esters give only 5 % yield of the desired amine.[19] Ruthenium,[20] iridium,[21] and boron[22] catalysts have also been studied by different groups with silanes as the H donor. These previous studies are summarized in Figure 1.

Although linear diamines have been produced from diesters by formation of the diazide followed by hydrogenation and used for polyamide synthesis with a variety of different chain length diesters,[23] as far as we know, there are no reported catalytic methods for the synthesis of linear diamines from linear dicarboxylic acids and their derivatives such as diesters or diamides, although we have recently reported that *N*-heterocycles can be obtained from diesters with 4-8 C atoms in the chain.[24] In some cases, linear diamines were formed as byproducts when excess amine was employed, but these reactions were not optimized.

Long chain diacids and diesters can be obtained sustainably from non-food biomass, for example, undecylenic acid, which could afford dodecanedioic acid and esters by a carboxylation reactions[25] can be derived from castor oil.[26] Tall oil fatty acid from waste tall oil contains mainly oleic acid, which can be converted into dimethyl 1, 19-nonadecanedioic by isomerizing methoxycarbonylation,[25] using the catalystic system derived from Pd / 1,2-*bis*(ditert-butylphoshinomethyl)benzene (BDTBPMB) / methane sulphonic acid (MSA) originally developed and commercialized for ethene methoxycarbonylation,[27] but subsequently shown to be highly effective for the production of terminal esters by isomerizing methoxycarbonylation of terminal or internal alkenes[28] or of α,ω-diesters from unsaturated esters[29] including methyl

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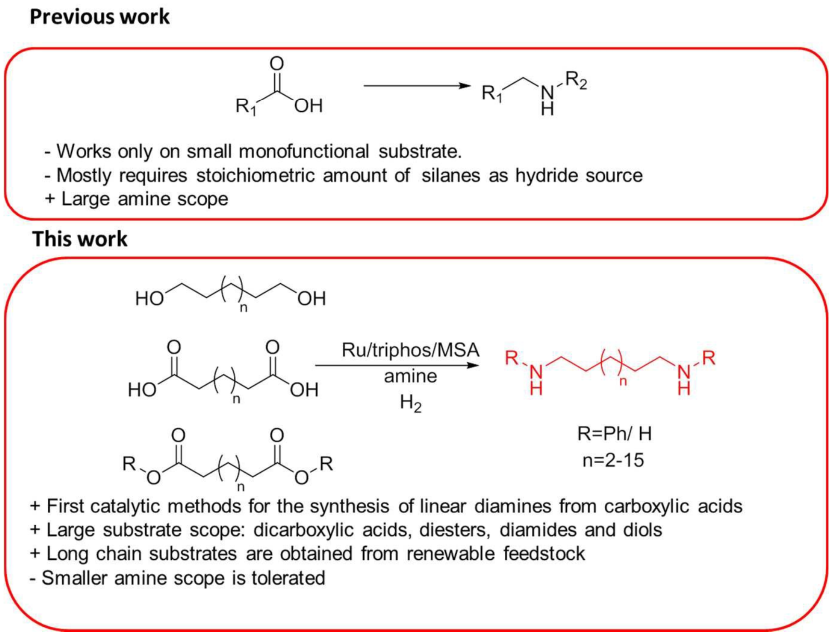
oleate,[30–38] high oleic sunflower oil[39–41], algal oils[42,43] for polymers such as polyamides, polyimides and polyureas.

Herein, we report a methodology to convert dicarboxylic acids, diesters and diamides to the desired diamines in the presence of the corresponding anilines or ammonia using a ruthenium catalyst (Figure 1) under the optimised conditions for amide hydrogenation.[5] Value added materials can be produced from waste bio feedstocks which makes this method attractive.

Figure 1. Brief summary of the current status of the formation of diamines from diacids and their derivatives compared with the work reported here.



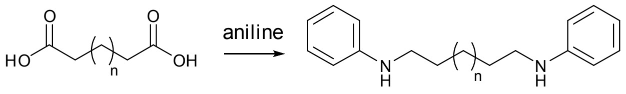
Results

Dicarboxylic acid derivatives as substrates

Initial studies were focused on the synthesis of *N*-substituted diamines as they could be used as precursors for *N*-substituted polymers.[44] Polyamides containing aromatic groups are known to be highly stable[44] and to be fire retardants,[45,46] therefore, *N*-phenyl polyamides are of potential interest. So far, di-(*N*-phenylamines) are only known to be produced from dibromoalkanes stoichiometrically[47] or by amination of linear diols using Pt-Sn/γ-Al_2O_3 in xylene.[48] Diamines can also be a product from amination of diols with excess aniline.[24]

Previous reports using molecular hydrogen as the reductant only managed to convert small monofunctional carboxylic acids to their corresponding amines.[5,16,17,49,50] Here, we report the first method for producing diamines from dicarboxylic acids and their derivatives in the presence of an amine source. The process works well even for very long chain fatty acids. *N*-phenyl diamines can be obtained from the hydrogenation of carboxylic acids in the presence of aniline using $[Ru(acac)_3]$ (acacH= 1,3-pentanedione) and triphos in excellent yields (Table 1, entry 1-4). Carbon chains with up to 19 carbons could be tolerated under the reaction conditions. Replacing aniline with water leads to diols (Table 1, entry 5). When using 1.5 equivalents of aniline with dodecanedioic acid, 52 % yield of the diamine was obtained (Table 1, entry 6), the cyclic product, which is formed for substrate chain lengths up to 7[24] was not observed. When 2-methyltetrahydrofuran (2-MeTHF) was used as solvent, very similar results were obtained to those obtained using 1,4-doxane (Table 1, entry 7 vs Table 1, entry 3). But in this case, 2-methyl-1-phenylpyrrolidine (from the reaction of 2-MeTHF with aniline) was also obtained as a side product (6 % relative to aniline).

Table 1. Hydrogenation of carboxylic acids and derivatives in the presence of aniline.[a]



Entry	n	Conv. (%)	Yield [b](%)
1	4	100	91
2	6	100	97
3	8	100	98 (95)
4	15	100	93 (86)
5[c]	8	97	95
6[d]	8	100	52
7[e]	8	100	97

[a] $[Ru(acac)_3]$ (2 mol%), triphos (4 mol%), MSA (2 mol%), 1,4-dioxane (15 mL), substrate (2.5 mmol), aniline (3 equiv.), H_2 (10 bar), 220 °C, 42 h. [b] NMR yield using 1,4-dinitrobenzene as internal standard, isolated yields in parenthesis. [c] omitting aniline, $[Ru(acac)_3]$ (1 mol%), triphos (2 mol%), MSA (1 mol%), 1,4-dioxane (15 mL), substrate (2.5 mmol), H_2O (10 mL), H_2 (10 bar), 220 °C, 20 h, major product is 1,12-dodecanediol. [d] As [a], aniline (1.5 equiv.). [e] As [a], 2-MeTHF (15 mL) was used as solvent.

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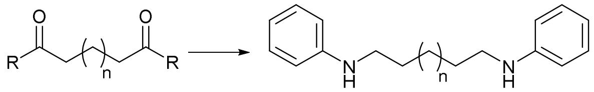
As esters are also wide spread in nature, we tested them as substrates. Reactions starting from dicarboxylic esters could also produce *N*-phenyl diamines in the presence of aniline. However, under the same reaction conditions as used for carboxylic acids, the diamine, **1**, was only obtained in 60 % yield (Table 2, entry 1). In this case, methyl 12-(phenylamino)dodecanoate, **2**, was also observed in 30 % yield. *N*-methyl aniline, and *N*,*N*-dimethylaniline were produced by methylation of aniline. The methyl groups were derived from methanol which was a byproduct from the methyl ester hydrogenation, as previously observed in the synthesis of *N*-heterocycles from short chain diesters[24]. As a result, the availability of aniline is reduced, lowering the yield of the desired diamine. Increasing the amount of aniline, and increasing the reaction time to 70 hours allowed the reaction to go to completion, and the desired diamine was obtained in 94 % yield. The longer reaction time required shows that esters are less reactive than carboxylic acids. Dimethyl dodecanedioate, **3**, can be converted to the N_1,N_{12}-diphenyldodecane-1,12-diamine, **1**, in 94 % yield after 70 hours (Table 2, entry 2). Replacing the methyl ester by diphenyl dodecanedioate, **4**, led to a similar result, and gave the desired product, **1**, in 95 % yield (Table 2, entry 4). In this case, phenol is obtained as the byproduct. No alkylation between phenol and aniline was observed because phenyl does not contain α-hydrogen atoms so the hydrogen borrowing mechanism *via* an aldehyde, required for alkylation of aniline by phenol, cannot take place.[24] Hydrogenation of diethyl ester, **5**, gave the product in 76 % yield (Table 2, entry 3) with ethyl 12-(phenylamino)dodecanoate, **6**, as the side product, which suggests a lower reaction rate in this case. Dimethyl nonadecanedioate, **7**, which can be obtained from waste tall oil,[51] can also be used as substrate for the production of N_1,N_{19}-diphenylnonadecane-1,19-diamine, **8**, in 98 % yield.

Extending the substrate scope, diamide, **9**, could also be hydrogenated to the corresponding diamine in a 56 % yield after 42 hours (Table 2, entry 6). Monohydrogenated amide, **10**, was also obtained in 37 % yield, see Scheme 2 for structures. By increasing the reaction time to 70 hours, the yield of the desired diamine, **1**, was increased to 98 % (Table 2, entry 7). Added aniline improved the selectivity of the reaction (Table 2 entries 7 and 8).

Table 2. Hydrogenation of carboxylic acids and derivatives in the presence of aniline.[a]



Entry	n	R	Equiv. aniline	Conv. (%)	Product	Yield (%)
1[b]	8	OMe **3**	3	100	**1**	60
2	8	OMe **3**	5	100	**1**	94
3	8	OEt **5**	5	100	**1**	76
4	8	OPh **4**	3	100	**1**	95
5	15	OMe **7**	5	100	**8**	96 (91)
6[b]	8	NPh **9**	3	95	**1**	56
7	8	NPh **9**	3	100	**1**	98
8[c]	8	NPh **9**	0	81	**1**	41

[a] [Ru(acac)$_3$] (2 mol%), triphos (4 mol%), MSA (2 mol%), 1,4-dioxane (15 mL), substrate (2.5 mmol), aniline (0-5 equiv.), H_2 (10 bar), 220 °C, 70 h; The conversion and yield are calculated by NMR with 1,4-dinitrobenzene as internal standard, isolated yields in parenthesis. [b] as [a], 42 h. [c] As [b] without added aniline. Other products include **10** (15 %) aniline and other products.

Different amines were also tested for this reaction starting from aniline derivatives. An electron donating methoxy group in the 4-position gave very similar results compared to the reaction with aniline (Table 1, entry 3 vs Table 3, entry 2). Weakly electron withdrawing 4-fluoro substitution also gave a similar result (97 %) (Table 3, entry 2), while stronger electron withdrawing groups (such as trifluoromethyl and nitro) did not produce the expected diamine (Table 3, entry 3 and 4).

Table 3. Other aniline derivatives.[a]

Entry	R	Conv.[b] (%)	Yield [b](%)
1	OMe	100	97
2	F	100	97
3	CF_3	100	0
4	NO_2	100	0

[a] [Ru(acac)$_3$] (2 mol%), triphos (4 mol%), MSA (2 mol%), 1,4-dioxane (15 mL), substrate (2.5 mmol), aniline (3 equiv.), H_2 (10 bar), 220 °C, 42 h. [b] NMR yield using 1,4-dinitrobenzene as internal standard.

The reaction works very well with aniline and some aniline derivatives, however, other amines such as aliphatic amines were less successful, (ESI, Table S2), diamides usually being the predominant product sometimes in complex mixtures although with isopropyl amine, the desired N_1,N_{12}-diisopropyldodecane-1,12-diamine was also produced (18 %)).

Although these *N*-arylated amines are of considerable interest for making stable polymers,[44] nylons are more usually made from primary diamines so we attempted the hydrogenation of dicarboxylic acids, esters and amides in the presence of aqueous ammonia. Although there was some evidence for diamine formation in some of these reactions, they were usually contained in complex mixtures and sometimes insoluble products, which appeared to be e. g. nylon 19 were formed.

Diols as substrates

Partly to obtain a better understanding of the reactions when using aniline and partly to try to synthesise di-primary amines in a two step process from dicarboxylic acid derivatives, diols were also studied as substrates. Diols can be synthesized from dicarboxylic acids by hydrogenation using a variety of catalysts including Ru/triphos. Ru/triphos is also efficient for the amination of alcohols *via* a hydrogenation borrowing

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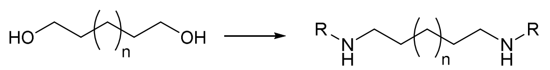
mechanism. For example, 1-octanol is known to be aminated to the corresponding octylamine using ammonia gas with the ruthenium/triphos system.[14] Long chain diamines have also been prepared by amination of diols using liquid ammonia catalysed by the Ru/triphos system in yields up to 68 %.[52]

It is known that alcohols are intermediates in the formation of amines by the hydrogenation of amides using the Ru/triphos system promoted by the Lewis acid, Yb(triflate)$_3$,[53] but we did not detect alcoholic intermediates in the Ru/triphos catalyzed hydrogenation of short chain dicarboxylic acid derivatives in the presence of aniline to give *N*-phenyl heterocycles.[24]

Reactions were firstly carried out using hydrogen to give comparable conditions to those used for diacids or esters. This allowed determination of whether the diol is a viable intermediate in the reactions starting from dicarboxylic acid derivatives.

Table 4. Amination of diols in the presence of an amine.[a]



Entry	n	R	Conv. (%)	Product	Yield (%)
1	8	Ph	100	**1**	98
2	15	Ph	100	**8**	98
3	8	Bn	100	**11**	86
4	8	^{i}Pr	100	**12**	62
5[b]	8	H	86	**13**	84
6[c]	8	H	88	**13**	86
7[d]	8	H	88	**13**	87
8[b]	2	H	93	**14**	64
9[g]	8	H	72	**13**	71
10[b]	15	H	92	**15**	76[h]
11[e]	8	Bn	100	**11**	33
12[f]	8	Bn	100	**11**	31
13[e]	8	Ph	100	**1**	45
14[f]	8	Ph	100	**1**	72

[a] [Ru(acac)$_3$] (1 mol%), triphos (2 mol%), MSA (1 mol%), 1,4-dioxane (15 mL), substrate (2.5 mmol), amine (3 equiv.), H_2 (10 bar), 220 °C, 20 h. The conversion and yield are calculated by NMR with 1,4-dinitrobenzene as internal standard. [b] [Ru(acac)$_3$] (2 mol%), triphos (4 mol%), MSA (2 mol%), 1,4-dioxane (20 mL), substrate (1.25 mmol), aq. ammonia (35 %, 30 mL), H_2 (10 bar), 220 °C, 20 h. [c] [Ru(acac)$_3$] (2 mol%), triphos (4 mol%), MSA (2 mol%), ammonia in 1,4-dioxane (0.5 M, 20 mL), substrate (1.25 mmol), aq. ammonia (35 %, 30 mL), H_2 (10 bar), 220 °C, 20 h. [d] Ru(acac)$_3$] (2 mol%), triphos (4 mol%), MSA (2 mol%), 1,4-dioxane (20 mL), substrate (1.25 mmol), aq. ammonia (35 %, 30 mL), H_2 (10 bar), 220 °C, 42 h. [e] Same as [a], Ar (1 bar) instead of H_2. [f] Same as [a], Ar (10 bar) instead of H_2. [g] Same as [b], 165 °C. [h] Isolated yield.

Amination of diols (C_{12} and C_{19}) with aniline gave excellent yields of the diamine (Table 4, entry 1,2). Reaction with other amines such as benzylamine afforded the N_1,N_{12}-dibenzyldodecane-1,12-diamine **11** in 86 % yield (Table 4, entry 3). **11** can itself be used as a precursor, or can be deprotected to the primary diamine. Other amines such as isopropylamine also produced the desired product, **12**, in reasonable yield (Table 4, entry 4). Control experiments showed, however, that hydrogen gas is necessary for these reactions. Much lower yields were obtained in the absence of hydrogen (Table 4, entry 11-14 compared with entry 3 and 1) when reacting diol with benzylamine or aniline.

Under these conditions we also managed to form the primary diamine using aqueous ammonia. Reaction of 1,12-dodecanediol with aqueous ammonia gave 86 % conversion and 84 % yield to the desired primary diamine, **13** (Table 4, entry 5). This is a significant improvement on the literature which has 68 % yield of the same product and requires liquid ammonia, which is more difficult to handle, as the amine source.[52] Slightly increasing the concentration of ammonia by using ammonia in 1,4-dioxane (0.5 M) instead of using 1,4-dioxane alone (aqueous ammonia was added in both cases) as the solvent gave a very similar result, **13** (86 % yield) (Table 4, entry 6). Increasing the reaction time did not improve the conversion, possibly because of an equilibrium between diol and diamine. When the reaction temperature was lowered to 165 °C, the conversion was slightly decreased (from 86 % to 72 %) after 20 hours (Table 4, entry 9). 1,6-Diaminohexane, **14**, is a very important precursor for the synthesis of nylon 6,6, and it can also be produced from 1,6- hexanediol using this method in good yield (64 %, Table 4, entry 8), with ε-caprolactam as a side product (15 %). Nylon 19 precursor, 1,19-nonadecanediamine **15**, was also obtained in this way in a good yield (76 %, Table 4, entry 10).

Sequential reactions

Since carboxylic acid derivatives can be hydrogenated to diols using Ru/triphos/MSA and since we have shown above that diols can be transformed into diamino alkanes by reaction with aqueous ammonia *under the same conditions,* we attempted the transformation of dicarboxylic acid derivatives to primary diamines by a two step reaction in one pot. This would remove the problem of intermolecular amide formation between molecules of the form $RO_2C(CH_2)_nNH_2$ to give polymers, which complicate a one pot synthesis.

The hydrogenation of 1,12-decanedoic acid or its dimethyl ester was carried out in the presence of water using the Ru/triphos/MSA system. At the end of the reaction, the reactor was depressurized, opened, aqueous ammonia and extra dioxane added. It was the repressurised with hydrogen and heated. Analysis of the product showed that 1,12-diaminodeodecane was formed in 83 or 79 % yield respectively, the main contaminant being diol (Scheme 1). With the same method, 1,19-dimethyl nonadecanedioate can also be successfully converted to 1,19-nonadecanediamine **15** in a one-pot reaction (78 % yield, Scheme 1).

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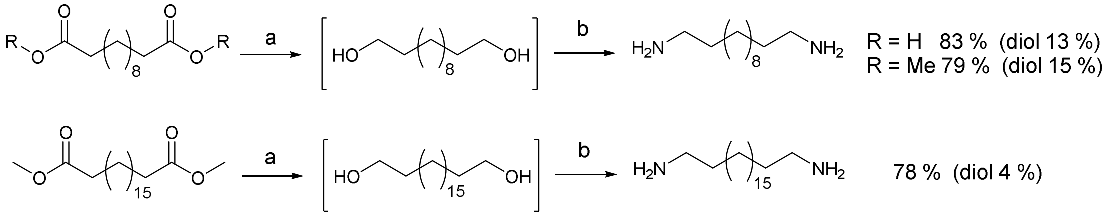
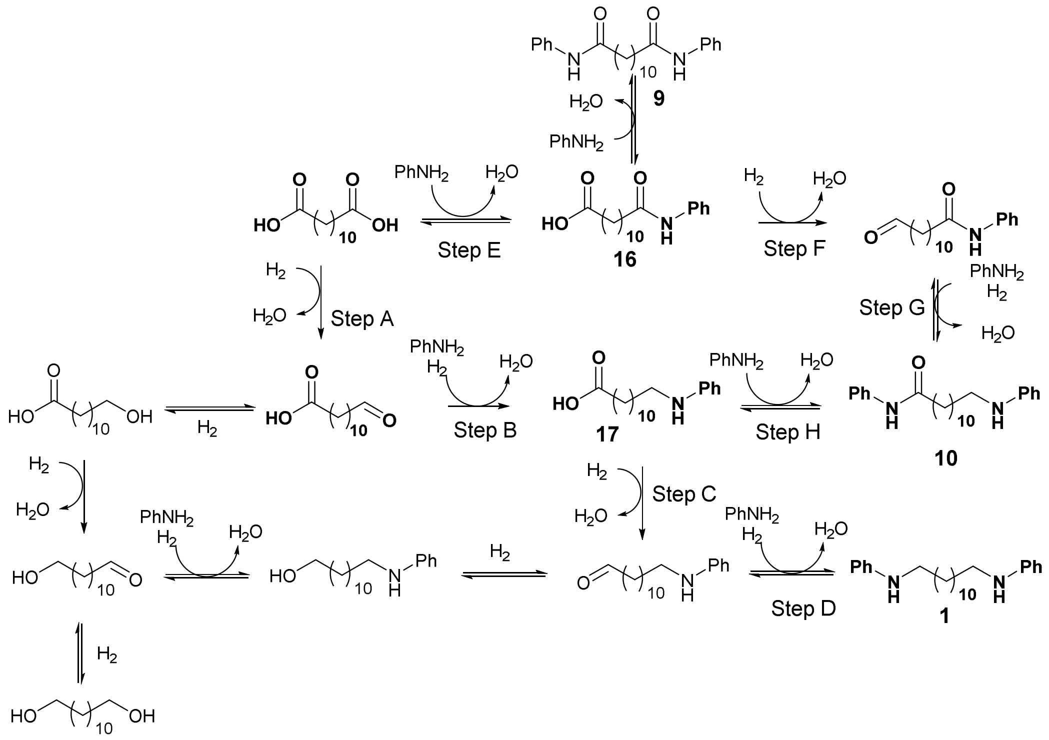


Scheme 1. ^{a} [Ru(acac)$_3$] (2 mol%), triphos (4 mol%), MSA (2 mol%), 1,4-dioxane (7.5 mL), substrate (1.25 mmol), distilled water (5 mL), H_2 (10 bar), 220 °C, 20 h. ^{b} 1,4-dioxane (12.5 mL), aq. ammonia (35 %, 30 mL), H_2, (10 bar), 220 °C, 20 h.



Scheme 2. Proposed reaction pathway for: the hydrogenation of 1,12-dodecanedioic acid in the presence of aniline to give **1** (Steps A-D and/or E-H, C, D, intermediates are bold), numbered compounds have been identified as being formed during the reaction; the reductive amination of 1,12-dodecanediol with aniline to give **1** (bottom) and the hydrogenation of 1,12-dodecanedoic acid to 1,12-dodecanediol (left hand side). The sequential reaction using ammonia proceeds through the hydrogenation to dodecanediol followed by reductive amination.

Discussion

Summarising the reactions above, polyamide precursors, primary and secondary diamines can be produced in high yields by hydrogenation of dicarboxylic acids, diesters, diols or diamides in the presence of aniline, aniline derivatives or aqueous ammonia (diols only or a 2 step reaction from diacids or diesters). Dodecanedioic is used as a model to discuss the results.

When hydrogenating dodecanedioic acid in the presence of aniline, acid amide, **16**, diamide, **9**, amide amine, **10**, and acid amine, **17**, were all observed after 20 hours, but not any intermediates containing an alcohol group at one or both ends. After 42 hours, full conversion to the *N*-phenyl diamine, **1**, was observed. Hydrogenation of diamide, **9**, under the same catalytic conditions (42 h) gave 95 % conversion and 56 % yield to the desired diamine **1**, the main other product being the aminoamide, **10** (37 % yield) (Table 2, entry 6). Increasing the reaction time to 70 hours, the substrate was fully converted with 98 % yield to the desired diamine, **1**. Although these observations suggest that diamide **9** may be an intermediate for this reaction, there must also be other faster routes which do not involve the diamide because the diacid is fully converted in 42 h whilst the diamide is not.

Hydrogenation of diamide, **9**, in the absence of aniline produces free aniline, which suggests that the partially hydrogenated amide undergoes some C-N bond cleavage to give aldehyde. In addition, it has been shown that for simple amines when using Lewis rather than Brønsted acid promoters,

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alcohols are intermediates.[53] We propose that the low energy pathways will follow Steps A-D or E-H then C, D (Scheme 2). Three of the compounds observed after shorter reaction times (**10**, **16** and **17**) are contained within these two alternative pathways. The diamide, **9**, is not within either pathway, consistent with its being observed after short reaction times, being formed by amidation of **16**, being hydrogenated to give **1** but not reacting as fast as the diacid. However, control reactions omitting aniline produce diol with high selectivity under the same reaction conditions as used for amine formation (Table 1, entry 5). Starting with diol and aniline under the same conditions gave 98 % yield of the desired diamine, **1**, after 20 hours (Table 4, entry 1). Thus, we cannot exclude pathways including alcohols, since the rapid rate of alcohol consumption would mean that the standing concentration of alcohol intermediates would be very small.

Conclusions

The hydrogenation of dicarboxylic acids and their esters in the presence of amines provides a new methodology for the synthesis of α,ω-diamines. Reaction of dicarboxylic acids and their derivatives with aniline in the presence of [Ru(acac)$_3$] and 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) gave good to excellent yields of the *N*-phenyl diamines with 8 to 19 carbon chains. Although primary diamines could not be obtained in a similar way using aqueous ammonia in place of aniline, they were formed from the reaction between diols and aqueous ammonia in very good yield and selectivity. They could also be formed in good yield by a sequential one pot reaction involving hydrogenation of the diacid or diester to the diol, addition of aqueous ammonia and further reaction to the diamine using the same catalyst. Renewable feedstocks can hence be converted to important precursors to polyamides.

Conflicts of interest

There are no conflicts to declare.

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