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Journal of
Applied
Chemical
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Journal of Applied Chemical Research, 18, 2, 81-92 (2024)

Optimized and Scalable Methods for the Synthesis of Lauryl Amine Anti-Cake using Diborane

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(Received 17 Nov. 2023; Final revised received 28 Feb. 2024)

Abstract

In this research, four improved and scalable methods for the synthesis of lauryl amine have been described. In this research, attempt has been by investigated the synthesis methods of lauryl amine, made to provide an easy and cost-effective method for the synthesis of lauryl amine as a surfactant and anti-cake with a wide range of applications. lauryl amine was synthesized from the primary materials of lauric acid, lauramide and lauronitrile in the presence of various catalysts and reducing agents. The advantages and disadvantages of each of these methods were investigated and compared to industrial methods. In the reduction of luramide and Lauronitrile to lauryl amine, diborane reductant was used as a new method for the first time. In this article, with an efficient and new method, lauryl amine was synthesized in the presence of ammonia and aluminum oxide with a overall yield of 63% from lauric acid. In this method, lauric acid is converted to Lauramide and finally reduced to lauryl amine.

Keywords: Lauryl amine, Anti-cake, Surfactant, Reducing agent, Diborane.

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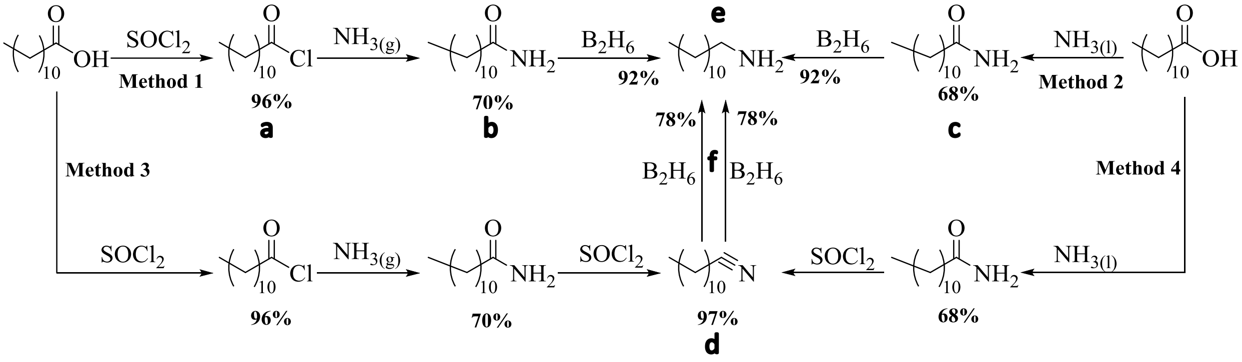
Introduction

Lauryl amine acts as a surfactant due to having a hydrophobic group, and for this reason, it has many applications in industry, agriculture, medicine, etc., some of them are discussed below. Perhaps the most important use of lauryl amine is its use as an anti-cake. By definition, caking may be viewed as the detrimental aggregation of particles, which transforms a readily free-flowing powder into a coherent solid [1]. Caking can affect the quality of powdered materials, especially energetic material and can also be costly and in some cases dangerous. To avoid these problems, organic compounds with at least one hydrophobic group and one group containing nitrogen are used. The most widely used of these compounds, are alkyl amines with alkyl chain of 12 to 18 carbon atoms, among which lauryl amine with 12 carbon atoms is the most widely used today as an anti-cake in energetic materials. Accordingly, lauryl amine has been used as an anti-cake of ammonium perchlorate [2], cyclotrimethylenetrinitramine (RDX) [3] and ammonium nitrate [4]. Another application of lauryl amine that has been very noticed in recent years is its use as a collector. Collectors are chemical compounds that are added to a mineral and create a hydrophobic property in the mineral. Today, lauryl amine has been used as a collector in the flotation of magnetite and dolomite [5], quartz [6], chlorite [7], albite and diatomite [8], magnetite [8] and etc. Lauryl amine is used to prevent corrosion of metals such as steel [9], iron [10] and copper [11] by new methods based on self-healing. In some cases, lauryl amine is also used as a surface modifier for the anti-tuberculosis drug rifampicin [12], the blood lipid drug fenofibrate [13] and the anti-inflammatory drug ibuprofen [14]. Lauryl amine is also widely used in paper industry [15], oil industry [16], antimicrobial coatings [17], engine oils and lubricants [18] and carbon black [19], etc. which makes it an important commercial material. The synthesis of lauryl amine has received much attention due to its wide range of applications, especially in recent years. In 1987 Bartra et al [20], In 1998 Fu et al [21], In 2002 Brown et al [22], In 2003 Wang et al[23], And in 2009 Prabhu et al [24] they were able to synthesize lauryl amine from its azide in the presence of Hydride donor compounds and catalyst which to not seem be suitable and cost-effective. In recent years, many attempts have been made to synthesize lauryl amine from nitrile using various reductants or catalysts in the presence of hydrogen gas, which has been more efficient than previous methods. For example in 2009, Singaram et al [25] using the Boron reducing compounds, in 2009 and 2014, Lemaire et al [26, 27] using the siloxane reducing and in 2010, Chen et al [28] using the Hydrogen gas, in 2013 to 2017, Beller et al [29-32] using the Hydrogen gas, in 2018 to 2020, Kirchner et al [33-35] using the Hydrogen gas and also in 2018, Jagadeesh et al [36] using the Hydrogen gas and in the presence of various catalysts, they were able to Synthesized lauryl amine from nitrile.

However, in the following, we will show the improved synthesis of lauryl amine from lauric acid in the presence of diborane reductant as a new efficient method and evaluate its performance compared to other reductants (Scheme 1).



Scheme 1. Methods of synthesis of lauryl amine.

Experimental

Material and Equipments

All compounds used, including raw materials and solvents, were obtained from Merck (Germany), and used without supernumerary purification. To remove water from tetrahydrofuran solvent and dichloromethane solvent from sodium and calcium chloride were used under reflux conditions. To analyze and identify synthetic products, device PerkinElmer-Spectrum 100 FTIR Spectrometer ،GC-Mas Agilent Technologies 7890B ,^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Varian Inova Bruker (Germany) has been used.

Synthesis of lauroyl chloride

5 g (25 mmol) of lauric acid and 15 ml of thionyl chloride with three drops of dimethylformamide were added to a 100 ml glass flask. Stirring was continued at -10 ° C for 20 min until the mixture was completely dissolved. Next, the solution was refluxed overnight at 80 ° C. Finally, the solution was transferred to a Rotary evaporator apparatus for one hour and its thionyl chloride was removed from the solution at 80 ° C. Thus, lauroyl chloride was obtained in the form of light brown oil.

Synthesis of lauramide from lauroyl chloride

To a 100 ml two necked glass flask was added 5 g of lauroyl chloride (25 mmol) (prepared in the previous step) along with 30 ml of dry dichloromethane. Then, Simultaneous with stirring at room temperature, ammonia gas was prepared from the reaction of liquid ammonia with sodium hydroxide, and when ammonia gas entered the reaction vessel, a white precipitate of lauramide appeared. For purification, the obtained lauramide precipitate was washed with n-hexane and diethyl ether and then extracted with ethyl acetate. Thus, after drying, white lauramide powder was obtained.

Synthesis of lauramide from lauric acid

To A 100 ml metal reactor was added 0.5 grams of lauric acid (2.5 mmol) and 0.5 g of aluminum oxide (5 mmol) with 10 ml of ammonia. The reactor was then transferred to the furnace and heated for 4 hours at a temperature of 250 ^{0}C. In the next step, the sample was removed from the furnace and the white sediment obtained in ethyl acetate was solved and then filtered to separate its aluminium oxide. Finally, the solution was transferred to the Rotary Evaporator, and its ethyl acetate was removed at 70 ° C to obtain a white precipitate appeared. For further purification, the combination of lauramide obtained by 20 ml Diethyl ether was washed and filtered.

Synthesis of lauronitrile

0.5 g (2.5 mmol) of lauramide and 5 ml of dry dichloromethane were added to a 50 ml glass flask, respectively. Then, while stirring, 1 ml (8 mmol) of thionyl chloride and a catalytic amount of dimethylformamide (three drops) were added and stirred at room temperature overnight. Was then transferred to a rotary evaporator and its excess dichloromethane was removed from the. Finally, a light yellow solution was obtained.

Synthesis of lauryl amine from luramide

In a 50 ml glass flask placed in an ice bath, 0.23 g (6 mmol) of Sodium borohydride and 10 ml of dry tetrahydrofuran were poured, respectively, and Simultaneous with stirring, in a catalytic amount Iodine was added and stirred until it changed color from red to white. After discoloration, the solution was came out from the ice bath and 0.4 g (2 mmol) of luramide was added to it at room temperature with stirring, and refluxed for 72 hours to obtain a uniform solution. The colorless solution was then transferred to a rotary evaporator and its tetrahydrofuran was removed from the solution at 70 ° C. In the next step, the solution was extracted three times each time with 20 ml of ethyl acetate and after drying by magnesium sulfate, the excess solvent was removed using a rotary evaporator for 30 minutes. Finally, lauryl amine was obtained as a white precipitate.

Synthesis of lauryl amine from lauronitrile

In a 50 ml glass flask placed in an ice bath, 0.23 g (6 mmol) of Sodium borohydride and 10 ml of dry tetrahydrofuran were poured, respectively, and at the same time as stirring, in a catalytic amount Iodine was added and stirred until it changed color from red to white. After discoloration, the solution was came out from the ice bath and 0.4 g (2 mmol) of lauronitrile was added to it at room temperature with stirring, and refluxed for 72 hours to change color from yellow to white. The yellow solution was then transferred to a rotary evaporator and its tetrahydrofuran was removed from the solution at 70 ° C. Then add 30 ml of water and stir for 30 minutes at room temperature to obtain a uniform solution. Finally, the solution was extracted three times each time with 20 ml of ethyl acetate and after drying by magnesium sulfate, the excess solvent was removed using a rotary evaporator for 30 minutes. Finally, lauryl amine was obtained as a white precipitate.

lauroyl chloride **(a)**

Light brown oil, Yield 4.8 g (96%). IR (KBr), (ν_{max}, cm^{-1}): 1803(C=O), 2852-2926(CH).

Synthesis of lauramide from lauroyl chloride **(b)**

White powder, mp 99˚C, yield: 4.20 g (95%). IR (KBr) (ν_{max}/cm^{-1}): 1630, 1663 (C=O), 3193-3363 (NH), 2852-2921 (CH). ^{1}H-NMR (500 MHz, CDCl3–d_6) δ, ppm: 0.87 (CH_3), 1.12-1.36 (CH_2), 1.62 (CH_2), 2.21 (CH_2), 5.63, 5.46 (NH_2) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$–d_6) δ, ppm: 14.2 (CH_3), 22.8 (CH_2), 31.9 (CH_2), 29.1-29.7 (CH_2), 39.3 (CH_2), 176.2 (C=O) ppm. -MS (EI, 70 eV): m/z (%): 199 ($M^{+\cdot}$ - $C_{12}H_{25}NO$), 183 ($M^{+\cdot}$ - $C_{12}H_{24}O$), 170 ($M^{+\cdot}$ - $C_{12}H_{25}$), 156 ($M^{+\cdot}$ – $C_{11}H_{24}$), 142 ($M^{+\cdot}$ – $C_{10}H_{22}$), 128 ($M^{+\cdot}$ – C_9H_{20}), 114 ($M^{+\cdot}$ – C_8H_{18}), 100 ($M^{+\cdot}$ – C_7H_{16}), 86 ($M^{+\cdot}$ – C_6H_{14}), 72 ($M^{+\cdot}$ – C_5H_{12}), 59 ($M^{+\cdot}$ – C_4H_{10}).

Synthesis of lauramide from lauric acid **(c)**

White powder, mp 99˚C, yield: 0.34 g (68%). IR (KBr) (ν_{max}/cm-1): 1633, 1660 (C=O), 3193-3366 (NH), 2849-2924 (CH). -MS (EI, 70 eV): m/z (%): 199 ($M^{+\cdot}$ - $C_{12}H_{25}NO$), 183 ($M^{+\cdot}$ - $C_{12}H_{24}O$), 170 ($M^{+\cdot}$ - $C_{12}H_{25}$), 156 ($M^{+\cdot}$ – $C_{11}H_{24}$), 142 ($M^{+\cdot}$ – $C_{10}H_{22}$), 128 ($M^{+\cdot}$ – C_9H_{20}), 114 ($M^{+\cdot}$ – C_8H_{18}), 100 ($M^{+\cdot}$ – C_7H_{16}), 86 ($M^{+\cdot}$ – C_6H_{14}), 72 ($M^{+\cdot}$ – C_5H_{12}), 59 ($M^{+\cdot}$ – C_4H_{10}).

Synthesis of lauronitrile **(d)**

Light yellow powder, mp 277˚C, yield: 0.44 g (97%). IR (KBr) (ν_{max}/cm^{-1}): 2858, 3363 (CH), 2246 (CN). ^{1}H-NMR (500 MHz, CDCl3–d_6) δ, ppm: 0.87 (CH_3), 1.15-1.36 (CH_2), 1.43 (CH_2), 1.64 (CH_2), 2.33, 5.46 (CH_2) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$–d_6) δ, ppm: 14.1 (CH_3), 22.6

(CH_2), 31.8 (CH_2), 28.1-29.9 (CH_2), 25.3 (CH_2), 17.1 (CH_2), 119.9 (CN) ppm. -MS (EI, 70 eV): m/z (%): 180 ($M^{+\cdot}$ - $C_{12}H_{23}N$), 166 ($M^{+\cdot}$ – $C_{11}H_{21}N$), 152 ($M^{+\cdot}$ – $C_{10}H_{19}N$), 138 ($M^{+\cdot}$ – $C_9H_{17}N$), 124 ($M^{+\cdot}$ – $C_8H_{15}N$), 110 ($M^{+\cdot}$ – $C_7H_{13}N$), 97 ($M^{+\cdot}$ – $C_6H_{11}N$), 82 ($M^{+\cdot}$ – C_5H_9N), 69 ($M^{+\cdot}$ – C_4H_7N), 55 ($M^{+\cdot}$ – C_3H_5N).

Synthesis of lauryl amine from luramide **(e)**

White powder, mp 32˚C, yield: 0.34 g (92%). IR (KBr) (ν_{max}/cm^{-1}): 3164, 3243 (NH), 2849, 2920 (CH). ^{1}H-NMR (500 MHz, CDCl3–d_6) δ, ppm: 0.87 (CH_3), 1.17-1.61 (CH_2), 2.74 (CH_2), 3.01 (CH_2), 5.37, 5.64 (NH_2) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$–d_6) δ, ppm: 14.0 (CH_3), 22.6 (CH_2), 31.9 (CH_2), 29.1-29.8 (CH_2), 40.5 (CH_2), 41.9 (CH_2), ppm. -MS (EI, 70 eV): m/z (%): 185 ($M^{+\cdot}$ - $C_{12}H_{27}N$), 170 ($M^{+\cdot}$ – $C_{11}H_{26}$), 156 ($M^{+\cdot}$ – $C_{10}H_{24}$), 142 ($M^{+\cdot}$ – C_9H_{22}), 128 ($M^{+\cdot}$ – C_8H_{20}), 114 ($M^{+\cdot}$ – C_7H_{18}), 100 ($M^{+\cdot}$ – C_6H_{16}), 86 ($M^{+\cdot}$ – C_5H_{14}), 69 ($M^{+\cdot}$ – C_4H_{12}), 55($M^{+\cdot}$ – C_6H_{10}).

Synthesis of lauryl amine from lauronitrile **(f)**

White powder, mp 32˚C, yield: 0.22 g (78%). -MS (EI, 70 eV): m/z (%): 185 ($M^{+\cdot}$ - $C_{12}H_{27}N$), 170 ($M^{+\cdot}$ – $C_{11}H_{26}$), 156 ($M^{+\cdot}$ – $C_{10}H_{24}$), 142 ($M^{+\cdot}$ – C_9H_{22}), 128 ($M^{+\cdot}$ – C_8H_{20}), 114 ($M^{+\cdot}$ – C_7H_{18}), 100 ($M^{+\cdot}$ – C_6H_{16}), 86 ($M^{+\cdot}$ – C_5H_{14}), 69 ($M^{+\cdot}$ – C_4H_{12}), 55($M^{+\cdot}$ – C_6H_{10}).

Results and discussion

Lauric acid was converted to lauroyl chloride in the presence of thionyl chloride and dimethylformamide. One of the important advantages of this reaction is the absence of solvent to perform the reaction. In this reaction, dimethylformamide was used in a catalytic amount (several drops), which significantly reduces the reaction time. The primary amides react with thionyl chloride to form imidoyl chlorides. These species are highly active and reactive and can be used to convert carboxylic acids to acyl chlorides. In the next step, lauryl chloride is converted to lauramide in the presence of gaseous ammonia. In this reaction, to prevent the production of by-products, gaseous ammonia was used instead of liquid ammonia, which was prepared simultaneously from the reaction of liquid ammonia with sodium hydroxide. Chlorine is a better Leaving group than OH and is easily replaced by NH_2. with the entry of ammonia gas into the flask, a color white precipitate is obtained over time in such a way that the rotation of the magnet becomes difficult and this indicates the synthesis of lauramide. In another way, lauric acid is converted to lauramide in the presence of liquid ammonia and Aluminium oxide. Using this method has eliminated the preparation step of lauroyl chloride from lauric acid.

Accordingly, the synthetic steps are shortened and the yield is increased. Lauramide synthesized from lauroyl chloride due to its impurities such as ammonium chloride, unused laurel chloride, etc. has several washing steps with n-hexane, diethyl ether and extraction with ethyl acetate, which makes purification difficult and reduces the yield but the lauramide synthesized from lauric acid does not have these problems and has a higher yield. In this method, an attempt was made to obtain optimized conditions by changing the reaction conditions including time, temperature, catalyst and different ratios. The results including yield and purity obtained from GC-Mas are given in the Table 1.

Table1. Results of changing conditions in the synthesis of luramide from lauric acid.

Purity (%)	**Yield** (%)	**Time**) **h**(	**Temperature**)^0**C**(	**Catalyst type**	**Ratio**		**Entry**
					Catalyst	**lauric acid**	
100	68	4	250	Al_2O_3	2	1	1
12	61	4	200	Al_2O_3	2	1	2
-	N.R	4	300	Al_2O_3	2	1	3
6	58	4	250	ZnO	2	1	4
31	65	4	250	CuO	2	1	5
27	63	4	250	-	-	-	6

Based on the results obtained in Table 1, the best conditions for reaction during 4 hours and with ratios of 1: 2 of lauric acid to aluminum oxide catalyst at 250 ° C (test 1). Reducing the reaction temperature to 200 degrees Celsius in the presence of aluminum oxide catalyst caused a sharp decrease in its yield (test 2) that indicating that the reaction could not be performed at a temperature below 250 degrees Celsius. In this method, we tried to use other catalysts that based on the results obtained in Table (1), the reaction yield relative to when aluminum oxide is used as a catalyst is significantly reduced. This reaction was carried out with similar conditions in the absence of catalyst, which did not result in not good yield despite perform the reaction (test 6). Therefore, the catalyst is essential for the complete progression of the reaction. In the next step, Lauramide was converted to lauronitrile in the presence of thionyl chloride and dimethylformamide. In this reaction, dimethylformamide is used in a catalytic amount (several drops), which significantly reduces the reaction time. This reaction was performed in the same conditions without the presence of solvent, which was less yield and purer than when the reaction was performed in the presence of solvent, according to the study of its mass spectra. This reaction takes place at ambient temperature and the increase in temperature and reflux causes the sample to destroy. In the last step, lauramide is converted to the product of lauryl amine in the presence of the reducing agent diborane. At this stage, the I_2/$NaBH_4$ system was used to reduce lauramide to lauryl amine. At the first stage, diborane prepared by the reaction of sodium borohydride with iodine in tetrahydrofuran solvent. After the addition of iodine to the solution of sodium borohydride and tetrahydrofuran, a rapid color change of the solution to red was observed along with the release of hydrogen gas, which after a few minutes of stirring at zero temperature, The color of the solution becomes completely white which indicates diborane has been prepared. Of course, at this stage, other solvents such as diethyl ether and triethylamine were also used to prepare diborane. After adding iodine to the solution of sodium borohydride and solvent, the color of the solution changed to red, but unlike tetrahydrofuran solvent, which after a few minutes the color of the solution changed to white and showed the formation of diborane in the solvent even after For several hours and with increasing temperature and distillation, no discoloration was observed as a sign of diborane formation. In the second step, lauramide was added to the borane which after addition, the oxygen of the carbonyl group of the lauramide was bonded to the empty orbital of boron and lauramide is reduced. The reaction is performed as a one-pot and there is no need to change the reaction container. In This method was tried, to obtain by changing the reaction conditions, including time, temperature, solvent and different proportions, optimal conditions. The results including yield and purity obtained from GC-Mas are given in the Table 2.

Table 2. Results of changing the synthesis conditions of lauryl amine from luramide.

Purity (%)	**Yield (%)**	**Time)h(**	**Mole ratio**		**Solvent**	**Entry**
			$NaBH_4$	**Lauramide**		
28	60	24	2	1	THF dry	1
45	94	72	2	1	THF dry	2
39	77	24	3	1	THF dry	3
72	92	72	3	1	THF dry	4
58	59	72	3	1	THF non-dry	5

63	88	24	5	1	THF dry	6
83	97	72	5	1	THF dry	7
86	98	72	5	1	THF dry	8
91	98	96	10	1	THF dry	9

Based on the results obtained in Table (2), the best reaction conditions are in 96 hours and the ratios of 1:5 of lauramide to sodium borohydride in dry tetrahydrofuran solvent are (test 8). A ratio of 1: 10 (test 9) compared to the ratio of 1: 5 (test 8) does not differ much in purity and yield, so the ratio is 1: 5 is more cost effective. Increase of time in ratios of 1: 3 at the same temperature from 24 (test 3) hours to 72 (test 4) hours increases the yield and purity. In this reaction, as shown in Table (2), an attempt was made to use non-dry tetrahydrofuran solvent. Based on the results, it was found that the reaction can also be performed in non-dried solvent (test 5). However, the percentage of purity and yield when using non-dry solvent was lower (58% purity and 59% yield) (test 5). Also, lauronitrile is converted to the product of lauryl amine in the presence of the reducing agent diborane. In this method, I_2 / $NaBH_4$ mixture in tetrahydrofuran solvent was used to reduce lauronitrile to lauryl amine, which leads to the preparation of diborane. After the addition of iodine to the solution of sodium borohydride and tetrahydrofuran, a rapid color change of the solution to red was observed with the release of hydrogen gas, which after a few minutes of stirring at zero degrees Celsius, the color of the solution becomes completely colorless (Indicates the preparation of diborane). In the second step, after preparing the diborane, lauronitrile is added to the same reaction flask and the reaction is performed as a one-pot. After the addition of lauronitrile to the diborane, the color of the solution first changes to a pale yellow, and by reflux it changes color to white over time, which can be considered as a sign of synthesis of lauryl amine. In This method was tried, to obtain by changing the reaction conditions, including time, temperature, solvent and different proportions, optimal conditions. The results including yield and purity obtained from GC-Mas are given in the Table 3.

Table 3. Results of changing the synthesis conditions of lauryl amine from lauronitrile.

Purity (%)	**Yield (%)**	**Time)h(**	**Temperature(^{0}c)**	**Mole ratio**		**Solvent**	**Entry**
				$NaBH_4$	**lauronitrile**		
38	72	4.5	75	3	1	THF dry	1
50	78	20	75	3	1	THF dry	2
21	69	24	75	4	1	THF dry	3
28	70	24	75	5	1	THF dry	4

Based on the results obtained in Table (3), the best reaction conditions are in 20 hours and 1: 3 ratios of lauronitrile to sodium borohydride in dry tetrahydrofuran solvent (test 2). In this reaction, an attempt was made to improve the reaction yield and purity by increasing the reducing ratio to lauronitrile or increasing the yield time. Unfortunately, contrary to expectations, the purity of the reaction decreased, and by repeating the reactions several times, no result was obtained, and this reaction did not show good reproducibility.

Conclusion

In sum we report an efficient and new method for the synthesis of lauryl amine from lauric acid. Examining the results of these four synthetic methods, it is observed that the best method for the synthesis of lauryl amine, is the use of liquid ammonia and aluminum oxide catalyst, at a temperature of 250 ° C and finally reduction lauramide to the lauryl amine is present in the presence of diborane reductant. This reaction has an overall yield of 63%. We report for the first time the reduction of Lauramide to lauryl amine using the diborane reductant and its optimization method.

Acknowledgements

We are grateful for the support of the faculty and chemistry research Institute of Imam Hossein Comprehensive University.

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