

# Simple conversion of fatty nitriles to primary fatty amines through iron(II)-tmphen catalyzed hydrosilylation

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**Abstract.** Hydrosilylation, a mild and save method, for reduction of fatty nitriles to primary fatty amines has been described. Using catalytic amount of iron(II)-tmphen complex, different long chain of fatty nitriles are reduced in good conversion number. The effect of the reaction times and the silane number toward the conversion was also studied in this work. The analysis by using gas chromatography showed that the the highest fatty nitriles conversion to its primary amines was achieved with nitrile:silane ratio 1:7 at 100°C for 24h under inert gas atmosphere. This commercially available and inexpensive catalyst and silane utilization offer a new method which is accessible for both laboratory and large scale primary fatty amines production.

## 1. Introduction

Fatty amine is a fatty acid derivative product which its demand is recently increasing. Amines is widely used as intermediate in many applications, such as surfactant, biocide, flotation agent, bitumen emulsifier, corrosion inhibitor, and also as solvent and polymer additive [1]. However, the increasing of fatty amine demand is not followed by its production. No contribution provided by the world major oil producer, Indonesia and Malaysia, is a factor which cause no significant increasing achieved in fatty amine number for 20 years [2]. In addition, a little development studied to find the most efficient method for production could be another factor.

There are some routes which can be applied for amine compound synthesis by using various methods, such as via amide [3-5], alcohol [6-8], nitro [9-11], and nitril [12-23]. The synthesis of amine via nitrile is widely applied because of its simplicity and less energy needed. A common method which has been applied for nitrile reduction is the use of metal hydride as the hydrogen source [17-20]. However, this method has some drawbacks, such as difficult handling and complicated post-reaction separation. Another method which could be applied is hydrogenation. However, this method commonly needs the presence of expensive metal catalyst, such as Pd [21], Ru [22], Ni, Co, and Pt [23], to increase the selectivity. In addition, the high temperature and pressure are often applied and this could increase the production cost.

In several years, hydrosilylation has attracted many reseachers because of its ability to reduce unsaturated compound in good chemo- and regioselectivity under milder conditions compared to the conventionally used reducing agents [24]. However, little is known about the hydrosilylation of C–N triple bonds, being the cyano group considered inert under the usual reaction conditions. The nitrile hydrosilylation had been investigated by using expensive cobalt complex [25], rhodium [26], ruthenium [27]. The study about nitrile hydrosilylation more focusing on aromatic nitriles conversion



and there is no one concern with fatty nitrile. In addition, recent study about fatty nitrile reduction more often applied hydrogenation method [28-29].

Recently, Das et al. [30] reported that hydrosilylation catalyzed by inexpensive transition metal compounds, like iron, could convert nitrile to primary amine in good yield. In their trial experiment which tried to reduce benzamide by inexpensive diethoxymethylsilane in the presence of ammonium hydridotriironundecarbonylate benzonitrile was the major product instead of the desired benzyl amine. On the other side, the trial which used benzonitrile as substrate and different iron complex as catalyst gave benzyl amine as mayor product up to 85%. Although Das et al. [30] more focusing on amide hydrosilylation, but those trial give important information for fatty nitrile reduction with saver, milder, and more inexpensive method than the other previous common method.

## 2. Experimental

### 2.1. Materials

Lauronitrile (dodecanenitrile), Pamitonitrile (hexadecanenitrile), and stearonitrile (octadecanenitrile) as substrates and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) as ligand was obtained from Tokyo Chemicals Industries. Iron(II) acetate ( $\text{Fe}(\text{OAc})_2$ ), diethoxymethylsilane, toluene, triethylamine, potassium hydroxide and ethyl acetate was purchased from Sigma Aldrich.

### 2.2. Instrumentation

Reduction yield in this work was analyzed using gas chromatography/mass spectrophotometer (GC/MS) and uncoupled gas chromatography. Fatty amine was isolated by preparative thin layer chromatography (TLC-P) and the isolate was analyzed by using GC/MS and nuclear magnetic resonance (NMR) spectroscopy.

### 2.3. Procedure

**2.3.1 Hydrosilylation of fatty nitriles.** The hydrosilylation procedure was adapted from Das et al. [30] procedure. Iron(II) acetate (10%mol), tmphen ligand (20%mol), 3mmol diethoxymethylsilane ( $(\text{EtO})_2\text{MeSiH}$ ) and 2mL dry toluene was added to a 25mL round-bottom flask. After that, the mixture was stirred for 15minutes at ambient temperature. Furthermore, 1mmol nitrile substrate (lauronitrile) was added to the flask, the the mixture was stirred again. After 10minutes, the mixture was started to heat up at  $100^\circ\text{C}$ . The reaction was stirred at constant temperature ( $100^\circ\text{C}$ ) for 24h under nitrogen atmosphere. After that, the mixture was cooled and 5mL potassium hydroxide solution (25% in MeOH) was added into the flask. Then, the mixture was stirred again for 3h. Note that every step was carried out under nitrogen atmosphere. Furthermore, the mixture was completely dried and the yield was extracted with ether. The extract solution was then filtered off using celite pad and washed with ether again. After then, the filtrate was dried using rotary evaporator for analysis. The yield was then analyzed using GC/MS Shimadzu-Qp-505 equipped with column HP-5MS and MS as detector.

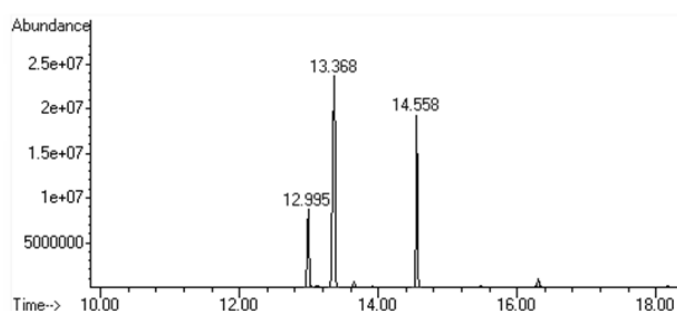
**2.3.2 Investigation of time reaction and silane number effect.** Reaction time was varied for 12h, 18h, and 24h, and another silane number (7mmol) was applied to investigate their effect toward the primary fatty amine yield. Every yield was then analyzed using gas chromatography equipped with column RTX-5 (Restec). Injection and column temperature was set  $250^\circ\text{C}$  and  $100^\circ\text{C}$  respectively and the mixture of nitrogen and air as a carrier. Column flow rate and linear velocity was set 1mL/minute and 27.7cm/s respectively. The best condition was then applied for other different long chain fatty nitriles.

**2.3.3 Isolation of primary fatty amines.** Fatty amine was isolated trough preparative thin layer chromatography (TLC) with the mixture of ethyl acetate-triethylamine as eluent. The isolation gave three spots on the TLC plate under ultraviolet 254nm. The isolate from each spots was gathered and redissolved into ether. After then, the isolates were analyzed using GC/MS.

### 3. Result and Discussion

#### 3.1. First trial of fatty nitriles hydrosilylation

Hydrosilylation of fatty nitriles in this study was carried out in nitrogen atmosphere to prevent oxidation which was not expected. Iron metal ions Fe(II) in complex is easy to be oxidized to Fe(III). In addition, atmospheric nitrogen was also required to prevent moisture that can cause damage to the silane. GC/MS analysis on the first trial of hydrosilylation result that we carried out for 24h with nitrile:silane ratio 1:3 toward lauronitrile substrate gave three main peaks in the chromatogram (Figure 1). Based on the MS database, each peak with a retention time of about 13.0, 13.4, and 14.5 minutes respectively show represent the primary amine product (dodecylamine), lauronitrile (substrate), and the secondary amine product (didodecylamine).

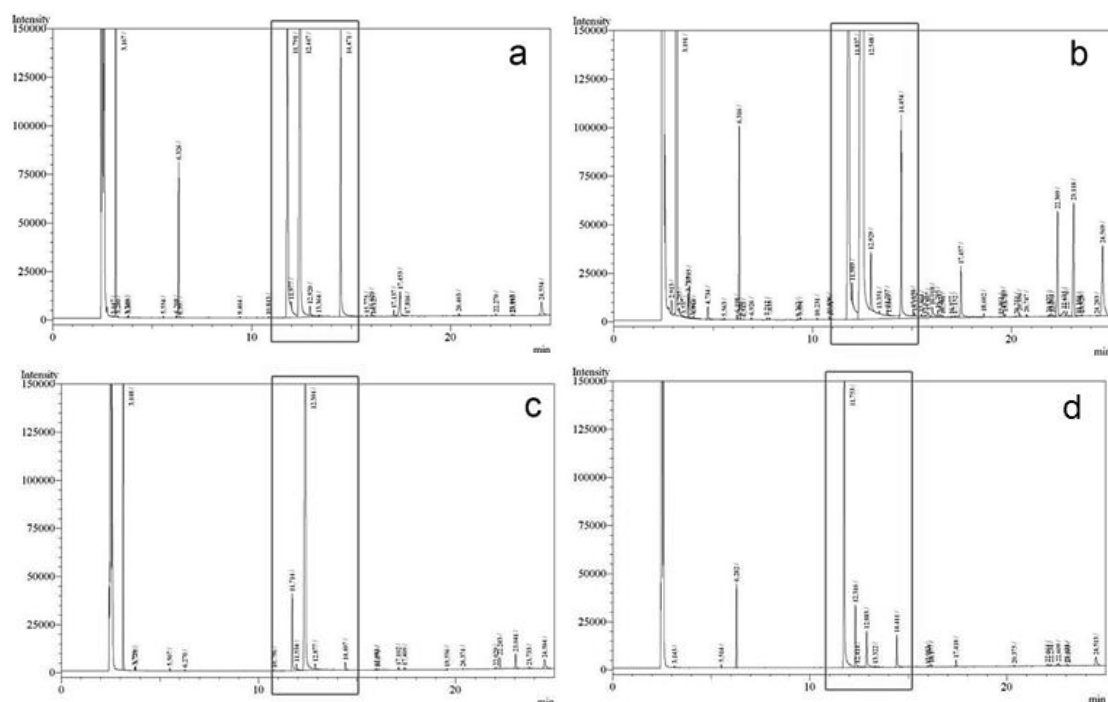


**Figure 1.** The chromatogram of the reaction mixture after hydrosilylation for 24h with nitrile:silane ratio 1:3.

The presence of dodecylamine compound was confirmed by fragmentation which let rearrangement resulting  $\text{CH}_2=\text{CHCH}_2^+$  ( $m/z$  41),  $\text{CH}_2=\text{CHCH}_2\text{CH}_2^+$  ( $m/z$  55)  $(\text{CH}_2)_5\text{NH}_2^+$  ( $m/z$  86),  $(\text{CH}_2)_5\text{CHNH}_3^+$  ( $m/z$  100) ion. Rearrangement has also occurred in lauronitrile fragmentation resulting  $\text{CH}_2=\text{C}=\text{NH}^+$ ,  $(\text{CH}_2)_3\text{C}=\text{NH}^+$ ,  $(\text{CH}_2)_5\text{C}=\text{NH}^+$ , and  $\text{CH}_2=\text{CH}-(\text{CH}_2)_5\text{C}\equiv\text{N}^+$  ion with  $m/z$  41, 69, 97, dan 124 respectively. In addition, the didodecylamine was confirmed by the fragment ion of  $(\text{CH}_2)_4\text{NH}^+$  ( $m/z$  71) and  $(\text{CH}_3(\text{CH}_2)_{10}\text{CH}=(\text{CH}=\text{CH}_2)\text{NH}^+$  ( $m/z$  210).

#### 3.2. Investigation of time reaction and silane number effect

Further analysis on the result of reaction time and nitrile:silan ratio effect investigation by only using gas chromatography was showed in Figure 2. Although we used different column from previous analysis but the chromatogram showed the same pattern. The peak with a retention time about 11.8, 12.5, and 14.5 minutes represent dodecylamine, lauronitrile, a didodecylamine respectively. Figure 2 showed that the reaction time gave a significant impact on the outcome of reduction through hydrosilylation. The longer reaction time, the higher primary amine yielded (Figure 2a-c). It could be explained as incomplete reaction occurred within 12h and 18h. This result was supported by the increasing of lauronitrile conversion number which is determined by comparing the area with the area of the standard (Table 1).



**Figure 2.** The chromatogram of lauritrile hydrosilylation with nitrile:silane ratio 1:3 for 24h (a), 18h (b), 12h (c), and with nitrile:silane ratio 1:7 (d) for 24h.

**Table 1.** Fatty nitriles conversion data from GC analysis.

Substrate	Treatment		% Conversion
	Nitrile:silane ratio	Time (h)	
Lauritrile (C12)	1:3	12	59.0
	1:3	18	60.0
	1:3	24	80.0
	1:7	24	99.4
Palmitonitrile (C16)	1:7	24	98.3
Stearonitrile (C18)	1:7	24	96.6

The conversion number in Table 1 showed no significant change for 12–18h but the chromatogram showed the increasing of didodecylamine peak (Figure 2b–c). It means that the formation of the secondary amine occurred over a period of 12–18h. Secondary amine is not an expected product in this study, but in some application it has been utilized since long ago. The sufficient availability of silane along the reaction was important for keeping lauritrile hydrosilylation providing its primary amine. It was proven with the yield resulted from the reaction with nitrile:silane ratio 1:7. The hydrosilylation with that ratio gave more than 99% nitrile conversion and high primary amine selectivity.

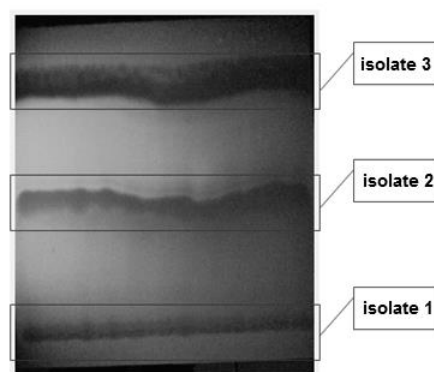
The hydrosilylation of the longer chain fatty nitriles (C16 and C18) showed a slightly decreasing on the conversion number but it was rated highly (> 97%) (Table 1). We supposed that this decreasing occurred because the steric effect began to emerge. However, the conversion of other longer chain fatty nitriles (> C18) is rarely carried out due to their little content number in palm oil. The conversion of the C16 and C18 gave very high primary hexadecylamine and octadecylamine with little secondary form.

The iron complex catalyst application in nitriles hydrosilylation showed the conversion number as good as the other previous catalyst [24]–[26]. However, by comparing the cost of the catalysts, this iron complex is still better than the other expensive catalysts. Comparing the methods for the same fatty nitrile substrates, the method in this work showed better conversion than the hydrogenation method

[[27]]–[[28]]. Besides, the addition of a large number of base, the high pressure and other special condition to achieve the best selectivity could raise the production cost which make these method disfavored. Thus, this research gave good information about an easier, saver, and milder method for the development of fatty amine production.

### 3.3. Isolation of primary fatty amine

The primary amines product in this work was isolated by using TLC preparative with ethyl acetate and triethylamine mixture (1:7) as a mobile phase. This separation of components in the post-hydrosilylation mixture, in this case lauronitrile as substrate, showed three spots under UV light with wavelength 254nm (Figure 3). Qualitative analysis was applied by comparing it with the spots of lauronitrile and the ligand. Thus, we recognized that the spot of isolate 1 and 3 represent the ligand and lauronitrile respectively. Although we could not ascertain what isolate 2 represent before but we supposed that it represented fatty amines.



**Figure 3.** Preparative TLC plate of the hydrosilylation product after isolation under UV light 254nm.

Further analysis by using GC/MS on the isolate 2 and 3 gave certainty that those spots represented dodecylamine (primary lauroamine) and lauronitrile respectively. The didodecylamine (secondary lauroamine) was not further analyzed in this work because it was a byproduct. However, we supposed that didodecylamine was separated in the area between the isolate 2 and isolate 3. In addition, the  $^1\text{H}$  NMR spectrum of the isolate 2 showed 5 signals at  $\delta = 0.84$  (3H,  $-\text{CH}_3$ ), 1.22 (18H,  $-\text{CH}_2$ ), 1.40 (2H,  $-\text{CH}_2$ ), 2.63 (2H,  $-\text{CH}_2$ ), and 4.92 (2H,  $-\text{NH}_2$ ).

## 4. Conclusion

Hydrosilylation catalyzed by iron(II)-tmphen complex could be applied as a saver, milder, and more inexpensive method in fatty nitriles reduction providing its analogue primary amines. Hydrosilylation with nitrile:silane ratio 1:7 for 24h at 100°C under nitrogen atmosphere gave high nitrile conversion and selectivity in producing primary fatty amines. The pure product could be obtained by chromatography separation using ethyl acetate:triethylamine mixture (1:7) as eluent.

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