Synthesis of R_2N-R' dissymmetric amines from nitriles and hexamethylenetetramine over nickel catalysts

X. Caillault, Y. Pouilloux, J. Barrault *

*Laboratoire de Catalyse, URA CNRS 350, ESIP, 40, avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

Abstract

The synthesis of methylated tertiary amines ($RN(CH_3)_2$ or R_2NCH_3) was carried out at low pressure and temperature ($P = 0.1$ MPa, $T \leq 160°C$) from fatty nitriles, hydrogen and hexamethylenetetramine (HMTA) over a nickel catalyst. HMTA, the methylating agent, is both very reactive and selective with the final selectivity depending on the experimental conditions. Indeed, over the same nickel catalyst, methyldidodecylamine is selectively obtained at 80–100°C while at 140–160°C dimethyldodecylamine is the main product starting from dodecylnitrile. These products would result from the reactions of didodecylamine or of dodecylamine (issued from the hydrogenation of dodecylnitrile) with methylimine ($CH_2=NH$) or with N-methylmethylimine ($CH_3-N=CH_2$) formed from the catalytic decomposition of HMTA.

1. Introduction

Fatty aliphatic amines which are important intermediates for the preparation of surfactants are generally prepared in multistep processes from fatty alcohols or acids [1]. In our laboratory, we studied the direct synthesis of dissymmetric tertiary amines (R_2NCH_3 or $RN(CH_3)_2$) from acids, esters or nitriles over multifunctional catalysts i.e.,

$$RC \equiv N + H_2 + \text{"Methylating agent"} \diagup^{(RCH_2)_2N-CH_3}_{\searrow RCH_2-N(CH_3)_2}$$
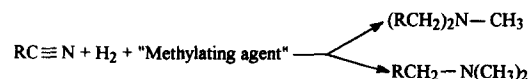
The selectivity of this type of reaction depends on the competitive steps of the methylation of the primary amine (steps 1 and 2) and of the conden-
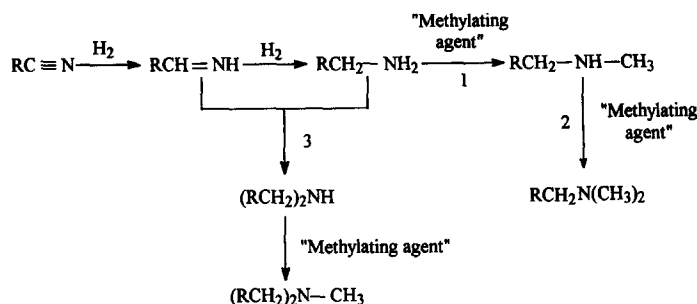
sation of the same primary amine with the corresponding imine (step 3) as depicted in Scheme 1.

The intermediate formation of $(RCH_2)_2NH$ has been described by Von Braun et al. [2] and more recently by Greenfield [3].

Generally, methanol is the methylating agent [4] but the alcohol dehydrogenation reviewed by Kliger et al. [5] or Baiker et al. [6] is the rate limiting step [7,8]. Moreover, water formed during the reaction is a strong catalyst modifier which minimizes both the activity and the selectivity [9]. It would be more convenient to use other methylating agents.

In the literature, hexamethylenetetramine (HMTA) [10], dimethylcarbonate [11] or syngas [12] are proposed for these reactions. Among them, HMTA which has numerous other applications [13] is potentially the most accurate com-

* Corresponding author.

$$RC \equiv N \xrightarrow{H_2} RCH = NH \xrightarrow{H_2} RCH_2 - NH_2 \xrightarrow[1]{\text{"Methylating agent"}} RCH_2 - NH - CH_3$$

$$RCH_2 - NH - CH_3 \xrightarrow[2]{\text{"Methylating agent"}} RCH_2N(CH_3)_2$$

$$\xrightarrow{3} (RCH_2)_2NH \xrightarrow{\text{"Methylating agent"}} (RCH_2)_2N - CH_3$$

Scheme 1.

pound and was recently used for the N-methylation of nitriles and amines involving a nickel catalyst [10]. In our laboratory, we studied the reactivity of HMTA with different nitrogen compounds over solid catalysts so as to increase the selectivity and to determine the substitution mechanism as well as the nature of the active sites. In this paper, we report the first results obtained in the reaction of dodecylnitrile with HMTA over a nickel hydrogenation catalyst.

2. Experimental

2.1. Catalytic reactions

The catalytic reactions were carried out at atmospheric pressure in a batch reactor with a continuous hydrogen flow. Dodecylnitrile $(C_{11}H_{23}C=N)$ and didodecylamine $((C_{12}H_{25})_2NH)$ were the reagents. At the start of the reaction, methanol or HMTA $((CH_2)_6N_4)$ used as methylating agents were introduced and mixed with the N-reagent and the solvent (dodecane).

The reaction mixture was continuously stirred with a magnetic agitation at 800 rpm. Moreover, we verified that the activity and the selectivity in the hydrogenation or methylation were independent of the agitation rate when it was above 600 rpm.

The liquid and gas phases were analyzed by off-line gas chromatographs respectively equipped with capillary columns (SGE-25 QC2/BP1–0.1 and SGE-25 QC3/BP1–5.0)

2.2. Nickel catalyst

The Ni 5256P catalyst (from Engelhard) used in these experiments was composed of nickel (31 wt%), nickel oxide (32 wt%), magnesium oxide (13 wt%) and silica (24 wt%) with a surface area of 250 $m^2 \cdot g^{-1}$ and a mean particle size of 150 μ. The solid was reduced with hydrogen at 420°C for 9 h before each catalytic test.

3. Results
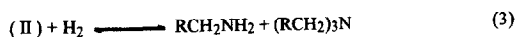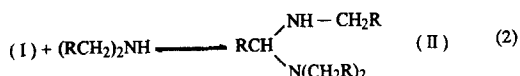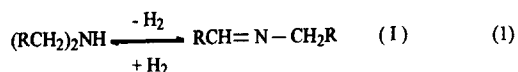
3.1. Preliminary study of the reactions of methanol or HMTA with amine or nitrile

In the first part of our work, we determined the rate of N-methylation of didodecylamine and dodecylnitrile with methanol or hexamethylenetetramine.

N-methylation of didodecylamine with methanol or HMTA

Results reported in Table 1 show that the N-methylation of didodecylamine is faster with HMTA than with methanol.

Indeed with methanol, the methyldidodecylamine selectivity was around 65% for a 20% conversion after 45 h reaction. On the other hand with HMTA, the selectivity was around 96% at complete conversion after only 10 h. The rate of N-methylation with HMTA was far greater than the rate of secondary amine dismutation via:

$$(RCH_2)_2NH \underset{+H_2}{\overset{-H_2}{\rightleftharpoons}} RCH=N-CH_2R \quad (I) \qquad (1)$$

$$(I) + (RCH_2)_2NH \longrightarrow RCH\begin{array}{l} {}^{\nearrow NH-CH_2R} \\ {}_{\searrow N(CH_2R)_2} \end{array} \quad (II) \qquad (2)$$

$$(II) + H_2 \longrightarrow RCH_2NH_2 + (RCH_2)_3N \qquad (3)$$

Thus the selectivity into $RN(CH_3)_2$ is also very low, which is quite in agreement with previous results [10].

N-methylation of dodecylnitrile with methanol or HMTA

When dodecylnitrile was used as starting material, the results presented in Table 2 show that the reaction rates are also different with CH_3OH and HMTA.

Moreover, due to the change of the product distribution with reaction time also reported in Table 2, we can observe that in the presence of methanol, the imine (I) is slowly hydrogenated into didodecylamine and enamine $[(C_{12}H_{25})_2N-CH=CH-C_{10}H_{21}]$ is then obtained from these two compounds. These results show that the rate of the methylation step with methanol is very slow.

On the other hand, with HMTA, dimethyldodecylamine is the main product (70%), and methyldidodecylamine the main side product (30%). In this case, the methylation of primary amine is faster than the formation of R_2NH (and of R_2N-CH_3).
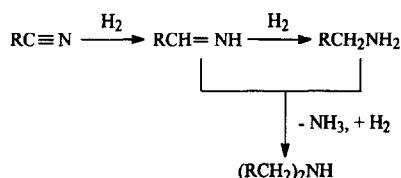
3.2. Reaction of dodecylnitrile or of HMTA in the presence of a nickel catalyst

In order to show the effect of HMTA on the activity and on the product distribution, we studied first the hydrogenation of nitrile and the hydrogenolysis of HMTA.

Hydrogenation of dodecylnitrile

The activity of the nickel catalyst and the main products obtained at 80°C and 140°C in the absence of HMTA are reported in Table 3.

The results show that dodecylamine and didodecylamine are the main products at low temperature. An increase of the reaction temperature from 80 to 140°C significantly changes the reaction, and didodecylamine is formed with a selectivity of 95%. At 140°C the rate of condensation of the primary amine with the corresponding imine is apparently increased significantly compared to the rate of nitrile hydrogenation;

$$RC\equiv N \xrightarrow{H_2} RCH=NH \xrightarrow{H_2} RCH_2NH_2$$

$$\downarrow \qquad \qquad \downarrow$$

$$\searrow \quad -NH_3, +H_2$$

$$(RCH_2)_2NH$$

This result is in agreement with those of previous work reported in the literature [14,15]

Hydrogenolysis of hexamethylenetetramine (HMTA)

This reaction has been studied under the same experimental conditions as the hydrogenation of nitrile.

In the absence of the nickel catalyst, the HMTA is not transformed.

In the presence of the catalyst, the results of Table 4 show that the HMTA is converted into monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA). (Ammonia is also formed during the reaction.)

Table 1
N-Methylation of didodecylamine with methanol or with HMTA

Methylating agent	Time (h)	Conversion of R_2NH (%)	Selectivity (%)		
			$RN(CH_3)_2$	R_2N-CH_3	R_3N
CH_3OH	1.5	1.4	–	100	–
	31	17.4	20.6	62.9	15.5
	45.5	19.4	21.6	62.3	16.1
HMTA	1	25.5	4.5	91.7	3.8
	6.5	96.3	2.4	96.3	1.3
	10	99	2.4	96.3	1.3

$w_{cata} = 0.2$ g; $V_{CH_3OH} = 2$ ml or $w_{HMTA} = 7$ g; $w_{R_2NH} = 3.2$ g. $V_{dodecane} = 65$ ml; $F_{H_2} = 21 \cdot h^{-1}$; $T = 140°C$.

Table 2
N-Methylation of dodecylnitrile with HMTA or methanol

Methylating agent	t	$C_{R'CN}$	Selectivity (%)							
	(h)	(%)	RNH_2	$RNH–CH_3$	$RN(CH_3)_2$	'imine'[a]	R_2NH	$R_2N–CH_3$	R_3N	'enamine'[b]
CH$_3$OH	1	30	18	–	–	74.9	3.2	–	–	3.9
	7	56.5	2.9	–	–	82	4.5	0.7	1	8.9
	32	79.4	5.8	1.3	–	66	9	1.9	3.9	12.1
	46	99	9	–	0.8	3.9	81.3	–	–	5
HMTA	1	38	–	15.6	43.8	23	8.6	5.2	–	3.8
	4	96.7	–	4.8	61	0.4	20.2	13	0.3	0.3
	7	100	–	–	69.4	–	9.2	21.1	0.3	–
	22	100	–	–	69.4	–	–	30.4	0.2	–

$w_{cata} = 0.2$ g; $V_{CH_3OH} = 2$ ml or $w_{HMTA} = 7.5$ g; $V_{R'CN} = 3.9$ ml. $V_{dodecane} = 65$ ml; $F_{H_2} = 2\ 1 \cdot h^{-1}$; $T = 140°C$.
[a] $C_{12}H_{25}N=CH–C_{11}H_{23}$.
[b] $(C_{12}H_{25})_2N–CH=CH–C_{10}H_{21}$.

Table 3
Hydrogenation of dodecylnitrile

Temperature	Time	Conversion of R'CN	Selectivity (%)				
(°C)	(h)	(%)	RNH_2	'imine'[a]	R_2NH	R_3N	'enamine'[b]
80	1	90.5	58.3	16.1	17.8	0.4	7.4
	7	100	54.4	–	44.8	0.8	–
	22	100	50.3	–	48.3	1	0.4
140	1	98.6	36.7	2	58.6	1.8	0.9
	7	100	5.4	–	91.5	3.1	–
	23	100	0.9	–	95.3	3.8	–

$w_{cata} = 0.2$ g; $V_{R'CN} = 3.9$ ml; $V_{dodecane} = 65$ ml; $F_{H_2} = 2\ 1 \cdot h^{-1}$.
[a] $C_{12}H_{25}N=CH–C_{11}H_{23}$.
[b] $(C_{12}H_{25})_2N–CH=CH–C_{10}H_{21}$.

If the rate of reaction was low at 80°C, we observed a significant increase at 140°C. Moreover the product distribution is also largely modified because DMA instead of TMA is the main product. In fact, besides the formation of TMA as a primary product there must be also the formation of MMA, DMA and NH$_3$. We suggest therefore that secondary transformations of MMA, DMA into TMA occur specially at low temperature. At higher temperatures the rates of these reactions are different and the selectivity of MMA or DMA increases. But at 140°C the development of the selectivity with reaction time also shows that there is a modification of the catalyst and perhaps a decrease of the secondary reactions of MMA or DMA into TMA.

Table 4
Hydrogenolysis of HMTA

Temperature	Time	Conversion of HMTA	Selectivity (%)		
(°C)	(h)	(%)	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
80	1	0.3	–	–	100
	7	1.5	–	–	100
	23	3.6	–	–	100
140	1	1.6	4.5	13.6	81.9
	7	11.4	6.3	30.4	63.3
	22	23.5	8.7	48.5	42.8

$w_{cata} = 0.2$ g; $w_{HMTA} = 7.5$ ml; $V_{dodecane} = 65$ ml; $F_{H_2} = 2\ 1 \cdot h^{-1}$.

Table 5
Transformation of HMTA in the presence of dodecylnitrile

Temperature	Time	Conversion of HMTA	Selectivity (%)		
(°C)	(h)	(%)	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
80	1	0.1	–	–	100
	7	1	–	–	100
	23	2.2	–	–	100
140	1	2.6	21.6	27.9	50.5
	7	13.9	18.7	41.7	39.6
	22	24.8	7.4	47.5	45.1

$w_{cata} = 0.2$ g; $w_{HMTA} = 7.5$ g; $V_{R'CN} = 3.9$ ml; HMTA/R'CN = 3 (mol). $V_{dodecane} = 65$ ml; $F_{H_2} = 2$ l·h^{-1}.

Conclusion

With these experiments at low temperature (80°C), the dodecylnitrile is mainly hydrogenated into dodecylamine while HMTA is transformed into TMA. At 140°C, the didodecylamine is the main product and HMTA is converted more rapidly into DMA and TMA.

3.3. Reaction of dodecylnitrile with hexamethylenetetramine

Hydrogenolysis of hexamethylenetetramine in the presence of dodecylnitrile

From results reported in Table 5, the rate of transformation of HMTA at 80°C is not modified by the presence of nitrile (see also Table 4) and TMA is always the major product. At 140°C, if the conversion of HMTA is also more or less the same in the presence of the nitrile, we observe at the beginning of the reaction a significant change of selectivity. Indeed DMA and especially MMA are produced faster in the presence of the dodecylnitrile. It seems that the competitive adsorption of nitrile and/or of the reaction products modify the secondary reactions starting from MMA and DMA. Moreover the selectivity changes with reaction time are important (see figure 1) and will be discussed later.

N-Methylation of dodecylnitrile with HMTA

From results reported in Table 6, we can see that at a temperature of 80–100°C, didodecylamine and methyldidodecylamine are the main prod-

ucts while at 140–160°C dimethyldodecylamine is obtained with a selectivity of more than 80%.

From the general scheme presented in the introduction for the formation of these amines, we can observe that: at 80°C, in the presence of HMTA, the rate of step 3 (of condensation of amine) is more significant than the rate of methylation of the primary amine (steps 1 and 2). In fact this result is due to the very low conversion of HMTA and to the small formation of MMA and DMA which are the true methylating agents (see also Table 5).

At 140°C we can observe from Table 3 that dodecylnitrile was selectively transformed into didodecylamine. When the reaction is carried out in the presence of HMTA, nitrile is converted into dimethyldodecylamine (Table 6). This result means that, according to the reaction scheme presented above, the methylation (steps (1) and (2)) becomes faster than the amine condensation (step 3). In fact, the transformation of HMTA into MMA and DMA is more significant at 140°C than at 80°C and the intermediate primary amine is methylated more rapidly.

The decrease of the nitrile conversion when the temperature rises from 80°C to 140°C could be also due to the large increase of the conversion of HMTA. Indeed the competitive adsorption on active sites of HMTA, light amines and nitrile could decrease significantly the nitrile coverage.

If we now compare at a temperature of 140°C the changes with reaction time, of the products distribution from HMTA (Fig. 1) and from dodecylnitrile (Fig. 2) it seems that:

1. During the first part of the reaction, MMA and/or DMA are consumed both for the methylation of the dodecylamine and for the formation of TMA. Indeed statistically the decomposition of HMTA produces TMA with a molar selectivity of 25% which would be the maximum value obtained (see reactions below).

2. When the hydrogenation of N-dodecyldodecylimine into didodecylamine occurs, followed by the consecutive N-methylation, the relative formation of TMA and MMA decreases while there is a continuous increase of the DMA. It can be

Table 6
N-Methylation of dodecylnitrile with HMTA

Temperature	Time	$C_{R'CN}$	Selectivity (%)					
(°C)	(h)	(%)	RNH_2	$RNH–CH_3$	$RN(CH_3)_2$	R_2NH	$R_2N–CH_3$	Others
80	1	31.5	31.4	–	3.4	24.3	4.3	36.6
	7	99	13.9	1.7	3.3	64.6	10.6	5.9
	23	100	–	1.2	7.8	59.9	24.1	7
100	1.5	65.8	16.3	4.2	10.5	39	13.1	16.9
	6	100	1.5	2.8	18.5	47	26.5	3.7
	23	100	–	–	21.1	8.8	65.6	4.5
140	1	38	–	15.6	43.8	8.6	5.2	26.8
	6	99	–	–	68.3	13	18.4	0.3
	22	100	–	–	69.4	–	30.4	0.2
160	1	29.9	4.1	18.8	54.3	2.4	3.3	17.1
	6	86.4	0.5	7	75	8.4	6.3	2.8
	23	99.6	–	–	83	5	10	2

$w_{cata} = 0.2$ g; $w_{HMTA} = 7.5$ g; $V_{R'CN} = 3.9$ ml; HMTA/R'CN = 3 (mol) $V_{dodecane} = 65$ ml; $F_{H_2} = 2 \, 1 \cdot h^{-1}$.
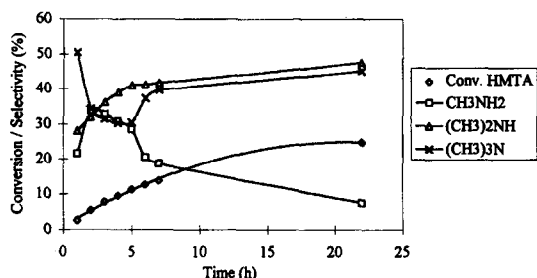

Fig. 1. Transformation of HMTA in the presence of dodecylnitrile at 140°C.
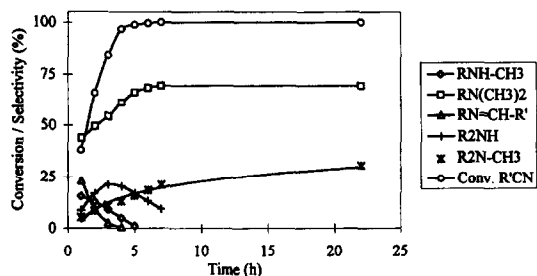

Fig. 2. Reaction of dodecylnitrile with HMTA at 140°C.

concluded that MMA rather than DMA is involved in the methylation of the secondary amine; otherwise the selectivity to DMA and to MMA would vary in the opposite way.

4. Discussion

We have shown in this work that HMTA can act as a methylating reagent of fatty amines and

that this reaction is catalyzed with a nickel catalyst. More precisely the catalytic decomposition of HMTA forms MMA and DMA which are the 'real' methylating reagents.

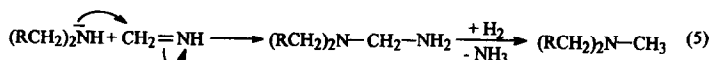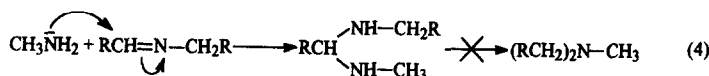These light amines, TMA and ammonia are formed from HMTA via the following reactions;
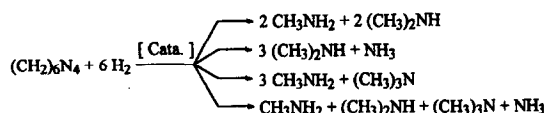
As TMA was the main product at 80°C, MMA and DMA are also converted into TMA;

$$3MMA \rightarrow TMA + 2NH_3$$

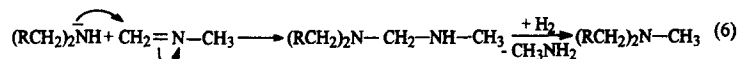$$2DMA \rightarrow TMA + MMA$$

$$MMA + DMA \rightarrow TMA + NH_3$$
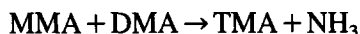
On the other hand at 140°C, the product distribution is modified significantly; MMA and DMA appear in the gas phase in amounts such that the rate of decomposition of HMTA in these products is higher than the rate of reconversion, especially in the presence of nitrile. Among all of these possible reactions, it is difficult to propose the preferential way(s) of HMTA hydrogenolysis.

Nevertheless if we consider methylamine and didodecylamine as reagents, two methylation steps can be proposed: the reaction of methyla-

$$CH_3\overset{\frown}{N}H_2 + RCH=N-CH_2R \longrightarrow RCH\overset{NH-CH_2R}{\underset{NH-CH_3}{}} \xrightarrow{\times} (RCH_2)_2N-CH_3 \quad (4)$$

$$(RCH_2)_2\overset{\frown}{N}H + CH_2=NH \longrightarrow (RCH_2)_2N-CH_2-NH_2 \xrightarrow[-NH_3]{+H_2} (RCH_2)_2N-CH_3 \quad (5)$$

Scheme 2.

$$(RCH_2)_2\overset{\frown}{N}H + CH_2=N-CH_3 \longrightarrow (RCH_2)_2N-CH_2-NH-CH_3 \xrightarrow[-CH_3NH_2]{+H_2} (RCH_2)_2N-CH_3 \quad (6)$$

Scheme 3.

mine with N-dodecyldodecylimine ($RCH=N-CH_2R$) or the reaction of methylimine (resulting from the catalytic dehydrogenation of methylamine) with didodecylamine. However, only the second reaction can explain the formation of methyldidodecylamine (Scheme 2) as well as the formation of methyldodecylamine or of dimethyldodecylamine from dodecylamine and methylimine.

From dimethylamine (and the intermediate N-methylmethylimine), similar reactions lead to methyldidodecylamine when didodecylamine is the reagent or to methyldodecylamine and dimethyldodecylamine when the reagent is dodecylamine. However the variation of the MMA selectivity observed during the reaction of dodecylnitrile with HMTA seems to indicate that the step (6) (Scheme 3) is less important than the step (5) Scheme 2.

5. Conclusion

Methyldodecylamine(s) can be prepared from the hydrogenation and N-methylation of dodecylnitrile with HMTA in the presence of a nickel catalyst.

Moreover, it is possible to obtain selectively either the methyldidodecylamine at low temperature (80–100°C) or the dimethyldodecylamine at a higher temperature (140–160°C)

This work also demonstrates that during the reaction, hexamethylenetetramine is transformed into light amines (MMA, DMA and TMA) and ammonia. Two of these amines DMA and especially MMA could act as methylating reagents (via the corresponding imines) of the intermediate dodecylamine and didodecylamine.

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