

# Amine synthesis via carbonylation reactions: aminomethylation

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## Abstract

The preparation of aliphatic amines and alicyclic diamines by reaction of olefins, synthesis gas and dimethylamine, known as aminomethylation, was investigated. Synthesis involves homogeneous rhodium and ruthenium catalysts or mixtures thereof at very low concentrations. Employing 3–12 ppm Rh and 50–100 ppm Ru results in up to 97% selectivity towards the amines at conversions of up to 98% if aliphatic mono-olefins are used as starting materials. At high catalyst concentrations (173 ppm Rh, 2660 ppm Ru) the corresponding diamine is obtained from dicyclopentadiene in 89% yield. The influence of reaction parameters and catalyst ratios on the *n/i*-selectivity of the product indicates the scope as well as the limits of such a multi-step synthesis for a commercial process. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Amine synthesis; Hydroformylation; Aminomethylation

## 1. Introduction

Since its discovery in 1938 by Otto Roelen at Ruhrchemie, the hydroformylation reaction has grown to become one of the most important homogeneously catalysed processes with about  $7 \times 10^6$  t/a of total capacity today [1–3]. This reaction, also known as “oxo synthesis”, is important in many multi-step and multi-component syntheses that have been developed subsequently. Examples are *N*-acetylated amino acids

from olefins, synthesis gas and amides, called amidocarbonylation [4,5], or amines from olefins, synthesis gas and ammonia or derivatives thereof, called aminomethylation or oxoamination [6–8].

The aminomethylation reaction using ammonia or primary or secondary amines as an alternative to the commercially employed routes such as ammonolysis of alcohols, reductive amination of aldehydes or hydrogenation of nitriles (Fig. 1) has been described recently both in the literature and patents [9–13]. Most examples reveal the use of high catalyst concentrations of up to several thousand parts per million of active metals with respect to olefins.

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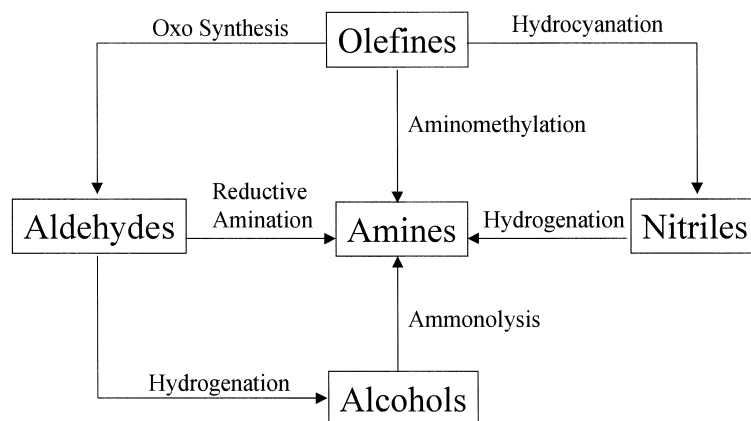
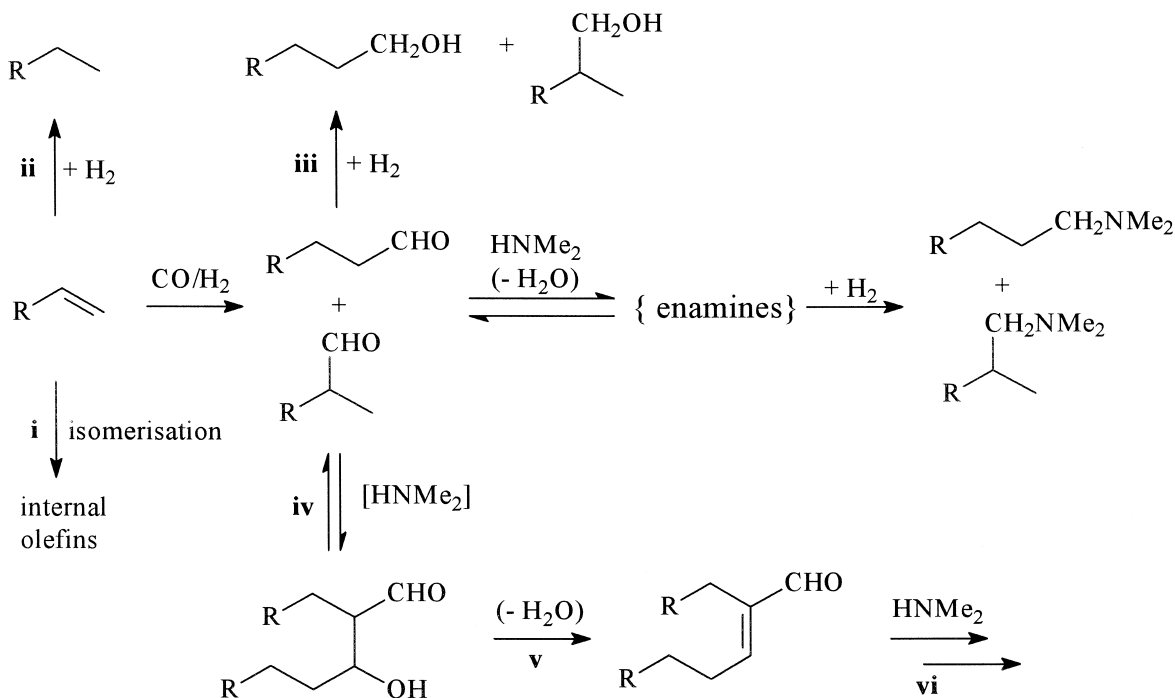


Fig. 1. Syntheses pathways to amines.

In this paper, we describe early results for the preparation of tertiary aliphatic monoamines by aminomethylation from 1-olefins using very low catalyst concentrations and the synthesis of bis-*N,N*-dimethylaminomethyl-tricyclodecane from

dicyclopentadiene (DCP). In the interests of constant product quality emphasis is placed on control of the *n/i*-selectivity. Therefore, the influence of reaction parameters and catalyst concentration on the *n/i*-selectivity is discussed



Scheme 1. Main reaction pathways in aminomethylation reaction.

Table 1  
Syntheses of *N,N*-dimethylalkylamines from olefins, syngas and dimethylamine

Entry	Rh <sup>a</sup> [ppm]	Ru <sup>b</sup> [ppm]	Ru/ Rh	Olefin	Olefin [g]	Olefin/Rh [m/m] (Olefin/Ru)	DMA [g]	<i>i</i> -C <sub>3</sub> -ol [g]	Reaction conditions	Conversion <sup>c</sup> [%]	Selectivity <sup>d</sup> [%] ( <i>n/iso</i> -ratio)
1	6	50	8.3	1-Hexene	168	198000	120	200	150 bar, 150°C, 5 h	97	95
2	6	50	8.3	1-Hexene	336	396000	240	–	150 bar, 150°C, 8 h	92	93
3	60	–	–	1-Hexene	168	19800	90	200	100 bar, 140°C, 3 h	66	42
4	120	–	–	1-Hexene	168	9900	90	200	100 bar, 140°C, 3 h	96	49
5	180	–	–	1-Hexene	168	6600	90	200	100 bar, 140°C, 3 h	98	83
6	240	–	–	1-Hexene	168	5000	90	200	100 bar, 140°C, 3 h	98	88
7	6	50	8.3	1-Octene	168	150000	90	200	150 bar, 150°C, 5 h	90	97
8	6	50	8.3	1-Octene	336	300000	180	–	150 bar, 150°C, 8 h	97	72
9	40	–	–	1-Dodecene	336	14900	90	200	100 bar, 140°C, 3 h	98	81
10	60	–	–	1-Dodecene	336	9900	90	200	100 bar, 140°C, 3 h	98	87
11	80	–	–	1-Dodecene	336	7500	90	200	100 bar, 140°C, 3 h	99.5	93
12	100	–	–	1-Dodecene	336	5900	90	200	100 bar, 140°C, 3 h	99.5	97
13	3	50	17	1-Dodecene	336	198000	120	–	150 bar, 150°C, 6 h	87	94
14	6	50	8	1-Dodecene	336	99000	120	–	150 bar, 150°C, 6 h	95	93
15	10	50	5	1-Dodecene	336	59500	120	–	150 bar, 150°C, 6 h	90	93
16	3	50	17	1-Dodecene	168	198000	60	200	150 bar, 150°C, 5 h	92	96 (0.98–1.0)
17	3	50	17	1-Dodecene	168	198000	60	200	100 bar, 150°C, 5 h	61	94
18	3	50	17	1-Dodecene	168	198000	60	200	50 bar, 150°C, 5 h	54	90
19	6	60	10	1-Dodecene	168	99000	60	200	150 bar, 150°C, 5 h	96	95.5 (1.08–1.25)
20	10	50	5	1-Dodecene	168	59500	60	200	150 bar, 150°C, 5 h	98	95 (1.28–1.33)
21	10	100	10	1-Dodecene	168	59500	60	200	150 bar, 150°C, 5 h	97.5	96 (1.36–1.42)
22	12	60	5	1-Dodecene	168	49600	60	200	150 bar, 150°C, 5 h	98.5	96
23	–	100	–	1-Dodecene	168	(5900)	60	200	150 bar, 150°C, 5 h	77	95
24	–	60	–	1-Dodecene	168	(9900)	60	200	150 bar, 150°C, 5 h	73	96
25	–	50	–	1-Dodecene	168	(11900)	60	200	150 bar, 150°C, 5 h	68	96

<sup>a</sup>Concentration with respect to olefin. Rh as RhCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> or Rh(2-ethylhexanoate)<sub>3</sub>.

<sup>b</sup>Concentration with respect to olefin. Ru as RuCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> or Ru(acetylacetonate)<sub>3</sub>.

<sup>c</sup>Conversion of olefin.

<sup>d</sup>Selectivity to *N,N*-dimethyl-*n/iso*-alkylamines.

in some detail. Such amines are of potential interest, e.g., for manufacturing surfactants or as template components in zeolite syntheses.

## 2. Experimental

Synthesis gas (CO/H<sub>2</sub>; 1:1 molar ratio) supplied from internal sources was used. All other reagents were used as received from external suppliers and were not further purified. A typical procedure for the preparation of *N,N*-dimethyl-*n,iso*-tridecylamine from 1-dodecene, syngas and dimethylamine is as follows.

A stainless steel pressure reactor (1 l) was charged under a nitrogen atmosphere with 200 ml isopropanol, 33.1 mg (83 mmol) Ru(acac)<sub>3</sub><sup>1</sup>, 4.3 mg (16.3 mmol) RhCl<sub>3</sub>·(H<sub>2</sub>O)<sub>3</sub>, 168 g (1 mol) 1-dodecene and 60 g (1.33 mol) dimethylamine and then heated to 150°C under a CO/H<sub>2</sub> pressure of 20 bar with vigorous stirring. On reaching the reaction temperature, the pressure was raised to 150 bar CO/H<sub>2</sub> and held constant for 5 h. After cooling to ambient temperature, the remaining gas was vented from the

<sup>1</sup> acac: acetylacetonate.

Table 2  
Isomerisation of 1-dodecene<sup>a</sup>

Product	3 ppm Rh			50 ppm Ru			3 ppm Rh/ 50 ppm Ru		
	Time [h]								
	4	8	12	4	8	12	4	8	12
1-Dodecene	93.8	93.4	92.5	27.0	26.6	26.9	80.9	60.1	53.4
Internal dodecenes	1.6	2.0	2.9	69.1	70.4	69.2	14.5	35.2	41.6

<sup>a</sup>Educt composition: 95% 1-dodecene, 0.5% internal dodecenes, 4% branched C<sub>12</sub>-olefins, 0.5% C<sub>10</sub>- and C<sub>14</sub>-olefins. Reaction conditions: 150°C, 150 bar N<sub>2</sub>. All values are in % by GC.

reactor and the mixture removed from the autoclave. The products were analysed by gas chromatography. Water contents were determined using standard procedures (Karl Fischer titration). Rh and Ru contents of the aqueous and organic phases were determined by atomic absorption spectroscopy analysis.

### 3. Results and discussion

Emphasis was placed on the preparation of tertiary amines and di-tertiary diamines from linear 1-olefins and DCP via aminomethylation reaction. The main reaction pathways are depicted in Scheme 1. Besides the desired reaction to form the aminomethylation products, several side-reactions have to be considered:

- (i) isomerisation of the olefin,
- (ii) hydrogenation of the olefin,
- (iii) hydrogenation of the in situ formed aldehydes to the corresponding alcohols,
- (iv) aldol reaction of the formed aldehydes,
- (vi) dehydration of the aldol adducts, and
- (vii) reaction of the resulting enal product with the amine.

The reaction of several olefins such as 1-hexene, 1-octene, 1-dodecene and DCP with CO/H<sub>2</sub> and dimethylamine in the presence of rhodium and/or ruthenium catalysts was investigated. The reactions were performed with isopropanol as solvent or without solvent. Reactions take place at 20–250 bar and temperatures from 90 to 160°C. Some of the experimental

results are shown in Tables 1 and 2. The major products with respect to the starting olefins are linear and branched *N,N*-dimethylalkylamines. Dimethylamine also reacts to some extent with carbon monoxide to form dimethylformamide. Under certain conditions, this becomes the main reaction pathway for dimethylamine, resulting in a significant deficiency of this reactant. Therefore, increased formation of other by-products, such as alcohols or aldol reaction products, was observed.

#### 3.1. Aliphatic 1-olefins

Typical results with 1-olefins are summarised in Table 1. From this and other experiments, we found 100 bar syngas pressure and 140°C to be the best reaction conditions if rhodium is the sole catalyst employed (entries 3–6; 9–12). If a mixture of Rh and Ru catalysts is used, the best results were obtained at higher pressure (150 bar) and temperature (150°C). With ruthenium as the sole catalyst, less conversion was observed with the same reaction conditions. It is clearly evident that a combination of rhodium and ruthenium leads to higher catalyst activity. A total amount of 3 ppm Rh with respect to 1-dodecene and a Ru/Rh ratio of about 17/1 shows high activity and selectivity, especially if a solvent like isopropanol is used (entry 16). In general, the use of isopropanol results in higher conversion and slightly higher selectivity. Based

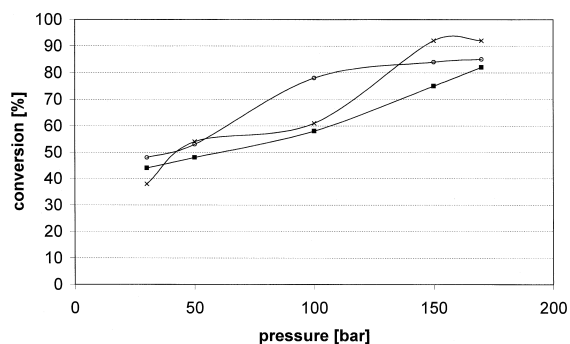


Fig. 2. Aminomethylation of 1-dodecene. Conversion to *N,N*-dimethyl-1-*n*,*iso*-tridecylamine vs. pressure at different temperatures: (□) 100°C; (○) 125°C; (×) 150°C.

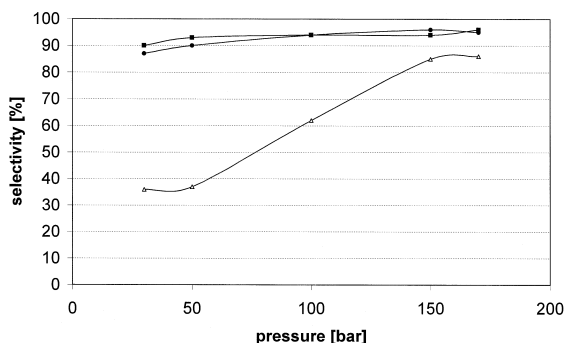


Fig. 3. Aminomethylation of 1-dodecene. Selectivity to *N,N*-dimethyl-*n,iso*-tridecylamine vs. pressure at different temperatures: ( $\Delta$ ) 100°C; ( $\blacksquare$ ) 125°C; ( $\bullet$ ) 150°C.

on the metal concentration, the activity is also higher. Even higher conversions are obtained by increasing the catalyst concentration to 6–12 ppm Rh and using Ru/Rh ratios of 5–10/1 (entries 19–22). For 1-hexene (entries 1, 2) or 1-octene (entries 7, 8), the best results were obtained with 6 ppm Rh and a Ru/Rh ratio of about 8/1.

For 1-dodecene, the influence of reaction temperature and pressure on conversion and selectivity is illustrated in Figs. 2 and 3. Using 3 ppm Rh and 50 ppm Ru, the selectivity at 125°C is only slightly affected by the total pressure, whereas conversion increases with higher pressure. At 100°C, the selectivity to *N,N*-dimethyl-*n/iso*-tridecylamine is much more dependent on the pressure, thus forming significant amounts of the corresponding enamines, hydrocarbons and heavy ends (high boiling products) at low pressure.

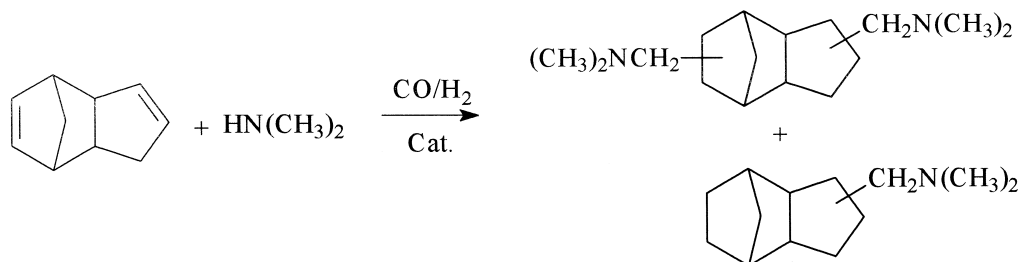
Means to control the *n/iso* ratio of the product formed by hydroformylation are well known [3]. With constant reaction conditions, total conversion and constant selectivity the *n/iso* ratio of the amine product formed can be controlled by catalyst concentration and Ru/Rh ratio within a range from 0.98 to about 1.4 (entries 16, 19–22).

### 3.2. Side-reactions

Terminal olefins usually react faster in hydroformylation than internal ones. Thus, the rate of hydroformylation vs. isomerisation of the olefin is an important component for the overall selectivity observed.

The isomerisation rate of 1-dodecene to internal dodecenes at various catalyst concentrations was examined. As shown in Table 2, the isomerisation of 1-dodecene is caused mainly by the Ru catalyst, with only limited isomerisation being due to the Rh catalyst. Employing 50 ppm Ru, the isomerisation of 1-dodecene towards the thermodynamic equilibrium was largely completed within a reaction time of 4 h, and 70% internal dodecenes were found. This may account for the relatively low conversion observed when Ru catalyst is used alone (Table 1, entries 23–26). If Ru and Rh are present at the same time, the isomerisation rate is significantly lower. This effect enables the *n/iso*-selectivity to be controlled by varying the Ru/Rh ratio within certain limits.

By employing only Rh, the isomerisation rate is much lower and therefore the conversion to



Scheme 2. Aminomethylation of dicyclopentadiene to 3(4),8(9)-bis(*N,N*-dimethylaminomethyl)-tricyclo[5.2.1.0<sup>2,6</sup>]decane and to 3(4)-*N,N*-dimethylaminomethyl-tricyclo[5.2.1.0<sup>2,6</sup>]decane.

Table 3

Syntheses of bis-(*N,N*-dimethylaminomethyl)-tricyclodecane from dicyclopentadiene, syngas and dimethylamine

Entry	Rh <sup>a</sup> [ppm]	Ru <sup>b</sup> [ppm]	Ru/ Rh	DCP [g]	DCP/Rh [m/m]	DMA [g]	Reaction conditions	Conversion <sup>c</sup> [%]	Selectivity mono-/ di-amine <sup>d</sup> [%]
1	173	2660	15	15	4350	11	150 bar, 140°C	100	38/43
2	173	2660	15	15	4350	10	150 bar, 145°C	100	7/89
3	173	2660	15	15	4360	12	150 bar, 150°C	100	0.5/30
4	87	1330	15	15	8700	11	150 bar, 145°C	100	20/65
5	173	1330	8	15	4360	10	150 bar, 145°C	100	50/43
6	350	2660	8	15	2200	12	150 bar, 140°C	100	13/54

<sup>a</sup>Concentration with respect to olefin. Rh as RhCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> or Rh(2-ethylhexanoate)<sub>3</sub>.<sup>b</sup>Concentration with respect to olefin. Ru as RuCl<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> or Ru(acetylacetonate)<sub>3</sub>.<sup>c</sup>Conversion of olefin.<sup>d</sup>3(4)-*N,N*-dimethylaminomethyl-tricyclo[5.2.1.0<sup>2,6</sup>]decane and 3(4),8(9)-bis(*N,N*-dimethylaminomethyl-tricyclo[5.2.1.0<sup>2,6</sup>]decane).

aldehydes is more efficient. The lower selectivity to the amines observed in this case (e.g., entries 3–6, Table 1) is due to the lower hydrogenation rates of the enamines formed (Scheme 1), causing unwanted by-products. This is partly compensated at higher catalyst concentrations, but in these circumstances aldol adducts and derivatives are also more likely to be formed because of the higher ratio of more reactive linear aldehydes formed. This is even more the case with more reactive aldehydes such as heptanal compared with tridecanal (entries 3–6 vs. entries 9–12).

### 3.3. DCP

It is well known that non-conjugated double bonds of dienes exhibit different reactivity in the hydroformylation reaction [3]. Converting the second double bond requires more drastic conditions. This may lead to subsequent reactions of the previously introduced formyl group. Thus, the aminomethylation of dienes like DCP becomes even more challenging (Scheme 2). Some experiments are described in Table 3. By varying the concentration, the Ru/Rh ratio as well as other reaction parameters, mixtures of diaminomethylated DCP were obtained in high yields (> 89%). Compared to the reactions of the aliphatic mono-olefins significantly higher catalyst concentrations have to be used. The best results were obtained by employing 173

ppm Rh and 2660 ppm Ru catalyst at 145°C and 150 bar pressure (entry 2).

Temperatures above or below 145°C lead to decreased diamine selectivity (entries 1, 3). Lower catalyst concentrations (either of Rh or Ru) lead to lower yields (entries 4, 5) which was surprisingly also observed when the Ru/Rh ratio was changed from 15/1 to 8/1 by raising the Rh concentration (entry 6). Main by-products formed are dimethylformamide (carbonylation of dimethylamine) and heavy ends.

## 4. Conclusion and outlook

Aminomethylation of linear 1-olefins also proceeds very well with low catalyst concentrations. By using a mixture of Rh and Ru catalyst, the activity is raised significantly compared with the sole use of Rh or Ru. In this case, also specific control of the *n/iso* ratio in the amine product can be achieved by varying catalyst concentrations and Ru/Rh ratio.

The conversion of DCP to the corresponding diamine requires still higher catalyst concentrations, even if Rh and Ru are employed. This makes effective catalyst separation and recycling even more important. Since water is formed during synthesis, which separates from the organic product, modification of the catalyst with water-soluble phosphine ligands offers one opportunity to solve this problem. Results using

such modified catalysts in the aminomethylation reaction as well as catalyst separation and recycling will be reported separately.

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