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Primary amine syntheses from syngas, olefins and ammonia

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Abstract

The selective preparation of aliphatic primary amines from alpha-olefins, synthesis gas (CO/H_2) and ammonia has been developed involving the use of homogeneous cobalt, rhodium and ruthenium catalysis. The modes by which these products are generated is discussed. An alternative, two-step procedure requiring initial olefin hydroformylation, followed by reductive amination of the linear aldehyde intermediate, is also described.

Keywords: Primary amine; Syngas; Ammonia

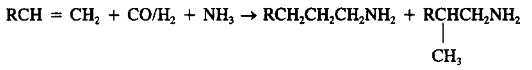
1. Introduction

There is continuing research interest regarding the conversion of synthesis gas to higher-value specialty and commodity chemical intermediates. In recent years our efforts have been directed to using CO/H_2 as a building block for the production of various aliphatic amine and amidocarbonylation chemistries [1,2]. In this paper we discuss various options for the generation of aliphatic amines, particularly linear alkyl primary amines, from synthesis gas, ammonia, plus the appropriate alpha-olefin building block.

2. Results and discussion

Three alternative approaches have been considered by us for the selective generation of primary amines from syngas, olefins and ammonia. They are:

1. A one-step synthesis starting from an aliphatic alpha-olefin substrate and involving homogeneous cobalt, rhodium and ruthenium catalysis [3] typified by Eq. (1):



$$RCH = CH_2 + CO/H_2 + NH_3 \rightarrow RCH_2CH_2CH_2NH_2 + R\underset{\substack{|\\ CH_3}}{C}HCH_2NH_2 \qquad (1)$$

2. A two-step process requiring initial olefin hydroformylation, followed by amination of the intermediate aldehyde [4], as depicted in Eq. (2):

$$RCH = CH_2 + CO/H_2 \rightarrow RCH_2CH_2CHO \xrightarrow[H_2]{NH_3} RCH_2CH_2CH_2NH_2 \qquad (2)$$

3. Aminomethylation of certain unsaturated, olefinic, materials with carbon monoxide plus water, and a nitrogen source, in the presence

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Table 1
Hydroformylation of 1-heptene to octylaldehydes

Example	Catalyst precursor [a,b]	Heptene conversion (%)	Octylaldehyde yield (mol%)	Selectivity to 1-octylaldehyde
1	$PtCl_2(PPh_3)_2 + SnCl_2$ (1:5)	100	85	90
2	$PtBr_2(PPh_3)_2 + SnBr_2$ (1:5)	100	64	85
3	$PtI_2(PPh_3)_2 + SnI_2$ (1:5)	< 2	0.6	
4	$PtCl_2(PPh_3)_2 + GeCl_2$ (1:5)	14	14	98
5	$PtCl_2(PPh_3)_2 + SnCl_4$ (1:5)	100	50	84
6	$PtCl_2(AsPh_3)_2 + SnCl_2$ (1:5)	100	46	75
7	$PtCl_2(SbPh_3)_2 + SnCl_2$ (1:5)	94	61	75
8	$PtCl_2[P(p\text{-}CH_3 \cdot C_6H_4)_3]_2 + SnCl_2$ (1:5)	90	78	93
9	$PtCl_2[PCl(Ph)_2]_2 + SnCl_2$ (1:5)	100	72	89
10	$PtCl_2[P(n\text{-}Bu)_3]_2 + SnCl_2$ (1:5)	100	83	89
11	$PtCl_4K_2 + SnCl_2$	99	60	73

[a] Batch experiments using rocking autoclave: 1-heptene/[Pt] initial molar ratio 200:1, solvent, methyl isobutyl ketone, H_2/CO (1:1).
[b] Hydroformylation conditions: 1500 psi, 66°C, 3 h.

of certain transition-metal compounds as catalyst.

$$\mathrm{RCH{=}CH_2 + 3\,CO + H_2O + HN\langle \;\rightarrow\; RCH_2CH_2CH_2N\langle + 2CO_2} \qquad (3)$$

Aminomethylation (Eq. (3)) catalyzed by iron pentacarbonyl was first discovered by Reppe to produce amines, but in low yields [5]. Since then rhodium, ruthenium and iridium [6], as well as mixed ruthenium/iron carbonyls [7], have been shown to catalyze reaction (3). While this synthesis is best suited for the generation of tertiary amines [8], we have also developed a two-step procedure for the production of secondary amines from olefins and a primary amine involving the intermediate generation of isolatable imine intermediates [9]. Where the N-coreactant is ammonia, however, the product mix contains only very low concentrations of desired primary amines [10].

A far more promising approach to the production of linear alkyl primary amines from α-olefins involves initial hydroformylation of the alkene substrate in the presence of ligand-stabilized platinum(II) halide catalysts, coupled with Group IVB metal halide cocatalysts, to yield the corresponding aldehyde intermediate [11], followed by reductive amination of said aldehydes in the presence of bulk-metal oxide catalysts. Some typical results for both the initial alkene hydroformylation step and the subsequent aldehyde reductive amination to desired primary amine are summarized in Tables 1 and 2, respectively. The preferred homogeneous oxonation catalyst in this work is bis(triphenyl-

Table 2
Reductive amination of octylaldehydes to octylamines

Example	Catalyst precursor [a,b]	Octylaldehyde conversion (%)	Total octyaldehyde yield (mol%)	Selectivity to n-octylamine
12	Ni-Al-Cr [c]	> 98	48	89
13	Ni-Ba-Cr	> 98	64	86
14	Ni-Mg-Cr	> 98	48	88

[a] Bulk metal oxide catalysts prepared by coprecipitation of metal nitrate solutions with hot sodium bicarbonate solution, followed by filtration, washing, drying, calcining and reduction under hydrogen at 325°C.
[b] Reductive amination conditions: 1500 psi, 100°C, 4 h.
[c] Analyses: Ni, 54.7%, Al, 11.4%; Cr, 4.7%.

phosphine)platinum(II) chloride plus tin(II)chloride [11]. This precursor provides high yields of linear aldehyde intermediate under relatively mild hydroformylation conditions (see Table 1, ex. 1). The related Pt[P(p-$CH_3 \cdot C_6H_4)_3]_2$–$SnCl_2$ and $PtCl_2[P(n\text{-}Bu)_3]_2$–$SnCl_2$ combinations are also very effective (see ex. 8 and 10). A nickel–aluminum–chromium bulk oxide catalyst proved satisfactory for the second-stage amination (Eq. (2)) to desired linear alkyl primary amines (see Table 2). Linearity of the final product was typically in the high 80%s. Where ease of aldehyde product-Pt catalyst separation is critical, and it is desirable not to use a solvent-solubilized catalyst system, then the application of low-melting dispersions of bis(triphenylphosphine)platinum(II) chloride in tetraethylammonium trichlorostannate(II) is particularly advantageous (Table 3). The reductive amination step is most readily conducted in an inert alkanol solvent; syntheses of C_3–C_{14} linear aliphatic amines has been demonstrated [4].

We have also investigated the direct, one-step, preparation of primary amines from an olefin, synthesis gas and ammonia (Eq. (1)) which leads to improved selectivities to the desirable primary amine products [3]. Previously, workers at Mitsubishi Petrochemical had reported [12] the synthesis of primary amines in approx. 30% yields from α-olefins, syngas and ammonia using a homogenous cobalt-phosphine catalyst solubilized in ethanol.

The focus of our work has been the preparation of primary amines using combinations of homogeneous cobalt catalysts, phosphine ligands and ether/acetamide solvent systems. Syntheses comprise reacting olefin, syngas and ammonia in the presence of cobalt octacarbonyl, a p-dioxane/tetraglyme/acetamide solvent, and a tertiary phosphine ligand (Ph_3P or n-Bu_3P), at a pressure of preferably 500–2000 psi and an operating temperature of 150–250°C. The major products are primary amines (Eq. (1)), particularly primary aliphatic amines having a carbon number either one greater (C_{n+1}) than the starting olefin substrate (C_n), and/or a carbon number of two or three greater than twice or thrice the carbon number (C_{2n+2} or C_{3n+3}) of the starting olefin. The principal by-products are oftentimes the corresponding alkanols. Where, for example, 1-hexene is the olefin substrate, the major products are the heptyl primary amines (Eq. (1)) and the tetradecyl primary amines. The heptylamine fraction generally comprises both primary and secondary alkyl primary amines, with the linear heptylamine predominating. The by-products are then the C_7- and C_{14}-alcohols with some hydrocarbon being detected in most cases.

Typical syntheses are summarized in Table 4. For the dicobalt octacarbonyl-triphenylphosphine catalyst combination of ex. 15, the principal derivatives are (in descending order): C_7-primary amines, C_{14}-primary amines, C_{14}-hydrocarbon and C_7-primary alcohols. A typical selectivity to primary amines is 57% [13]. Generally, our parameter and kinetic studies [3] have served to reconfirm initial conclusions (based upon data such as in Table 4) that to achieve selective oxoamination of olefins to primary amines it is necessary to have the ammonia, syngas, olefin and homogeneous cobalt

Table 3
Propylene hydroformylation catalyzed by bis(triphenylphosphine)platinum(II) chloride dispersed in tetraethylammonium trichlorostannate(II)

Catalyst cycle [a,b]	n-Butyraldehyde selectivity (%)	Isolated yield of butyraldehydes (mol%)	Purity of isolated butyraldehydes (%) [c]
1	82	48	99
11	83	34	99
111	82	10	98

[a] Batch experiments using stirred autoclave: $(PPh_3)_2PtCl_2$, 4 mmol; $[Et_4N][SnCl_3]$, 40 mmol; C_3H_6, 1 mol; CO/H_2 (1:1).
[b] Hydroformylation conditions: 1260 psi, 80°C, 5 h.
[c] Product butyaldehydes isolated by fractional distillation.

Table 4
Primary amines syntheses from olefins, syngas and ammonia

Example	Catalyst precursor	Solvent (g)	1-Hexene (g)	Ammonia (g)	Reaction conditions	Hexene conv. (%)	Product selectivities (%)	
							$C_7H_{15}NH_2$	$C_{14}H_{29}NH_2$
15	$Co_2(CO)_8$-PPh_3 [a]	p-Dioxane (7.0)	7.0	10.0	2000 psi, 200°C, 4 h	85	32	25
16	$Co_2(CO)_8$-PBu_3	p-Dioxane (14.0)	14.0	13.0	1650 psi, 200°C,4 h	73	6	4
17	$Co_2(CO)_8$-PBu_3	p-Dioxane (14.0)	14.0	40.0	2000 psi, 200°C, 4 h	30	28	1
18	$Co_2(CO)_8$-PBu_3	p-Dioxane (14.0) + Acetamide (1.0)	14.0	12.5	2000 psi, 200°C, 4 h	81	7	7
19	$Co_2(CO)_8$-PBu_3	Tetraglyme (14.0)	14.0	20.0	2000 psi, 200°C, 4 h	47	13	8
20	$Co_2(CO)_8$-PBu_3	p-Dioxane (20.0)	20.0	20.0	2000 psi, 180°C, 6 h	69	18	11
21	$Co_2(CO)_8$-PBu_3 [b]	p-Dioxane (20.0)	20.0	20.0	2000 psi, 180°C, 6 h	56	26	5
22	$Co_2(CO)_8$-DIPHOS [c]	p-Dioxane (20.0)	7.0	10.0	2000 psi, 180°C, 4 h	None	–	–

[a] Batch experiments using rocking autoclave, $Co_2(CO)_8$ (2.0 mole), PR_3 (2.0-16.0 mmole)
[b] Batch experiments using stirred autoclave.
[c] 1,2-Bis(diphenylphosphino)ethane.

catalyst in a delicate balance of initial molar ratios such that there is sufficient ammonia present at all times to aminate a substantial portion of the intermediate aliphatic aldehyde but not so much that the ammonia interferes with the initial hydroformylation step and/or with the formation of the necessary quantities of active cobalt carbonyl-tertiary phosphine homogeneous catalysts.

A combination of ^{1}H-NMR, ^{13}C-NMR, GLC and GC-MS analyses have served to establish that the C_{18} and C_{27} amine fractions are each a complex mix of linear and branched, primary and secondary amines. Both fractions are likely formed through a combination of:

- Aldol condensation of linear and branched aldehydes followed by reductive amination to give a range of aliphatic primary amines, as illustrated by Eqs. (4) and (5).
- Schiff base condensation followed by imine reduction of a variety of linear and branched amine-aldehyde combinations to give linear and branched secondary amines, as generalized in Eqs. (6)–(8).

The extension of this technology to the oxoamination of C_4 olefins (1-butene, 2-butene and isobutylene) has proven more complicated than at first expected. Homogeneous cobalt, ruthenium and rhodium catalyst precursors have all proven effective, with the order of productivity being:

$Ru < Co < Rh$.

Rhodium catalysis, for example, using solutions of $Rh(acac)_3$–PPh_3 and $RhHCO(PPh_3)_3$ in p-dioxane ([Rh] 7–43 mM) under the general oxoamination conditions of Table 4, but lower operating temperatures (130°C, 2000 psi, 4 h), produces very high liquid yields (100–130% liquid weight gains) with all three C_4-olefins. Glc, gc-ms and NMR analyses, however, confirm a large number of products. The expected tri(isopentyl)amine has been identified as a primary product from isobutylene oxoamination using $NH_3/CO/H_2$ and fractional distillation of typical crude products has led to the identification of aliphatic, highly branched, primary, secondary and tertiary amines.

Further parameter studies with linear 1-olefin substrates have served to confirm that:

1. Olefin isomerization to internal isomers is rapid within the time frame of oxoamination.
2. Excess ammonia (e.g., a 10-fold molar excess over olefin) may completely shut down oxo and oxoamination activity.
3. Oxoamination and oxo alcohol product formation rates appear comparable only where the initial ammonia charge is less than stoi-

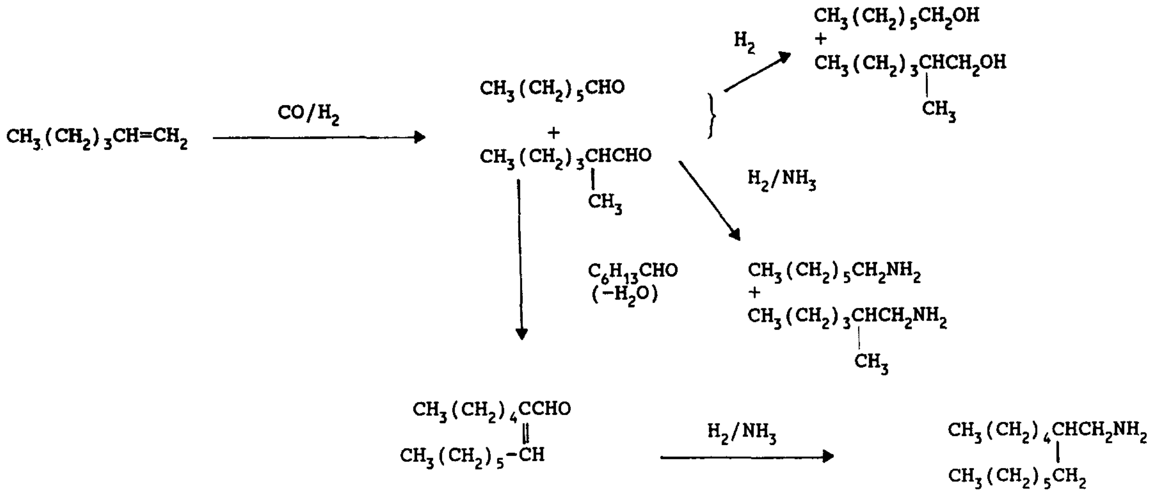


Fig. 1. Aliphatic primary amines form 1-hexene, syngas, and ammonia — the principle reaction paths.

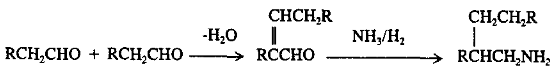
chiometric with respect to olefin, otherwise amine products predominate.

4. At 200°C operating temperature, it is possible to achieve quantitative olefin conversions after 4 h with ≥ 40% concentration of total aliphatic amines in the crude effluent product [3]. Primary amine selectivities and yields may then reach 60–65 mol%. Lower temperatures (200 → 160°C) lead to significantly lower rates of hydroformylation and amination.

These results and product distributions may be rationalized in terms of initial olefin oxonation followed by reductive amination to give desired aliphatic primary amines, as depicted in Fig. 1, with aldehyde hydrogenation to the corresponding alcohol and base-catalyzed aldol condensation as parallel paths. Not included in this schematic are competing olefin double bond isomerization and Schiff base condensation. Under normal oxonation conditions the initial hydroformylation step controls the product regioselectivity and is the slow, rate-determining, step. It is bracketted by a more rapid olefin double bond isomerization and aldehyde amination. The spectra of typical reaction solutions show the presence of $[Co(CO)_4]^-$ and $HCo(CO)_3(PPh_3)$ moieties, plus additional ~ (CO) bands attributable to other cobalt carbonyl amine species. The mechanism of intermediate aldehyde formation is likely then to be very similar to the well understood cobalt carbonyl-phosphine oxo catalysis [14–16]. p-Aryl orthometalation and subsequent benzene elimination [17] does not appear to be a major problem in the case of $Co_2(CO)_8$–PPh_3 oxoamination. Regioselectivity to linear primary alkyl primary amines (Eq. (1) and Fig. 1) is typically approx. 70–75%.

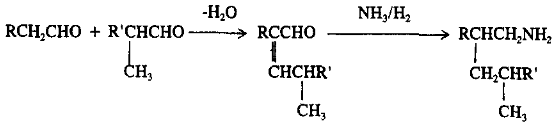
It is evident from these discussions that, whichever of these three approaches to primary amine syntheses (Eqs. (1)–(3)) are taken, although considerable progress has been made in recent years, more selective and more facile catalysts are still waiting to be discovered and developed.

2.1. Primary amines



$$\mathrm{RCH_2CHO + RCH_2CHO \xrightarrow{-H_2O} \overset{CHCH_2R}{\overset{\|}{RCCHO}} \xrightarrow{NH_3/H_2} \overset{CH_2CH_2R}{\overset{|}{RCHCH_2NH_2}}}$$

(4)

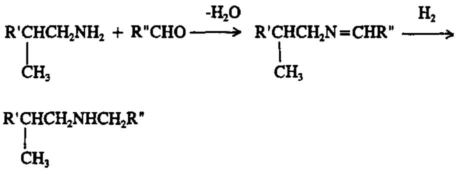


$$\mathrm{RCH_2CHO + \underset{\underset{CH_3}{|}}{R'CHCHO} \xrightarrow{-H_2O} \underset{\underset{\underset{CH_3}{|}}{CHCHR'}}{\underset{\|}{RCCHO}} \xrightarrow{NH_3/H_2} \underset{\underset{\underset{CH_3}{|}}{CH_2CHR'}}{\underset{|}{RCHCH_2NH_2}}}$$

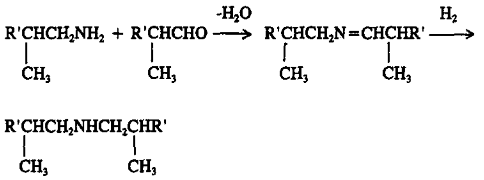
(5)

2.2. Secondary amines

$$RCH_2NH_2 + R''CHO \xrightarrow{-H_2O} RCH_2N = CHR'' \xrightarrow{H_2} RCH_2NHCH_2R''. \tag{6}$$



$$R'\underset{CH_3}{C}HCH_2NH_2 + R''CHO \xrightarrow{-H_2O} R'\underset{CH_3}{C}HCH_2N{=}CHR'' \xrightarrow{H_2} R'\underset{CH_3}{C}HCH_2NHCH_2R'' \tag{7}$$



$$R'\underset{CH_3}{C}HCH_2NH_2 + R'\underset{CH_3}{C}HCHO \xrightarrow{-H_2O} R'\underset{CH_3}{C}HCH_2N{=}CH\underset{CH_3}{C}HR' \xrightarrow{H_2} R'\underset{CH_3}{C}HCH_2NHCH_2\underset{CH_3}{C}HR' \tag{8}$$

3. Experimental

Synthesis gas (CO/H_2, 1:2 molar ratio) was purchased from Big Three Industries, all other reagents were used as received from the suppliers.

A typical synthesis procedure for the generation of C_7/C_{14} amines from 1-hexene, syngas, and ammonia is as follows:

A glass-lined pressure reactor (183 ml) was charged with a mixture of dicobalt octacarbonyl (0.34 g, 1.0 mmol), triphenylphosphine (0.80 g, 4.0 mmol), 1-hexene (7.0 g) and p-dioxane (7.0 g). The reactor was purged of air and then charged with anhydrous ammonia (ca. 10 g) plus syngas ($CO/H_2 = 1:2$ molar ratio) to 500 psi. The reactor was heated to 200°C while it was agitated by rocking. The pressure was brought up to 2000 psi by the addition of CO/H_2 mixtures. The reaction was held at temperature for 4.0 h; during this period the pressure dropped to 1500 psi. The reactor was allowed to cool to room temperature. The excess gas was vented from the reactor, following which 13.0 g of yellow solution with a ca. 0.3 g bottom layer was recovered. A metal deposit on the wall of glass liner was observed.

The product liquid was analyzed by glc. The conversion of 1-hexene was calculated to be ca. 85%. The principal products and their selectivities were assigned as shown in Table 4.

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