

The selective preparation of n-propylamines by the rhodium catalysed reaction of ethylene and syngas with alkylamines

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Abstract

The aminomethylation of ethylene with a primary amine has been shown to provide a highly selective route to n-propylamines; the rhodium catalysed reaction of n-propylamine with ethylene and syngas (2/1, H₂/CO) affords di-n-propylamine with 98% selectivity (with respect to ethylene). The reaction of amines of the type RR¹NH with the ethylene/syngas mixture and a rhodium catalyst provides a highly selective and general route to the n-propylamines RR¹NPr (R = Pr, R¹ = H; R = t-Bu, R¹ = H; R = n-Bu, R¹ = H; R = C₈H₁₇, R¹ = H, R = R¹ = Pr; R = HOCH₂CH₂, R¹ = H, and R = PhCH(OH)CH₂, R¹ = H).

Introduction

Amines are important compounds for large scale and fine organic synthesis. Together with their derivatives they are employed, in particular, as antioxidants in fuel oils, as rubber stabilisers, and in the manufacture of water-impermeable fabrics, herbicides, and medicinal drugs [1]. Many methods are known for manufacturing amines from a variety of starting materials; the principal methods are the amination of alcohols, halogeno compounds and carbonyl compounds, and the reduction of nitriles.

Ethylene has a well established carbonylation chemistry involving syngas [2], and in the presence of rhodium or cobalt catalysts undergoes hydroformylation to propanal. Primary, secondary, and tertiary amines can be prepared by the reaction of aldehydes with ammonia or amines with cobalt or rhodium carbonyls as homogeneous hydrogenation catalysts [3]. This paper describes the remarkably selective synthesis of predominantly secondary amines by reaction of an amine with an ethylene/syngas feed.

Results and discussion

Several papers have described the transition metal-catalysed reductive alkylation of secondary amines by alkenes, carbon monoxide, and water according to eq. 1,

Table 1

Reaction of PrNH₂ with H₂/CO/C₂H₄PrNH₂ (0.15 mmol), EtOH (60 cm³), [RhCl(CO)₂]₂ (0.04 g, 0.1 mmol) 6/3/1, H₂/CO/C₂H₄, 59 bar, 115 °C, 1h

Product	% selectivity with respect to	
	PrNH ₂	C ₂ H ₄
Pr ₂ NH	99	98
Pr ₃ N	1	2
% Conv.	40	56

referred to as aminomethylation of alkenes [4–8].

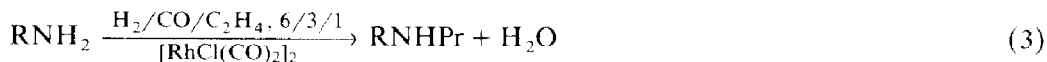


A disadvantage of this system is the uneconomic oxidation of carbon monoxide to carbon dioxide, via the water-gas shift reaction. Very little work has been carried out on systems which use gaseous hydrogen (eq. 2) [9–12]. This reaction has the advantage that it makes more economic use of carbon monoxide.



In initial experiments to assess the effectiveness of reaction 2, *N,N*-diethylpropylamine was obtained from the reaction of a 6/3/1 H₂/CO/C₂H₄ gas mixture with diethylamine in the presence of a cobalt carbonyl catalyst. However, the selectivity for tertiary amine formation was rather low (54% with respect to diethylamine), and high temperature and pressure (210 °C, 280 bar) were necessary. Di-*n*-propylamine is the largest bulk *n*-propylamine manufactured (ca. 11000 t/a in the USA), and so a study was made to investigate the conversion of *n*-propylamine into di-*n*-propylamine rather than tri-*n*-propylamine, for which there is little demand. The results of a typical reaction are summarised in Table 1 and show that [RhCl(CO)₂]₂ catalyses the aminomethylation of ethylene to di-*n*-propylamine with 98% selectivity under relatively mild conditions (115 °C, 59 bar).

The ability of rhodium to act as a catalyst for the synthesis of di-*n*-propylamine from *n*-propylamine having been established, a study was made of the generality of the reaction. Thus, a number of primary and secondary amines were treated with an ethylene/syngas mixture and a rhodium catalyst, and Table 2 summarises the results obtained. Again the reaction is very selective at converting a primary amine into a secondary amine rather than a tertiary amine (eq. 3). *t*-Butyl-*n*-propylamine is



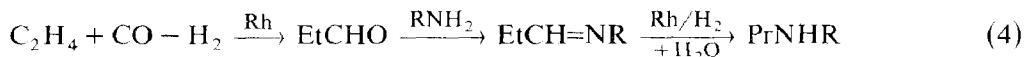
obtained with 99.7% selectivity from the reaction of *t*-butylamine with the ethylene/syngas mixture, and the ethylene conversion is high (75%). Surprisingly, under analogous conditions di-*n*-propylamine is converted into tri-*n*-propylamine with 100% selectivity; again the ethylene conversion is good (67%).

The system [RhCl(CO)₂]₂/PrNH₂ catalysed the hydroformylation of ethylene with moderate ethylene conversion (43%) in 1 h. The selectivity for *n*-propanal formation is high (99%), and the only other product detected by GC/MS is the

Table 2
Rhodium catalysed aminomethylation reactions
Catalyst (ca. 0.1 mmol), + solvent (60 cm³) + amine (ca. 0.15 mol, except example 2) + H₂/CO/C₂H₄ 6/3/1, ca. 50 bar.

Example	Amine	Catalyst	Solvent	T (°C)	Run time (h)	%C ₂ H ₄ conversion	Product	% selectivity with respect to C ₂ H ₄
1	n-BuNH ₂	[RhCl(CO) ₂] ₂	EtOH	110	1	56	n-BuNHPr	87
2	t-BuNH ₂	[RhCl(CO) ₂] ₂	t-BuNH ₂	100	1	75	t-BuNHPr	99.7
3	C ₈ H ₁₇ NH ₂	[RhCl(CO) ₂] ₂	MeOH	110	1	90	C ₈ H ₁₇ NHPr	75
4	HOCH ₂ CH ₂ NH ₂	[RhCl(CO) ₂] ₂	EtOH	110	2	41	HOCH ₂ CH ₂ NHPr	74
5	Pr ₂ NH	[RhCl(CO) ₂] ₂	EtOH	115	1.5	67	Pr ₃ N	100
6	PhCH(OH)CH ₂ NH ₂	[RhCl(CO) ₂] ₂	EtOH	110	1	43	PhCH(OH)CH ₂ NHPr	89.6
7	—	[RhCl(CO) ₂] ₂ /PrNH ₂	EtOH	110	1	43	EtCHO	99

acetal, 1,1-diethoxypropane (1%). The fact that the $[\text{RhCl}(\text{CO})_2]_2/\text{PrNH}_2$ system is an effective hydroformylation catalyst suggests that the aminomethylation reactions proceed via an initial hydroformylation of ethylene to give propanal. The condensation reaction of aldehydes with amines to form imines is well documented, and a subsequent rhodium catalysed hydrogenation of the carbon–nitrogen double bond would afford the *n*-propylamine, eq. 4.



If secondary amines are alkylated, enamines are believed to be the intermediates in the aminomethylation reaction, and it is the carbon–carbon double bond which has to be hydrogenated [3].

Functionalised primary amines are selectively converted into the *n*-propylamine derivatives under mild conditions. Thus, *n*-propylethanolamine is obtained with 74% selectivity (with respect to ethylene) from the reaction of ethanolamine with the ethylene/syngas mixture. Similarly, 2-amino-1-phenylethanol reacts to give 2-(*N*-propylamino)-1-phenylethanol with 90% selectivity.

Ammonia reacted with the syngas/ethylene mixture in the presence of a rhodium catalyst to give dipropylamine and tripropylamine, but the selectivity for formation of these compounds was low, and a number of by-product were detected by GLC. These by-products were also formed in the reaction of ammonia with propanal, and are thought to be imine polymerisation products [13]. Ammonium carbamate is also produced in this reaction, and is presumably formed by reaction of ammonia with carbon dioxide, the carbon dioxide being generated in a rhodium catalysed water gas shift reaction, eq. 5.



The results of an assessment of commonly used homogeneous organometallic catalysts aimed at establishing the relative merits of individual complexes, are summarised in Table 3. These results show that rhodium is the preferred metal, and losses of selectivity and conversion were encountered only with a rhodium phosphine catalyst (example 11); interestingly this is a very efficient hydroformylation

Table 3

Results of catalyst screening programme

Catalyst + EtOH (60 cm³) + H₂/CO/C₂H₄, 6/3/1 ca. 50 bar, 110 °C, 1h

Example	Amine (0.15 mol)	Catalyst (mmol)	%C ₂ H ₄ conver- sion	Product (selectivity %) with respect to C ₂ H ₄
8	PrNH ₂	[RhCl(CO) ₂ (<i>p</i> -toluidine)] (0.3)	55	Pr ₂ NH (98), Pr ₃ N (2)
9	PrNH ₂	[RhCl(CO) ₂] ₂ (0.09)	56	Pr ₂ NH (98)
10	BuNH ₂	[RhCl(COT) ₂] ₂ (0.07)	58	BuNHPPr (100)
11	BuNH ₂	[RhH(CO)(PPh ₃) ₃] (0.03) + PPh ₃ (0.2)	29	BuNHPPr (60)
12	BuNH ₂	[Co ₂ (CO) ₈] (1.96) + PBu ₃ (3.95)	0	
13	PrNH ₂	[RuCl ₂ (PPh ₃) ₄] (0.09)	0	
14	PrNH ₂	[IrCl(COD)] ₂ (0.1)	0	

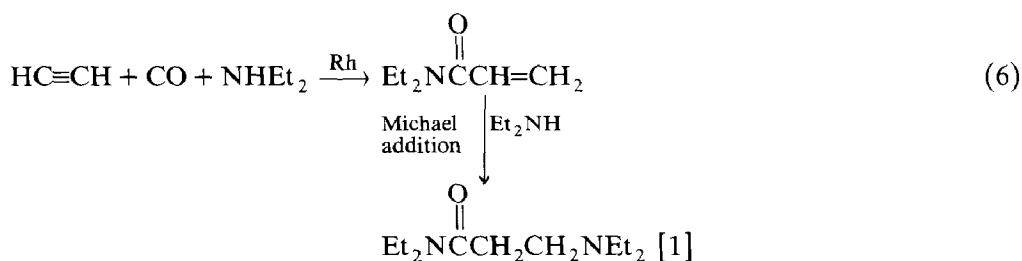
Table 4

Reaction of Et₂NH with H₂/CO/C₂H₂/C₂H₄Et₂NH (9.7 mmol), toluene (25 cm³), [Rh₆(CO)₁₆] (0.05 g, 0.05 mmol), H₂/CO/C₂H₂/C₂H₄ (61/20/3/3), 8.8 bar, 60 °C, 3h

Product	%selectivity with respect to C ₂ H ₂
$\text{Et}_2\text{N}\overset{\text{O}}{\parallel}\text{CCH}=\text{CH}_2$	27
$\text{Et}_2\text{N}\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{NEt}_2$	73
% Conv. of C ₂ H ₂	17

catalyst [2]. With regard to the cobalt carbonyl catalyst, which was only active at very high temperatures and pressures, it should be noted that strongly basic amines are regarded as catalyst poisons for cobalt catalysed hydroformylation reactions owing to the formation of [BH]⁺[Co(CO)₄]⁻ salts [3].

A brief study was made to see if acetylene could be carbonylated in the presence of a secondary amine, and the results are summarised in Table 4. Two acetylene derived products were obtained, *N*-diethyl acrylamide and the amide [1], presumably formed by a Michael addition of diethylamine to the acrylamide, equation 6.



Interestingly no ethylene derived products were observed by GC/MS.

Conclusions

The rhodium catalysed aminomethylation of ethylene in the presence of H₂/CO (2/1) and an alkylamine produces *n*-propylamines with good selectivity under mild conditions. However, ammonia is not a suitable nitrogen source for these reactions due to carbamate formation.

Experimental

1. Equipment

All of the reactions were carried out in a 300 ml (nominal volume) stainless steel autoclave. The autoclave was equipped with a magne-drive stirrer, cooling coil, and a facility for collection of gas samples.

2. Procedures

Breathing apparatus was used whilst loading and discharging autoclaves because of the toxic nature of alkyl amines and carbon monoxide. The procedure was similar in all cases. The catalyst, amine, and solvent were charged to the autoclave, which was then purged with carbon monoxide, then pressurised with the reactant gas, and heated to the required temperature.

Once the reactions were complete, the mixture was cooled to ambient temperature and the gas and liquid phases were fully analysed. Results and reactor charges are summarised in Tables 1 to 4.

3. Definitions

The reaction time refers to the time period during which the autoclave is at the selected reaction temperature. Selectivity is quoted in % molar terms with respect to one of the reactants.

4. Product Analysis

All liquid products were analysed by GC/MS or by GLC using a Pye Unicam 4500 instrument equipped with a FID detector. Analyses were performed with a 6×2 mm ID column packed with Chromosorb 103, using a temperature programme (120°C , 3 min, rise to 225°C at $6^\circ\text{C}/\text{min}$, 225°C , 25 min). Gas analyses were carried out using a Pye Unicam 4500 instrument equipped with a thermal conductivity detector and a $6' \times 3$ mm ID column packed with Porapak Q. The chromatographs were temperature programmed (85°C , 4 min, rise to 105°C at $8^\circ\text{C}/\text{min}$, 105°C , 8 min).

Acknowledgements

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