Unexpected products of the allyldiethylamine hydroformylation homogeneously catalyzed by rhodium complexes

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Attempts to carry out the hydroformylation of allyldiethylamine homogeneously catalyzed by rhodium complexes led to unexpected formation of N,N,N′,N′-tetraethyl-1,4-diaminobutane and 4-(diethylamino)-1-butanole as final products. The role of the catalyst on the product formation and the reaction mechanism are briefly discussed.

Keywords: Hydroformylation; allylamines; N,N,N′,N′-tetraethyl-1,4-diaminobutane; 4-(diethylamino)-1-butanole; homogeneous catalysis; rhodium complexes

1. Introduction

Carbonylation of allylamine or secondary N-alkylallylamines homogeneously catalyzed by cobalt or rhodium complexes leads to cyclization to N-alkylpyrrolidones, which are important in the petrochemical industry [1]. Reaction proceeds under milder conditions in the presence of hydrogen, which indicates its possible involvement in the reaction mechanism [2]. Besides possible reactions on the amino group [1–3], the use of the CO/H_2 mixture enables hydroformylation of the double bond as a side or even dominant reaction [2,4]. Aldehydes react with the NH group of amines to form enamines [2,4] and enamines are formed also by the catalyzed isomerisation of the allyl group [5,6]. Further reactions of enamines, as reactions with aldehydes or in situ hydrogenation [2,4,7], lead to a wide variety of products which can be found after completion of the catalytic reactions.

In order to gain some insight into the mechanism of the hydroformylation of the allyl group of allylamines and to avoid possible interferences of the reactivity of

the NH group, we have attempted to carry out the hydroformylation of tertiary N-allyldiethylamine as described in this paper.

2. Experimental

2.1. CHEMICALS

N-allyldiethylamine was prepared according to the published method [8] and distilled prior to use; its purity was >99% by GC. Known methods were also used for the preparation and purification of $Rh_4(CO)_{12}$ [9] and $RhCl(CO)L_2$, L = PPh_3 [10]. A mixture of CO/H_2 (50.8% CO, 46.8% H_2, 2.1% N_2, 0.3% O_2, VÚP Prievidza, Czechoslovakia) was used. Solvents, (Lachema, Czechoslovakia) were purified and dried by usual methods and distilled under nitrogen prior to use.

2.2. ANALYSIS

Gas chromatography of reaction products was carried out using a Chrom 31 instrument (Laboratory Instruments Prague, Czechoslovakia), equipped with an FID detector and a glass column packed with 2.5% KOH and 10% Versamide on Chromosorb W mesh 80–100 (Carlo Erba). IR spectra were recorded with a Perkin Elmer 684 spectrometer connected to a PE 3600 data station, NMR experiments and mass spectra were measured using a Varian XL-200 and Jeol 100 spectrometers; TMS and perfluorokerosene were used as internal standards.

2.3. CATALYSIS

Preliminary experiments were carried out in a 50 ml stainless-steel autoclave, 20 mm i.d., in an inner 5 ml glass vessel (Reacti-Vial, Pierce) with PTFE beaker. The autoclave was heated by an oil bath and stirred magnetically. Preparative experiments were carried out in a 750 ml autoclave (Berghof, Germany), equipped with an inner PTFE vessel heated by a programmable oven and stirred magnetically.

3. Results and discussion

In our previous study we used N-alkylallylamines as substrates for the catalytic carbonylation with a CO/H_2 mixture [2]. Cyclization of N-alkylallylamines to N-alkyl-2-pyrrolidones was in that case complicated by the simultaneous hydroformylation of the allyl group and by a number of consecutive reactions of NH and CHO groups. With allyldiethylamine used in this study in order to eliminate the interferences of NH group, the aminoaldehydes were the expected products. The

present study followed the same choice of catalysts and reaction condition as described previously. Since the simple assumption of unambiguous reaction step failed, new unexpected products were isolated preparatively.

To the 750 ml autoclave were added 100 ml of 0.5 M allyldiethylamine in benzene, 1 mmol of $RhCl(CO)(PPh_3)_2$ and 2 mmol of PPh_3 (Fluka, Switzerland) (substrate/catalyst = 50). Based on preliminary experiments, reaction was allowed to run for 3 h at 9 MPa CO/H_2 1 : 1 and 100°C. After completion of catalytic reaction, benzene was distilled off at an ambient pressure and a single product was obtained by vacuum distillation at 60°C, 0.23 kPa; yield was about 30%. Based on the absence of bands characteristic for double bonds in IR spectra, fragmentation in MS spectra and interpretation of NMR spectra, the product was identified as N,N,N′,N′-tetraethyl-1,4-diaminobutane. [^{1}H NMR (ppm), $CDCl_3$, 23°C: ethyls 1.01 t (7 Hz), 2.51 q (7 Hz), $\delta(Et_2N\underline{CH_2})$ 2.42 m, $\delta(Et_2NCH_2\underline{CH_2})$ 1.44 m, ^{13}C NMR: ethyls 11.77 q, 52.95 t, $\delta(Et_2N\underline{CH_2})$ 46.91 t, $\delta(Et_2NCH_2\underline{CH_2})$ 25.19 t, MS: $C_{12}H_{28}N_2^{+\cdot}$ (m/z 200), $(M-Et)^+$ (m/z 171), $(M-C_6H_{16}N)^+$ (m/z 98), $C_5H_{12}N^+$ (m/z 86), $C_3H_8N^+$ (m/z 58)]. Under the presence of phosphines, the expected 4-(diethylamino)-1-butanal was detected by NMR [$CDCl_3$, δ(CHO) 9.57 t], however, its yield represented only 30% of reaction products.

To the 750 ml autoclave were added alternately 100 ml of 0.5 M allyldiethylamine in benzene and 1/4 mmol of $Rh_4(CO)_{12}$ (substrate/catalyst = 50). Reaction was allowed to run for 3 h at 9 MPa CO/H_2 1 : 1 and 100°C. After completion of catalytic reaction, benzene was distilled off at an ambient pressure and one fraction was obtained by vacuum distillation at 63°C, 0.26 kPa; yield was about 40%. Based on GC, fraction contained 56% of N,N,N′,N′-tetraethyl-1,4-diaminobutane and 44% of a compound identified as 4-(diethylamino)-1-butanole. [^{1}H NMR (ppm), $CDCl_3$, 23°C: ethyls 1.05 t (7 Hz), 2.55 q (7 Hz), $\delta(Et_2N\underline{CH_2})$ 2.40 m, $\delta(Et_2NCH_2\underline{CH_2}\underline{CH_2})$ 1.65 m, $\delta(Et_2N(CH_2)_3\underline{CH_2})$ 3.55 m, ^{13}C NMR: ethyls 10.70 q, 53.31 t, $\delta(Et_2N\underline{CH_2})$ 46.12 t, $\delta(Et_2NCH_2\underline{CH_2}\underline{CH_2})$ 32.70, $\delta(Et_2N(CH_2)_3\underline{CH_2})$ 62.50 t]. The presence of 4-(diethylamino)-1-butanole as one of principal products probably reflects the general tendency of "unmodified" carbonyls to work equally well as hydrogenation catalysts, which was described for aldehydes, olefins as well as enamines.

The formation of N,N,N′,N′-tetraethyl-1,4-diaminobutane formally resembles to the origin of N-alkyl-tetrahydropyrrole formed in the course of hydroformylation of N-alkyldiallylamines [4]. According to the mechanism suggested in ref. [4], reaction with N-allyldiethylamine should proceed through steps (1)–(4):

$$Et_2N(CH_2)_3-CHO + Et_2NCH_2-CH=CH_2 \rightarrow Et_2N(CH_2)_3-CH(O^-)-N^+(CH_2-CH=CH_2)Et_2, \quad (1)$$

$$Et_2N(CH_2)_3-CH\,(O^-)-N^+(CH_2-CH=CH_2)Et_2 \rightarrow Et_2N(CH_2)_3CH(O-CH_2-CH=CH_2)-NEt_2, \quad (2)$$

$$Et_2N(CH_2)_3CH(O-CH_2-CH=CH_2)-NEt_2 \rightarrow Et_2N(CH_2)_2-CH=CH-NEt_2 + CH_2=CH-CH_2-OH\,, \quad (3)$$

$$Et_2N(CH_2)_2-CH=CH-NEt_2 + H_2 \rightarrow Et_2N(CH_2)_4NEt_2\,. \quad (4)$$

To prove this mechanism we allowed N-allyldiethylamine to react with similar aldehydes separately (10 mmol of N-allyldiethylamine, 20 mmol of freshly distilled *n*-propanal or *n*-butanal, sealed glass ampoule, N_2, 4.5 h, 85°C). Since no reaction occurred, we consider the alternative mechanism following steps (5)–(7):

$$Et_2NCH_2-CH=CH_2 \rightarrow Et_2NCH=CH-CH_3\,, \quad (5)$$

$$Et_2NCH=CH-CH_3 + Et_2N(CH_2)_3-CHO \rightarrow Et_2NCH=CH-(CH_2)_2NEt_2 + CH_3CH_2CHO\,, \quad (6)$$

$$Et_2NCH=CH-(CH_2)_2NEt_2 + H_2 \rightarrow Et_2N(CH_2)_4NEt_2\,. \quad (7)$$

The mechanism assumes isomerisation of the allyl group as a first step of reaction (5), which is well documented in literature [5,6]. Since enamine is a product of a balance (8), trans-enamination as a type of electrophilic substitution [8] is suggested as a second step (6):

$$Et_2NCH=CH-CH_3 + H_2O \rightarrow Et_2NH + CH_3CH_2CHO\,. \quad (8)$$

In both ways, the hydrogenation of enamine is a terminal step of the reaction. Hydrogenation of enamines under hydroformylation conditions was recently found to occur with side products of hydroformylation of N-alkyldiallylamines [4] and N-alkylallylamines [2] and the catalyst structure–hydrogenation activity relationship was studied also with 1-(1-cyclohexenyl)piperidine [7].

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