Journal of Organometallic Chemistry, 206 (1981) 393—397
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CARBONYLATION OF AMINES AND DIAMINES CATALYZED BY NICKEL CARBONYL

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(Received July 15th, 1980)

Summary

The carbonylation of amines and diamines was carried out using nickel carbonyl as the catalyst. Reaction of butylamine, diethylamine, and diphenylamine with carbon monoxide all lead exclusively to the corresponding formamide derivative. Benzylamine reacts with carbon monoxide to yield urea and 1,2-diphenylethane. Diamines such as ethylenediamine, 1,2-diaminopropane, and 1,3-propylenediamine react to yield a cyclic condensation product, a cyclic urea, and a carbamic acid.

Introduction

Reactions of amines with carbon monoxide, catalyzed by various transition metal complexes, are well known [1,2]. Generally, the products obtained are formamides, but ureas, and even oxamides, depending on the conditions and the catalyst, can be produced.

Metal carbonyls are known to catalyze the carbonylation of amines; both dicobalt octacarbonyl [3] and iron pentacarbonyl [4] lead to formamides but dimanganese decarbonyl produces ureas [5,6].

Carbonylation reactions of diamines have not been studied extensively. In one report where $Mn_2(CO)_{10}$ was used as the catalyst, variable results were obtained depending on the diamine. Thus, no reaction occurred for ethylenediamine and 1,4-diaminobutane; 1,3-diaminopropane led to the cyclic urea and the cyclic condensation product while *N*,*N*-dimethyl-1,3-diaminopropane gave the corresponding formamide. Hexamethylenediamine yielded a polyurea when treated with carbon monoxide in the presence of manganese carbonyl [6].

This paper reports the results of the reaction of several amines and diamines with carbon monoxide catalyzed by nickel carbonyl. Particularly interesting are the reactions of the diamines, which show a consistency in reactivity and selectivity.

Experimental

Solvents and starting materials. Toluene was distilled over $LiAlH_4$, and absolute ethanol was distilled over CaO, immediately before use as solvents. Diphenylamine, diethylamine and benzylamine were used as received from the suppliers. n-Butylamine was distilled from KOH, and anhydrous ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, and 1,6-diaminohexane were distilled over CaH_2, prior to use.

Physical methods and analyses. Nuclear magnetic resonance (NMR) spectrometry was carried out on a Varian EM 360 NMR spectrometer using tetramethylsilane as the internal standard. Infrared spectra were taken on a Perkin-Elmer 597 grating spectrophotometer. Mass spectra were obtained on a Finnigan 1015 mass spectrometer. Elemental analyses and molecular weights were determined by Galbraith Laboratories Inc., Knoxville, Tenn.

General description of the reactions. All reactions were carried out in a 300 ml, glass-lined, autoclave (Autoclave Engineers). Temperature was controlled by a thermocouple connected to an automatic temperature regulator.

Carbonylation of n-butylamine. The autoclave was charged with 30 ml (22.2 g, 0.3 mol) of n-butylamine, 30 ml of toluene and 0.08 g (0.5 mmol of $Ni(CO)_4$. The autoclave was flushed well with CO, then pressurized to 750 psig of CO. The reaction mixture was heated at 160° C for 20 h with constant, rapid stirring. After that time, the autoclave was allowed to cool to room temperature, and the contents were fractionally distilled to yield 16.0 g of n-butylformamide (52% yield), which was identified by comparing its infrared and NMR spectra with those of an authentic sample.

Carbonylation of diethylamine. A reaction mixture containing 30 ml (21.3 g, 0.3 mol) of diethylamine, 30 ml of toluene and 0.08 g $Ni(CO)_4$ was heated to 180° C for 24 h under 750 psig CO. Fractional distillation of the product mixture yielded 16.7 g (55%) of *N,N*-diethylformamide, identified by a comparison of its spectra with those of an authentic sample.

Carbonylation of diphenylamine. Conditions similar to those of the carbonylation of n-butylamine were applied to 21.3 g of diphenylamine. After work-up, 15.5 g of *N,N*-diphenylformamide was recovered (62%).

Reaction of benzylamine. Conditions similar to those in other carbonylation reactions were applied to 29.4 g of benzylamine. Fractional distillation yielded 17.2 g (70.4%) of 1,2-diphenylethane (b.p. 96° C/10 mmHg). Anal. Found: C, 92.38; H, 7.39%. $C_{14}H_{14}$ calcd.: C, 92.31; H, 7.69%; An NMR spectrum of the sample was consistent with that of 1,2-diphenylethane. Urea, 3.5 g (11.6%) was also recovered from the reaction mixture.

Carbonylation of ethylenediamine. A mixture composed of 30 ml of absolute ethanol, 30 ml (26.1 g, 0.44 mol) of ethylenediamine and 0.08 g of $Ni(CO)_4$ was heated at 160° C for 18 h under 750 psig CO with constant stirring. The autoclave was allowed to cool to room temperature and opened. A white solid was collected from the top of the reaction chamber and identified as the carbamic acid derivative of ethylenediamine, *N*-β-aminoethylcarbamic acid (14.5 g, 31.7%). Anal. Found: C, 34.58; H, 7.81; N, 26.89%. $C_3H_8N_2O_2$ calcd.: C, 34.64; H, 7.74; N, 26.91%. Recovered by fractional crystallization from the reaction mixture were two compounds: the cyclic urea, 2-imidazolidone (4.0 g, 10.6%), and the cyclic condensation product, 2-imidazoline (8.5 g, 28.0%). The cyclic urea was identified by spectral properties and elemental analysis. Anal. Found: C, 42.08; H, 7.13; N, 32.17%. $C_3H_6N_2O$ calcd.: C, 41.86; H, 6.98; N, 32.50%. The imidazoline, which showed a melting point of ca. 40° C, was converted to the picrate, which is a known compound, and exhibited a melting point at 201—202° C (lit., 202° C) [7].

Carbonylation of 1,2-diaminopropane. Similar conditions as described above for ethylenediamine were applied to a reaction mixture of 1,2-diaminopropane. Isolated were the carbamic acid, presumed to be composed of a mixture of the isomers $^+H_3NCH(CH_3)CH_2NHCOO^-$ and $^+H_3NCH_2CH(CH_3)NHCOO^-$, the cyclic urea, and the isomeric cyclic condensation products, methylimidazoline. The carbamic acid isomers gave the following elemental analysis. Anal. Found: C, 40.59; H, 8.53; N, 23.69%. $C_4H_{10}N_2O_2$ calcd.: C, 40.68; H, 8.47; N, 23.64%. The cyclic urea showed infrared spectral properties in accordance with the proposed structure, and a mass spectrum of the compound showed the parent ion peak at *m/e* 100. The presumed mixture of the methyl imidazolines showed a parent ion peak at *m/e* 84 in the mass spectrum.

Carbonylation of 1,3-diaminopropane. The autoclave was charged with 30 ml (26.7 g, 0.36 mol) of 1.3-diaminopropane, 30 ml of toluene and 0.08 g $Ni(CO)_4$. The autoclave was pressurized to 750 psig CO, then heated at 150° C for 20 h with constant stirring. The autoclave was allowed to cool to room temperature, and the pressure was released. Found at the top of the reaction vessel was a white compound identified as 1,3-diaminopropane carbamic acid. This compound, which is not stable at room temperature, yielded CO_2 and 1,3-diaminopropane upon acidification. Fractional crystallization of the reaction mixture led to the isolation of two compounds: the cyclic urea, 2-pyrimidone (3,2 g, 8.9%), and the cyclic condensation product, 1,4,5,6-tetrahydropyrimidine (12.2 g, 40.8%). The cyclic urea showed a parent ion peak at *m/e* 100 in its mass spectrum. Anal. Found: C, 47.93; H, 8.44; N, 27.91%. $C_4H_8N_2O$ calcd.: C, 48.00; H, 8.08; N, 28.02%. The final compound, 1,4,5,6-tetrahydropyrimidine, was identified by comparing its infrared spectrum with that of the known compound [8], and by the melting point of its picrate derivative (278—280° C; lit., 280° C) [7].

Carbonylation of 1,6-diaminohexane. A solution containing 25 g (0.22 mol) of 1,6-diaminohexane, 30 ml toluene, and 0.08 g $Ni(CO)_4$ was heated at 170° C for 20 h under 750 psig CO with constant stirring. The insoluble product was filtered from solution and identified as a polyurea (14.2 g, 45.5%) by its infrared spectrum. When 30 ml of 70% 1,6-diaminohexane in water was subjected to the same conditions, 16.2 g of 1,6-diaminohexane carbamic acid was obtained. Anal. Found: C, 52.24; H, 17.82; N, 19.98%. $C_7H_{16}N_2O_2$ calcd.: C, 52.50; H, 17.50; N, 20.00%.

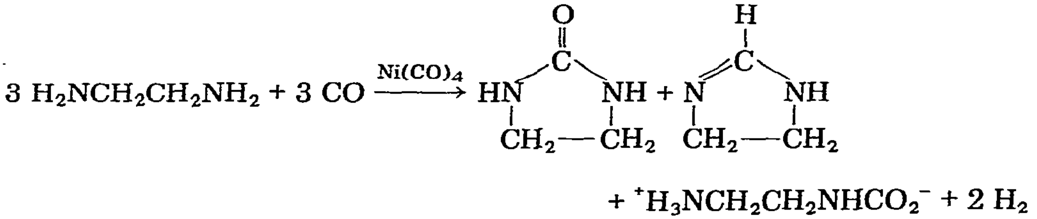
Carbonylation of ammonia. The autoclave was charged with 15 g of liquid ammonia and 0.08 g $Ni(CO)_4$ and heated at 100° C for 24 h under 750 psig CO. The only product obtained from the reaction was urea (7.9 g, 30%). When the same reaction was carried out using ammonium hydroxide solution (30 ml, 28.7% NH_3), 3.6 g of urea was recovered.

Results and discussion

Primary and secondary amines react with CO in the presence of $Ni(CO)_4$ to yield the corresponding formamides. The formation of other types of molecules such as ureas or oxamides was not detected. Thus, nickel carbonyl acts more in accord with cobalt and iron carbonyls, rather than manganese carbonyl, to produce formamides.

A mechanism based on that advanced for iron carbonyl [4] for the formation of formamides would appear likely for the $Ni(CO)_4$-catalyzed system as well. Since it has been shown that coordinated amine or amide does not migrate onto coordinated CO to form a carbamoyl group [9], direct attack of the amino group on a carbonyl group must be involved, as proposed for the iron carbonyl system.

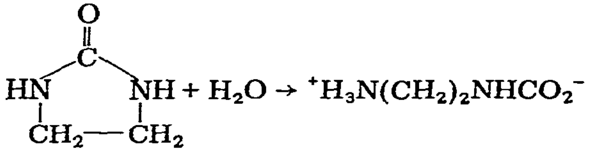
The reaction of diamines with CO in these systems is very interesting. The overall reaction of ethylenediamine is shown below, although the evolution of hydrogen was not investigated.



The reaction of 1,2-diaminopropane led to products analogous to those of the ethylenediamine reaction, with a presumed mixture of isomers for the cyclic condensation product and carbamic acid. 1,3-Diaminopropane led to analogous products based on six-membered rings. Besides the carbamic acid, the cyclic urea (2-pyrimidone) and the cyclic condensation product (1,4,5,6-tetrahydropyrimidine) were also isolated and identified.

Mechanistic details of the formation of the cyclic products and carbamic acid were not investigated in this work. However, 1,3-diaminopropane led to the same cyclic products where $Mn_2(CO)_{10}$ was used as the catalyst [6]. Therefore, it is possible that attack on coordinated carbonyl by one end of the diamine to form a carbamoyl group followed by reaction of the free amino group on carbamoyl to condense water would give, in the case of ethylenediamine, 2-imidazoline. The cyclic urea, 2-imidizolidone, could arise if the carbamoyl intermediate releases an isocyanate ($OCNCH_2CH_2NH_2$), followed by reaction with the free amino end of the molecule. This process was suggested for the $Mn_2(CO)_{10}$-catalyzed system [6].

The carbamic acid could be produced from at least two different processes. Once again using the ethylenediamine system as example, the cyclic urea 2-imidazolidone could react with the water produced in the formation of 2-imidazoline.



This reaction was confirmed in a separate experiment. When 2-imidazolidone was treated with water under experimental conditions, a quantitative conversion to the carbamic acid occurred.

A second possibility for the production of the carbamic acid arises from consideration of $Ni(CO)_4$ as a catalyst for the water-gas shift reaction: $H_2O + CO \rightarrow H_2 + CO_2$. Carbon dioxide produced in the reaction could react with the amine to produce the carbamic acid. In preliminary experiments, it was found that nickel carbonyl indeed is active in promoting the water-gas shift reaction.

A polyurea is produced when 1,6-diaminohexane reacts with CO under catalytic conditions, which is the same reaction observed with $Mn_2(CO)_{10}$ as the catalyst [6].

$$x\ H_2N(CH_2)_6NH_2 + x\ CO \rightarrow [-NH(CH_2)_6NHCO-]_x + x\ H_2$$

In the presence of water, 1,6-diaminohexane reacts with CO to yield the carbamic acid exclusively; this was observed when a 70% solution of the diamine in water was used.

Anomalous results were observed in the reaction of benzylamine with carbon monoxide; the products were 1,2-diphenylethane and urea. Additional studies are required before comment on the mechanism of this reaction can be made.

Acknowledgement

The authors are grateful to Dow Chemical, U.S.A., for support of this research.

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