CARBONYLATION REACTION

COMMUNICATION 11. CARBONYLATION OF AMINO ALCOHOLS AND SOME CYCLIC AMINES WITH CARBON MONOXIDE IN THE PRESENCE OF MERCURIC ACETATE

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Aliphatic alcohols [1] and amines [2] react with CO in the presence of Hg(OCOCH₃)₂ to give symmetrical dialkyl carbonates and N-alkylformamides. In the present paper we studied the possibility of carbonylating the amino alcohols: ethanolamine, 3-amino-1-propanol and 3-amino-1-butanol, and also some cyclic amines: morpholine and cyclohexylamine. The reaction was run at 100-200°C and 100-150 atm of CO. It was established that the amino alcohols react with CO at the NH₂ group to give the corresponding N-hydroxyalkylformamide. The hydroxyl group does not take part in the carbonylation reaction. The amino alcohol and CO react in a 1:1 ratio. The yield of the carbonylation products is 1.4-2.5 M/M of reacted Hg(OCOCH₃)₂. On the example of ethanolamine it was shown that increasing the reaction temperature up to 200° facilitates an increase in the amounts of reacted CO and amino alcohol by a factor of 2 and 4, respectively. Here the yield of N-(β -hydroxyethyl)formamide decreases and the yield of the high-molecular condensation products, which contain CO (1660-1680 cm⁻¹), NH (3400-3450 cm⁻¹), and OH (3600-3660 cm⁻¹) groups, increases sharply. These condensation products are soluble in water, dilute alkali and acid solutions, and are insoluble in the common organic solvents. The yield of the water that is liberated during the condensation of N-(β -hydroxyethyl)formamide increases by ~20 times when the temperature is raised from 100 to 200°. The other reaction products are the salt of the amino alcohol, Hg and CH₃COOH.

Morpholine is carbonylated with the formation of two products: the formyl derivative and 4,4'-carbonyldimorpholine. An increase in the temperature in the range 150-200° facilitates the carbonylation: the amount of reacted CO and the yields of formylmorpholine and 4,4'-carbonyldimorpholine increase by ~ 2 times. Cyclohexylamine reacts with CO almost completely to give N-cyclohexylformamide and 1,3-di-cyclohexylurea in a 1:1.8 ratio.

Previously we had shown [2] that aliphatic and cycloaliphatic amines, which are strong Lewis bases, are easily carbonylated by CO in the presence of $Hg(OCOCH_3)_2$ to give predominantly the formamide derivative. Amino alcohols behave in a similar manner, in which connection the NH_2 group takes part in the formation of the intermediate complex [3]. Dehydration condensation of the carbonylation products occurs at high temperatures, and probably of the starting amino alcohol, with involvement of the hydroxyl groups.

The insertion of a second heteroatom into the cycloaliphatic amine molecule, for example oxygen, changes the direction of the carbonylation. Thus, if in the reaction products the ratio of the formamide and urea derivatives during the carbonylation of piperidine is 5-7:1, then during the carbonylation of morpholine this ratio is $\sim 1:1$. This is apparently explained by a decrease in the basicity of the amine. Actually, the pK_a value of morpholine is equal to 8.64, and that of piperidine is 11.8. It is known [2] that a decrease in the basicity of the amine favors the formation of the urea derivative. Thus, in the carbonylation of aniline (pK_a 4.6) the sole reaction product is 1,3-diphenylurea, while formanilide is not formed at all. Together with the urea derivative, cyclohexylformamide is formed in the carbonylation of cyclohexylamine (pK_a 10.64).

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T., °C	Amount reacted, M		[Obtained			
			Amount	N-(β-Hydroxyethyl)formamide		in Mark readed	
	CO	ethanol- amine	of H ₂ O formed,M	М	in %of reacted ethanolamine	ethanolamine	
100 170 200	0,31 0,67 0,75	0,33 0,66 1,24	$0,05 \\ 0,20 \\ 0,94$	0,26 0,36 0,12	91,5 64,5 5,3	8,5 34,4 94,0	

TABLE 1. Carbonylation of Ethanolamine in the Presence of 0.09 M Mercuric Acetate at 150 atm of CO

TABLE 2. Carbonylation of Morpholine in the Presence of 0.09 M Mercuric Acetate at 100 atm of CO

	Anount	reacted,M	Amount formed, M			
т., °С	CO	morpho- line	formy1- morpholine	4,4-carb- onyldimorph- oline	tar	
150 170 200	$0,12 \\ 0,21 \\ 0,37$	$0,28 \\ 0,35 \\ 0,55$	0,10 0,12 0,20	0,02 0,09 0,08	0,02 0,02 0,02	

EXPERIMENTAL METHOD

Into a rotated 0.25 liter steel autoclave were charged ~0.1 M of $\text{Hg}(\text{OCOCH}_3)_2$ and 0.5-1.2 M of the amino alcohol or amine, the system was purged with CO (99% pure), the CO pressure was raised to 100-150 atm, and the autoclave was heated for 5-6 h. The reaction products were separated from the Hg and fractionally distilled in a Favorskii flask using a vacuum of 10-20 mm. The fractions, corresponding to the carbonylation products, were purified by re-

peated vacuum-distillation. The IR spectra were taken on a UR-20 instrument, and the NMR spectra were taken on an RS-60 instrument in CD_3CO solution relative to HMDS. The solid carbonylation products were purified by recrystallization from the appropriate solvent.

<u>Carbonylation of Ethanolamine</u>. The carbonylation was run at 150 atm in the range 100-200° (Table 1). The main product at low temperatures was N-(β -hydroxyethyl)formamide (bp 186-188° (18 mm), n_D²⁰ 1.4782, d₄²⁰ 1.1514. Found: C 40.50; H 8.30; N 14.89%. C₃H₇NO₂. Calculated: C 40.44; H 7.86; N 15.73%). NMR spectrum (δ , ppm): 7.6 (singlet, NH), 3.9 (singlet, OH), 3.0 (multiplet, HOCH₂), 2.8 (multiplet, CH₂N). At 170° the yield of N-(β -hydroyethyl)formamide when based on the starting monoethanol-amine is 1.5 times greater, but here the yield of the tarry condensation products increases sharply. At 200° the yield of N-(β -hydroxyethyl)formamide decreases sharply, but here the ethanolamine reacts almost completely, being converted to tarry condensation products to the extent of 94%.

<u>Carbonylation of 3-Amino-1-propanol.</u> At 120° and 105 atm of CO the amount of absorbed CO was 0.12 M, and the amount of liberated H_2O was 1.0 g. After separating the Hg and unreacted 3-amino-1-propanol the reaction products were found to contain 0.12 M of N-(γ -hydroxypropyl)formamide (viscous liquid with bp 210-212° (25 mm), n_D^{20} 1.4800, which crystallized on standing. Found: C 46.20; H 8.95; N 14.02%. C₄H₉NO₂. Calculated: C 46.60; H 8.73; N 13.59%) and 0.04 M of tar (when based on the 3-amino-1-propanol).

Carbonylation of 3-Amino-1-butanol. At 180° and 100 atm of CO the amount of absorbed CO was 0.1 M, and the amount of liberated H_2O was 1.0 g. After separating the Hg and unreacted 3-amino-1-butanol the reaction products were found to contain 0.1 M of N-(α -methyl- γ -hydroxypropyl)formamide (viscous liquid with bp 205-210° (30 mm). Found: C 51.72; H 9.92; N 11.40%. $C_5H_{11}NO_2$. Calculated: C 51.28; H 9.40; N 11.96%) and 0.1 M of tar.

<u>Carbonylation of Morpholine</u>. The carbonylation products of morpholine at 100 atm of CO in the range 150-200° were (Table 2): formylmorpholine [4] (bp 136-139° (30 mm), n_D²⁰ 1.4815, d₄²⁰ 1.1268. Found: C 69.52; H 8.95; N 14.23%. C₅H₉NO₂. Calculated: C 69.69; H 9.09; N 14.14%); 4,4'-carbonyldimorpholine [4], obtained as crystals with mp 143° (from acetone) (Found: C 54.08; H 8.12; N 14.06%. C₃H₁₆ \cdot NO₃. Calculated: C 54.00; H 8.00; N 14.00%), and a small amount of tar.

<u>Carbonylation of Cyclohexylamine</u>. The amount of CO absorbed at 180° and 100 atm of CO was 0.15 M. In the reaction products after separating the Hg were found 0.07 M of cyclohexylformamide (bp 132-136° (18 mm). Found: C 66.40; H 10.35; N 11.52%. $C_7H_{13}NO$. Calculated: C 66.14; H 10.28; N 11.03%), and 0.125 M of dicyclohexylurea [5] with mp 233°.

CONCLUSIONS

Primary amino alcohols react with CO in the presence of mercuric acetate at 100-200° and a pressure of 100-150 atm to give the corresponding N-(hydroxyalkyl)formamides in a yield of 1.4-2.5 M/M of reacted $Hg(OCOCH_3)_2$. Morpholine under analogous conditions forms the corresponding formyl derivative and the urea derivative in a 1.2-5:1 ratio, while cyclohexylamine forms the same derivatives in an ~0.7:1 ratio.

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