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HOMOGENEOUS REDUCTIVE AMINATION WITH COBALT AND RHODIUM CARBONYLS AS CATALYSTS

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Summary

Primary, secondary and tertiary amines may be prepared with high yields from aldehydes or ketones and ammonia or amines using cobalt and rhodium carbonyls as homogeneous hydrogenation catalysts. Reaction conditions are similar to those used in hydroformylation so aldehydes may be prepared in situ from olefins, carbon monoxide and hydrogen.

The heterogeneous catalytic hydrogenation of aldehydes and ketones in the presence of ammonia or amines ("reductive amination") to obtain primary, secondary or tertiary amines is a well-known process of industrial importance but, as far as we know, no homogeneous catalytic version of this reaction has been reported.

It was found that reductive amination can be achieved with rather good yields (70-100%) under homogeneous catalytic conditions using one of the following three procedures:

(a) $Co_2(CO)_8$ + PR_3 (R = alkyl or aryl, P/Co = 2/1) catalyst, 150-200°C, 100-300 atm H_2, solvent ethanol;

(b) $Co_2(CO)_8$ catalyst, 150-180°C, 100-300 atm H_2 + CO(1/1), solvent benzene;

(c) $Rh_6(CO)_{16}$ catalyst, 110-160°C, 100-300 atm H_2 + CO(1/1), solvent hexane.

Some representative experiments and yields of amines obtained are collected in Table 1.

As shown by GLC, Schiff bases are intermediates in the reaction if primary amines are used as starting components. Since imines may similarly be assumed to be the intermediates in the formation of primary amines, the metal carbonyls function in these cases as catalysts for the hydrogenation of the C=N double bond. In accordance with this observation, Schiff bases prepared separately from

TABLE 1

HOMOGENEOUS REDUCTIVE AMINATION OF ALDEHYDES AND KETONES[a]

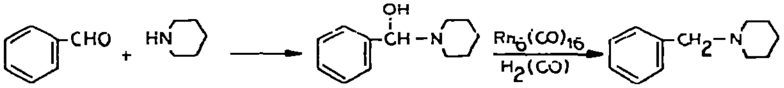
Starting materials		Carbonyl/ amine molar ratio	Catalyst	Product amine	Yield of product (%)	
Carbonyl Compound	Amine				Determined by GLC	Obtained by distillation
C_6H_5CHO	n-$C_4H_9NH_2$	1/1.5	$Co_2(CO)_8 + PBu_3$ 1/4	$C_6H_5CH_2NHCH_2CH_2CH_2CH_3$	100	86
Furfural	$C_6H_5NH_2$	1/1.5		$C_4H_4OCH_2NHC_6H_5$	100	49
$C_6H_5COCH_3$	NH_3	1/1.2		$C_6H_5CH(CH_3)NH_2$	69	65
				$[C_6H_5CH(CH_3)]_2NH$	23	
$C_6H_5COCH_3$	NH_3	1/0.67		$C_6H_5CH(CH_3)NH_2$	31	
				$[C_6H_5CH(CH_3)]_2NH$	56	52
$CH_3(CH_2)_3CH(C_2H_5)CHO$	$(CH_3)_2CHNH_2$	1/1.5	$Rh_6(CO)_{16}$	$CH_3(CH_2)_3CH(C_2H_5)CH_2NHCH(CH_3)_2$	08	82
Cyclohexanone	$(CH_3)_2CHNH_2$	1/1.5		$C_6H_{11}NHCH(CH_3)_2$	100	83
$(CH_3)_2CHCHO$	Piperidine	1/0.67		$(CH_3)_2CHCH_2NC_5H_{10}$	90	
C_6H_5CHO	Piperidine	1/0.83		$C_6H_5CH_2NC_5H_{10}$	100	
$(CH_3)_2CHCHO$	$C_6H_5NHCH_3$	1/1.2	$Co_2(CO)_8$	$C_6H_5N(CH_3)CH_2CH(CH_3)_2$	66	

[a] Reaction time in all cases 6 h. Other reaction conditions see text. Products were identified by GLC and MS.

primary amines and carbonyl compounds (e.g. benzilidene aniline) were successfully hydrogenated under the conditions employed for reductive amination.

If secondary amines are alkylated, enamines are found to be the intermediates and it is the carbon—carbon double bond which has to be hydrogenated. The activity of the cobalt-containing catalysts used in our experiments has been amply documented in the literature[1] for this type of hydrogenation, but with rhodium carbonyls hydrogenation of the olefinic double bond is usually very limited under hydroformylation conditions. Since we observed no hydroformylation of the enamine double bond, the amino group must have a pronounced influence on the reactivity of the intermediate alkylrhodium species.

If an aromatic aldehyde and a secondary amine are used, neither a Schiff base nor an enamine may be formed. $Rh_6(CO)_{16}$ is a useful catalyst in this case too, however, apparently promoting the hydrogenolysis of the intermediate benzyl alcohol derivative:



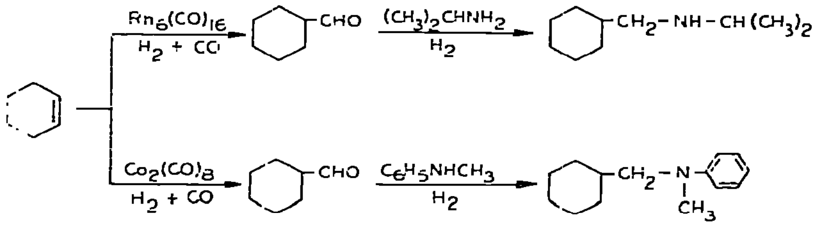
Since benzyl alcohol is not hydrogenated to toluene under similar conditions, this observation again emphasizes the influence of the nitrogen atom in the substrate on the reaction path.

Each of the catalysts has its advantages and restrictions. Thus the cobalt + phosphine catalyst is to be preferred if primary amines are the desired products and ammonia is used as one of the reactants whereas the cobalt carbonyl or rhodium carbonyl catalyst is more suitable if primary or secondary amines are to be transformed into secondary or tertiary amines, respectively. Furthermore, both cobalt-containing catalysts are effective only if aromatic compounds are the desired products (i.e. derivatives of aniline or benzylamine) while rhodium carbonyl is useful for the preparation of purely aliphatic amines too.

The activity of the $Co_2(CO)_8 + PR_3$ catalyst is significantly influenced by the structure of the phosphine. Aryl phosphines are much less suitable than alkyl phosphines as is observed when the same catalyst system is applied to the hydrogenation of ketones[2]. This effect may be due to the decreased stability of the cobalt complexes containing aromatic phosphines, since using PPh_3 a practically complete decomposition of the complexes to metallic cobalt could be observed under the reaction conditions. Most experiments were therefore performed with tributylphosphine as a catalyst component. Infrared spectra of the products, and of samples taken from the high pressure reactor during the reaction, showed a very strong band around 1885 cm^{-1}, characteristic of the $Co(CO)_4^-$ anion, and much weaker bands at 2000 and 1954 cm^{-1} which may be attributed to the $Co(CO)_3(PR_3)_2^+$ cation and to $Co_2(CO)_6(PR_3)_2$ complexes, respectively. This suggests that most of the cobalt is present in the form of a $[BH]^+[Co(CO)_4]^-$ [$B = NH_3$ or RNH_2] ionic complex and some doubt may arise about the role of the phosphine in the catalyst. No hydrogenation could be achieved with H_2 alone in experiments without added phosphine, however, despite the fact that the reaction mixture contained $Co(CO)_4^-$ in large amounts also in these cases. This suggests that a phosphine-containing complex [probably $CoH(CO)_3(PR_3)$] is the actual catalyst, despite its relatively small concentration.

With regard to the $Co_2(CO)_8$ catalyst, it should be mentioned that strongly basic amines are regarded as catalyst poisons for hydroformylation because of the formation of $[BH]^+[Co(CO)_4]^-$ salts [3]. In accordance with this, no reaction was observed if aliphatic amines were used and the IR spectrum of the reaction mixture showed all cobalt to be present in the form of the tetracarbonylcobaltat anion. With the much less basic aromatic amines, however, a significant amount of the cobalt remained in the form of $Co_2(CO)_8$ which could function as the active catalyst for hydrogenation.

The reaction conditions used in the case of $Co_2(CO)_8$ and $Rh_6(CO)_{16}$ are practically identical with those necessary for hydroformylation with the same catalysts. This circumstance enables the combination of hydroformylation and reductive amination to produce amines from olefins, carbon monoxide, dihydrogen and amines in one step. Using cyclohexene and isopropylamine or *N*-methylaniline as starting compounds, hexahydrobenzyl isopropyl amine and *N*-methyl-*N*-hexahydrobenzylaniline were both obtained in nearly quantitative yield:



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