Journal of Organometallic Chemistry, 420 (1991) 119–123
Elsevier Sequoia S.A., Lausanne
JOM 22084

The role of alcohol in the catalytic reductive carbonylation of nitrobenzenes to carbamates in the presence of $Rh(CO)_4^-$ or $Ru_3(CO)_{12}$

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(Received April 12th, 1991)

Abstract

The selectivity of *N*-phenylcarbamate from the reductive carbonylation of nitrobenzene using $Rh(CO)_4^-$ or $Ru_3(CO)_{12}$-$Et_4N^+Cl^-$ as the catalyst is much higher in t-butyl alcohol than in primary or secondary alcohols; the latter two alcohols are readily involved in the reduction of nitrobenzene to aniline leading to lower selectivity of the corresponding carbamates. For example, when 2-butanol was used as the solvent for the reductive carbonylation of nitrobenzene, 2-butanone and aniline were observed in a molar ratio of 1:1. Similarly, the reductive carbonylation of *p*-nitrotoluene to give the corresponding carbamate in t-butyl alcohol is also higher in yield than in 2-butanol or in butanol. However, for dinitroarenes the selectivity of carbamates is low using either ^{t}BuOH or other primary and secondary alcohols.

Introduction

The reductive carbonylation of aromatic nitro compounds to the corresponding carbamates [1]

$$ArNO_2 + 3CO + ROH \rightarrow ArNHCOOR + 2CO_2 \qquad (1)$$

is a subject of great interest both from the mechanism and the application viewpoints. In spite of extensive research on the selectivity of this reductive carbonylation, little is known regarding the nature of the selectivity. In this paper, we report the use of complexes $Ru(CO)_4^-$ and $Ru_3(CO)_{12}$ for the catalysis of reaction 1 and the drastic effect of alcohol on the selectivity of carbamates. The results clearly indicate that low selectivity of carbamate is closely related to the ability of alcohol to reduce nitoarenes to amino derivatives. Consequently, the employment of an alcohol which can not reduce nitroarene greatly increases the selectivity of carbamate.

Experimental section

Materials

The following compounds were obtained from the indicated suppliers: $RhCl_3 \cdot H_2O$, $Ru_3(CO)_{12}$, bis(triphenylphosphine) iminium chloride (Strem); methanol,

ethanol, butanol, 2-butanol and t-butyl alcohol (Merck); CO (Matheson); tetra-n-butylammonium iodide (Fluka); nitrobenzene, *p*-nitrotoluene, *m*-nitrotoluene, *o*-nitrotoluene, 2,4-dinitrotoluene, 1,3-dinitrobenzene, 4,4'-dinitrobiphenyl and 2,2'-dinitrobiphenyl (TCI). $Rh(CO)_4PPN$, $Rh_2(CO)_4Cl_2$ were prepared according to methods reported previously [2]. All solvents were dried by known procedures prior to use.

General procedures

Infrared spectra were recorded on a Perkin Elmer 781 spectrophotometer, while ^1H NMR spectra were obtained on a Bruker AM-400 system. A Shimadzu GC-8A gas chromatograph equipped with a flame-ionization detector and an OV-17(5%) on Chromosorb W-HP (100/80 mesh) column (6 ft) in conjuction with a Shimadzu model chromatopac C-R1B microprocessor was employed for the analysis of carbamates and anilines. Mass spectral data were obtained on a Jeol JGC-20k/JMS-D100 GC/MS system. A Parr model 4561 mini reactor with a 4842 controller was used for the catalytic reductive carbonylation of nitroarenes.

Catalytic carbonylation of nitrobenzene

To a 300-ml Parr pressure reactor containing $Rh(CO)_4PPN$ (2.00×10^{-4} mol), nitrobenzene (1.00×10^{-2} mol), and aniline (7.5×10^{-4} mol) was added 30.0 ml of t-butyl alcohol. The system was charged with one atmosphere of CO and was then evacuated. The procedure was repeated twice to remove all the air in the reactor. Finally, the system was pressured up to 400 psi with CO and was heated with mechanical stirring at 140 °C for 12 h. The solution was analyzed on an NMR spectrometer using DMF as an internal standard to give t-butyl phenylcarbamate 96% and aniline 8% in yield. Essentially the same results were obtained by using GC to analyze the solution.

Similar procedures were employed for the reductive carbonylation of other mononitroarenes and the detailed conditions and the results are presented in Table 1.

Results and discussion

The rhodium carbonyl anion, $Rh(CO)_4(PPN)$, is an efficient catalyst precursor in various alcohol solutions at 140 °C and 10 ~ 30 atm CO (room temperature pressure) for the reductive carbonylation of nitrobenzene to the corresponding alkyl phenylcarbamate. Under the same reaction conditions, $Ru_3(CO)_{12}$ is also active with an activity approximately 1/3 that of $Rh(CO)_4^-$, but $Rh_2(CO)_4Cl_2$ and $RhCl_3 \cdot 3H_2O$ do not catalyze the reaction.

With methanol, ethanol, butanol or 2-butanol as the solvents and $Rh(CO)_4(PPN)$ as the catalyst, the reductive carbonylation of nitrobenzene to the corresponding carbamates is low in selectivity. The reaction is accompanied by the formation of a substantial amount of aniline. To see whether aniline is produced from the reduction of nitrobenzene by CO and water, extra water was added to the catalytic solution, the yield of aniline was greatly enhanced and the formation of carbamate was totally inhibited (run 5). Moreover, the selectivity of aniline was clearly higher in wet solvent than in dried solvent (runs 7–9). These observations indicate that in

Table 1

Carbonylation of nitroarenes in various alcohols [a]

Run	$ArNO_2$	ROH	Temp.	Catalyst	Time (h)	Conversion (%)	Selectivity [b]	
							$PhNH_2$ (%)	$PhNHCO_2R$ (%)
1	$PhNO_2$	MeOH	140	$Rh(CO)_4^-$	4	51	50	50
2	$PhNO_2$	EtOH	140	$Rh(CO)_4^-$	4	100	64	36
3	$PhNO_2$	^nBuOH	140	$Rh(CO)_4^-$	4	100	51	34
4	$PhNO_2$	2-BuOH	140	$Rh(CO)_4^-$	4	100	66	31
5 [c]	$PhNO_2$	2-BuOH	140	$Rh(CO)_4^-$	4	100	94	0
6	$PhNO_2$	^tBuOH	140	$Rh(CO)_4^-$	6	41	0	95
7	$PhNO_2$	^tBuOH	140	$Rh(CO)_4^-$	12	84	7	85
8 [d]	$PhNO_2$	^tBuOH	140	$Rh(CO)_4^-$	12	100	8	96
9 [e]	$PhNO_2$	^tBuOH	140	$Rh(CO)_4^-$	12	100	39	61
10	$PhNO_2$	^tBuOH	160	$Rh(CO)_4^-$	6	97	16	85
11	$PhNO_2$	^tBuOH	140	$Rh(CO)_4^-$ [a]	6	74	0	100
12	$PhNO_2$	MeOH	140	$Ru_3(CO)_{12}$ [a]	4	76	67	32
13	$PhNO_2$	^tBuOH	140	$Ru_3(CO)_{12}$ [a]	6	100	3	97
14	*o*-$MeC_6H_4NO_2$	2-BuOH	140	$Rh(CO)_4^-$	4	100	68	31
15	*m*-$MeC_6H_4NO_2$	2-BuOH	140	$Rh(CO)_4^-$	4	100	73	27
16	*p*-$MeC_6H_4NO_2$	2-BuOH	140	$Rh(CO)_4^-$	4	100	70	28
17	*p*-$MeC_6H_4NO_2$	^tBuOH	160	$Rh(CO)_4^-$	6	100	1	72 [f]

[a] Reaction conditions: $Rh(CO)_4(PPN)$ or $Ru(CO)_{12}$, 0.2 mmol; alcohol, 30 ml; $PhNO_2$, 10.0 mmol; CO, 400 psi; temp. 140 °C; Et_4NCl, 1.4 mmol if used (runs 11–13). Except otherwise mentioned, all solvents were dried using standard methods. [b] Selectivities are determined by NMR methods. [c] Water (22 mmol) was added to the solution. [d] Aniline (0.75 mmol) was added to the solution. [e] The alcohol was used as purchased and was not further dried. [f] The reaction also produced 30% di-*p*-tolyl urea.

the presence of water a modified water-gas-shift reaction [3–5] (eq. 2) occurs during the catalysis of reaction 1.

$$C_6H_5NO_2 + 3CO + H_2O \rightarrow C_6H_5NH_2 + 3CO_2 \qquad (2)$$

However, even if the solvents used were carefully dried, aniline still appeared in substantial amount in the product solution (runs 1–4). These results strongly imply that the alcohol solvents are also involved in the reduction of nitrobenzene to aniline.

Evidence supporting the notion that alcohols may act as a reducing agent was obtained from analyzing the product solution using 2-butanol as the solvent (run 4) by GC and by ^1H NMR spectroscopy. In addition to the carbamate and 2-butanol expected, the solution was found to consist of 6.6 mmol of aniline and 6.7 mmol of 2-butanone. This observation may be rationalized in terms of the reduction of nitrobenzene by 2-butanol as shown by the following reaction (eq. 3):

$$C_6H_5NO_2 + 3CH_3CH_2CHOHCH_3 \rightarrow C_6H_5NH_2 + 3CH_3CH_2COCH_3 + 2H_2O \qquad (3)$$

$$C_6H_5NO_2 + 2CO + CH_3CH_2CHOHCH_3 \rightarrow C_6H_5NH_2 + CH_3CH_2COCH_3 + 2CO_2 \qquad (4)$$

Stoichiometrically, the reduction of nitrobenzene to aniline by 2-butanol requires 3 mol of the alcohol for each mole of aniline produced [6,7] (eq. 3). However, since CO and the produced H_2O further react with nitrobenzene rapidly to give aniline

[2,8,9] (eq. 2), the overall reaction is the stoichiometry shown in eq. 4. This is in agreement with the observed results, which show that the molar ratio of aniline to 2-butanone is nearly 1:1. Similarly, when ethanol or butanol was used as the solvent for the catalysis of reaction 1, the corresponding aldehyde was also formed, but the ratio of aldehyde to aniline is lower than 1:1 presumably due to the secondary reaction of the aldehyde under the reaction conditions.

The reduction of nitroarenes by alcohols in the presence of Rh and Ru complexes has been demonstrated in our previous report [6]. Primary and secondary alcohols that possess a hydrogen on the α-carbon are able to reduce nitroarenes to the corresponding anilines at 150 °C. A β-hydrogen elimination mechanism is believed to occur in the dehydrogenation of alcohol to ketone or aldehyde during the reduction.

The above observations lead us to employ t-BuOH which does not have a hydrogen on the α-carbon for the reductive carbonylation of nitrobenzene. As shown in runs 6–8, a much higher selectivity of carbamate was achieved by using this alcohol. The addition of a small amount of aniline to the reaction solution further increases the selectivity of carbamate [1c]. Similarly, a much greater selectivity of carbamate by using the known catalyst system $Ru_3(CO)_{12}$–$Et_4N^+Cl^-$ [1b,1h] was also observed in ^{t}BuOH than in MeOH under the present reaction conditions.

The temperature employed for the catalysis of reaction 1 using ^{t}BuOH as the solvent has great effect on the selectivity of carbamate. It appears that 140 °C is the most suitable for the catalysis in terms of catalytic rate and selectivity. For example, at 120 °C the catalytic rate is too slow to be efficient, while at 160 °C the selectivity of carbamate drops significantly. The yield of aniline increases as the temperature further increases, even though the ^{t}BuOH was carefully dried. One possible reason for this unexpected result is that ^{t}BuOH undergoes dehydration significantly at a temperature higher than 160 °C to give water and 2-methylpropene. The produced water and CO then reduce nitrobenzenes to aniline in the presence of catalyst (eq. 2). Unfortunately, we were unable to detect 2-methylpropene from the solution. Further investigation is necessary to understand the cause for the low selectivity of carbamate in ^{t}BuOH at high temperature.

The reduction of dinitroarenes in the presence of CO, ^{t}BuOH and $Rh(CO)_4^-$ does not produce the corresponding carbamate. For 1,3-dinitrobenzene and 2,3-dinitrotoluene the observed products were the corresponding aminonitro or diaminoarene. The corresponding dicarbamate was isolated in the 4% yield from the reductive carbonylation of 4,4′-dinitrobiphenyl, while compounds **1** and **2** were isolated in 55% and 43% yields, respectively, from 2,2′-dinitrobiphenyl. Both compounds **1** and **2** were identified by comparing their NMR spectra with those of authentic samples *.

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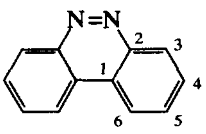
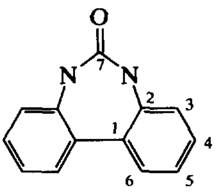
* The spectral data of **1**. MS: 180 (M^+), 152, 76. ^{1}H NMR ($CDCl_3$): δ 8.77 ~ 8.74 (m, 2H, H(3)), 8.59 ~ 8.56 (m, 2H, H(6)), 7.92 ~ 7.89 (m, 4H, H(4), H(5)). ^{13}C NMR: δ 145.55 (s, C(2)), 131.71 (d, C(5)), 131.48 (d, C(4)), 129.39 (d, C(6)), 121.55 (d, C(3)), 121.03 (s, C(1)). IR (aromatic) 750 cm^{-1}. M.p. 156 °C. The spectral data of **2**. MS: 210 (M^+), 168. ^{1}H NMR (DMSO): δ 8.81 (bs, 2H, H–N), 7.47 (d, $J = 7.8$ Hz, 2H, H(6)), 7.32 (t, $J = 7.6$ Hz, 2H, H(4)), 7.17 (t, $J = 7.5$ Hz, 2H, H(5)), 7.11 (d, $J = 7.9$ Hz, 2H, H(3)). ^{13}C NMR: δ 164.83 (s, C(7)), 140.43 (s, C(1)), 129.61 (s, C(2)), 129.27 (d, C(4)), 128.86 (d, C(6)), 124.32 (d, C(5)), 121.09 (d, C(3)); IR ν(N–H): 3230, ν(CO) 1680, ν(C–N) 1420 cm^{-1}. M.p. > 310 °C. HRMS: $C_{13}H_{10}N_2O$ calc.: 210.0794. Found: 210.0810.



(1)



(2)

In conclusion, for reductive carbonylation of mononitroarenes the use of t-butyl alcohol can drastically improve the selectivity of carbamate. An alcohol which would not undergo dehydrogenation under the catalytic conditions is necessary to obtain high yield of carbamate. However, for dinitroarenes the use of t-butyl alcohol does not significantly improve the selectivity of carbamate. It appears that other unknown factors predominate for the reductive carbonylation of dinitroarenes.

Acknowledgment

We thank the National Science Council of the Republic of China for support of this research.

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