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DIRECT SYNTHESIS OF N-ARYL BENZAMIDES BY REDUCTIVE CARBONYLATION OF NITROARENES CATALYZED BY RHODIUM CARBONYLS IN BENZENE

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The reactions of nitroarenes, carbon monoxide, and benzene in the presence of $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$ give N-aryl benzamides via the reductive carbonylation of nitroarenes and subsequent addition of benzene to the resulting aryl isocyanates.

Under pressure of carbon monoxide rhodium carbonyl catalysts such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ activate a carbon-hydrogen bond of an aromatic compound to allow the interaction with unsaturated compounds.1)-3) In this catalytic system N-aryl benzamides can be obtained from aryl isocyanates and benzene.1) It has been recently explored that the reductive carbonylation of nitroarenes with carbon monoxide in the presence of various group VIII metal catalysts give aryl isocyanates.4) These results prompted us to examine direct synthesis of N-aryl benzamides from nitroarenes, CO, and benzene via the reductive carbonylation of nitroarenes and subsequent addition of benzene to the resulting aryl isocyanates. In this communication we wish to report that the reductive carbonylation of nitroarenes catalyzed by the rhodium carbonyls in benzene leads to the direct synthesis of N-aryl benzamides.

When a mixture of nitrobenzene (10mmol), benzene (100ml), and $Rh_4(CO)_{12}$ (0.05 mmol) was heated at 220°C for 6hr under pressure of CO ($50 Kg/cm^2$ at room temperature), benzanilide was obtained in a 43% yield (based on an amount of the nitrobenzene converted (69%)), together with aniline (17%)5) and N,N'-diphenylurea (8%).5)

$$C_6H_5NO_2 \quad + \quad C_6H_6 \quad + \quad 3\ CO \xrightarrow{Rh_4(CO)_{12}} C_6H_5NHCOC_6H_5 \quad + \quad 2\ CO_2$$

The pressure of CO in the range of $30\text{-}100 Kg/cm^2$ and the reaction temperature at 220-240°C were suitable for this reaction. $Rh_6(CO)_{16}$ also showed the same catalytic activity as that of $Rh_4(CO)_{12}$. On the other hand, use of $Rh_2(CO)_4Cl_2$ as a catalyst resulted in the low conversion of nitrobenzene (27%) and no formation of benzanilide.

Similarly, the reductive carbonylation of substituted nitrobenzenes in benzene, except p-N,N-dimethylaminonitrobenzene, gave the corresponding N-aryl benzamides in 32-54% yields. These results are summarized in Table 1. In the reactions of nitrobenzenes having a substituent at the para-position, the conversion of nitrobenzenes and the yields of benzamides increase in the following order of the substituents; $-N(CH_3)_2 < -OCH_3 \simeq -Cl < -CH_3 < -H < -CN < -COCH_3 < -CO_2CH_3$. This order shows that the presence

Table 1. Reductive Carbonylation of Substituted Nitrobenzenes ($R-C_6H_5NO_2$) Catalyzed by Rhodium Carbonyl in Benzene.[a)]

Nitrobenzene (R)	Conversion (%)[b)]	Product Yield (%)[c)] $R-C_6H_4NHCOC_6H_5$	$R-C_6H_4NH_2$	$(R-C_6H_4NH)_2CO$
$p-(CH_3)_2N-$	34	-	100	-
$p-CH_3O-$	46	45	10	34
p-Cl-	47	35	20	11
$p-CH_3-$	54	45	12	25
H-	69	43	17	8
p-NC-	73	42	22	-
$p-CH_3CO-$	83	50	24	-
$p-CH_3O_2C-$	96	54	26	-
$m-CH_3-$	61	48	14	10
$o-CH_3-$	57	32	13	11

a) The reaction of the nitrobenzene (10mmol) with benzene (100ml) in the presence of $Rh_4(CO)_{12}$ (0.05mmol) was carried out at 220°C for 6hr under pressure of CO ($50Kg/cm^2$ at room temperature).

b) Based on an amount of the nitrobenzene used. Determined by GLC.

c) Based on an amount of the nitrobenzene converted. Benzamides and ureas were isolated and the yields were calculated from the amounts, and the yields of anilines were determined by GLC.

of electron-withdrawing groups facilitates the reductive carbonylation of nitrobenzene and/or subsequent addition of benzene.

N-Aryl benzamides are usually prepared from benzoyl halide and the corresponding anilines. It is interesting to note that the present method for preparing N-aryl benzamides from nitrobenzenes, CO, and benzene is more direct than the known method. Further studies on the detailed mechanism and extension of this reaction are in progress.

References and Notes

1) P. Hong, H. Yamazaki, K. Sonogashira, and N. Hagihara, Chem. Lett., 535 (1978).
2) P. Hong, B-R. Cho, and H. Yamazaki, Chem. Lett., 339 (1979).
3) P. Hong and H. Yamazaki, Chem. Lett., 1335 (1979).
4) W. B. Hardy and R. P. Bennet, Tetrahedron Lett., 961 (1967); F. J. Weigert, J. Org. Chem., 38, 1316 (1973); B. K. Nefedov and V. I. Manov-Yuvenskii, Izv. Akad. Nauk SSSR, Ser. Khim., 585 (1979); K. Unverferth, R. Hoentsch, and K. Schwetlick, J. Prakt. Chem., 321, 86 (1979) and references cited therein.
5) The formations of aniline and diphenylurea in the reduction of nitrobenzene with CO have been reported; A. F. M. Iqbal, Chem. Technol., 4, 566 (1974).

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