Journal of Organometallic Chemistry, 219 (1981) 125—127
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

HETEROGENEOUS COBALT CARBONYL-NITROARENE REACTIONS. A SIGNIFICANT DIFFERENCE FROM THE HOMOGENEOUS PROCESS

HOWARD ALPER * and MADHUBAN GOPAL

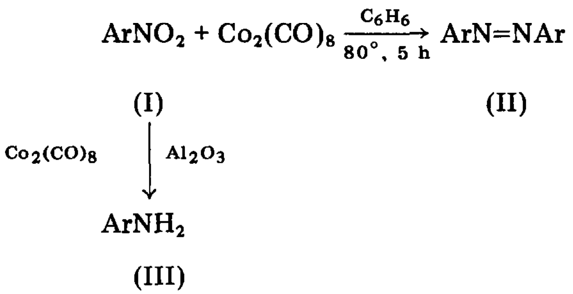
Department of Chemistry, University of Ottawa, Ottawa, Ontario, K1N 9B4 (Canada)

(Received February 27th, 1981)

Summary

Nitroarenes are converted to aromatic amines using dicobalt octacarbonyl on alumina. Product yields are dependent on the temperature at which the oxide is dried, as well as on the nature of the support. These results contrast with the homogeneous reaction which affords azo compounds.

In 1978, one of us described the conversion of nitrobenzenes (I) to azo compounds (II) with dicobalt octacarbonyl in refluxing benzene [1]. A number of publications have appeared in recent years concerning the use of metal carbonyls, deposited on refractory oxides such as silica or alumina, for effecting deoxygenation [2], olefin isomerization and disproportionation [3], desulfurization [4], dehalogenation [5], Fischer-Tropsch [6], and metathesis [7] reactions. It was of interest to learn the influence of an oxide on the nitroarene-$Co_2(CO)_8$ reaction. In other words, is the heterogeneous process similar to, or different from, the homogeneous one? We now report the results of this study.



$$\begin{tikzcd} \underset{(I)}{\mathrm{ArNO_2}} + \mathrm{Co_2(CO)_8} \arrow[r, "\mathrm{C_6H_6}", "80^\circ,\ 5\ \mathrm{h}"'] \arrow[d, "\mathrm{Al_2O_3}", "\mathrm{Co_2(CO)_8}"'] & \underset{(II)}{\mathrm{ArN{=}NAr}} \\ \underset{(III)}{\mathrm{ArNH_2}} & \end{tikzcd}$$

---

[*] E.W.R. Steacie Fellow, 1980—1982.

0022-328X/81/0000—0000/$02.75

A rapid color change occurs when a hexane solution of $Co_2(CO)_8$ is exposed to alumina at room temperature. When *p*-nitrotoluene was added and the reaction mixture was stirred overnight at room temperature, *p*-toluidine (III, Ar = *p*-$CH_3C_6H_4$) was isolated in 60% yield with the azo compound II (Ar = *p*-$CH_3C_6H_4$) being obtained as a low-yield by-product. The alumina used in this experiment was dried at 150°C under reduced pressure. The yield of *p*-toluidine decreased to 35% when the reaction was effected in a carbon monoxide atmosphere. A similar reduction in yield (to 38%) occurred using a nitrogen atmosphere but first drying the alumina at 550°C instead of at 150°C. Other oxides, including silica and Florisil, afforded *p*-toluidine from *p*-nitrotoluene, but in lower yields than in the case of alumina (Table 1).

Good yields of aromatic amines were also attained from a variety of nitroarenes and $Co_2(CO)_8/Al_2O_3$ (Table 1). Functionalities such as chloro, ketone, and ether were unaffected under these reaction conditions. Only starting material was recovered when the nitroarene was exposed to alumina in the absence of dicobalt octacarbonyl. Bis(tributylphosphine) dicobalt hexacarbonyl and tetracobalt dodecacarbonyl on alumina were less effective reagents (7—45% yields of III) than dicobalt octacarbonyl for the reduction of I.

That the reduction process is heterogeneous was clearly demonstrated by the following experiment: after stirring the mixture of $Co_2(CO)_8$ and alumina in hexane for 2 hours, the solid and liquid phases were separated by filtration (N_2 atmosphere). Each phase was treated separately with *p*-nitrotoluene in benzene. While *p*-toluidine was clearly formed using the solid phase, the liquid phase only afforded recovered nitro compound.

Clearly, the heterogeneous process is different from the homogeneous pathway. It is therefore likely that the intermediates involved in the two reactions are not the same. A key observation, noted above, is that an increase in the temperature at which the alumina is dried results in a decrease in the yield of amine, indicating that the hydroxyl groups, which are present on the surface of the oxide, participate in the reaction. (There are more such OH groups present

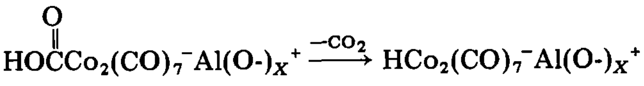
TABLE 1

REACTION OF I WITH $Co_2(CO)_8$

I, Ar =	Oxide [a]	Product [b]	Yield [c] (%)
p-$CH_3C_6H_4$	Al_2O_3	*p*-Toluidine	60
		4,4'-Azotoluene	6
	Al_2O_3(550°C)	*p*-Toluidine	38
	Al_2O_3	*p*-Toluidine	35 [d]
	SiO_2	*p*-Toluidine	40
	Florisil	*p*-Toluidine	35
p-$CH_3OC_6H_4$	Al_2O_3	*p*-Anisidine	62
		4,4'-Azoanisole	3
	Al_2O_3(550°C)	*p*-Anisidine	39
p-ClC_6H_4	Al_2O_3	*p*-Chloroaniline	62
p-$PhCOC_6H_4$	Al_2O_3	*p*-Aminobenzophenone	71
m-$CH_3C_6H_4$	Al_2O_3	*m*-Toluidine	70
2-Fluorene	Al_2O_3	2-Aminofluorene	77

[a] The oxides were dried at 150°C except where noted. [b] Products were identified by comparison of physical data with those for authentic materials. [c] Yields are of isolated, pure products. [d] CO atmosphere.

at 150°C than at 550°C). It is conceivable that attack by one of these hydroxyl groups on a cobalt carbonyl carbon would afford IV, which on loss of carbon dioxide generates the binuclear cobalt hydride V. The latter can then convert nitroarene to aromatic amine.



$$HO\overset{O}{\overset{\|}{C}}Co_2(CO)_7^-Al(O\text{-})_X^+ \xrightarrow{-CO_2} HCo_2(CO)_7^-Al(O\text{-})_X^+$$

(IV) (V)

In conclusion, nitroarenes can be reduced to amines under very mild conditions using $Co_2(CO)_8/Al_2O_3$. Regardless of the mechanistic details, the heterogeneous and homogeneous reactions are fundamentally different.

Experimental

Spectral data were recorded with a Unicam SP-1100 infrared, Varian T-60 nuclear magnetic resonance, and Varian MS9 mass spectrometers. The nitro substrates and cobalt carbonyls were commercial products, and were used as received. The oxides used were: Al_2O_3 (Fisher adsorption 80—200 mesh), SiO_2 (Bio-rad), and Florisil (Fisher, 60—200 mesh). All reactions were run under an atmosphere of dry nitrogen (except for one experiment using carbon monoxide).

General procedure for the reaction of nitroarenes with $Co_2(CO)_8/Al_2O_3$

Alumina (20 g) was dried by heating overnight at 150°C (3—6 mmHg). A mixture of $Co_2(CO)_8$ (3.0 mmol) and alumina in hexane (60 ml) was stirred at room temperature for two hours. To this deep red mixture was added the nitroarene (2.3 mmol) dissolved in the minimum amount of benzene or tetrahydrofuran, and stirring was continued for 16—18 hours. The mixture was filtered, the oxide was treated with ether or ethyl acetate until it was free of product(s), and the washings were added to the filtrate. The crude amine, obtained by rotary evaporation of the filtrate, was purified by recrystallization or by chromatography on silica gel using hexane-ether as eluant.

Acknowledgement

We are grateful to the Natural Sciences and Engineering Research Council for support of this research.

References

1 H. Alper and H.N. Paik, J. Organometal. Chem., 144 (1978) C18.
2 H. Alper and M. Gopal, J. Chem. Soc., Chem. Commun., (1980) 821.
3 A. Brenner and R.L. Burwell, Jr., J. Catal., 52 (1978) 364.
4 H. Alper and C. Blais, J. Chem. Soc., Chem. Commun., (1980) 169.
5 H. Alper and L. Pattee, J. Org. Chem., 44 (1979) 2568.
6 D. Commereux, Y. Chauvin, F. Hugues, J.M. Basset, and D. Olivier, J. Chem. Soc., Chem. Commun., (1980) 154.
7 A.A. Olsthoorn and J.A. Moulijn, J. Mol. Catal., 8 (1980) 147.