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THE CATALYTIC TRANSFORMATION OF NITROSOBENZENE INTO AZOXY AND AZOBENZENE

F. PORTA, M. PIZZOTTI and S. CENINI

Istituto di Chimica Generale and CNR Center, Via Venezian 21, 20133 Milano (Italy)

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Summary

Nitrosobenzene is converted into azoxybenzene in alcoholic media in the presence of $Ru(CO)_3(PPh_3)_2$ as catalyst and under an inert atmosphere; $Fe(CO)_3(PPh_3)_2$ and palladium complexes such as PdL_2Cl_2 (L = PhNO, p-$MeC_6H_4NH_2$, PPh_3) and $Pd_3(CO)_3(PPh_3)_4$, are less active as catalysts. Under CO pressure and with $Ru(CO)_3(PPh_3)_2$ as catalyst, nitrosobenzene is converted into azobenzene and aniline, while azoxybenzene gives azobenzene.

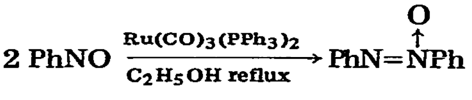
Introduction

The catalytic transformations of organic functional groups by transition metal complexes have recently received much attention [1]. Usually milder conditions and better selectivities can be achieved in this way. As a continuation of our investigations on metal-assisted reactions, particularly these involving nitrogen-containing organic functions [2], we have studied the reactions of nitrosobenzene in the presence of transition metal complexes. It was previously reported that nitrosobenzene gives azobenzene in a stoichiometric reaction with $Fe(CO)_5$ in boiling butyl ether [3]. More recently, the carbonylation of nitroso compounds to the corresponding isocyanates by CO in the presence of rhodium and iridium carbonyl derivatives has been studied [4].

Results and discussion

i) Reactions at atmospheric pressure

By heating nitrosobenzene in ethanol in the presence of catalytic amounts of $Ru(CO)_3(PPh_3)_2$, azoxybenzene can be obtained in good yields (eq. 1) (Table 1, runs 1 and 2):



$$2\ PhNO \xrightarrow[C_2H_5OH\ reflux]{Ru(CO)_3(PPh_3)_2} PhN{=}\overset{\overset{O}{\uparrow}}{N}Ph \qquad (1)$$

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TABLE 1

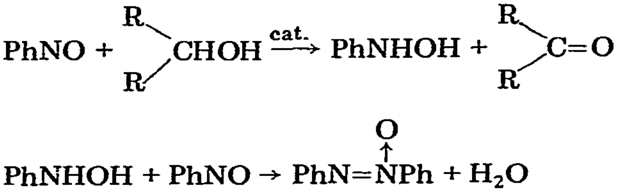
CONVERSIONS OF PhNO INTO $PhN{=}\overset{O}{\overset{\uparrow}{N}}Ph$ WITH $Ru(CO)_3(PPh_3)_2$ AS CATALYST; [PhNO]/[cat.] = 50

Run	1	2	3	4	5	6	7	8
PhNO (mmol)	7.06	7.06	7.06	7.06	7.06	7.06	7.06	2.234 [b]
cat. (mmol $\times 10^2$)	14	14	14	14	14	14	14	4
toluene (ml)	—	—	20	20	—	20	20	20
ethanol (ml)	20	20	—	—	20	—	5	—
T (°C)	reflux	reflux	80	80	75	80	80	80
t (h)	6	6	6	6	3	3	7	3
p_{N_2} (atm)	1	—	1	—	—	—	—	—
p_{CO} (atm)	—	1	—	1	10	30	60	30
conversion (%)	90.8	ca. 90	15.15	ca. 50	100	100	100	—
azoxybenzene (%) [c]	65.5	68.1	15.1	[a]	67	19.5	—	—
azobenzene (%) [c]	—	—	—		traces	34.5	main	20.5
aniline (%) [c]	—	—	—		—	10.1	30.1	traces

[a] Not determined. [b] mmol of azoxybene. [c] With respect to the intiial PhNO or azoxybenzene.

The reaction is insensitive to whether the atmosphere used is dinitrogen or carbon monoxide. Control experiments showed that nitrosobenzene undergoes no significant reaction in ethanol or in benzene-ethanol at 75—80° C in the absence of the catalyst and under nitrogen. The iron complex $Fe(CO)_3(PPh_3)_2$ proved to be much less active than its ruthenium analogue in this reaction. With toluene as solvent (runs 3 and 4) much lower yields were obtained under a nitrogen atmosphere, while in the presence of carbon monoxide the degree of conversion was increased to 50%. However, control experiments showed that nitrosobenzene in toluene at 75—80° C reacts with carbon monoxide in the absence of the catalyst to give a mixture of products and with a degree of conversion of ca. 25%.

Although these results indicate that CO acts as a reducing agent in non protic solvents (the formation of CO_2 was confirmed by the usual tests), in protic media the reaction could proceed via the proton transfer from the solvent to nitrosobenzene, with the intermediate formation of hydroxylamine (eq. 2):



$$\begin{gathered} PhNO + \begin{matrix} R \\ R' \end{matrix}\!\!>\!CHOH \xrightarrow{cat.} PhNHOH + \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}O \\ PhNHOH + PhNO \rightarrow PhN{=}\overset{\overset{\displaystyle O}{\uparrow}}{N}Ph + H_2O \end{gathered} \qquad (2)$$

In one experiment conducted with a slow stream of dinitrogen, the gas was passed through a trap cooled with dry/ice acetone. The resulting condensed liquid was shown by mass spectrometry to be a very complex mixture. Treatment of this liquid with 2,4-dinitrophenylhydrazine gave only small amounts of the corresponding hydrazone of acetaldehyde. Similarly, with isopropanol as solvent and a nitrogen atmosphere, acetone was obtained in only small amounts, together with azoxybenzene. Proton transfer from the alcohols has been used to reduce other organic compounds such as ketones [5] and alkenes [6] in the presence of transition metal complexes, and is reminiscent of the Meerwein-Ponndorf reaction, where a ketone is reduced to the corresponding alcohol by use of aluminium isopropanolate. In our case the absence of significant amounts of acetone among the products indicates that this is not the main reaction path. Moreover, only traces of nitrobenzene were produced in the catalytic reactions. Analyses of the gas evolved during the catalytic reactions conducted in alcoholic media under nitrogen showed the formation of carbon dioxide, but again its quantity was less than that calculated on the basis of the PhNO converted.

At the end of the catalytic reaction a ruthenium-carbonyl complex was isolated (IR evidence), and this did not show any catalytic activity. Furthermore, upon addition of fresh nitrosobenzene at high conversions no further reaction occurred. Since it was proved that azoxybenzene does not poison the catalyst, this result is probably to be ascribed to a slow decomposition of the catalyst or to the presence of large amounts of another product, which is reduced in preference to nitrosobenzene. When acetone was added in amounts equivalent in molar terms to the nitrosobenzene, to the catalytic system in isopropanol the conversion of nitrosobenzene was not significantly changed.

TABLE 2

CONVERSIONS OF PhNO INTO $PhN{=}\overset{O}{\overset{\uparrow}{N}}Ph$ WITH PALLADIUM COMPLEXES AS CATALYSTS

Run[a]	1	2	3	4	5	6[b]	7[b]
Cat. (mmol X 10^2)	$PdCl_2(PhNO)_2$ (25.6)	$PdCl_2(PhNO)_2$ (6.39)	$Pd(PPh_3)_2Cl_2$ (14.26)	$Pd(PPh_3)_2Cl_2$ (14.2)	$Pd(p\text{-}CH_3C_6H_4NH_2)_2Cl_2$ (25)	$Pd(PhNO)_2Cl_2$ (25.6)	$Ph(PhNO)_2Cl_2$ (25.6)
PhNO (mmol)	12.78	12.78	7.13	7.22	2.56	2.56	2.56
Benzene (ml)	—	—	15	12.5	15	20	20
Ethanol (ml)	—	—	15	12.5	—	—	—
Isopropanol (ml)	25	25	—	—	—	—	—
T (°C)	80	80	75	75	80	80	80
P_{N_2} (atm)	1	1	—	1	1	1	—
P_{CO} (atm)	—	—	1	—	—	—	1
Azoxybenzene (%)[c, d]	25.7	38.3	35.12	24.2	60	58.85	39.6

[a] Reaction time: 4 hours. [b] In these experiments 3.06 mmol of $p\text{-}CH_3C_6H_4NH_2$ were also added, and 19.2% of $C_6H_5N{=}NC_6H_4CH_3\text{-}p$ was obtained (run 7). [c] $Pd_3(CO)_3(PPh_3)_4$ gave 20.8% of azoxybenzene under the conditions of run 4. [d] run 4: conversion = 48.7%; run 5: conversion = 65%.

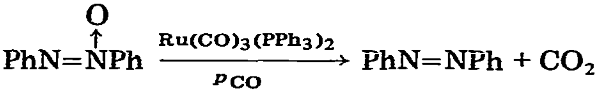
We also examined the catalytic activity of a series of palladium complexes in this reaction (Table 2). We observed generally lower conversions to azoxybenzene, but in some cases the catalysts were only partially soluble in the reaction medium (runs 1, 5, 6 and 7). In two experiments (runs 6 and 7) p-$MeC_6H_4NH_2$ was also added in molar amounts equivalent to the PhNO, free and complexed. At the end of the reaction the original catalyst, $Pd(PhNO)_2Cl_2$, was partly recovered as the amine complex, $Pd(p\text{-}MeC_6H_4NH_2)_2Cl_2$. Azoxybenzene was again the main product, but in run 7, conducted under a carbon monoxide atmosphere, significant amounts of $C_6H_5N{=}NC_6H_4Me$-p were also produced.

ii) Reactions under CO pressure

We also carried out some reactions under CO pressure and with $Ru(CO)_3(PPh_3)_2$ as catalyst. At ten atmospheres (Table 1, run 5), complete conversion of the nitrosobenzene was achieved, and azobenzene was detected together with the main product, which is still azoxybenzene. Upon increasing the CO pressure to 30 atmospheres (run 6), the amount of azobenzene produced is increased, but aniline is also formed even though toluene was used as solvent.

Finally at 60 atm of CO (run 7), large amounts of aniline were obtained, while azobenzene was the only product of the coupling.

The formation of aniline under CO pressure might indicate that a nitrene species is formed as an intermediate, but reacts further in its triplet state by hydrogen abstraction from the solvent. On the other hand, the formation of azobenzene cannot be ascribed to a coupling of two RN residues. It was also shown that $Ru(CO)_3(PPh_3)_2$ is also able to catalyze the reduction of azoxybenzene to azobenzene under CO pressure (Table 1, run 8):



$$PhN{=}\overset{\overset{\displaystyle O}{\uparrow}}{N}Ph \xrightarrow[p_{CO}]{Ru(CO)_3(PPh_3)_2} PhN{=}NPh + CO_2 \qquad (3)$$

Conclusions

We have shown that $Ru(CO)_3(PPh_3)_2$ is an efficient catalyst for the conversion of nitrosobenzene into azoxybenzene in alcoholic media. The catalytic deoxygenation of azoxybenzene to azobenzene under CO pressure has few precedents, although it is likely that other metal carbonyls will exhibit the same type of activity. This reaction has been observed with $Fe(CO)_5$ under stoichiometric conditions [3] and also catalytically at high temperatures and CO pressures [7].

Experimental

The complexes $Ru(CO)_3(PPh_3)_2$, $Pd(PhNO)_2Cl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd_3(CO)_3(PPh_3)_4$ were prepared by standard methods. $Pd(p\text{-}CH_3C_6H_4NH_2)_2Cl_2$ was isolated from one reaction in which $Pd(PhNO)_2Cl_2$ was used as catalyst (run 6, Table 2). At the end of the reaction the yellow compound was filtered off, washed with n-hexane and dried in vacuo. [Found: C, 43.2; H, 4.9; N, 6.9. Calcd. for $C_{14}H_{18}Cl_2N_2Pd$: C, 43.0; H, 4.6; N, 7.1%. $\nu(NH) = 3295, 3220, 3130$

cm^{-1}, in Nujol.] $\mathrm{PhN{=}\overset{\overset{O}{\uparrow}}{N}Ph}$, PhN=NPh and $PhN{=}NC_6H_4Me$-*p* were identified by their m.p. and IR spectra, which were taken on a Beckman 4210 spectrophotometer.

GLC measurements were carried out with a Dani 3600 gas chromatograph, using a 2 m column filled with 20% weight silicone oil 702 on Chromosorb W 60-80 mesh, with $PhNO_2$ as internal standard, for nitrosobenzene-aniline analyses. A 2.5 m column filled with 30% weight Carbowax 1500 on Chromosorb W 60—80 mesh treated with DMCS with toluene as internal standard, was used for acetone/isopropanol analyses.

Reaction mixtures, filtered if insoluble materials were present, were evaporated to dryness and chromatographated on silica gel with elution with n-hexane, 1/1 benzene/n-hexane, and benzene. In the experiments conducted at atmospheric pressure, in glass vessels, samples of the solution were periodically removed with a syringe through a serum cap and analysed by GLC. High pressure reactions were carried out in a 100 ml stainless steel autoclave. The reagents were placed under nitrogen in a glass liner constructed to fit the autoclave. The autoclave was charged with CO at the desired pressure. Magnetic stirring was begun and the autoclave was heated to the desired temperature.

Acknowledgement

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References

1 See for example: I. Wender and P. Pino (Eds.), Organic Syntheses via metal carbonyls, Vols. I, 1968 and II, 1977, John Wiley and Sons, New York.
2 (a) G. La Monica and S. Cenini, J. Chem. Soc. Dalton, (1980) 1145. (b) P.L. Bellon, S. Cenini, F. Demartin, M. Manassero, M. Pizzotti and F. Porta, J. Chem. Soc. Dalton, (1980) 2060 and references therein. (c) G. La Monica and S. Cenini, J. Organometal. Chem., 216 (1981) C35.
3 H. Alper and J.T. Edward, Canad. J. Chem., 48 (1970) 1543.
4 Von K. Unverferth, C. Ruger and K. Schwetlick, J. Prakt. Chem., 319 (1977) 841.
5 A. Camus, G. Mestroni and G. Zassinovich, J. Molec. Catal., 6 (1979) 231 and references therein.
6 C. Fragale, M. Gargano and M. Rossi, J. Molec. Catal., 5 (1979) 65 and references therein.
7 J.E. Kmiecik, J. Org. Chem., 30 (1965) 2014.