J. CHEM. SOC., CHEM. COMMUN., 1986

Deoxygenation Reactions of *ortho*-Nitrostyrenes with Carbon Monoxide Catalysed by Metal Carbonyls: a New Route to Indoles

Corrado Crotti,ª Sergio Cenini,*ª Bruno Rindone,^b Stefano Tollari,^b and Francesco Demartin^c

^a Dipartimento di Chimica Inorganica e Metallorganica and CNR Center, ^b Dipartimento di Chimica Organica e Industriale, and ^c Istituto di Chimica Strutturistica Inorganica, Via Venezian 21, 20133 Milano, Italy

The metal carbonyls $Fe(CO)_5$. $Ru_3(CO)_{12}$, and $Rh_6(CO)_{16}$ are catalysts for the deoxygenation of *ortho*-nitrostyrenes under carbon monoxide pressure to give indole derivatives; the crystal structure of a non-catalytically active rhodium complex obtained during the synthesis of (**5e**) is reported.

The catalytic carbonylation of aromatic nitro compounds is an area of current interest, from both the academic and industrial points of view.^{1,2} We have recently reported on the carbonylation of aromatic nitro compounds catalysed by ruthenium carbonyls in toluene–methanol, to give carbamates.² This method avoids the use of phosgene for the synthesis of these important chemicals, used as pesticides. The discovery of new synthetic methods for the construction of the indole nucleus under non-acidic conditions is also of current interest.

The intramolecular cyclization of nitrenes obtained either from deoxygenation of *o*-nitrostyrenes by trialkyl phosphites³

or from thermal or photochemical decomposition of *o*azidostyrenes⁴ has been described. Moreover, under hydroformylation conditions, using supported rhodium on carbon as catalyst, *o*-nitrostyrene is converted into skatole, by a reaction involving formation of 2-(*o*-nitrophenyl)propionaldehyde, reduction of the nitro group, and ring closure *via* thermal dehydration.⁵

We report here that the metal carbonyls $Fe(CO)_5$ (1), $Ru_3(CO)_{12}$ (2), and $Rh_6(CO)_{16}$ (3) are catalysts for the deoxygenation of nitrostyrenes (4), to afford directly the indoles (5) (Table 1) (Scheme 1).

Table 1. Conversion of ortho-nitrostyrenes (4)	4) i	into indoles catalysed by	y	$Fe(CO)_5(1)$), 1	$Ru_3(CO)_{12}$	(2)	, and	Rh ₆ (CO)16	(3)).a
--	--------------	---------------------------	---	---------------	------	-----------------	-----	-------	-------------------	-------	-----	-----

Substrate	Catalyst	Cat.: substrate ratio	Conversion (%)	Indole (%) ^b	Amine (%) ^b	Other products (%) ^b
(4 a)	(2)	1:50	100	(5a) 18.1	(6a) 33.3	с
`,,`	(3)	1:50	100	(5a) 25.0	(6a) 41.8	с
(4b)	(2)	1:25	100	(5b) 68.6	(6b) 10.9	(10) 11.7
(4c)	(1)	1:10	100	(5c) 74.9	(6c) 2.5	с
`,,`	(2)	1:25	100	(5c) 32.6	<u> </u>	(7) 39.3
				. ,		(12) 9.6
,,	(3)	1:50	100	(5c) 58.8		(7) 24.5
(4d)	(2)	1:25	100	(5d) 71.5	(6d) 17.3	с
(4e)	(1)	1:10	100	(5e) 58.9	(6e) 17.8	с
`,,`	(2)	1:25	100	(5e) 63.1	(6e) 15.1	с
,,	(3)	1:50	71.5	(5e) 35.2	(6e) 5.0	(11) 17.3
(4f)	(2)	1:25	100	(5f) 56.2	(6f) 20.1	$\begin{cases} (8) & 6.3 \\ (9) & 3.7 \end{cases}$
(4 g)	(2)	1:25	100	(5g) 57.7	(6g) 13.9	c

^a See text for conditions. ^b Calculated with respect to converted ortho-nitrostyrenes and showing selectivities. ^c Not identified.



The catalysts (1)---(3) were used in a molar ratio ranging from 1:10 to 1:50 relative to the nitrostyrenes (4), with a concentration of 0.1 M of substrate in toluene, at 220 °C, for 5 h, under 80 atm of carbon monoxide. Substrates (4a)---(4g) were prepared by using a modified Wittig reaction^{6,7} and n.m.r. spectroscopy showed that they were a *ca.* 85:15 *trans-cis*-mixture, except for (4g), for which the n.m.r. spectrum cannot clarify the structure.

The products were mainly the indoles (5a)—(5g), derived by attack of an intermediate nitrene on the β -carbon atom of the styrene double bond. With substrates (4f) and (4g), having a β , β -disubstituted styrene double bond, a 1,2-shift of one substituent occurs during the reaction, phenyl undergoing rearrangement in preference to methyl. Other products were the amines (6) corresponding to the starting nitro-derivatives, and derived from hydrogen abstraction effected by the intermediate nitrene. The amine corresponding to (4c) is also probably formed as an intermediate, but under the reaction conditions *cis-trans* isomerization occurs, followed by intramolecular amidation to give the quinolone (7). Other products were observed in some instances. Compound (4f) also gave





compounds (8) and (9), derived by hydrogenation of the 2,3-double bond of the indole (5f) and of the amine (6f). Carbon-carbon bond coupling was also observed in the case of (5b) to give (10). Finally (4e) and (4c) also gave the quinolone (11) and the 3,4-dihydroquinolone (12), which may be formed by reaction of the intermediate nitrene with carbon monoxide to give an isocyanate, followed by cyclization and reduction of the double bond in the case of (12).

Table 1 shows the quantitative results obtained after

785



Figure 1. ORTEP view of $Rh(CO)_2$ (indolato) (13). Selected distances and angles with estimated standard deviations are: Rh-N(1) 2.103(5), Rh-N(15) 2.040(5), Rh-C(20) 1.866(7), C(20)-O(20) 1.129(8), Rh-C(21) 1.868(7), C(21)-O(21) 1.143(8), N(1)-C(6) 1.368(8), C(6)-C(7) 1.440(7), N(15)-C(7) 1.351(7), C(14)-N(15) 1.384(7), C(7)-C(8) 1.355(8), C(8)-C(9) 1.419(8), C(9)-C(14) 1.389(9) Å; N(1)-Rh-N(15) 78.7(2), $C(20)-Rh-C(21) 87.9(3)^{\circ}$.

silica-gel chromatography of the reaction products. The low yield of (5a) must be attributed to the formation of unidentified high molecular weight products and to some oxidation of (5a) occurring during work-up. The indole is the major product in most cases, and Fe(CO)₅ seems to be the most selective catalyst. Nevertheless, in these reactions some iron oxides were formed, and it is known that they catalyse the insertion of the intermediate nitrenes into the aromatic C-H bond.⁸ The cluster catalysts (2) and (3) seem to be of comparable selectivity. The i.r. spectra of the solutions at room temperature and atmospheric pressure at the end of the reactions with (2) as catalyst show the presence of Ru(CO)₅, which rapidly trimerises to give (2). In some experiments rhodium metal was detected at the end of the reaction where (3) was used as catalyst. However in one case, during the synthesis of (5e), a well defined rhodium complex (13) could be isolated. Compound (13) (v_{co} 2067s and 2000s cm⁻¹, in toluene) was shown by X-ray structure analysis to be a bis(carbonyl) indolato rhodium(I), having the pyridine nitrogen atom of the \mathbb{R}^2 substituent co-ordinated to rhodium.^{†‡} However, when compound (13) was used as catalyst in the place of compound (3), it showed a very low activity, indicating that (13) is not the complex catalytically active during the reactions carried out with (3) as catalyst.

In conclusion, this catalytic method has the advantage of a better selectivity and simpler work-up procedure over the analogous stoicheiometric trialkyl phosphite deoxygenation of o-nitrostyrenes.³ Preliminary results have shown that compound (2) is also active as a catalyst for the deoxygenation of 1-phenyl-2-nitroethylene.

Received, 23rd December 1985; Com. 1810

References

- 1 A. F. Iqbal, Chem. Tech., 1974, 566.
- 2 S. Cenini, M. Pizzotti, C. Crotti, F. Porta, and G. La Monica, J. Chem. Soc., Chem. Commun., 1984, 1286, and references cited therein.
- 3 R. J. Sundberg, J. Org. Chem., 1965, 30, 3604.
- 4 R. J. Sundberg, H. F. Russel, W. V. Ligon, jr., and Long Su Lin, J. Org. Chem., 1972, 37, 719; G. L. Abbé, Chem. Rev., 1969, 69, 345.
- 5 E. Ucciani and A. Bonfand, J. Chem. Soc., Chem. Commun., 1981, 82.
- 6 W. S. Wadsworth and W. D. Emmons, J. Am. Chem. Soc., 1961, 83, 1733.
- 7 D. H. Wadsworth, O. E. Schupp, III, E. J. Seus, and J. A. Ford, jr., J. Org. Chem., 1965, **30**, 680.
- 8 R. A. Abramovitch and B. A. Davis, Chem. Rev., 1964, 64, 149.

9 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 1983, 39, 159.

 \dagger Elemental analyses and ${}^{1}H$ n.m.r. and mass spectra are in agreement with the structure (13).

‡ Crystal data: C₁₅H₉N₂O₂Rh, M_r = 352.16, orthorhombic, space group Pnma (No. 62), a = 9.739(2), b = 6.434(1), c = 20.860(4) Å, U = 1307(1) Å³, Z = 4, µ(Mo-K_α) = 12.86 cm⁻¹, D_c = 1.789 g cm⁻³. 1239 intensity data were collected on a CAD-4 Enraf-Nonius diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and were corrected for absorption as described in ref. 9. The structure was solved and refined using the SDP software by a combination of Patterson, difference Fourier, and full-matrix least-squares methods. The final conventional residuals were R = 0.039 and R_w = 0.050 for 873 observations having I ≥ 3 σ (I), and 121 variables. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.