Journal of Organometallic Chemistry, 307 (1986) C35—C37
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

COBALT ATOMS AS CATALYSTS OF THE SYNTHESIS OF PYRIDINES FROM NITRILES AND ACETYLENES

GIOVANNI VITULLI, SERGIO BERTOZZI, RAFFAELLO LAZZARONI and PIERO SALVADORI

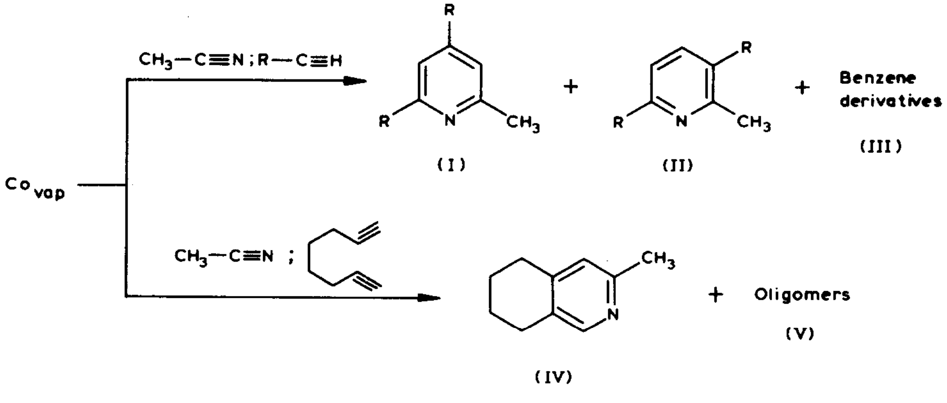
Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, 56100 Pisa (Italy)

(Received February 25th, 1986)

Summary

Cobalt atoms have been found to provide efficient and selective catalysts for the synthesis of pyridines from nitriles and acetylenes; the reaction conditions are milder than those reported for other cobalt-containing catalysts.

Extensive studies have been made on cobalt-catalyzed synthesis of pyridines from alkynes and nitriles [1]. With the exception of the difficult to handle [1] cyclopentadienylbis(ethylene)cobalt [2], the previously described cobalt catalysts were not active at room temperature [1]. We show here that cobalt atoms promote the synthesis of pyridines from acetonitrile and acetylenes or diacetylenes even at room temperature (Scheme 1).



SCHEME 1. R = C_3H_7; C_4H_9.

0022-328X/86/$03.50

Cobalt metal (0.05 g; 0.8 mg-atom) was evaporated during 40 min and co-condensed with acetonitrile (21.4 g; 520 mmol) and 1-hexyne (4.2 g; 52 mmol) by introducing them simultaneously, at liquid nitrogen temperature, using a glass metal atom reactor [3]. The mixture was allowed to warm to room temperature and the resulting brown solution filtered under nitrogen then set aside at room temperature or at 80 or 120°C for two days.

The results obtained for the reaction of 1-pentyne, 1-hexyne and 1,7-octadiyne with acetonitrile are summarized in Table 1. In the cyclocotrimerization of 1-pentyne and 1-hexyne with CH_3CN, the chemoselectivity of the reaction, i.e. the molar ratio of pyridines to benzene derivatives, is high and increases with the temperature, rising from ca. 5 at 25°C to ca. 7 at 120°C. The reaction gives two isomeric pyridine derivatives (I and II) (Scheme 1), with the symmetrically substituted species I, as the major product. The regioselectivity of the reaction, (I/II ca. 2) is independent of the temperature.

Co atoms are also useful in effecting the cyclocodimerization of 1,7-octadiyne with acetonitrile to give 5,6,7,8-tetrahydro-2-methylisoquinoline (IV) (Scheme 1). Reaction at 25°C for 48 h gives a diyne conversion of ca. 37%, with the pyridine derivative as the main product (ca. 86%), along with some diyne oligomers (ca. 14%) (Table 1). At 80°C the conversion is higher, but the diyne is mainly oligomerized (78%) and the yield of the pyridine derivative is only 22%.

TABLE 1

SUBSTITUTED PYRIDINES OBTAINED ACCORDING TO SCHEME 1[a]

Alkyne (mmol)	Temperature (°C)	Conversion of alkyne (%)	Products (%)[b]		Chemo-selectivity[c]	Regio-selectivity[d]
			Pyridines	Benzenes		
1-Pentyne	25	40	84	16	5.2	2.1
(60)	80	59	85	15	5.6	2.0
	120	84	87	13	6.7	2.2
1-Hexyne	25	35	82	18	4.6	2.1
(52)	80	56	85	15	5.6	2.0
	120	74	88	12	7.3	2.0
1,7-Octadiyne[g]	25	37	86	14[e]	6.1[f]	[h]
(30)	80	80	22	78[e]	0.3[f]	[h]

[a] CH_3CN/alkyne (mol/mol) = 10; Co metal vaporized 50 mg (0.8 mg-atom); reaction time ca. 48 h; work-up by acid—base separation. [b] Molar composition determined on isolated products. [c] (I + II)/III (mol/mol). [d] Ratio I/II (mol/mol) as indicated by GLC. [e] Yield of oligomers calculated as moles of diyne oligomerized; the structure of oligomers was not determined. [f] Ratio of moles of pyridine to moles of diyne oligomerized. [g] CH_3CN/diyne (mol/mol) = 5; toluene as solvent. [h] The only cyclocodimerization product was IV.

For the cyclocotrimerization reaction of 1-hexyne with CH_3CN, comparative studies using Co atoms and some usual cobalt catalysts, such as $CoCl_2 \cdot 6H_2O$/$NaBH_4$ and CpCoCOD (Cp = cyclopentadienyl, COD = cycloocta-1,5-diene) were carried out. At room temperature or 80°C the catalytic activity of the usual catalysts is almost negligible. The results obtained at 120°C, which is the temperature used for most common Co-containing catalytic systems, are reported in Table 2. Catalysts derived from Co atoms give high conversions with pronounced chemoselectivity (ca. 7) and regioselectivity (ca. 2). Use of the CpCoCOD complex under the same conditions results in a slightly higher activ-

TABLE 2

SYNTHESIS OF PYRIDINES FROM 1-HEXYNE AND CH_3CN (Scheme 1), USING VARIOUS CATALYTIC PRECURSORS AT 120°C[a]

Catalyst Co (mg-atom)	Conversion of hexyne (%)	Chemoselectivity[b]	Regioselectivity[c]
Co_{vap} (0.8)	74	7.3	2.0
CpCoCOD (0.8)	82	8.1	1.1
$CoCl_2 \cdot 6H_2O/NaBH_4$ (1.2)	41	1.2	1.7

[a] Reaction conditions: 1-hexyne (6 ml, 52 mmol), CH_3CN (27.5 ml, 520 mmol); reaction time 48 h.
[b] (I + II)/III (mol/mol), determined on isolated products. [c] Ratio I/II (mol/mol) as indicated by GLC.

ity (alkyne conversion ca. 82%) and high chemoselectivity (8.1) but almost no regioselectivity (I/II = 1.1). The $CoCl_2 \cdot 6H_2O/NaBH_4$ system gives low conversion, moderate chemoselectivity, and a regioselectivity lower than that for Co vapour.

The cyclocodimerization of 1,7-octadiyne with CH_3CN to IV has also been reported to take place with $CpCo(CO)_2$ as catalyst at ca. 150°C [4], but a very low catalytic efficiency was observed. With $CpCo(CO)_2$ as catalyst we found that no reaction occurs at room temperature, and at 80°C only octadiyne oligomers are obtained.

The results show that Co atoms act as convenient precursors of catalysts for the synthesis of pyridines from acetylenes and nitriles, enabling the reaction to be carried out under very mild conditions and with high selectivities.

Acknowledgements. This work was carried out with support from the research program "Progetto Finalizzato del C.N.R. per la Chimica Fine e Secondaria".

References

1 H. Bönnemann and W. Brijoux, The Cobalt Catalyzed Synthesis of Pyridines and Its Derivatives, in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, 5 (1984) 75 and ref. therein.
2 K. Jonas and C. Kruger, Angew. Chem. Int. Ed. Engl., 19 (1980) 708.
3 K.J. Klabunde, P. Timms, P.S. Skell and S.D. Ittel, Inorg. Synth., 19 (1979) 59.
4 A. Naiman and K.P.C. Vollhard, Angew. Chem. Int. Ed. Engl., 16 (1977) 708.