CHEMISTRY LETTERS, pp. 505-506, 1986.

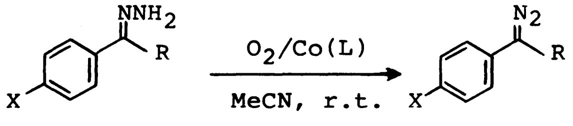
A CONVENIENT SYNTHESIS OF DIAZO COMPOUNDS BY CATALYTIC DEHYDROGENATION OF HYDRAZONES WITH COBALT SCHIFF BASE COMPLEX-OXYGEN SYSTEM

Akira NISHINAGA,* Shigekazu YAMAZAKI, and Teruo MATSUURA
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto 606

Cobalt Schiff base complex catalyzed oxidation of hydrazones is found to be a convenient method for the synthesis of diazo compounds.

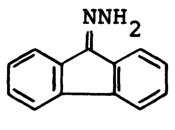
Aryldiazoalkanes are useful compounds in organic syntheses including the synthesis of peptides.[1] The oxidations of hydrazones by a variety of metal oxides, lead tetraacetate, and peroxides were applied to the synthesis of diazo compounds.[1] However, these methods lack laboratory convenience in respect of cost, efficiency, or manipulation of the oxidants. Few catalytic methods have been known for the dehydrogenation of hydrazones.[2—4]

We now find that N, N'-ethylenebis(salicylideneiminato)cobalt(II), Co(L^1), a readily available Schiff base complex, and its derivatives are excellent catalysts for the dehydrogenation of hydrazones with oxygen under mild neutral conditions to give diazo compounds. A typical procedure: Co(L^2) (0.1 mmol) was suspended in acetonitrile (30 cm^3) and 1-methylimidazole (MeIm) as a ligand (0.2 mmol) was added. Oxygen was bubbled through this mixture until a clear solution was obtained. To the resulting solution was added 4-nitroacetophenone hydrazone (**1a**) (0.5 mmol) at once and oxygen bubbling was continued at room temperature until the reaction was complete. (15 min). Filtration of the mixture through a short Florisil column to remove the metal complex followed by evaporation of the solvent gave orange crystals, which were composed of 1-(4-nitrophenyl)-1-diazoethane (**2a**) (90%) and 4-nitroacetophenone (10%). Similar results were obtained with Co(L^1)-(MeIm), although Co(L^3) was less effective. Five coordination structure of the cobalt complex was essential for the selective formation of **2a** as rationalized by

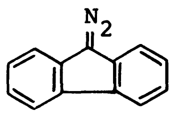


1 **2**

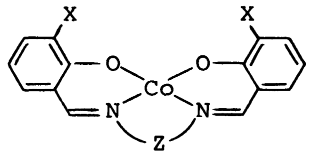
a; R = Me, X = NO$_2$ **b**; R = Ph, X = NO$_2$ **c**; R = H, X = NO$_2$
d; R = COPh, X = H **e**; R = Ph, X = H **f**; R = Ph, X = Cl



3



4



Co(L^1); Z = (CH$_2$)$_2$
X = H
Co(L^2); Z = (CH$_2$)$_2$
X = OMe
Co(L^3); Z = (CH$_2$)$_3$NH(CH$_2$)$_3$
X = H

Table 1. Oxidation of Hydrazones Catalyzed by Cobalt Schiff Base Complexes a)

Substrate	Co(L)	[Co]/[Sub.]	Additive	[Add.]/[Co]	Reaction time/min b)	Product yield/% Diazo	Product yield/% Ketone
1a	$Co(L^2)$	0.1	MeIm	2	50c)	78d)	22d)
1a	$Co(L^2)$	0.2	MeIm	2	15	90d)	10d)
1a	$Co(L^2)$	1.0	MeIm	2	5	96d)	4d)
1a	$Co(L^2)$	1.0	Py	2	5	77d)	23d)
1a	$Co(L^2)$	1.0	None	-	20	0	100
1a	$Co(L^1)$	1.0	MeIm	2	10	91d)	9d)
1a	$Co(L^3)$	1.0	-	-	120	60d)	34d)
1b	$Co(L^2)$	0.4	MeIm	2	10	92e)	
1c	$Co(L^2)$	0.2	MeIm	2	30	44e)	
1d	$Co(L^2)$	0.2	MeIm	2	10	87e)	
1d	$Co(L^2)$	0.025	MeIm	2	30f)	75e)	
1e	$Co(L^2)$	2.0	MeIm	2	15	70e)	
1f	$Co(L^2)$	2.0	MeIm	2	20g)	67e)	
3	$Co(L^2)$	0.2	MeIm	2	20	88e)	

a) Substrate (0.5 mmol) in MeCN (30 cm^3) at room temperature. b) Required for complete conversion. c) Conv. 73%. d) Determined by the ^1H NMR of isolated crystalline product. e) Isolated yield of acetate obtained by the addition of AcOH to the reaction mixture. f) Conv. 90%. g) Conv. 86%.

the effectiveness of the additive, whereas $Co(L^2)$ itself gave only the parent ketone (Table 1). The oxidation of other hydrazones (1b-f, 3) also gave diazo compounds (2b-f, 4) (Table 1). The use of a stoichiometric amount of the complex brought about a considerable reduction in the reaction time with higher yield of 2, but with less than 20 mol% catalyst concentration the reaction was incomplete and the selectivity in the diazo formation was somewhat reduced (Table 1) probably due to the formation of catalytically inactive cobalt(III) species. In the oxidation of acetophenone hydrazone and its 4-methoxy derivative, where the diazo products are unstable, the parent ketones were mainly obtained. The present oxidation of hydrazones to give diazo products required a half mol of oxygen as determined by gas volumetry. The catalytically active species should be $Co^{III}(L)(OH)$5) as rationalized by the fact that 1a was oxidized with two equivalents of $Co^{III}(L^2)$-(OH) under nitrogen atmosphere to give 2a and $Co^{II}(L^2)$. The reaction path may involve $Co^{III}(L)(S^-)$, formed by an acid-base reaction between $Co^{III}(L)(OH)$ and the substrate (SH), which undergoes homolysis and further oxidation under oxygen.

References

1) L. Lapatsanis, G. Milias, and S. Paraskewas, Synthesis, 1985, 513; and references therein.
2) M. Regitz, "The Chemistry of Diazonium and Diazo Groups," Part 2, Ed. S. Patai, John Wiley & Sons, Chichester-New York-Brisbane-Toronto (1978), p. 659; B. Eistert, M. Regitz, G. Heck, and H. Schwall, "Methoden der Organischen Chemie (Houben Weyl)," Georg Thieme Verlag, Stuttgart (1968), Vol. 10/4, p. 567.
3) W. Fischer and J. -P. Anselme, J. Am. Chem. Soc., 89, 5312 (1967); B. P. Giri, G. Prasad, and K. N. Mehrotra, Can. J. Chem., 57, 1157 (1979).
4) J. Tsuji, H. Takayanagi, and T. Kajimoto, Tetrahedron Lett., 1973, 4573.
5) A. Nishinaga, T. Kondo, and T. Matsuura, Chem. Lett., 1985, 905.

(Received January 16, 1986)