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.<sup>1)</sup> The oxidations of hydrazones by a variety of metal oxides, lead tetraacetate, and peroxides were applied to the synthesis of diazo compounds.<sup>1)</sup> 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.<sup>2</sup>

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<sup>3</sup>) 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 (<u>la</u>) (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

|           |                     |             |          | _           |                                    |                   |                   |
|-----------|---------------------|-------------|----------|-------------|------------------------------------|-------------------|-------------------|
| Substrate | Co(L)               | [Co]/[Sub.] | Additive | [Add.]/[Co] | Reaction <sub>b)</sub><br>time/min | Product<br>Diazo  | yield/%<br>Ketone |
| la        | Co(L <sup>2</sup> ) | ) 0.1       | MeIm     | 2           | 50 <sup>C</sup> )                  | 78 <sup>d)</sup>  | 22 <sup>d</sup> ) |
| la        | Co(L <sup>2</sup> ) | 0.2         | MeIm     | 2           | 15                                 | 90 <sup>d)</sup>  | 10 <sup>d)</sup>  |
| la        | Co(L <sup>2</sup> ) | ) 1.0       | MeIm     | 2           | 5                                  | 96 <sup>d)</sup>  | 4 <sup>d)</sup>   |
| la        | Co(L <sup>2</sup> ) | ) 1.0       | Ру       | 2           | 5                                  | 77 <sup>d)</sup>  | 23 <sup>d)</sup>  |
| la        | Co(L <sup>2</sup> ) | ) 1.0       | None     | -           | 20                                 | 0                 | 100               |
| la        | Co(L <sup>1</sup> ) | ) 1.0       | MeIm     | 2           | 10                                 | 91 <sup>d)</sup>  | 9 <sup>d)</sup>   |
| la        | Co(L <sup>3</sup> ) | ) 1.0       | -        | -           | 120                                | 60 <sup>d</sup> ) | 34 <sup>d)</sup>  |
| 1b        | Co(L <sup>2</sup> ) | ) 0.4       | MeIm     | 2           | 10                                 | 92 <sup>e)</sup>  |                   |
| lc        | Co(L <sup>2</sup> ) | ) 0.2       | MeIm     | 2           | 30                                 | 44 <sup>e)</sup>  |                   |
| lđ        | Co(L <sup>2</sup> ) | ) 0.2       | MeIm     | 2           | 10                                 | 87 <sup>e)</sup>  |                   |
| 14        | Co(L <sup>2</sup> ) | 0.025       | MeIm     | 2           | 30 <sup>f)</sup>                   | 75 <sup>e)</sup>  |                   |
| le        | Co(L <sup>2</sup> ) | ) 2.0       | MeIm     | 2           | 15                                 | 70 <sup>e)</sup>  |                   |
| lf        | Co(L <sup>2</sup> ) | 2.0         | MeIm     | 2           | 20 <sup>g)</sup>                   | 67 <sup>e)</sup>  |                   |
| 3         | Co(L <sup>2</sup> ) | 0.2         | MeIm     | 2           | 20                                 | 88 <sup>e)</sup>  |                   |
|           |                     |             |          |             |                                    |                   |                   |

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

a) Substrate (0.5 mmol) in MeCN (30 cm<sup>3</sup>) at room temperature. b) Required for complete conversion. c) Conv. 73%. d) Determined by the <sup>1</sup>H 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<sup>III</sup>(L)(OH)<sup>5)</sup> as rationalized by the fact that  $\underline{la}$  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<sup>III</sup>(L)(S<sup>-</sup>), formed by an acid-base reaction between Co<sup>III</sup>(L)(OH) and the substrate (SH), which undergoes homolysis and further oxidation under oxygen.

## References

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(Received January 16, 1986)