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An Effective Oxidation of Dihydrazones to Acetylenes with Cobalt(II) Schiff's Base Complexes

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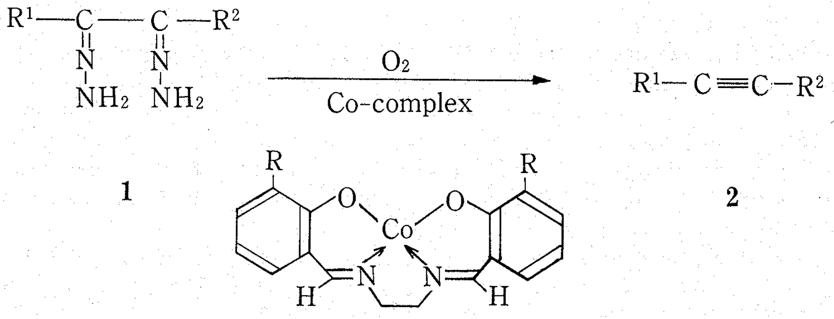
Facile oxidations of dihydrazones of α-diketones to acetylenes were performed with a catalytic amount of bis(salicylidene)ethylenediaminatocobalt(II) and bis(3-methoxysalicylidene)ethylenediaminatocobalt(II) under mild conditions in 88—98% yields.

Keywords——cobalt complex; oxidation; dihydrazone; diarylacetylene; catalytic reaction

The oxidation of organic substances catalyzed by transition metal complexes which are able to interact reversibly with molecular oxygen is of particular interest in relation to biological oxidations and organic syntheses.[1] In the previous report,[2] we described the effective dehydrogenation of indoline to indole catalyzed by cobalt(II) Schiff's base complexes. This paper describes a further successful application of the Co(II)-complex catalyst system to the oxidation of dihydrazones of diaryl α-diketones to diarylacetylenes.

The oxidation reaction proceeded upon simple mixing of the substrate, diaryl α-diketone dihydrazones (**1a**—**f**), and the catalyst, bis(salicylidene)ethylenediaminatocobalt(II) [Co-

TABLE I. Oxidation of Dihydrazones (**1**) to Acetylenes (**2**) with Co(II) Schiff's Base Complexes[a]



A : R=H, Co(salen)
B : R=MeO, Co(MeO salen)

Substrate (1)	% yield of (2)		Other reagent
	A	B	
a : $R^1=R^2=Ph$	98	95	85 (CF_3COOAg)[6] 97 (Cu_2Cl_2-pyridine)[8] 94 (4 equiv. $Cu(OAc)_2$)[9] 78 (0.2 equiv. $Cu(OAc)_2$)[9] 61 (NiO_2)[10]
b : $R^1=R^2=p\text{-}CH_3\text{-}Ph$	94	90	
c : $R^1=R^2=p$-MeO-Ph	91	94	85[6]
d : $R^1=R^2=p\text{-}(CH_3)_2N\text{-}Ph$	97	93	
e : $R^1=Ph$, $R^2=p\text{-}(CH_3)_2N\text{-}Ph$	90	88	
f : $R^1=Ph$, $R^2=p$-Cl-Ph	92	94	

[a] The catalytic activities of Co(II)-complexes were taken from the literature.[3]

(salen)] or bis(3-methoxysalicylidene)ethylenediaminatocobalt(II) [Co(MeO salen)],[3] in MeOH–benzene solution[4] under an O_2 atmosphere. Both catalysts showed the same oxidative activity on all of the substrates.

When the catalyst amount was 1/5 of the substrate amount, the reaction was completed in 2 h at ambient temperature in quantitative yield. The product, diarylacetylene (**2a**—**f**), was purified by passing the reaction mixture through a silica gel column without any difficulty, and no such product was obtained by reaction in the absence of the catalyst.

The table summarizes the yields of **2** for each substrate (**1**), obtained by the procedure described in "Experimental."

The oxidation of dihydrazones of α-diketones to acetylenes has been achieved by using various oxidizing agents, such as HgO,[5] CF_3COOAg,[6] $Pb(OAc)_4$,[7] Cu_2Cl_2–pyridine complex,[8] $Cu(OAc)_2$,[9] and NiO_2.[10]

However, the Co(II)-complex catalyzed oxidation is superior to those using other reagents, shown in the table, in that the reaction proceeds under milder conditions with a catalytic amount of complex in high yield.

It should be mentioned here that Co(II)-complex catalysis in the oxidation of dihydrazones is so far restricted to the dihydrazone of benzil, while significant oxidation did not take place with those of methyl phenyl and di-*n*-pentyl α-diketones. By a similar procedure, hydrazobenzene was oxidized to azobenzene in quantitative yield.

Experimental

All melting points are uncorrected. IR spectra were measured on a Hitachi 215 spectrometer. ^{1}H-NMR spectra were taken on a JEOL JNM-PMX 60 spectrometer with TMS as an internal standard. MS were recorded on a Shimadzu LKB 9000 spectrometer.

Oxidation of Dihydrazones (1) to Acetylenes (2)——The general procedure is as follows. Co (salen) or Co (MeO salen) (each 0.4 mmol) was suspended in MeOH (20 ml) under a fine stream of O_2, then a solution of **1** (2 mmol) in benzene (10 ml) and MeOH (20 ml) was added dropwise in 15 min at room temperature under vigorous stirring. The resulting suspension was bubbled through with O_2 for an additional 2 h. The reaction mixture was then evaporated down and the residue was purified on a short silica gel column with the appropriate solvent to give diarylacetylene (**2**).

Oxidation of Hydrazobenzene to Azobenzene——Co (salen) or Co (MeO salen) (0.4 mmol) was added to a solution of hydrazobenzene (2 mmol) in MeOH (50 ml), and the resulting suspension was bubbled through with O_2 for 1 h. After removal of the solvent by evaporation, the residue was purified by filtration on a short column of silica gel with hexane–benzene (1/1) to give azobenzene in quantitative yield.

Characterization and Identification of Products——Compound **2a** and azobenzene were identified by comparing them with authentic commercial samples. Compounds **2b**,[11] **2c**,[6] and **2f**[6] were identified by the comparison of physical data with the data in the literature.

Di-*p*-dimethylaminophenylacetylene (2d)——mp 231—232°C ($MeOH–CH_2Cl_2$). *Anal.* Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60. Found: C, 81.77; H, 7.59; N, 10.69. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1610. MS *m/e*: 264 (M^+, 100). NMR ($CDCl_3$) δ: 3.0 (12H, s, 2×NMe_2), 6.50—6.83 (4H, m, ArH), 7.17—7.50 (4H, m, ArH).

***p*-Dimethylaminophenyl Phenyl Acetylene (2e)**——mp 113—114°C ($MeOH–CH_2Cl_2$). *Anal.* Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.77; H, 6.96; N, 6.37. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2200, 1610, 1590. MS *m/e*: 221 (M^+, 100). NMR (CCl_4) δ: 2.97 (6H, s, NMe_2), 6.50—6.83 (2H, m, ArH), 7.17—7.67 (7H, m, ArH).

References and Notes

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