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A NOVEL SYNTHESIS OF NITRILES FROM ALDEHYDES USING COBALT AMMINE COMPLEXES

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Although various N-unsubstituted imines are formed easily from the reaction of aldehydes with ammonia and are assumed to have unique reactivities in organic reactions, they have been received only limited attention from organic chemists because of the instability, tendency to facile cyclization and so on (1).

In recent years unstable molecules such as cyclobutadiene (2), benzyne (3), carbene (4) and trimethylene methane (5) have been successfully stabilized by the complex formation with transition metals and several unique reactions using these complexes have been reported (6).

From the view point of synthetic organic chemistry it is very interesting to study the possibility of stabilizing the N-unsubstituted imines by the coordination to transition metal. We have found that N-unsubstituted imine cobalt complexes were prepared by the reaction between aldehydes and cobalt hexaammine complexes and were stable enough to allow for a long time storage under inert gas atmosphere at room temperature.

In this paper, we wish to report the formation of N-unsubstituted imine cobalt complexes and furthermore the synthesis of nitriles in excellent yields by bromine oxidation of the complexes as one of the applications of imine transition metal complexes into organic synthesis.

Dry ammonia was bubbled into n-hexane solution of dicobalt octacarbonyl $\left[Co_2(CO)_8\right]$ (5.0g, 14.6 mM) to precipitate white solid. After the hexane solution became colorless,excess of ammonia and the solvent were completely removed under reduced pressure. The resulting white solid (cobalt hexaammine bis-tetracarbonyl cobaltate, $Co(NH_3)_6\left[Co(CO)_4\right]_2$, (8)) was easily soluble in polar solvents and stable under inert gas but decomposed immediately in air. The reaction mixture from benzaldehyde and $Co(NH_3)_6\left[Co(CO)_4\right]_2$ in acetonitrile at 40° for 15 hr. showed the presence of N-H (3480 and 3300 cm^{-1}), Co-CO (1840~1930 cm^{-1}) and C=N (1630 cm^{-1}) in ir-spectra. After removal of solvent from the reaction mixture, benzene extract was analyzed and was found to contain trace amounts of benzaldehyde but imine derivatives were not detected. These results show that benzaldehyde reacts well with $Co(NH_3)_6\left[Co(CO)_4\right]_2$ to give benzalimine, as a stable species by complex formation with cobalt (7).

When the imine complex obtained by the same reaction described above was oxidized by bromine and then was dealed with ordinary method, benzonitrile was produced in a yield of 70.0 %. This result prompted us to study the synthesis of nitriles from other aldehydes. The structures of the products obtained were confirmed by ir, nmr, mass, glc and elemental analysis and these results are summarized in Table I.

Table I Synthesis of nitriles from aldehydes

R-CHO	Solv.	Temp. (°C)	hr.	Product (%)[*1]	
				R-CN	$(PhCH=N)_2CHPh$[*2]
C_6H_5-	DMSO	40	6	20.0	50.5
C_6H_5-	DMF	40	6	42.7	42.0
C_6H_5-	CH_3CN	40	6	52.1	0
C_6H_5-	CH_3CN	40	15	70.0	0
C_6H_5-	CH_3CN	30	100	77.0	0
C_6H_5-	CH_3CN	50	100	110.0	0
$C_6H_5CH=CH$-	CH_3CN	15	15	21.0	polymer
$C_6H_5CH_2CH_2$-	CH_3CN	0 ~ 5	6	70.5	-

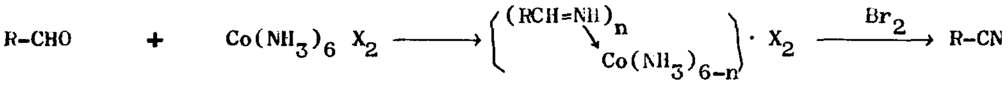
*1 Based on the moles of $Co(NH_3)_6\{Co(CO)_4\}_2$ formed quantitatively according to the following equation (8);

$$3Co_2(CO)_8 \quad + \quad 12\ NH_3 \xrightarrow{\qquad} 2\ Co(NH_3)_6\{Co(CO)_4\}_2 \quad + \quad 8\ CO$$

*2 It was considered that this product was formed from the reaction of aldehyde with ammonia (9) which was freed from the cobalt by the coordination of solvents with strong coordinating ability such as DMSO and DMF.

As shown in Table I, the corresponding nitriles were yielded from aromatic, α,β-unsaturated and aliphatic aldehyde in mild condition. It should be noted that benzonitrile was given in a yield of 110 %, and this result shows that more than one of the ammonia coordinated to cobalt could be used for the formation of nitriles. To clarify the effect of anion $\{Co(CO)_4^-\}$ in the cobalt hexaammine complex, the similar reaction using cobalt(II) hexaammine dichloride (10) was carried out in acetonitrile at 40 ~ 45° for 24 hr.. The reaction mixture was decomposed by bromine to give benzonitrile in a yield of 74.5 %. Therefore, it is assumed that the effect of anion is not important in these reactions.

A simple scheme for the formation of nitriles from aldehydes is depicted as follows;



$$R\text{-}CHO \quad + \quad Co(NH_3)_6\ X_2 \longrightarrow \left\{ \begin{array}{l} (RCH{=}NH)_n \\ \qquad\searrow \\ \qquad Co(NH_3)_{6-n} \end{array} \right\} \cdot X_2 \xrightarrow{Br_2} R\text{-}CN$$

The conversion of aldehydes into nitriles has been so far reported by several workers, and the reactions tend to be divided into three types as follows; (a) preparation of oximes from aldehydes, followed by oxidation with various reagents (11). (b) aldehydes itself are treated with ammonia in the presence of iodine and sodium methoxide (the yields of nitriles are low) (12). (c) in the presence of cupric chloride, the reaction of aldehyde with ammonia, sodium hydroxide and oxygen (13).

Our method seems to resemble to the reaction of type (c) in view of the use of auxilary metallic reagent but is very unique and novel one, admitting the reaction to proceed under mild condition and giving high yields of nitrils.

Further application of the N-unsubstituted imine-transition metal complexes into organic synthesis is now under investigation and will be reported in the near future.

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