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The Oligomerization and Co-oligomerization of Active Methylene Compounds and Isocyanides Catalyzed by Octaisocyanidedicobalt[1)]

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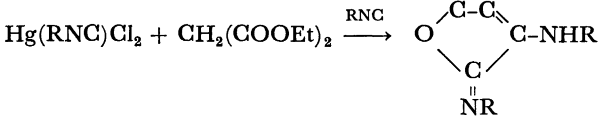
The reactions of RNC with $CH_2R^1R^2$ ($R=2,6\text{-}Me_2C_6H_3$; R^1, R^2=COOMe, COOEt, CN) in the presence of $Co_2(RNC)_8$ or $Co_2(CO)_8$ gave cyclic compounds in a 4:1 molar ratio. $Co_2(RNC)_8$ also catalyzed $CH_2(CN)_2$ to give a pyridine derivative.

Octacarbonyldicobalt has been widely used as a precursor of the catalyst of the hydroformylation of olefins and the carbonylation of various unsaturated organic compounds.[2)] Recently we have reported the synthesis and characterization of $Co_2(RNC)_8$, by analogy with $Co_2(CO)_8$.[3)] From the versatile reactivities of $Co_2(CO)_8$, one can expect catalytic actions similar to those of the corresponding isocyanide complexes. In fact, we established the hydrogenation of acetylene and the co-oligomerization of acetylene or azobenzene with isocyanide, catalyzed by $Co_2(RNC)_8$.[4,5)]

The compounds with an active methylene group, such as the malonic ester, malononitrile, and the cyanoacetic ester, have become keystones for syntheses of a heterocyclic system.[6)] Saegusa *et al.* reported that the reactions of *t*-butyl isocyanide with active methylene compounds gave three substituted olefins in the presence of Cu_2O (Eq. 1).[7)]

$$CH_2XY + t\text{-BuNC} \longrightarrow XYC{=}CHNHBu\text{-}t \qquad (1)$$

Sawai and Takizawa have described producing a 2:1 cyclic adduct consisting of RNC and CH_2XY by the reactions of isocyanide–mercury(II) chloride complex with active methylene compounds in the presence of Et_3N (Eq. 2).[8)]



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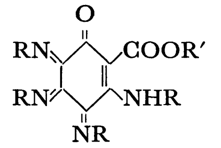
We wish here to report on cyclo-cooligomerization reactions between CH_2XY and RNC and on the oligomerization of an active methylene compound in the presence of a catalytic amount of $Co_2(RNC)_8$.

Results and Discussion

A mixture of $CH_2(COOMe)_2$, $2,6\text{-}Me_2C_6H_3NC$, and $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ was heated in toluene at 120—125 °C.[9)] The subsequent chromatography of the mixture on alumina gave two compounds: a reddish brown compound **1a**, formulated as $(C_9H_9N)_4(C_4H_4O_3)$ from the mass spectrum, M^+ 624 (624.75), and brown crystals, **2**, with the empirical formula of $(C_6H_6N)_6$. Compound **2** was identical with the compound obtained from the oligomerization of 2,6-xylyl isocyanide with $HgCl_2$ by Sawai and Takizawa.[10)] The infrared spectrum of **1a** showed an absorption at 3403 cm^{-1} due to a NH group, two bands at 1712 and 1688 cm^{-1} due to the carbonyl groups, and two broad bands at 1616 and 1593 cm^{-1} due to the C=N groups. The ^{1}H NMR spectrum showed four singlets, at δ 1.90, 2.03, 2.19, and 2.39, due to the *o*-methyl groups, a singlet at δ 3.21 due to a methoxycarbonyl group, and a broad signal at δ 4.91 due to a NH group. These spectral characteristics suggest a cyclic imino derivative. The other derivatives **1b** and **1c** were also prepared from the reaction of $CH_2(COOEt)_2$ with 2,6-xylyl isocyanide, or from that of $CH_2(COOMe)_2$ with *o*-tolyl isocyanide in the presence of $Co_2(CO)_8$, respectively. However, a similar reaction with *t*-butyl isocyanide led to the recovery of the starting material without undergoing a cyclic cooligomerization.



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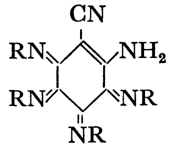

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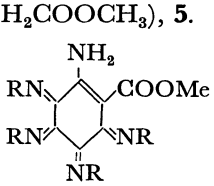
a $R=2,6\text{-}Me_2C_6H_3$, $R'=Me$
b $R=2,6\text{-}Me_2C_6H_3$, $R'=Et$
c $R=4\text{-}MeC_6H_4$ $R'=Me$

When malononitrile was treated with 2,6-xylyl isocyanide at 120—125 °C in the presence of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ or $Co_2(CO)_8$, two compounds, **3** and **4**, were isolated as brown and pale yellow crystals respectively. Compound **3** was formulated as a 1:4 adduct of malononitrile and 2,6-xylyl isocyanide. The infrared spectrum showed the presence of the C≡N, C=N, and NH groups. The ^{1}H NMR spectrum showed four bands, at δ 1.90, 2.01, 2.23, and 2.44, due to the ortho-methyl groups and a broad singlet at δ 4.67 due to the NH group. Compound **4** was a trimer of malononitrile and was identified as 4-cyanomethyl-2,6-diamino-3,5-dicyanopyridine by a comparison of its infrared and UV spectra with those of an authentic sample.[6)] When the reactions were carried out in the absence of isocyanide, a trimerization of malononitrile occurred to give **4**. The results are listed in Table 1. The reaction of 2,6-xylyl isocyanide with methyl cyanoacetate in the presence of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ gave a yellow compound consisting with the formula of $(C_9H_9N)_4(NCCH_2COOCH_3)$, **5**. The infrared spectrum showed the presence of the NH and methoxy-



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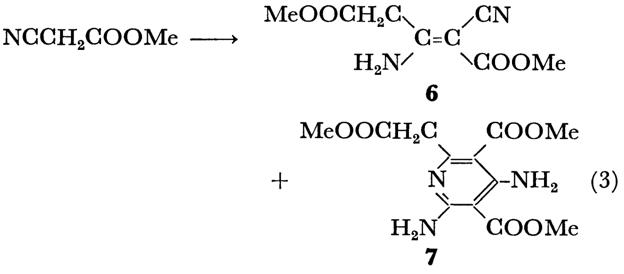
$R=2,6\text{-}Me_2C_6H_3$

TABLE 1. TRIMERIZATION OF MALONONITRILE

Catalyst[a]	Temp/°C	Time/h	Yield/%
$Co_2(2,6\text{-}Me_2C_6H_3NC)_8$	r.t.	15	0
$Co_2(2,6\text{-}Me_2C_6H_3NC)_8$	80	2	51
$Co_2(t\text{-}BuNC)_5Co(CO)_4$[b]	80	2	56
$Co_2(2,6\text{-}Me_2C_6H_3NC)_8$	120	1	65
$Co_2(2,6\text{-}Me_2C_6H_3NC)_8$[c]	120	1.5	73

a) Catalyst: 0.15 mmol. $CH_2(CN)_2$; *ca.* 13 mmol. b) *t*-BuNC (0.3 mmol) was added. c) $2,6\text{-}Me_2C_6H_3NC$ (0.2 mmol) was added.

carbonyl groups, but the absence of the C≡N group. The ^{1}H NMR spectrum showed four bands, at δ 2.01 (bs, 2-CH_3), 2.12 (s, CH_3), and 2.23 (s, CH_3) due to the ortho-methyl groups, a singlet at δ 3.83 due to the methoxycarbonyl group, and a broad signal at δ 3.55(2H) due to the NH groups. The treatment of methyl cyanoacetate with $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ in the absence of 2,6-xylyl isocyanide gave a dimer, **6**, and a trimer, **7**, of methyl cyanoacetate in low yields. The dimer, **6**, was identified as a tetrasubstituted olefin; it is obtained from methyl cyanoacetate and bases. The trimer, **7**, was tentatively identified as a pyridine derivative by a comparison of its UV spectrum with that of **4**.



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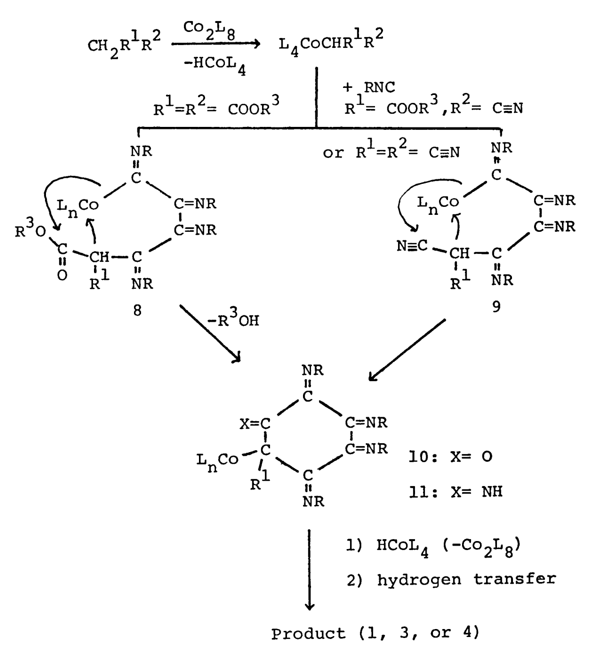
(3)

The initial step of the co-oligomerization is probably the formation of $HCo(RNC)_4$ and $R^1R^2HCCo(RNC)_4$ by a cleavage of the metal-metal bond, followed by a successive insertion of isocyanide molecules into a carbon-metal bond. The step-by-step insertion of isocyanide has been explored in various alkyl metal complexes.[11] The intermediates, **10** and **11**, are generated by a nucleophilic attack of a tertiary carbon on the cobalt atom, accompanied by ring closure through an elimination of ROH or a transfer of hydrogen onto the cyano group. The resulting tetraimino cyclic intermediates are reduced with the $HCo(RNC)_4$ formed in the initial step. Thus, the reactions are achieved by a transfer of hydrogen to an imino nitrogen. The $Co_2(RNC)_8$ reformed in these reactions again undergoes a cleavage of a metal-metal bond, and the catalytic cycle is complete. Pyridine derivatives are probably formed by a transformation similar to that of the base-promoted reaction of active methylene compounds.[6]

Experimental

The reactions were carried out under an atmosphere of nitrogen. The melting points are uncorrected. The IR spectra were recorded with a Shimadzu IR-27G spectrometer. The NMR spectra were measured with a JEOL C-60HL apparatus. The mass spectra were measured on a JEOL Type JPS-1S mass spectrometer with a directinlet system. The isocyanides were prepared according to the literature.[12] The $Co_2(CO)_8$[13] and $Co_2(RNC)_8$[3] were prepared by procedures described in the ilterature.



Scheme 1. Possible path for the formation of tetraiminocyclic compounds.

Reactions of Isocyanides with Active Methylene Compounds. Some representative examples will be described below.

Reaction of 2,6-Xylyl Isocyanide with Dimethyl Malonate. A mixture of $2,6\text{-}Me_2C_6H_3NC$ (0.21 g, 1.6 mmol), $CH_2(COOMe)_2$ (1.3 g, 10 mmol), and $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ (0.16 g, 0.10 mmol) in toluene (10 ml) was heated at 120—125 °C for 4 h. The solvent was then removed *in vacuo*, and the residue was chromatographed on alumina. Compounds **1a** (0.12 g, 48%) and **2** (0.07 g, 7%) were isolated by using benzene or benzene–CH_2Cl_2 (10:1) respectively as the eluents. **1a** (mp 244—246 °C). Found: C, 76.35; H, 6.43; N, 8.95%. Calcd for $C_{40}H_{40}N_4O_3$: C, 76.89; H, 6.45; N, 8.87%. By using an analogous procedure except for the use of $Co_2(CO)_8$ instead of $Co_2(RNC)_8$, the following compounds were prepared.

1b (51%, mp 247—248 °C). NMR ($CDCl_3$): δ 1.20 (t, 3.5 Hz, Me), 1.87, 2.02, 2.19, 2.38 (s, *o*-Me), 3.71 (q, 3.5 Hz, CH_2), 4.89 (b, NH), and 6.5—7.3 (c, aromatic protons). IR (KBr): 3398 (NH), 1713, 1689, 1676, 1615, and 1591 (C=O and C=N) cm^{-1}. Mass: 638 (668.78). Found: C, 77.04; H, 6.63; N, 8.77%. Calcd for $C_{41}H_{42}N_4O_3$: C, 77.09; H, 6.63; N, 8.77%. **1c** (43%, mp 186—188 °C). IR (KBr): 3498 (NH), 1740, 1693, 1625, and 1598 (C=O and C=N) cm^{-1}. Mass: 568 (568.65). Found: C, 76.32; H, 5.76; N, 9.98%. Calcd for $C_{36}H_{32}N_4O_3$: C, 76.03; H, 5.67; N, 9.85%.

Reaction of 2,6-Xylyl Isocyanide with Malononitrile. A mixture of $Co_2(CO)_8$ (0.035 g, 0.1 mmol) and 2,6-xylyl isocyanide (0.21 g, 1.6 mmol) was stirred in toluene (10 ml) at reflux. After 0.5 h, $CH_2(CN)_2$ (0.7 g, 10.6 mmol) was added to the solution. After the reaction was over (2 h), the resulting solids, **4** (0.03 g, 13%), identified as 4-cyanomethyl-2,6-diamino-3,5-dicyanopyridine, were removed by filtration. The orange-brown solution was chromatographed on alumina, CH_2Cl_2 being used as the eluent. The subsequent removal of the solvent and crystallization of the residue from benzene–hexane gave **3** (0.1 g, (42%), mp 265 °C) as brown crystals. NMR ($CDCl_3$): δ 1.90, 2.01, 2.23, 2.44 (s, *o*-CH_3), 4.67 (b, NH_2), and 6.5—7.4 (c, aromatic protons). IR (KBr): 3310 (NH), 2195 ($C\equiv N$), 1625, 1610, and 1590 (C=N) cm^{-1}. Mass: 590 (590.78). Found: C, 79.27; H, 6.46; N, 14.43%. Calcd for $C_{39}H_{38}N_6$: C, 79.26; H, 6.48; N, 14.23%.

5 (45%, mp 203—204 °C) was obtained from 2,6-Me_2-C_6H_3NC (0.22 g), methyl cyanoacetate (0.5 g), and $Co_2(CO)_8$ (0.04 g). IR (KBr): 3350 (NH), 1755, 1740, 1623, and 1595 (C=O and C=N) cm^{-1}. Mass: 623 (623.77). Found: C, 76.80; H, 6.65; N, 11.09%. Calcd for $C_{40}H_{41}N_5O_2$: C, 77.02; H, 6.46;, N, 10.95%.

Oligomerization of Methyl Cyanoacetate. A mixture of $CH_2(CH)(COOMe)$ (0.5 g, 5.0 mmol) and $Co_2[2,6\text{-}Me_2C_6H_3NC]_8$ (0.2 g, 0.17 mmol) in toluene was stirred in toluene (10 ml) at reflux for 2 h. The solvent and the unreacted ester were then removed *in vacuo*. The residue was chromatographed on alumina, CH_2Cl_2–benzene and CH_2Cl_2 being used as the eluents. The dimer, **6** (0.03 g, 12%), from the first band was isolated. The product, **7**, from the second band was a trimer (0.01 g, (6%), mp 114—119 °C). IR (KBr): 3510, 3430 (NH), 1735, 1683, 1632, 1586, and 1538 (C=O and C=N) cm^{-1}. Mass: 297 (297.26). UV (CH_3OH): λ_{max} 244 (ε 8400), 260 (ε 7300), and 324 (ε 2800). Found: C, 48.15; H, 5.03; N, 13.78%. Calcd for $C_{12}H_{15}N_3O_6$: C, 48.48; H, 5.09; N, 14.14%.

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