Isomerization and Hydrogenation of Dimethyl Maleate and 1,5-Cyclooctadiene by Nickel Cyanide Complex

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The selective isomerization and hydrogenation of monoenes, dienes and their derivatives by nickel cyanide complex and excess sodium borohydride were the subject of our investigations,[1,2] in which it was suggested that the stability of the intermediary hydridonickel or alkylnickel complex plays a significant role in determining the distribution of products. The present work was undertaken to confirm such selectivity revealed by nickel cyanide complex for the isomerization and hydrogenation of dimethyl maleate (DMM) and of 1,5-cyclooctadiene (1,5-COD), respectively.

Nickel complexes investigated here were dicyano-(1,10-phenanthroline)nickel (II), $Ni(CN)_2(phen)$, tetracyanonickelate(II), $Ni(CN)_4^{2-}$, and dicyano-bis(triphenylphosphine)nickel(II), $Ni(CN)_2(P\phi_3)_2$. Previous investigation[1] revealed that hydrogenation activity increases according to the sequence: $Ni(CN)_2(P\phi_3)_2 < Ni(CN)_4^{2-} < Ni(CN)_2(phen)$ while isomerization activity is reversed.

DMM or 1,5-COD was introduced in a water-isopropanol (10 : 25) solution containing a given nickel cyanide complex and excess sodium boro-hydride at 0°C or 10°C. After a certain reaction interval, products were extracted with chloroform for DMM and petroleum ether for 1,5-COD respectively and analyzed by gas chromatography. The method of preparation of the nickel cyanide complexes, apparatus and experimental procedure were almost the same as those described earlier.[1]

The isomerization and hydrogenation of DMM took place rapidly with the three nickel cyanide complexes, i.e. more than 90% DMM was found to convert to dimethyl fumarate (DMF) and dimethyl succinate (DMS) within 30 min. However, product distribution differed with the kind of nickel cyanide employed. Typical data, obtained after 30 min, are illustrated in Table 1.

TABLE 1. PRODUCT COMPOSITION FOR THE ISOMERIZA-
TION AND HYDROGENATION OF DIMETHYL MALEATE
BY THE NICKEL CYANIDE COMPLEXES AT 10°C

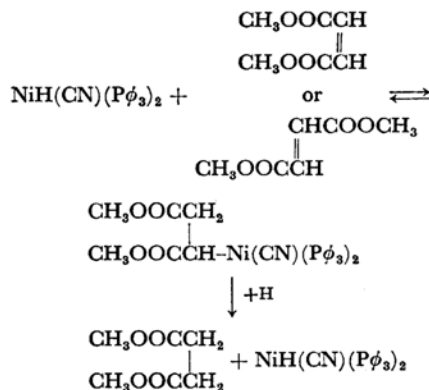|	Product composition %		Substrate converted %
	DMF	DMS	DMM
$Ni(CN)_2(phen)$	28	72	90
$Ni(CN)_4^{2-}$	88	12	89
$Ni(CN)_2(P\phi_3)_2$	95	5	95

It is apparent from Table 1 that $Ni(CN)_2(phen)$ gives rise to the hydrogenation of DMM in preference to $Ni(CN)_2(P\phi_3)_2$, while the latter is quite active for the isomerization of DMM to give DMF.

1) H. Samejima, T. Mizuta and T. Kwan, *Nippon Kagaku Zasshi* (*J. Chem. Soc., Pure Chem. Sect.*), **89**, 1028 (1968).

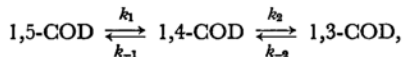2) T. Mizuta, H. Samejima and T. Kwan, This Bulletin, **41**, 727 (1968).

This result is in line with that of the previous report[1] which concerned the isomerization and hydrogenation of 1-butene.

The isomerization and hydrogenation of DMM would probably follow the hydride elimination-addition mechanism:

$$NiH(CN)(P\phi_3)_2 + \quad \begin{matrix} CH_3OOCCH \\ \parallel \\ CH_3OOCCH \end{matrix} \quad or \quad \begin{matrix} CHCOOCH_3 \\ \parallel \\ CH_3OOCCH \end{matrix} \quad \rightleftharpoons$$

$$\begin{matrix} CH_3OOCCH_2 \\ | \\ CH_3OOCCH-Ni(CN)(P\phi_3)_2 \end{matrix}$$

$$\downarrow +H$$

$$\begin{matrix} CH_3OOCCH_2 \\ | \\ CH_3OOCCH_2 \end{matrix} + NiH(CN)(P\phi_3)_2$$

Let us investigate 1,5-COD as the substrate; 1,5-COD is expected to convert to 1,4-COD and 1,3-COD or even to cyclooctene in the presence of the nickel cyanide complex and excess sodium borohydride. Indeed, experiments indicated that 1,4-COD is formed first and then followed by 1,3-COD. No cyclooctene was detected with $Ni(CN)_2$-$(P\phi_3)_2$. On the other hand, cyclooctene was produced more or less with the other two com-complexes, of which $Ni(CN)_2$(phen) gave rise to more cyclooctene. The result is again consistent with the isomerization and hydrogenation data of DMM mentioned above.

In Fig. 1 is plotted the composition of 1,4-COD and 1,3-COD produced against the degree of conversion of 1,5-COD for $Ni(CN)_2(P\phi_3)_2$ at 0°C. Assuming now that the isomerization of 1,5-COD obeys a consecutive, reversible first-order kenetics as

$$1,5\text{-COD} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1,4\text{-COD} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 1,3\text{-COD},$$

rate constants were calculated according to the
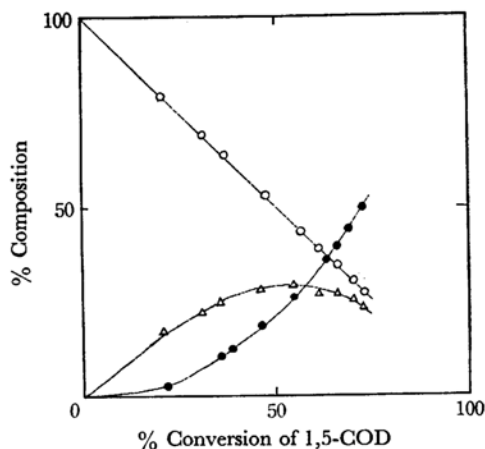

Fig. 1. Catalytic isomerization of 1,5-COD to give 1,4-COD and 1,3-COD in the presence of Ni-$(CN)_2(P\phi)_2$ and excess $NaBH_4$ at 0°C.
1,5-COD: 8.3 mmol,　$NaBH_4$: 2.0 mmol, $Ni(CN)_2(P\phi_3)_2$: 0.1 mmol.
○: 1,5-COD, △: 1,4-COD, ●: 1,3-COD.

Runge-Kutta-Gill method.[3] That is, k_{-1}, k_2 and k_{-2} were computed so as to best fit the experimental plots of Fig. 1 with the aid of the observed value for k_1, the k_1 being evaluated from the initial rates for 1,5-COD decay. These values are shown below.

$$k_1 = 2.53 \times 10^{-3} \quad\quad k_{-1} = 4.25 \times 10^{-5}$$
$$k_2 = 4.25 \times 10^{-3} \quad\quad k_{-2} = 4.25 \times 10^{-6}\ sec^{-1}$$

The solid lines of Fig. 1 refer to concentrations of substrate and products as calculated by the rate constants. Here, k_{-1} and k_{-2} should be regarded as only upper limit since lower values appeared also well suited. The validity of these values are still under investigation.

3) A. Ralton and H. S. Wilf, "Mathematical Methods for Digital Computers," John Wiley & Sons Inc., New York (1960), p. 110. A HITAC-5020 computer of The University of Tokyo was used in performing numerical calculations.