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Transfer-hydrogenation and Transfer-hydrogenolysis. I. Transfer-hydrogenation of Cyclooctadienes Catalyzed by Dichlorobis(triphenylphosphine)iron(II)

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Hydrogen transfer from a number of organic compounds to olefins in a homogeneous system was studied. In the case of hydrogen transfer to 1,5-cyclooctadiene, using dichlorobis(triphenylphosphine)iron(II) as the catalyst, dihydroxybenzenes, such as pyrocatechol and hydroquinone, were much superior to *prim*- and *sec*-alcohols, 1-dodecanethiol, and cyclohexene as hydrogen donors.

In almost all catalytic hydrogenations of olefins, molecular hydrogen has been used as the hydrogen source. However, the hydrogenation in which hydrogen transfer from organic compounds takes place has also been reported;[1] it has been called transfer-hydrogenation,[2] transhydrogenation[3] or conjugated hydrogenation.[4] Transfer-hydrogenation has several advantages because it needs no hydrogen gas. For example, the experimental operation is easy, and a completely homogeneous system is made available. It has been reported that primary alcohols, secondary alcohols,[4,5] and six-membered cyclic olefins[2] donate hydrogen to olefins to give aldehydes, ketones, and aromatic compounds respectively in the presence of heterogeneous catalysts, such as metallic palladium and nickel. As for the reactions of homogeneous systems, Itatani and Bailar have reported that methyl linoleate[6] or soybean oil[7] are hydrogenated to monoenes selectively under the pressure of nitrogen gas when benzene–methanol is used as the solvent and platinum or palladium complexes as the catalysts. In this case, methanol is inferred to be the hydrogen souce. It has also been reported that the hydrogenation of methyl linoleate occurs in the presence of dihalobis(triphenylphosphine)nickel(II) as the catalyst and tetrahydrofuran or benzene as the solvent.[8] Studies of homogeneous transfer-hydrogenation have thus far been performed incidentally to hydrogenation by molecular hydrogen; no systmatic investigation of the reaction conditions or the reaction mechanism has yet been undertaken. We also found that the olefin linkages of methyl linoleate were reduced in 2-propanol in the presence of bis(2,4-pentanedionato)nickel(II) under an atmosphere of nitrogen; however, the reproducibility of the reaction was discouragingly bad, perhaps because the catalyst decomposed to give an insoluble substance.[9]

The work reported here was undertaken in order to study transfer-hydrogenation systematically; some of the results have been reported in a preliminary communication.[10] There it was shown that $FeBr_2(PPh_3)_2$ and $FeCl_2(PPh_3)_2$ are the most active catalysts of the $MX_2(PPh_3)_2$ complexes, where M is Fe(II), Co(II), or Ni(II), and where X is Cl, Br, or I, and that 1,5-cyclooctadiene (1,5-COD), which is presumed to have the strongest coordinating ability of all the cycloolefins attempted, is most readily reduced.

Results and Discussion

The experiments in this study were carried out under conditions such as follows, unless otherwise noted. For instance, a dioxane solution of 1,5-COD (concn., 0.5M), dichlorobis(triphenylphosphine)iron(II) (0.05M), and pyrocatechol (2.0M), sealed in a Pyrex glass tube under a vacuum (10^{-2} mmHg), was heated at 200±1°C for six hours. Though the catalyst did not dissolve completely at room temperature, it did so at once at the reaction temperature and gave no insoluble materials until the end of the reaction. In this reaction, not only the hydrogenation of 1,5-COD to cyclooctene (COE) and cyclooctane (COA), but also the isomerization to 1,4- and 1,3-cyclooctadiene (1,4-COD and 1,3-COD), occurred. From the composition of the reaction mixtures, the following reaction parameters were derived: the selectivity is the percentage of COE in the reduced products, and the percentage of hydrogenation was calculated on the assumption that both double bonds of cyclooctadienes (COD) are reduced. (See the footnotes of Table 1.) Therefore, if the selectivity is 100%, the reaction may be regarded as having been completed at 50% hydrogenation. The percentage of conversion is the percentage of the 1,5-COD consumed. A part of the results are summarized in Table 1.

Hydrogen Donors. At first, *prim*- and *sec*-alcohols, and cyclohexene, which have been reported as hydrogen donors, were examined, but their ability to donate hydrogen was quite weak. Then, taking a hint from

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[8] H. Itatani and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 1600 (1967).

[9] S. Nanya, M. Hanai, and K. Fukuzumi, *Kogyo Kagaku Zasshi*, **72**, 2005 (1969).

[10] T. Nishiguchi and K. Fukuzumi, *Chem. Commun.*, **1971**, 139.

TABLE 1. TRANSFER-HYDROGENATION OF 1,5-COD CATALYZED BY $FeCl_2(PPh_3)_2$[a)]

No.	Gas in sealed tube	Hydrogen donor	React. temp. °C	Yield of products, %				% Conv.[b)]	% Conv. of COD[c)]	% Hyd.[d)]	Selectivity[e)] %
				COA	COE	1,3-COD	1,4-COD				
1	None	o-$C_6H_4(OH)_2$	160	5	6	1	5	16	11	8	53
2	None	o-$C_6H_4(OH)_2$	180	22	8	6	10	46	30	26	27
3	None	None	180	3	5	1	5	14	8	5	64
4	None	o-$C_6H_4(OH)_2$	200	57	9	22	9	97	66	62	14
5	O_2	o-$C_6H_4(OH)_2$	200	55	9	22	9	95	64	60	14
6	Air	o-$C_6H_4(OH)_2$	200	57	9	22	9	97	66	62	15
7	N_2	o-$C_6H_4(OH)_2$	200	58	9	22	8	97	67	64	13
8	CO_2	o-$C_6H_4(OH)_2$	200	57	9	20	9	95	66	62	15
9	None	1,2,3-$C_6H_3(OH)_3$	200	63	6	14	9	92	69	65	8
10	None	p-$C_6H_4(OH)_2$	200	53	8	24	10	96	61	57	13
11	None	2-C_3H_7OH	200	3	1	1	7	12	4	3	21
12	None	1-$C_8H_{17}OH$	200	3	8	1	8	20	11	6	73
13	None	2-$C_8H_{17}OH$	200	4	1	2	11	17	5	4	13
14	None	1-$C_{12}H_{25}OH$	200	3	1	1	7	11	3	3	16
15	None	1-$C_{12}H_{25}SH$	200	6	7	4	18	33	13	9	56
16	None	1-$C_{12}H_{25}NH_2$	200	1	1	1	5	6	1	1	f)
17	None	Cyclohexene	200	4	1	1	9	15	5	4	20
18	None	None	200	11	3	4	14	30	14	12	16
19	None	1,2,3-$C_6H_3(OH)_3$	240	75	23	2	1	99	98	87	22
20	None	o-$C_6H_4(OH)_2$	240	71	14	14	2	99	85	77	16
21	None	p-$C_6H_4(OH)_2$	240	68	15	13	3	98	83	75	18
22	None	1-$C_7H_{15}OH$	240	6	3	3	10	12	9	8	33
23	None	None	240	32	9	20	11	72	42	37	22

a) 1,5-COD (concn., 0.5M), hydrogen donors(2.0M) and the catalyst (0.05M) were heated in dioxane for 6 hr.

b) Conversion of 1,5-COD to COA, COE, 1,3-COD and 1,4-COD.

c) Conversion of COD to COA and COE.

d) This is given by $\frac{2\times \text{COA}+\text{COE}}{2}$.

e) Given by $\frac{\text{COE}}{\text{COA}+\text{COE}}\times 100$.

f) The yield was too low to evaluate.

the reaction in which p-benzoquinone abstracts hydrogen from organic compounds to form hydroquinone,[1)] we tried to use polyhydroxybenzenes with hydroxyl groups at the *ortho* or *para* positions as hydrogen donors; we founs that they were much superior to the other organic compounds tried. That is, the percentage of hydrogenation was 64—57% in the case of the polyhydroxybenzenes (Nos. 4—10 in Table 1), while it was less than 10% in the cases of the other compounds (Nos. 11—18). The order of the ability to give hydrogen, based on the percentage of hydrogenation, was found to be as follows: pyrogallol>pyrocatechol> hydroquinone≫n-dodecanethiol>1-octanol>cyclohexene>2-octanol>n-dodecanol>n-dodecyl amine. When *prim*- or *sec*-alcohols were used, small amounts of aldehydes or ketones were detected by IR analysis. However, when the polyhydroxybenzenes were used, a tarry material was formed and no quinones were identified. This might be at least partly attributable to the thermal instability of the quinones, though further study is needed. In fact, o- and p-benzoquinone gave tarry substances when heated in dioxane at 200°C.

Unexpectedly, as is shown in Table 1 and Figs. 5 and 6, not only were COA and COE formed, even if no hydrogen donor was added especially, but also the percentage of hydrogenation was higher in these cases (Nos. 18 and 23) than in the cases where the alcohols, n-dodecanethiol, cyclohexene and n-dodecyl amine, were used (Nos. 11—17 and 23). Hydrogen transfer from the solvent, dioxane, to 1,5-COD was inferred, for the possibility of the disproportionation of the diene may be rejected on the following grounds: cyclooctatrienes, which would result from the disproportionation of the diene, were not detected by gas-chromatographic analysis, and the total amount of the detected eight-membered cyclic hydrocarbons was almost equal to the amount of 1,5-COD charged as a reactant.

Effect of Gases in the Sealed Tubes. It is well known that some metal complexes react with oxygen or nitrogen,[11)] and that radical reactions are apt to be influenced by the presence of oxygen. Therefore, the experiments under atmosphers of oxygen, air, nitrogen, and carbon dioxide were carried out (Nos. 5—8), and compared with the one done under a vacuum. The results showed that the compositions of the reaction mixtures were identical within the limits of experimental error under any gas or in a vacuum.

Reaction Temperature. The percentage of conversion was 16% at 160°C, 46% at 180°C, 97% at 200°C, and more than 99% at 240°C. As the reac-

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[11)] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

tion temperature was raised, the percentage of hydrogenation also increased, but the selectivity had almost no connection with the reaction temperature at relatively high conversions.

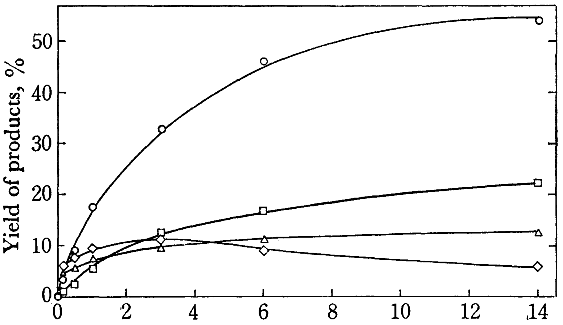

Fig. 1. Time dependence of the yield of the products.
○: COA, △: COE, □: 1,3-COD, ◇: 1,4-COD

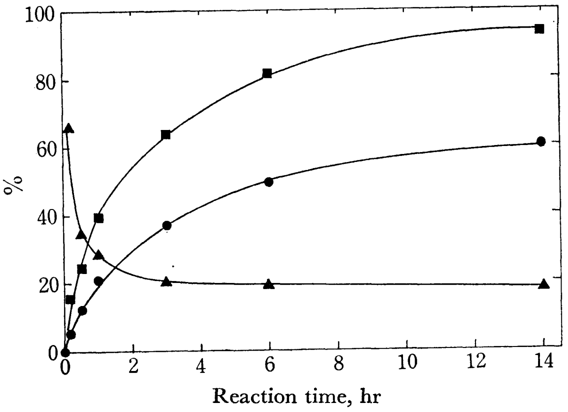

Fig. 2. Time dependence of the reaction parameters.
●: % Hydrogenation, ▲: Selectivity, ■: % Conversion

Reaction Time. At an early stage of the reaction, all the reaction parameters except that of the selectivity were in proportion to the reaction time (Figs. 1 and 2). The lack of an induction period suggests that the time for the formation of an active species is short, though induction periods have been reported in a few homogeneous hydrogenations.[12]

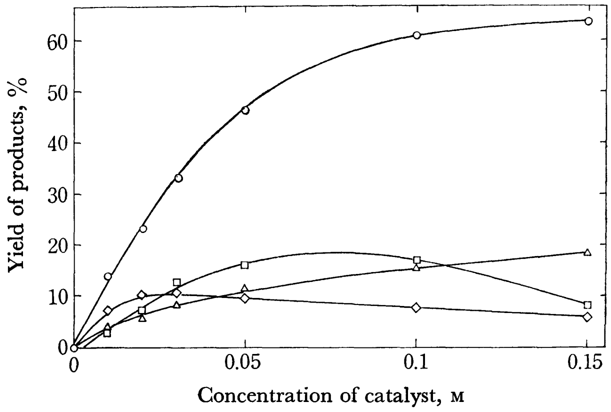

Fig. 3. Dependence of yield of the products on initial concentration of the catlyst.
○: COA, △: COE, □: 1,3-COD, ◇, 1,4-COD

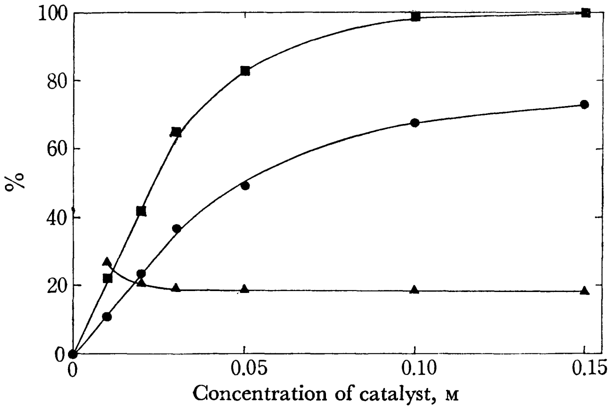

Fig. 4. Dependence of the reaction parameters on initial concenttation of the catalyst.
●: % Hydrogenation,
■: % Conversion, ▲: Selectivity

Concentration of the Catalyst. The percentage of hydrogenation and the percentage of conversion were proportional to the initial concentration of the catalyst below 0.05M (Figs. 3 and 4). This fact suggests that the rate of the hydrogenation is first order in relation to the initial concentration of the catalyst.

Concentration of Pyrocatechol. The influence of the

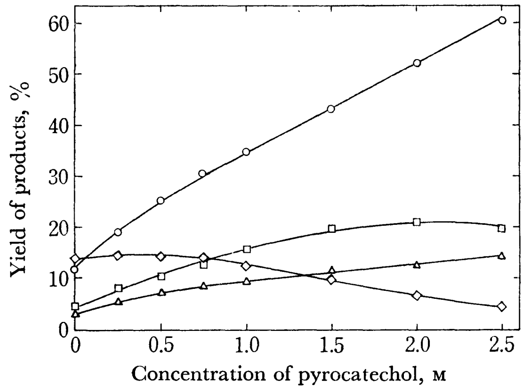

Fig. 5. Dependence of yield of the products on initial concentration of pyrocatechol.
○: COA, △: COE,
□: 1,3-COD, ◇: 1,4-COD

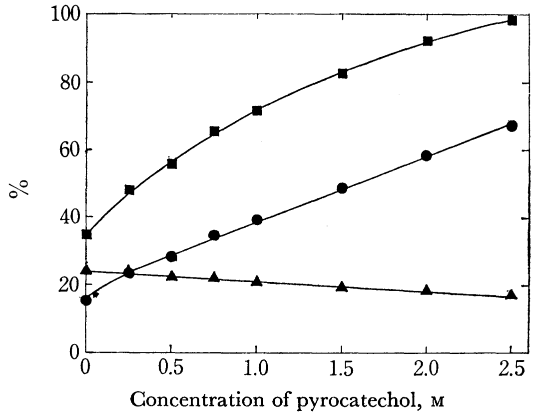

Fig. 6. Depencence of the reaction parameters on initial concentration of pyrocatechol.
●: % Hydrogenation,
■: % Conversion, ▲: Selectivity

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[12] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc., A*, **1968**, 3143.

initial concentration of a hydrogen donor was examined by the use of pyrocatechol, which has a strong ability to supply hydrogen and a high solubility (Figs. 5 and 6). The interpretation of the results was complicated by the fact that the solvent, dioxane, gave some hydrogen, as has been mentioned previously. If the hydrogen-donating capacity of the solvent is equal to that of pyrocatechol at a concentration of about 0.8M in the solvent, the percentage of hydrogenation and the percentage of conversion may have a linear relation to the initial concentration of pyrocatechol.

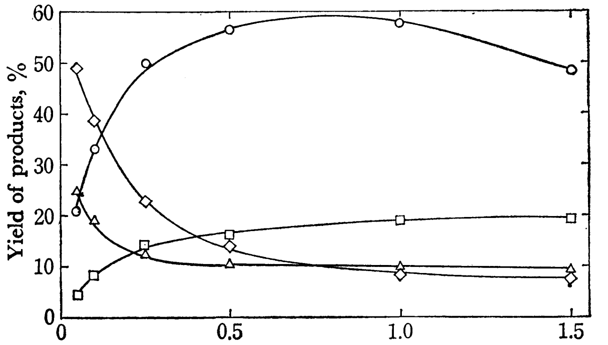

Fig. 7. Depencence of yield of the products on initial concentration of 1,5-COD.
○: COA, △: COE, □: 1,3-COD,
◇: 1,4-COD

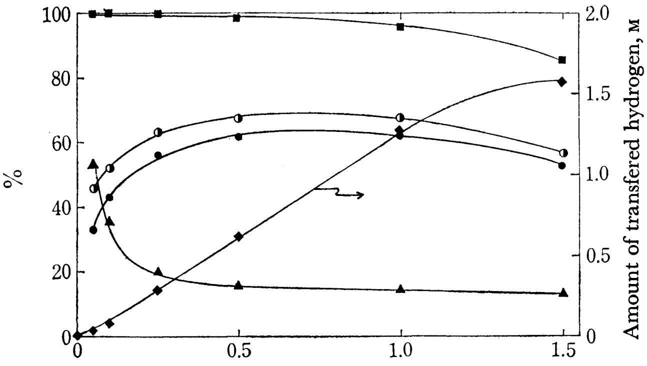

Fig. 8. Depencence of the reaction parameters and the amount of transfered hydrogen on initial concentration of 1,5-COD.
●: % Hydrogenation, ■: % Conversion,
◐: % Conversion of COD, ▲: Selectivity, ◆: Amount of transfered hydrogen which is given by [% Hydrogenation] × [Initial concentration of 1,5-COD] × 1/100

Concentration of 1,5-COD. The percentage of hydrogenation and the percentage of conversion of COD were found to have maximum values against the initial concentration of 1,5-COD (Figs. 7 and 8). That is, the higher the concentration, the larger the degree of the hydrogenation, until it decreased, perhaps because of the deficiency of the hydrogen donor. This fact suggests that at least two 1,5-COD molecules are involved in the reduction and that they act not only as hydrogen acceptors, but also as ligands having the function of co-catalysts, for if merely one molecule of 1,5-COD is involved, the lower values of the parameters at the lower concentration of 1,5-COD cannot be explained. Therefore, it is difficult to decide whether the susceptibility of 1,5-COD to the reduction is due to its nature as a hydrogen acceptor or as a ligand in activating the catalyst. The amount of transferred hydrogen which caused the reduction was roughly proportional to the initial concentration of 1,5-COD at concentrations from 0.3M to 1.0M.

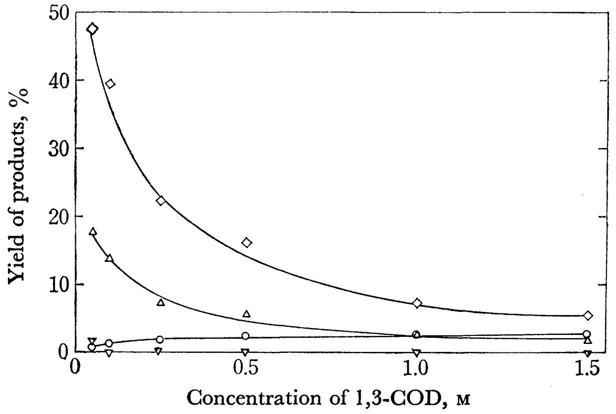

Fig. 9. Depencence of yield of the products on initial concentration of 1,3-COD.
○: COA, △: COE, ▽: 1,5-COD,
◇: 1,4-COD

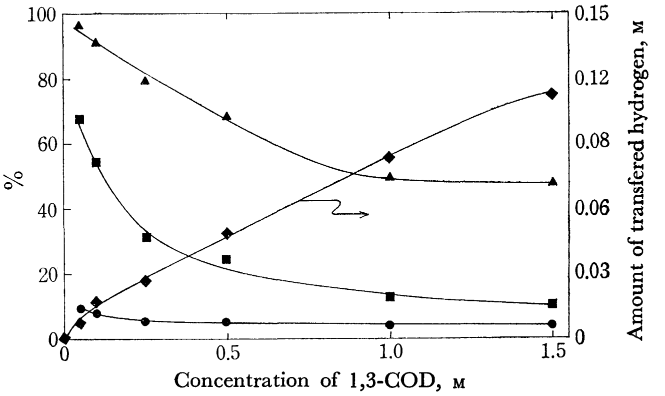

Fig. 10. Depencence of the reaction parameters and the amount of transfered hydgogen on initial concentration of 1,3-COD.
●: % Hydrogenation of 1,3-COD, ■: % Conversion of 1,3-COD, ▲: Selectivity, ◆: Amount of transfered hydgogen which is given by [% Hydrogenation] × [Initial concenration of 1,3-COD] × 1/100

The lower the initial concentration of 1,5-COD, the higher the ratio of 1,4-COD in the reaction mixture. It can thus be inferred that the lower the concentration of COD at constant concentrations of the catalyst and the hydrogen donor, the easier it is to reach an equilibrium among COD. From this inference and our observations, the isomerization of 1,3-COD to 1,4-COD can be expected to occur more easily at a lower initial concentration of the conjugated diene; this expectation was confirmed (Figs. 9 and 10). 1,3-COD did not show such a co-catalystic action as 1,5-COD did, and the percentage of hydrogenation decreased constantly as the initial concentration of 1,3-COD increased.

General Discussion. It is well known that hydrido complexes are formed as active species not only in homogeneous hydrogenation by molecular hydrogen, but also in the isomerization of olefins, where alcohols act as co-catalysts.[4,13] Moreover, hydrido complexes are obtained in the reaction of Rh(I), Os(I), Ir(I), and Pt(II) complexes with alcohols.[14] In analogy with these reactions, a hydrido complex is presumed to be involved as an active species in the transfer-hydrogenation.

It has been reported that alcohols give molecular hydrogen and carbonyl compounds when heated in the presence of catalysts in not only a heterogeneous but also in a homogeneous system.[15] Therefore, the evolution of molecular hydrogen during the transfer-hydrogenation reaction may not be so unreasonable. However, perhaps hydrogen is not transferred in the gaseous form in the reaction, for the evolution of molecular hydrogen from pyrocatechol was not observed upon heating at 200°C without the catalyst, and the hydrogenation of 1,5-COD by molecular hydrogen did not take place without the catalyst. Such a reaction as is shown in the following equation should not be regarded as a transfer-hydrogenation *via* molecular hydrogen.

$$\begin{tikzcd}
\begin{array}{c}\text{Hydrogen donor}\\ +\\ \text{Catalyst}\end{array} \arrow[r, shift left] & \begin{array}{c}\text{Hydrido}\\ \text{complex}\end{array} \arrow[l, shift left] \arrow[r, "\text{Olefin}"] \arrow[d, shift left] & \begin{array}{c}\text{Paraffin}\\ +\\ \text{Other compounds}\end{array} \\
 & H_2 + \text{Other compounds} \arrow[u, shift left] &
\end{tikzcd}$$

The mechanistic study of the transfer-hydrogenation is now in progress.

Experimental

Materials. The dichlorobis(triphenylphosphine)iron(II) was prepared according to the method of Pignolet *et al.*[15] and was recrystallized from toluene. The dioxane, 1,5-COD, 1,3-COD and cyclohexene were purified by distillation over metallic sodium. The purified 1,5-COD was found to be contaminated with 0.2% of COA, 0.7% of COE, 0.5% of 1,3-COD, and 0.9% of 1,4-COD. The Pyrocatechol, hydroquinone, and pyrogallol were purified by recrystallization from benzene. All the other reagents were of a commercial G. R. grade. The mixture of cyclooctatrienes was prepared by the method of Cope and Hockstein.[16]

An Example of Transfer-hydrogenation. 1,5-COD (0.0541 g, 0.5 mmol), pyrocatechol (0.22 g, 2.0 mmol), and $FeCl_2(PPh_3)_2$ (0.0326 g, 0.05 mmol) were put into a Pyrex glass tube which had been sealed at one side. Into the mixture, dioxane was then stirred with a wire, and the total volume of the solution was made 1.0 m*l*. The solution was degassed with a Dry Ice-acetone bath and a vacuum line, and sealed in a vacuum (10^{-2} mmHg). The sealed tube was heated for 6 hr in a silicon-oil bath kept at 200±1°C. To analyze the reaction mixture, gas chromatography was performed at 80°C with a Hitachi Perkin-Elmer instrument equipped with a flame ionization detector. A 2 m×6 mm stainless steel column packed with 25% of 1,2,3-tris(2-cyanoethoxy)-propane on Celite 545 was used.

The other transfer-hydrogenations were carried out in the same way.

When the glass tubes were sealed under gases, the volume of the gases in the reaction vessels was three times that of the solution.

An Attempted Hydrogenation by Molecular Hydrogen without Catalysts. A dioxane solution of 1,5-COD (0.5M, 10 m*l*) was placed in a 50 m*l* stainless steel autoclave, and the air in the vessel was replaced with hydrogen of 10 atm. After being heated for 6 hr at 180°C, the solution was analyzed by gas chromatography.

An Examination to Test the Evolution of Hydrogen. A dioxane solution of pyrocatechol (1.0M) was sealed in a Pyrex glass tube under a vacuum and was then heated at 200°C for 4 hr. When the sealed tube was then broken in water, no evolution of gas was observed.

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