

Homogeneous Transfer-hydrogenation of Olefins Catalysed by Fe^{II}, Co^{II}, and Ni^{II} Complexes: *o*- and *p*-Dihydroxybenzene as Hydrogen Donors

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Summary In the homogeneous hydrogenation of eight-membered cyclo-olefins, *o*- and *p*-dihydroxybenzene were superior to alcohols as hydrogen donors, and FeCl₂(PPh₃)₂ and FeBr₂(PPh₃)₂ were the most active catalysts of the complexes MX₂(PPh₃)₂, where M is Fe^{II}, Co^{II}, and Ni^{II}, and X is Cl⁻, Br⁻, and I⁻.

olefin (0.5 M), hydrogen donor (2.0 M) and catalyst (0.05 M) in dioxan, were heated under vacuum for 6 h. The fact that the pressure in the reaction vessel was unchanged throughout the reaction suggested that no molecular hydrogen was formed during the reaction.

TABLE I

Transfer-hydrogenation of cyclo-octa-1,5-diene catalysed by FeCl₂(PPh₃)₂

Hydrogen donor	Reaction temp. (°C)	Yield of products (%)			
		(4)	(3)	(2)	(5)
None	180	3	5	1	5
<i>o</i> -C ₆ H ₄ (OH) ₂	200	22	8	6	10
.. ..	200	54	12	20	5
.. ^a	200	3	5	2	5
.. ..	240	71	14	13	2
<i>p</i> -C ₆ H ₄ (OH) ₂	240	68	15	12	3
<i>n</i> -C ₇ H ₁₅ OH	240	6	3	3	10
cyclo-C ₈ H ₁₁ OH	240	37	10	23	8

^a Triphenylphosphine (0.2M) was added.

In almost all catalytic hydrogenations of olefins, molecular hydrogen has been used as the hydrogen source. However, transfer-hydrogenation in which organic compounds are employed as hydrogen donors has the advantage of milder reaction conditions. Although several investigations of heterogeneous transfer-hydrogenation in which six-membered cyclo-olefins¹ and alcohols² are used as the hydrogen source, have been carried out, few studies of the homogeneous reaction of olefins have been reported. Itatani and Bailar³ have reported that the formation of an olefin from methyl linoleate is effected by dihalogenobis(triphenylphosphine)nickel(II) in tetrahydrofuran or C₆H₆ under N₂. We also found that the olefin linkages of methyl linoleate were reduced in PrⁱOH in the presence of Ni(acac)₂,⁴ but the reproducibility of the reaction was discouragingly bad, perhaps because the catalyst decomposed to give an insoluble substance.

We now report the transfer-hydrogenation of cyclo-octa-1,5-diene (1) and -1,3-diene (2) to cyclo-octene (3) and cyclo-octane (4), and that of (3) to (4). In the reaction of (1) or (2), the isomerization to other cyclo-octadienes including cyclo-octa-1,4-diene (5) also took place. The

As hydrogen donors, *o*- and *p*-dihydroxybenzene were better than cyclohexanol which, in turn, was superior to heptan-1-ol. It may be inferred that the hydroxy compounds are dehydrogenated to give *o*- and *p*-benzoquinone, heptanal, and cyclohexanone. The aldehyde and the ketone were identified by i.r. analysis, but the quinones were not, presumably because they are unstable at the high

temperatures. In fact, they decomposed to form a tarry material on heating in dioxan at 200°. The solvent, dioxan, was considered to be a poor hydrogen donor on the grounds

activity of $\text{FeX}_2(\text{PPh}_3)_2$ ⁷ and $\text{CoX}_2(\text{PPh}_3)_2$ was $\text{X} = \text{Cl}^- \gg \text{Br}^- > \text{I}^-$ for the nonconjugated olefins (1) and (3) and $\text{I}^- > \text{Br}^- > \text{Cl}^-$ for the conjugated diene (2) while that of

TABLE 2
Transfer-hydrogenation catalysed by various complexes^a

Catalyst	(1)			(2)			(3)
	Hyd. ^b	Sel. ^c	Iso. ^d	Hyd. ^b	Sel. ^c	Iso. ^d	Hyd. ^b
$\text{FeCl}_2(\text{PPh}_3)_2$	77	16	98	17	71	2	26
$\text{FeBr}_2(\text{PPh}_3)_2$	79	15	98	18	67	9	23
$\text{FeI}_2(\text{PPh}_3)_2$	62	7	55	35	96	8	8
$\text{CoCl}_2(\text{PPh}_3)_2$	35	11	40	2	e	1	7
$\text{CoBr}_2(\text{PPh}_3)_2$	32	10	28	2	e	0	3
$\text{CoI}_2(\text{PPh}_3)_2$	11	30	9	3	e	1	2
$\text{NiCl}_2(\text{PPh}_3)_2$	14	20	21	3	e	0	2
$\text{NiBr}_2(\text{PPh}_3)_2$	35	26	69	6	78	1	3
$\text{NiI}_2(\text{PPh}_3)_2$	43	69	91	31	94	55	5

^a The reactions were carried out at 240° and *o*-dihydroxybenzene was used as the hydrogen donor.

^b Percentage of hydrogenation: it is defined as $[(3) + 2 \times (4)]/2$ for the hydrogenation of (1) and (2) where the reduction to (4) may require two moles of hydrogen donor, and as the yield of (4) from (3).

^c Selectivity: percentage of (3) in the hydrogenated products.

^d Percentage of isomerization: percentage of isomerized cyclo-octadiene from the reactions.

^e The yield of (3) and (4) was too low to evaluate selectivity.

that in a blank experiment little hydrogenation took place. Cyclo-octatrienes which would result from the disproportionation of cyclo-octadienes were not detected.

The fact that the addition of triphenylphosphine retarded the hydrogenation suggests that there is reversible dissociation of the ligand from $\text{FeCl}_2(\text{PPh}_3)_2$ as in the case of $\text{RhCl}(\text{PPh}_3)_3$.⁵ The results shown in Table 2 may be summarized as follows: (a) the order of the susceptibility of the olefins to reduction was (1) > (2) > (3) and this is similar to their affinity to metal ions;⁶ (b) the order of the catalytic

$\text{NiX}_2(\text{PPh}_3)_2$ was $\text{I}^- > \text{Br}^- \gg \text{Cl}^-$ for all the olefins, though the reverse order has been reported in the reduction of methyl linoleate by hydrogen;³ (c) the selectivity was high for the conjugated diene (2) but low for the nonconjugated diene (1).

The metal complexes isolated from the reaction mixture were not identical with the original ones and their i.r. spectra showed several peaks characteristic of the dihydroxybenzenes, *e.g.*, a strong broad peak at 3340 cm^{-1} .

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¹ E. A. Braude, R. P. Linstead, and P. W. D. Mitchell, *J. Chem. Soc.*, 1954, 3578, and references therein.

² K. Sakai, T. Ito, and K. Watanabe, *Bull. Chem. Soc. Japan*, 1966, 39, 2230.

³ H. Itatani and C. Bailar, jun., *J. Amer. Chem. Soc.*, 1967, 89, 1600.

⁴ S. Nanya, M. Hanai, and K. Fukuzumi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1969, 72, 2005.

⁵ J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.

⁶ M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, 1962, 84, 4679.

⁷ L. H. Pignolet, D. Forster, and W. D. Horrocks, Jun., *Inorg. Chem.*, 1968, 7, 828.