

HOMOGENEOUS SELECTIVE HYDROGENATION OF 1,3-OR 1,4-DIENES TO MONOENES  
BY  $(C_5H_5)_2MoH_2$  AS CATALYST<sup>1,2)</sup>

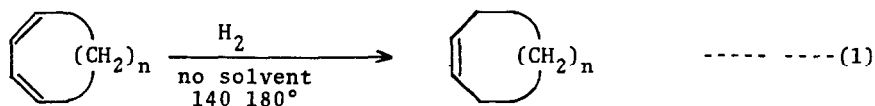
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Selective partial hydrogenation of dienes to monoenes has been achieved using partially poisoned heterogeneous catalyst<sup>3)</sup> under controlled conditions or using homogeneous catalysts active only for dienes.<sup>4-13)</sup> Selective hydrogenation of polyenes is of practical importance; in particular, the hydrogenation of cyclopentadiene to cyclopentene has been a subject of a number of patents<sup>14)</sup> for the cycloolefin affords a useful polymer "cyclopentenamar". We have found that  $(h^5-C_5H_5)_2MoH_2$  ( $Cp_2MoH_2$ ) acts as a novel selective homogeneous catalyst active only for 1,3- or 1,4-dienes and for some  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>2d)</sup>

Freshly distilled dicyclopentadiene containing 0.2 mole % of  $Cp_2MoH_2$  was heated at 180° under 160 atm of hydrogen for 4 hr. The brown reaction mixture contaminated with some polycyclopentadienes was distilled to give a liquid which consists of cyclopentene (55%), cyclopentadiene (~1%) and dicyclopentadiene (1.5%). A fully hydrogenated product, cyclopentane, was practically absent. The relatively high reaction temperature (180°) shifts the thermal



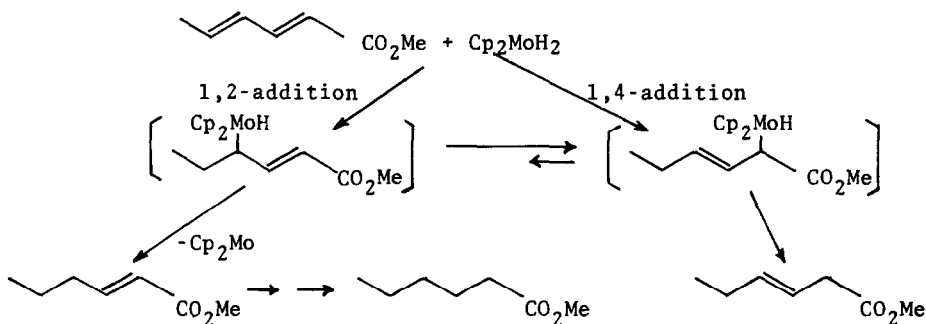
equilibrium between dicyclopentadiene and the monomer toward the monomer side. Therefore, thermal cracking to the monomer prior to the hydrogenation is not

necessary. This high-temperature hydrogenation may have advantage over hitherto known low-temperature method<sup>9,12)</sup> (e.g. at 0°~20°) since the endothermic cracking partially compensates the heat of hydrogenation facilitating temperature control in a large scale reaction. Use of solvent such as acetic acid or chlorobenzene gives cyclopentene in reduced yields (10~20%). Aromatic solvents such as benzene, toluene, etc inhibit the catalytic hydrogenation. With a catalytic amount of  $\text{Cp}_2\text{MoH}_2$  ( 0.2 mole %) 1,3-or 1,4-cyclohexadiene, 1,3-cycloheptadiene, norbornadiene, or 1,3-cyclooctadiene are also successfully hydrogenated at 140°~180° without solvent to the corresponding cyclic monoenes in good yields (50~90%). Cycloheptatriene is stepwisely hydrogenated. At 140°, a mixture of 1,3-cycloheptadiene and cycloheptene is obtained, but at 180° only cycloheptene with some cycloheptane results. The absence of 1,4-cycloheptadiene indicates 1,2-or 1,6-addition of hydrogen to the triene. A 1,5-diene, cycloocta-1,5-diene, is not hydrogenated at all even at 180°. The result shows no isomerization of the olefin at the hydrogenation condition even though hydrogen and metal hydride species are involved.

Similar metallocene hydrides such as  $\text{Cp}_2\text{WH}_2$  or  $\text{Cp}_2\text{ReH}$ , or a metallocene,  $\text{Cp}_2\text{Cr}$ , were inactive.

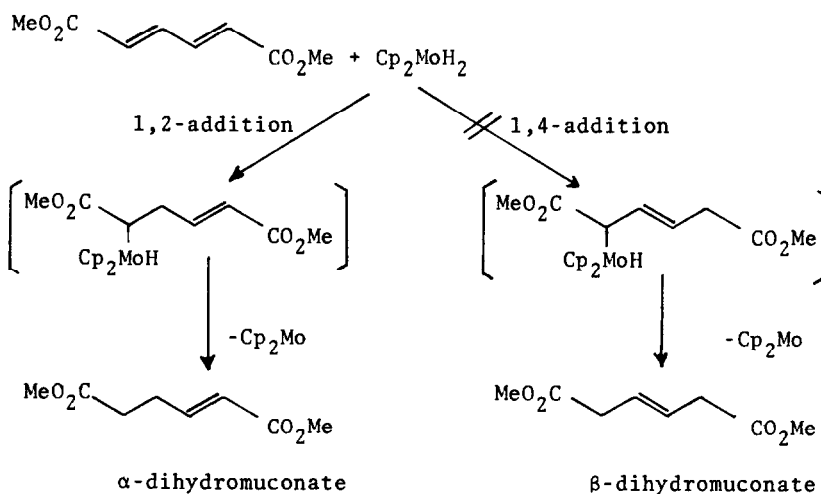
Methyl acrylate, methyl crotonate, crotonaldehyde or mesityl oxide is hydrogenated at 140~50° without solvent to the corresponding saturated compounds. Methyl sorbate gave a mixture of products (cf. Scheme 1); the ratio is sensitive to the solvent and temperature. Although the formation of methyl 3-hexenoate

Scheme 1



in a minor amount may imply 1,4-addition of hydrogen to the diene part, it can also be formed via an initial formation of a  $\alpha$ -metalated product followed by allyl migration to an  $\alpha$ -metalated one as shown in Scheme 1. A direct route for the  $\alpha$ -metalated complex unlikely as described below. Absence of 1,4-addition receives support from the result of stoichiometric reaction. Thus methyl sorbate with  $\text{Cp}_2\text{MoH}_2$  gave almost the same product distribution as found in the catalytic reaction. Further, dimethyl muconate with  $\text{Cp}_2\text{MoH}_2$  gave exclusively dimethyl  $\alpha$ -dihydromuconate. A separate experiment confirmed that no isomerization of dimethyl  $\beta$ -dihydromuconate occurs in the presence of  $\text{Cp}_2\text{MoH}_2$  at the same condition. The above results of catalytic hydrogenation are explicable with the stepwise hydrogenation mechanism already proposed by us<sup>2)</sup> in stoichiometric reactions. A chelating coordination of a 1,3-diene as a tetrahapto ligand, to the metal in  $\text{Cp}_2\text{MoH}_2$  is sterically impossible and the diene is

Scheme 2



forced to behave as dihapto-ligand. Our proposal of absence of 1,4-hydrogenation even for conjugated dienes is thus supported and  $\text{Cp}_2\text{MoH}_2$  may be utilized as a selective catalyst for 1,2-hydrogenation in suitable conditions.

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