Mechanism of Hydrogen Transfer Reactions in 1,4-Cyclohexadiene and 1,4-Hexadiene Catalyzed by Tricarbonyl Chromium Complexes

Deuterium tracer studies showed previously that the specific homogeneous hydrogenation of methyl sorbate catalyzed by methyl benzoate–$Cr(CO)_3$ occurs by 1,4-addition of H_2 (*1*). In a study of the scope of this reaction (*2*), we have found that: (a) both 1,4- and 1,3-cyclohexadienes are selectively reduced to cyclohexene; (b) the products from acyclic 1,4-dienes are those expected if hydrogenation is preceded by isomerization to the 1,3-dienes; and (c) 1,4-addition is the dominant mechanism of reduction of both 1,4- and 1,3-dienes. These findings led to our investigation of the catalytic isomerization of cyclic and acyclic diolefins with arene–$Cr(CO)_3$ complexes. This report deals with the isomerization of 1,4-cyclohexadiene and 1,4-hexadiene catalyzed by methyl benzoate–$Cr(CO)_3$ in the absence of H_2. Under these conditions disproportionation of cyclohexadiene is observed. Other reports have described the homogeneous isomerization and disproportionation of 1,4-cyclohexadiene but with Ir–PPh_3 complexes (*3*) and with Rh- and Ir-(1,3-cyclohexadiene)(pentamethylcyclopentadiene) complexes (*4*). These new transfer reactions observed in the absence of H_2 may be of significance in the elucidation of the mechanism of catalytic homogeneous hydrogenation by arene–$Cr(CO)_3$ complexes.

The 1,4-cyclohexadiene was heated with methyl benzoate–$Cr(CO)_3$ in an autoclave under N_2 pressure. After a 2-hr induction period, 1,4-cyclohexadiene was smoothly isomerized to a mixture of 1,3- and 1,4-diene approaching a constant ratio of 1.6 to 1 with some accompanying disproportionation to benzene and cyclohexene (Fig. 1). A new carbonyl band at 1921 cm^{-1} appeared in the ir spectrum of the reaction mixture which corresponds to that of benzene–$Cr(CO)_3$. Concentrations of benzene–$Cr(CO)_3$ and methyl benzoate–$Cr(CO)_3$ complexes were estimated by the intensity

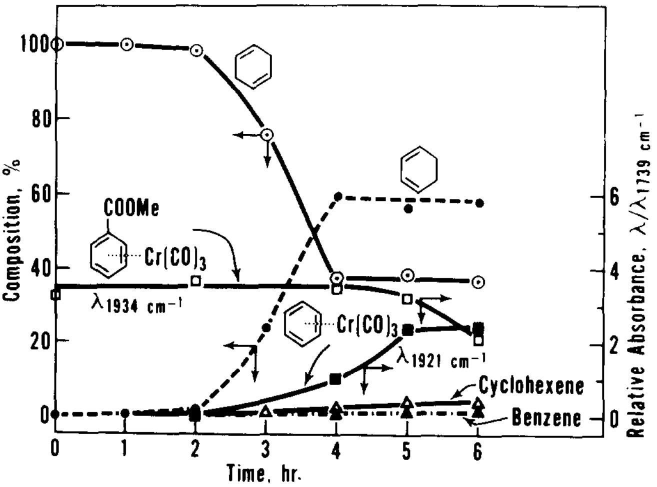


FIG. 1. Catalytic isomerization and disproportionation of 1,4-cyclohexadiene with methyl benzoate–$Cr(CO)_3$ at 160°C. [Reaction conditions: 9.5 mmol diene, 0.5 mmol catalyst, 50 ml *n*-pentane, initial N_2 pressure 50 psi, 150 ml Magne–Dash autoclave. Analyses: by glc and ir as described in (*2*).]

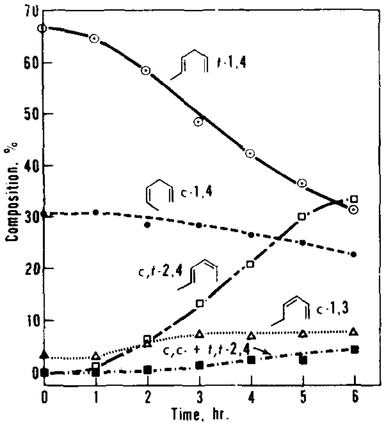


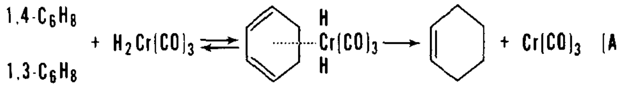
FIG. 2. Catalytic isomerization of 1,4-hexadiene with methyl benzoate-$Cr(CO)_3$ at 175°C. (Reaction conditions and analyses: See Fig. 1).

of the respective bands at 1921 and 1934 cm^{-1} (relative to a band at 1739 cm^{-1} which remained constant). The formation of benzene–$Cr(CO)_3$ corresponded to a decrease in methyl benzoate–$Cr(CO)_3$ (Fig. 1). The concentration of benzene–$Cr(CO)_3$ in the final reaction product was estimated at 11% based on calibrations with pure complex. Apparently, benzene from disproportionation of 1,4-cyclohexadiene forms a $Cr(CO)_3$ complex by ligand exchange with the methyl benzoate–$Cr(CO)_3$ catalyst. Ligand exchange between catalyst and substrate is an important feature of homogeneous hydrogenation catalyzed by $Fe(CO)_5$ (*5*) and diene–$Fe(CO)_3$ complexes (*6*).

Figure 2 shows kinetic data on the isomerization of a mixture of *trans*-1,4- and *cis*-1,4-hexadiene with methyl benzoate–$Cr(CO)_3$. *trans*-1,4-Hexadiene is much more reactive than *cis*-1,4-hexadiene in yielding *cis*-2,*trans*-4-hexadiene as the major product. Minor products include *cis*-1,3- and *cis*,*cis*- plus *trans*,*trans*-2,4-hexadienes.

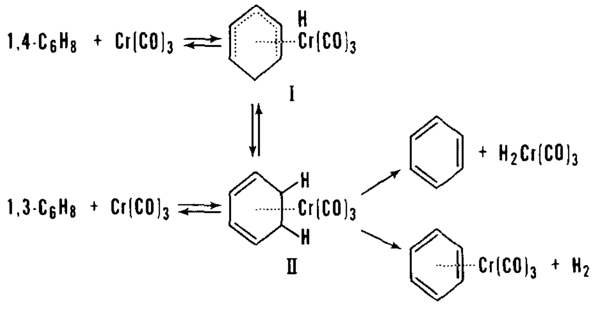
Catalyst activation in the mechanism of homogeneous hydrogenation for both $RhCl(PPh_3)_3$ (*7*) and $IrCl(CO)(PPh_3)_2$ (*8*) involves PPh_3 dissociation, making available a coordination site on the metal complex for reaction with H_2 and/or olefin. This "coordination unsaturation" is now considered as a key step in many homogeneous catalytic systems (*9*, *10*). Formation of a metal–olefin complex which reacts with H_2 is the preferred path ("unsaturate route") for the Ir complex (*8*). Formation of a solvated metal–hydride complex which reacts with the olefin ("hydride route") by solvent displacement is favored for the Rh complex (*11*).

If dissociation of the arene–$Cr(CO)_3$ complex is assumed as the initial step (*1*), the $Cr(CO)_3$ intermediate can either react with H_2 or the diene. In the presence of H_2, the formation of cyclohexene from both 1,4- and 1,3-cyclohexadiene indicates that $H_2Cr(CO)_3$ is the preferred catalytic intermediate (A).

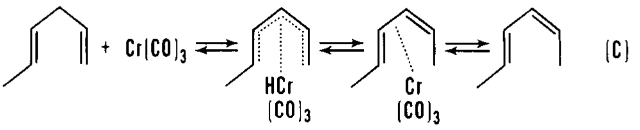


[A]

In the absence of H_2, disproportionation of cyclohexadienes to benzene supports the formation of a cyclopentadienyl hydride complex (I) yielding 1,3-cyclohexadiene–$Cr(CO)_3$ (II) as intermediate which can either dissociate or undergo H-abstraction at C-5 and C-6 to give benzene and $H_2Cr(CO)_3$ (B).



[B]



III

Accordingly, ligand exchange occurs either via complex II to form benzene–Cr(CO)$_3$ and H_2 or benzene reacts directly with Cr(CO)$_3$. Reduction of cyclohexadienes would occur through the dihydride.

These results provide further support for the hydrogenation mechanism involving $H_2Cr(CO)_3$ (*1*, *2*). If complex II was an intermediate, the formation of benzene–Cr(CO)$_3$ would be expected during the hydrogenation of 1,3- and 1,4-cyclohexadienes. The absence of benzene–Cr(CO)$_3$ under hydrogenation conditions (*2*) shows that H_2 effectively competes with the diene for the vacant coordination sites of Cr(CO)$_3$ and the formation of $H_2Cr(CO)_3$ is favored over that of complex II. In a similar way, with the RhCl(PPh$_3$)$_3$ catalyst, the "hydride route" was shown (*12*) to be promoted at high H_2 pressure and in alcohol solvents, and this path favored selectivity. Mechanistic paths may be thus significantly affected by the presence or absence of H_2.

The finding that *trans*-1,3-hexadiene and *trans,trans*-2,4-hexadiene form very slowly, if at all, in methyl benzoate–Cr(CO)$_3$ catalyzed isomerization of 1,4-hexadienes lends support for a mechanism involving pentadienyl hydride complex III (C). Steric interaction in the corresponding pentadienyl hydride complex from *cis*-1,4-hexadiene would account for the very slow interconversion into *cis,cis*-2,4- and *cis*-1,3-hexadienes.

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