Selective Hydrogenation of the Cyclohexadienes Catalyzed by trans-[IrCl(CO)(Ph₃P)₂]

The selective hydrogenation of unsaturated hydrocarbons using transition metal complexes is a rapidly expanding area of both synthetic and mechanistic interest (1, 2). The isomeric cyclohexadienes have proven to be interesting models for the study of the selective hydrogenation of a system of two equivalent double bonds. Various transition metal complexes are capable of hydrogenating 1,3- and 1,4-cyclohexadiene (CHD) but the selectivity and the mechanistic pathway varies considerably with the metal complex which is used. When complexes of nickel, palladium, and platinum are used (3), stepwise migration of unconjugated double bonds forms a conjugated diene which is hydrogenated to the monoene. It has been shown (4, 5a,b) that when an arenechromiumtricarbonyl is used, cis-1,4-addition of hydrogen to 1,3-CHD is the predominant pathway. Solutions of pentacyanocobaltate(II) also have been shown (6) to selectively hydrogenate 1,3-CHD to cyclohexene and the mode of hydrogen addition is dependent on the cyanide ion concentration.

The catalytic activity of Vaska's complex, trans-[IrCl(CO)(Ph₃P)₂] has been the subject of a series of elegant papers (7), which have demonstrated the versatility of this complex in a variety of reactions. Recent work by Strohmeier (8), and coworkers has extended the study of the iridium(I) system as a homogeneous hydrogenation catalyst. Nonetheless, the synthetic utility of this complex for selective hydrogenation has been virtually unexplored.

We wish to report that trans-[IrCl(CO)(Ph₃P)₂] catalyzes the hydrogenation of the isomeric cyclohexadienes smoothly and selectively under mild conditions to give cyclohexene as the predominant product (Table 1). Little or no isomerization or disproportionation (9) accompanies this reaction. Deuterium is incorporated predominantly (75%) into the allylic position of the product when 1,3-CHD is deuterated, whereas the deuterium is distributed randomly when 1,4-CHD is reduced. Hydrogen–deuterium exchange results in the incorporation of deuterium into unreduced 1,3-CHD, however, deuterium is not incorporated into unreduced 1,4-CHD to a significant extent during deuteration.

cat. = trans – [IrCl(CO)(Ph₃P)₂]
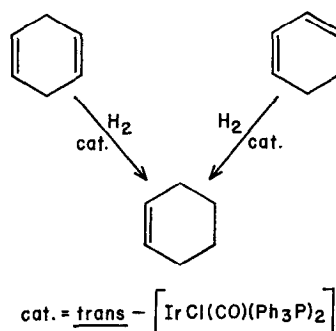
The observation that cyclohexene is selectively produced from either isomer without concurrent isomerization or disproportionation of the starting material suggested that competing H-transfer processes might not be occurring during hydrogenation. Results of reactions with deuterium (Table 2) showed that this was not the case. Addition of D₂ to 1,3-CHD in a 1,4-manner would yield only cyclohexene-d₂ with 100% of the heavy isotope in the α-methylene position whereas 1,2-addition would result in a product having 50% of the label in the α-methylene position and 50% at the β-methylene. If no other H-transfer oc-

490

TABLE 1

CATALYTIC HYDROGENATION[a] OF THE CYCLOHEXADIENES USING trans-[IrCl(CO)(Ph₃P)₂]

Diene	Solvent	[IrCl(CO)(Ph₃P)₂] M/L	Reaction time, hr	Conversion, %	Products, % yield	
					Cyclohexene	Cyclohexane
1,3-CHD	none	1.8×10^{-3}	3.5	80	100	—
1,3-CHD	DMA[b]	6.42×10^{-3}	5.0	69	99	1
1,4-CHD	none	2.3×10^{-3}	4.0	74	92	8
1,4-CHD	DMA[b]	6.14×10^{-3}	5.0	62	97	2
Cyclohexene	DMA[b]	6.30×10^{-3}	5.0	8	—	100

[a] Hydrogenations were carried out at 32 psi H_2 at 83°C in a Fisher–Porter aerosol tube with vigorous magnetic stirring. Product mixtures were analyzed by glpc using a 150 ft capillary column coated with UCON 550-X.

[b] Hydrogenation of 3.0 ml cyclohexadiene in 7.0 ml dry DMA was carried out as described in footnote a, above.

curred, the starting material should not undergo deuterium exchange during reaction. Addition of deuterium to 1,4-CHD in a 1,2-manner would yield only cyclohexene-d_2 with the label exclusively in the β-methylene position.

Reduction of 1,3-CHD with deuterium (32 psi, 83°C, 4.9 hr) in the presence of trans-[IrCl(CO)(Ph₃P)₂] gave deuterated cyclohexene (100%) as the sole reduction product (Table 2). The deuterated cyclohexene was isolated in greater than 99.5% purity by preparative glpc. Mass spectrometric analysis of the deuterated cyclohexene showed that although the major product (90%) was cyclohexene-d_2, smaller amounts of mono-, tri-, and tetradeuterated cyclohexene were also produced. The relative intensities of the Hnmr signals of protons in the vinyl ($\delta 5.58$), α-methylene ($\delta 1.97$), and β-methylene ($\delta 1.62$) positions were 2.0, 2.5, and 3.5, respectively. Thus, approximately 75% of the deuterium on an average was located at the α-methylene, 25% at the β-methylene, and little, if any, at the double bond. The mass spectrum and the nmr spectrum of unreduced 1,3-CHD (58%) indicated that there was a small amount of incorporation of deuterium into the starting material. Reduction of 1,3-CHD under identical conditions over a 7.3-hr period produced deuterated cyclohexene (99%) of which 83% was cyclohexene-d_2. The mass spectrum of unreduced 1,3-CHD (22%) indicated that there was substantial incorporation of deu-

terium into the starting material during the longer time period. These data demonstrate that H–D exchange processes were occurring during reduction without resulting in isomerization or disproportionation. Deuterium scrambling was even more pronounced when reaction was carried out in N,N-dimethylacetamide (DMA).
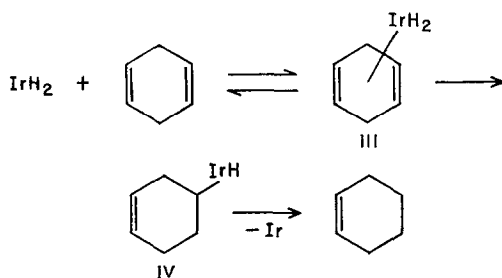
Our observations concerning the reduction of 1,3-CHD are accommodated by the reaction pathway postulated below. Intermediate π-allyl species have recently been
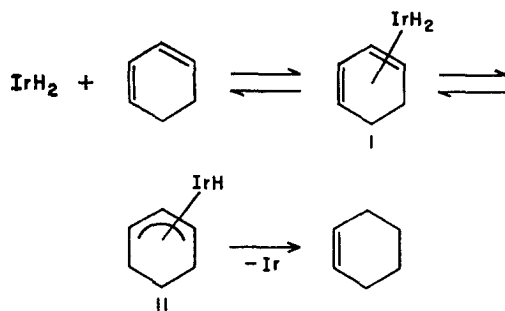
shown to be important (10) in other hydrogen transfer reactions catalyzed by trans-[IrCl(CO)(Ph₃P)₂]. Both hydrogenation and H–D exchange data are accounted for in this scheme, however, direct 1,2- and 1,4-addition of hydrogen may also occur to some extent.

During the reduction of 1,4-CHD by deuterium in the presence of trans-[IrCl (CO)(Ph₃P)₂], H–D exchange occurs to a greater extent than with 1,3-CHD. The isotopic distribution (Table 2) shows large

TABLE 2

Catalytic Deuteration[a] of the Cyclohexadienes Using trans-[IrCl(CO)(Ph₃P)₂]

| Diene | Solvent | [IrCl(CO)- (Ph₃P)₂] | Reaction time, hr | Conversion, % | Products, % yield | | Deuterated hydrocarbon | Isotopic distribution, mole% | | | | | | | |
					Cyclohexene	Cyclohexane		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_{av}
1,3-CHD	none	2.79×10^{-3}	4.9	41.0	100%	0%	1,3-CHD	97.8	1.9	0.3	—	—	—	—	0.03
							Cyclohexene	1.2	7.5	90.4	0.9	<0.1	—	—	1.91
1,3-CHD	none	2.86×10^{-3}	7.3	78.0	100%	0%	1,3-CHD	91.9	7.0	0.7	0.1	0.3	—	—	0.10
							Cyclohexene	5.4	8.8	82.8	2.9	0.2	—	—	1.84
1,3-CHD	DMA	6.42×10^{-3}	5.2	68.2	98%	0%	1,3-CHD	75.5	15.0	2.6	0.3	—	—	—	0.21
							Cyclohexene	7.7	14.6	70.5	6.3	0.9	—	—	1.78
1,4-CHD	DMA	6.14×10^{-3}	4.85	60.8	96.2%	2.6%	1,4-CHD	98.0	1.6	0.4	—	—	—	—	0.024
							Cyclohexene	10.8	21.6	27.9	21.0	12.8	4.8	1.4	2.24

[a] Deuterations were carried out in a manner identical to the hydrogenations (Table 1). Products were isolated by preparative glpc and identified by their ir and nmr spectra. The isotopic distribution of the deuterated products was determined from mass spectral data.

amounts of cyclohexene-d_0, d_1, d_3, and d_4 in the product monoene. The relative intensities of signals at $\delta5.88$, $\delta1.97$, and $\delta1.62$ in the deuterated monoene are 2, 4, and 4, respectively, indicating that the deuterium in the product is randomly distributed. Curiously, however, the mass spectrum of unreacted 1,4-CHD (39%) shows that there is almost no incorporation of deuterium into the starting material in this case. This necessitates an essentially irreversible step between reactants and intermediate species responsible for exchange. The extensive deuterium scrambling in this case might arise via complexes having extended conjugation such as V. Hydrogenation of 1,4-CHD probably proceeds in a
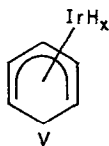
stepwise fashion similar to the pathway proposed by James and Memon (11). Conversion of the π-complex, III, to the σ-complex, IV, is represented as an irreversible step since the rate of abstraction of an allylic hydrogen from IV to give the 1,3-CHD complex, I, should be faster than abstraction of the non-allylic hydrogen leading back to III. Since this would result in competing isomerization to 1,3-CHD, it would appear that the rate of collapse of IV to cyclohexene is rapid compared with return to coordinated diene, I or III.

The absence of isomerization of either diene during hydrogenation using trans-[IrCl(CO)(Ph$_3$P)$_2$] is particularly interesting since: (a) hydrogen transfer is

occurring rapidly, (b) the ratio of 1,3-/1,4-CHD is 2/1 at equilibrium (12), and (c) the relative rates of hydrogenation of the two dienes are comparable.

The rapid rate of hydrogenation of the cyclohexadienes relative to cyclohexene in the presence of trans-[IrCl(CO)(Ph$_3$P)$_2$] is responsible for the selectivity of this reaction to yield monoene. This result stands in interesting contrast to results obtained using RhCl(Ph$_3$P)$_3$ as the catalyst, in which case the reduction of cyclohexene is 6 times faster than reduction of 1,3-CHD (13).

Finally, the absence of disproportionation (9) under hydrogenation conditions can be attributed to the suppression of the dehydrogenation step which is required for disproportionation in the presence of trans-[IrCl(CO)(Ph$_3$P)$_2$] (12).

In summary, Vaska's complex is an efficient catalyst for the selective hydrogenation of a conjugated and an unconjugated diene to the monoene. Although reaction is highly selective, deuteration studies revealed the existence of concurrent hydrogen exchange processes. It is expected that the selectivity observed in the hydrogenation of 1,3-CHD and 1,4-CHD will find synthetic utility in the partial reduction of other diene systems.

REFERENCES

1. LYONS, J. E., RENNICK, L. E., AND BURMEISTER, J. L., Ind. Eng. Chem. Prod. Res. Develop. 9, 2 (1970).
2. HARMON, R. E., GUPTA, S. K., AND BROWN, D. J., Chem. Rev. 73, 21 (1973).
3. TAYIM, H. A., AND BAILAR, J. C., JR., J. Amer. Chem. Soc. 89, 4330 (1967).
4. MIYAKE, A., AND KONDO, H., Angew. Chem. Inter. Ed. 7, 631 (1968).
5. (a) FRANKEL, E. N., AND BUTTERFIELD, R. O., J. Org. Chem. 34, 3930 (1969).
   (b) FRANKEL, E. N., SELKE, E., AND GLASS, C. A., J. Org. Chem. 34, 3938 (1969).
6. KWIATEK, J., Catal. Rev. 1, 37 (1967).
7. For a summary of reversible reactions of trans-[IrCl(CO)(Ph$_3$P)$_2$] with H$_2$, O$_2$, SO$_2$,

CO, C_2H_4, and other small molecules see: VASKA, L., *Accounts Chem. Res.* **1,** 335 (1968). For particular emphasis on hydrogen activation see: VASKA, L., AND WERNEKE, M. F., *Trans. N. Y. Acad. Sci.* 70 (1971) and references cited therein.

8. STROHMEIER, W., *J. Organometal. Chem.* **32,** 137 (1971) and references cited therein.

9. LYONS, J. E., *Chem. Commun.* 564 (1969).

10. UEDA, T., *Proc. 5th Internat. Congr. Catal.* **27,** 1 (1972).

11. JAMES, B. R., AND MEMON, N. A., *Can. J. Chem.* **46,** 217 (1968).

12. LYONS, J. E., *J. Catal.* **28,** 500 (1973).

13. JARDINE, F. H., OSBORN, J. A., AND WILKINSON, G., *J. Chem. Soc. (A)* 1574 (1967).

JAMES E. LYONS

Sun Research and Development Company
Corporate Research Department
Marcus Hook, Pennsylvania 19061
Received March 15, 1973