Catalytic Activation of the Carbon–Hydrogen Bond by Some Iridium(I) Complexes: Hydrogen Transfer Reactions in Cyclic Dienes

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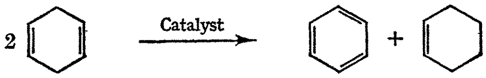
Summary Several iridium complexes are shown to be capable of catalysing the disproportionation of cyclohexa-1,4-diene to benzene and cyclohexene under mild conditions.

ALTHOUGH numerous accounts of homogeneous catalytic hydrogenation have appeared,[1] the catalytic dehydrogenation of olefins has not been investigated. Homogeneous transition-metal-catalysed disproportionation involving hydrogen redistribution in hydrocarbons has also been virtually unexplored to date. I report the first examples of intermolecular hydrogen transfer resulting in olefin disproportionation catalysed by Group VIII metal complexes. The iridium complexes, $IrX(CO)(Ph_3P)_2$, (X = halide), first prepared and studied by Vaska[2] are capable of converting cyclohexa-1,4-diene catalytically into benzene and cyclohexene. The results of these reactions which were run at 80° in a dry nitrogen atmosphere are tabulated below. Equimolar amounts of both the dehydrogenated and the hydrogenated products were observed. This reaction has long been known to occur over supported metals;[3] however, unlike the heterogeneous analogue, the iridium(I)-catalysed reactions reported here exhibited no tendency toward further disproportionation of the cyclohexene formed.



Accompanying disproportionation was a certain amount of isomerization to cyclohexa-1,3-diene. The extent of this competing reaction varied with the nature of the catalyst. The iridium hydrides (IV), (V), and (VI) were more effective isomerization catalysts than were the square-planar bistriphenylphosphine-carbonyliridium halides (I) and (II).

Cyclohexa-1,3-diene, however, did not readily undergo disproportionation in the presence of catalytic amounts of the co-ordinatively unsaturated iridium complexes (I) and

Disproportionation of cyclohexa-1,4-*diene catalysed by metal complexes*[a]

	Catalyst	Reaction time (hr.)	Disproportionation (%)[b,d]	Isomerization (%)[c,d]
(I)	$[IrCl(CO)Ph_3P)_2]$	90	30	8
	"	180	60	7
(II)	$[IrI(CO)(Ph_3P)_2]$	40	12	4
(III)	$[IrCl(CO)(Ph_3As)_2]$	70	3	10
(IV)	$[IrH_2Cl(CO)(Ph_3P)_2]$	24	1	4
	"	115	7	11
(V)	$[IrH_2Cl(Ph_3P)_2]$	47	—	17
(VI)	$[IrH(CO)(Ph_2P)_3]$	47	—	50

[a] The diene (5 ml.) was vacuum-transferred into the reaction vessel containing 5 mg. of the catalyst. Dry nitrogen was then admitted to the system and the clear yellow solution was stirred magnetically at 80° for the indicated time. The product mixtures were separated and analysed by g.l.c. using a 150 ft. capillary column coated with UCON 550-X. The identity of the products was confirmed by their i.r. spectra.

[b] % Disproportionation = % benzene + % cyclohexene in the reaction mixture. In all cases the yield of benzene was equal to that of cyclohexene.

[c] Isomerization = % cyclohexa-1,3-diene in the reaction mixture.

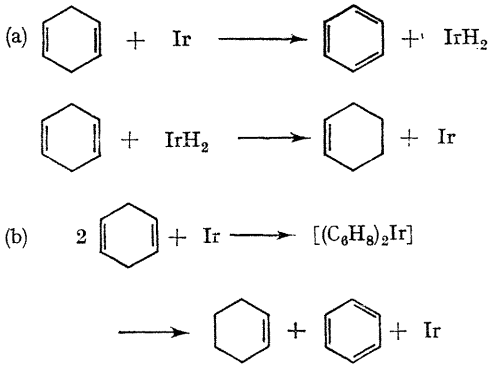
[d] Isomerization and disproportionation were the only reactions observed. In all cases (100 — % disproportionation — % isomerization) is equal to the % unreacted starting material.

(II). Little or no disproportionation of the 1,3-diene occurred over 90 hr. periods under conditions similar to those used in reaction of the 1,4-isomer. Thus the possibility that the 1,3-diene might have been an intermediate in the disproportionation of the 1,4-isomer may be excluded.

The transfer of two hydrogen atoms from one molecule to another might occur in either of two general ways: (a) hydrogen redistribution through separate stages of dehydrogenation and hydrogenation or (b) hydrogen transfer directly from one cyclohexadiene molecule to another. It is of interest that kinetic evidence for a mechanism similar to (a) has been obtained for the disproportionation of cyclohexa-1,3-diene on palladium films,[4] whereas the transfer of hydrogen directly from one adsorbed molecule to another has been postulated to account for the kinetics of the disproportionation of cyclohexene over palladium powder.[5]

Kinetic studies aimed at elucidating the mechanism of the homogeneous catalytic disproportionation reaction as well as extensions to other diene systems in the presence of a variety of Group VIII metal complexes are in progress and will be the subject of future publications.

I thank Mrs. Ruth Jenkins and Mr. Arthur Raymond for gas-chromatographic analyses of reaction mixtures.



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[1] For a review of homogeneous hydrogenation, see C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Academic Press, New York, 1967, ch. 10.

[2] (a) L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679; (b) L. Vaska and R. E. Rhodes, *ibid.*, 1965, **87**, 4970, and references cited therein.

[3] G. C. Bond, "Catalysis by Metals", Academic Press, New York, 1962. P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, 1967.

[4] V. M. Gryaznov and V. D. Yagodovskii, *Kinetika i Kataliz*, 1963, **4**, 404.

[5] S. Carra, P. Beltrame, and V. Ragaaini. *J. Catalysis*, 1964, **3**, 353.