

carbon tetrachloride for 2 days. The succinimide was filtered off and the remaining solution concentrated. In the absence of equilibration, this bromination could only give EE and ET products as well as 1,1,2-tribromo-1,3-diphenylpropane (15). The material 9 was isolated, 9.6 g, mp 181–182°, as well as 0.96 g of 10, mp 131–133°. A third fraction, mp 93–95°, 1.7 g, was a mixture of starting material and 10. The remaining oil (1.3 g) was a similar mixture with traces of 15 apparent.

Registry No.—4, 16793-35-4; 5, 16793-36-5; 6, 16793-37-6; 7, 16793-38-7; 9, 16793-39-8; 10, 16793-40-1.

Acknowledgment.—This work was supported by NSF Grant GP6765. This work was begun at Iowa State University. D. C. B. gratefully acknowledges the award of the Shell Fellowship.

The Hydrogenation of Dialkylcyclohexenes with Rhodium Catalysts¹

ALLEN S. HUSSEY, THOMAS A. SCHENACH, AND ROBERT H. BAKER

The Ipatieff Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received January 25, 1968

The *cis/trans* product ratios observed in the hydrogenation of six dialkylcyclohexenes on rhodium catalysts at 25° and 1 atm are given. These are compared with the results when platinum and palladium catalysts are used. The effect of temperature on the product ratios from three of these cycloalkenes with rhodium and platinum catalysts are reported, as are the results of their disproportionation and the hydrogenations of the corresponding arenes at 100°. Rhodium and platinum are found to be closely similar, and quite different from palladium, in their promotion of hydrogen addition to carbon unsaturation. Platinum appears to be the more effective of the two for the straightforward addition of hydrogen to 1,2-diadsorbed alkanes.

There have been several reports of the stereochemical results observed when platinum and palladium catalysts are used to effect the hydrogenation of dialkylcycloalkenes which can form *cis* and *trans* products.² It seems clearly established that palladium catalysts furnish a product mixture at pressures near one atmosphere which approaches equilibrium composition, whereas platinum catalysts lead to an entirely different mixture. Furthermore, isomerization of the initial cycloalkene has been found to be pronounced with palladium catalysts but to be relatively minor or insignificant for most cycloalkenes with platinum.^{2,3} The nonintervention of isomerization with platinum catalysts, even where this is thermodynamically favored, has been demonstrated in recent reports of the kinetics of this reaction⁴ and in studies of the competitive hydrogenation of pairs of cycloalkenes.⁵

It was of interest to compare the catalytic properties of rhodium catalysts with those of palladium and platinum. We report here the stereochemical results observed when several dialkylcyclohexenes are hydrogenated over rhodium, together with the effect of temperature on the product ratios using both rhodium and platinum.

Results

The data in Table I summarize the results of the hydrogenations of several dialkylcyclohexenes at 25° near one atmosphere with rhodium, platinum, and palladium catalysts. Most of these data are averages

TABLE I
HYDROGENATION OF DIALKYL CYCLOHEXENES WITH RHODIUM, PLATINUM, AND PALLADIUM CATALYSTS^a

Cyclohexene	% <i>cis</i> isomer ^b with		
	Rh ^c	Pt	Pd
1,4-DiMe	61	57 ^d	28 ^e
1-Me-4-Et	55	48 ^d	24
1-Et-4-Me	55	58 ^d	27
1,4-DiEt	54	49	25
1-Me-4- <i>i</i> -Pr	52	43 ^d	26 ^e
1- <i>i</i> -Pr-4-Me	54	58 ^d	21 ^e

^a In purified glacial acetic acid, 25° (1 atm). ^b Precision of analysis ±1%. ^c 5% on charcoal. ^d Data from ref 2d. ^e Data from ref 2e.

of replicate analyses of replicate hydrogenation experiments (usually three, occasionally more) and include, for rhodium and platinum, the results from several experiments interrupted between 15 and 50% hydrogenation. The data for the hydrogenations using palladium catalysts are all from complete hydrogenations; extensive isomerization of the cycloalkenes are observed with this catalyst and the *cis/trans* product ratios for the unsymmetrical dialkylcyclohexanes vary ±4–5% depending upon the extent of hydrogenation when samples are removed for analysis.^{2e} In contrast, isomerization is small at 25° when moderate amounts of rhodium catalysts are used (1–4% near 50% hydrogenation). Isomerization is unobservable with platinum at this temperature. When an excessive amount of rhodium catalyst is used, a hydrogen deficiency is created at the catalyst surface because of transport limitations⁶ and isomerization increases. This effect is less pronounced with platinum. However, as long as the amount of catalyst is reasonably small (10–40 mg), the product composition from reactions at 25° is the same, within the ±1% precision of our analyses, at various stages in the hydrogenations with both catalysts. This is not true with palladium.

The data in Table II summarize the effect of temperature with three of the cycloalkenes of Table I. At 50° and above, disproportionation to form arenes and cyclohexanes becomes competitive with the hy-

(1) Support of a part of this research through GP 4656 from the National Science Foundation is gratefully acknowledged.

(2) (a) S. Siegel, *J. Amer. Chem. Soc.*, **75**, 1317 (1953); (b) S. Siegel and M. Dunkel, *Advan. Catal.*, **9**, 15 (1957); (c) S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6082, 6087 (1960); (d) J-F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **82**, 6090 (1960); (e) J-F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **83**, 3874 (1961); (f) S. Siegel and B. Dmuchovsky, *ibid.*, **86**, 2192 (1964).

(3) (a) D. J. Cram, *ibid.*, **74**, 5518 (1952); (b) G. V. Smith and R. L. Burwell, *ibid.*, **84**, 925 (1962); G. C. Bond, J. J. Phillipson, P. B. Wells, and J. M. Winterbottom, *Trans. Faraday Soc.*, **60**, 1847 (1964); (d) G. V. Smith and J. R. Swoap, *J. Org. Chem.*, **31**, 3904 (1966); (e) A. W. Weitkamp, *J. Catal.*, **6**, 431 (1966).

(4) A. S. Hussey, G. W. Keulks, G. P. Nowack, and R. H. Baker, *J. Org. Chem.*, **33**, 610 (1968).

(5) A. S. Hussey, G. W. Keulks, and R. H. Baker, *J. Catal.*, **10**, 258 (1968).

(6) H. C. Yao and P. H. Emmitt, *J. Amer. Chem. Soc.*, **81**, 4125 (1959).

TABLE II
THE EFFECT OF TEMPERATURE ON HYDROGENATIONS
OF DIALKYL-CYCLOHEXENES WITH PLATINUM
AND RHODIUM CATALYSTS

Temp. °C	% <i>cis</i> isomer ^a					
	1,4-DiMe		1-Et-4-Me		1-Me-4-IsoPr	
	Pt	Rh	Pt	Rh	Pt	Rh
100	48	54	48	47	42	51
50	54		52			
25	57	61	58	55	43	52
18	59		59			
0	61	62	62	63	43	52
-17	63					
-30	66	66	67	68	46	51

^a Precision of analysis $\pm 1\%$.

drogenation reactions. It is most extensive with palladium, appreciably less with platinum, still less with rhodium. Isomerization of olefin also increases with increasing temperature with rhodium and it becomes easily detectable at 100° with platinum. It is still small at 100° with both of these catalysts relative to that observed with palladium at 25° however.^{2c} In order to minimize the contribution of cycloalkene isomers and arenes to the cycloalkane product ratios, the experiments at 50° and 100° in Table II were interrupted at 10 to 30% hydrogenation. Accordingly the data represent the stereochemical consequences of the hydrogen addition and disproportionation reactions with little contribution from the other two pathways.

At very low hydrogen pressures, the disproportionation reaction becomes the only pathway to dialkylcycloalkanes. In order to check the stereochemistry of this process, we carried out a number of disproportionation experiments in which the hydrogen atmosphere was replaced by nitrogen or helium. These reactions were interrupted in the early stages while isomerized olefin was still small, and below 30° the ratios of dialkylcycloalkanes were within experimental error of the values given in Table I. The values at 100° are slightly different and are summarized in Table III. At high conversions at this temperature, significantly more *cis* product is obtained. We also carried out the hydrogenation of the corresponding arenes at 100° and one atmosphere (Table IV).

TABLE III
STEREOCHEMICAL CONSEQUENCES OF THE DISPROPORTIONATION
OF DIALKYL-CYCLOHEXENES AT 100°

Cyclohexene	% <i>cis</i> isomer	
	Rh	Pt
1,4-Dimethyl	57	47
1-Ethyl-4-methyl	49	48
1-Methyl-4-isopropyl	53	41

TABLE IV
HYDROGENATION OF 4-ALKYLTOLUENES AT 100°

4-Alkyltoluene	% <i>cis</i> isomer	
	Rh	Pt
4-Methyl	70	61
4-Ethyl	72	59
4-Isopropyl	69	55

In several blank experiments with known mixtures of *cis* and *trans* products, of products with their unsaturated precursor, and of products with their arene counterparts, we determined that (1) there was no inci-

dental enrichment in one component as a result of differential vaporization at elevated temperatures; (2) the rate of isomerism of *cis* to *trans* product at 100° was too slow to effect the ratios observed if the reactions were allowed to go to completion; (3) there was no inadvertent change in the mixture compositions in the course of separating hydrocarbons from catalyst (filtration) and solvent (washing with water) prior to analysis by glpc.

Discussion

The results summarized in Table I and Table II furnish some empirical guidelines for the choice of catalyst and conditions for the preferential formation of one dialkylcyclohexane *via* the hydrogenation of its dialkylcyclohexene precursor. If a preponderance of the thermodynamically more stable cycloalkane is desired, the use of a palladium catalyst is indicated. The use of platinum or rhodium catalysts, on the other hand, will result in a larger proportion of a thermodynamically unstable *cis*-1,4-dialkylcyclohexane, and this proportion will often be increased by a hydrogenation procedure at low temperatures. Of these two catalysts, rhodium appears more likely to favor the formation of an unstable *cis* isomer from 1,4-dialkylcyclohexenes when the group at a distance from the double bond is larger than methyl. Platinum, on the other hand, is the catalyst of choice if desorption of isomerized olefin is to be avoided. Olefin isomerization is a minor surface reaction but it is detectable when rhodium catalysts are used; it is an exceptional olefin which isomerizes on platinum catalysts near room temperature.²⁻⁵ Olefin isomerization is very extensive when palladium catalysts are used.

The close resemblance of rhodium and platinum catalysts (and the difference of palladium) in the hydrogenation of cyclohexenes is also reflected in the hydrogenation of arenes. Here the order of effectiveness is Rh > Pt >> Pd.⁷ Similarly we have found the order of effectiveness in promoting the disproportionation of cyclohexenes to be Pd >> Pt > Rh. Clearly rhodium and platinum catalysts closely resemble one another while palladium catalysts are quite different.

In addition to the surface reactions which result in the hydrogenation of the original dialkylcyclohexane, three other surface reactions intervene to varying degrees with these three catalysts to lead to differences in the stereochemical results observed in the hydrogen addition reaction. All three of these reactions become pronounced, even with platinum and rhodium, in the higher temperature reactions summarized in Table II. At the outset, the second most important pathway is the disproportionation route through which one cyclohexene molecule furnishes the four hydrogen atoms necessary for the reduction of two others, and is itself converted into the arene. At more advanced stages of the higher temperature hydrogenation more and more of the product mixture is derived from isomers of the original cyclohexene (except for 1,4-dimethylcyclohexene, of course). Finally, when the cycloalkene is nearly gone, arene begins to hydrogenate to product also. At lower temperatures, all of these are minor processes with platinum and rhodium, and arene hydrogenation does not occur on palladium.

Although it seemed unlikely that the disproportionation reactions would generate a different dialkylcyclohexane isomer ratio than is observed from hydrogenations, we carried out a number of disproportionation experiments to check this. Below 30°, no significant difference in hydrogenation and disproportionation product ratios was observed, but at 100° higher proportions of *cis* isomers were formed when the disproportionation reactions were carried to completion. This probably results in part from hydrogen addition to the 4-methyl isomer^{2d} of 1-methyl-4-isopropylcyclohexene, but the observed increase of *cis*-1,4-dimethyl- and 1-ethyl-4-methylcyclohexane^{2d} can only come from the hydrogenation of some of the corresponding arenes.

We therefore carried out the hydrogenation of the three corresponding arenes at 100° and one atmosphere. The results of Table IV show that the increased *cis* product observed at high conversions can be ascribed, at least in part, to the hydrogenation of small amounts of the arenes generated by the disproportionation reactions. Without question, however, some of the additional *cis* product also stems from the 4-methyl isomer^{2d} of the last cycloalkene at higher conversions. Therefore the data given in Table II at the higher temperatures were obtained from experiments which were interrupted at low conversions when olefin isomerization was still small and arene hydrogenation could be ignored. The trend exhibited by two of the three cyclohexenes in Table II is therefore real and is worthy of brief discussion.

We have recently proposed that 1,2-diadsorbed cycloalkanes with alkyl groups in a *cis* configuration can interconvert on platinum surfaces with their *trans* counterparts.⁵ This proposal is consistent with the observed kinetics for the hydrogenation of cycloalkenes⁴ and with the results from the competitive hydrogenations of pairs of cycloalkenes.⁵ It also satisfactorily explains the pressure-variable *cis/trans* ratio both from the xylenes⁸ and from their tetrahydro counterparts² as well as the failure to observe isomerization of the latter.³⁻⁵ We choose to apply much the same explanation here.

We cannot demonstrate in an unequivocal way that the trend of the data in Table II does not simply reflect a temperature-variable equilibrium chemisorption of the cycloalkene in the two modes, along with different temperature coefficients for the rate constants for the over-all reactions.⁹ Nevertheless, we prefer to view the decrease in *cis* product with increasing temperature as a reflection of an increase in the surface concentration of hydrocarbon in a *trans* geometry which results from a *cis,trans* interconversion on the surface.⁵ Different temperature coefficients for the two hydrogen addition reactions may also be a contributing factor. We acknowledge that alkene does desorb to a small extent from rhodium at 25° and from platinum at higher temperatures. However, we hasten to point out that the trend continues as the temperature decreases below 25° (Table II) where no desorption is detectable

with either catalyst. The absence of a similar trend in the hydrogenation of 1-methyl-4-isopropylcyclohexene simply implies that the temperature coefficients for all of the steps in the *cis* and in the *trans* pathways, including the *cis,trans* surface interconversion, are identical over-all. The temperature response of rhodium and platinum emphasizes their similarity as catalysts for the addition of hydrogen to unsaturated hydrocarbons.

Experimental Section

Dialkylcyclohexenes.—The preparation and purification of most of the dialkylcyclohexenes used here have been described earlier.^{2d}

1,4-Diethylcyclohexene was prepared as follows. A solution of 31.5 g (0.250 mol) of 4-ethylcyclohexanone^{2d} in 150 ml of ether was added to a stirred solution of the Grignard reagent from 32.7 g (0.300 mol) of ethyl bromide in 200 ml of ether under nitrogen. After 1 hr, 30 ml of water was added dropwise with stirring. The ether solution was decanted and the precipitated magnesium salts were extracted with 4–100 ml portions of warm ether. The crude product weighed 45.0 g (99%) and this was distilled and redistilled to give 36.0 g (79%) of 1,4-diethylcyclohexanol: bp 98–101° (15 mm); n_D^{20} 1.4600. The latter was dehydrated by dropping it onto 50 g of sodium bisulfate and heated to 150° (120 mm) over 20 min. The alkene distilled as fast as it was formed at 98–100° and consisted mostly of 1,4-diethylcyclohexene (78%) and 4-ethylethylidene-cyclohexene (22%), with traces of other isomers (analysis through silver nitrate-triethylene glycol on 60–80 mesh firebrick). The 31.0 g (76%) of mixed cycloalkenes was distilled through a five-plate column and then redistilled through a 100-plate column. A 5.6-g middle fraction which distilled at 174.8° (747 mm) was of "single peak" purity by glpc (silver nitrate in triethylene glycol on firebrick).

Hydrogenation and Analyses.—The cyclohexenes were hydrogenated in purified glacial acetic acid, ethyl alcohol, or mixtures of the two in a microhydrogenation apparatus as described earlier.^{2d} Part hydrogenations were interrupted at 10–70% uptake of theoretical hydrogen. Analyses were by glpc procedures which had been found to be capable of separation of the several components in known mixtures.

Temperature control in these experiments was maintained in the reaction flask and only to $\pm 3^\circ$ in many of them. Initial experiments showed that the change of product ratios with temperature was small; hence it was not necessary to pay elaborate attention to temperature control.

For experiments carried out above 50°, the hydrogenation flask was fitted with a cold-finger condenser to return vaporized substrate and solvent. Experiments with prepared mixtures of known composition showed that there was no enrichment in one component as a result of vaporization at 100° or as a result of the method of isolation. Likewise the rate of isomerization of *cis* to *trans* was found to be too slow at 100° to be of significance.

Catalysts.—Several different samples of commercial 5% rhodium-on-carbon catalysts, several samples of commercial platinum oxide, and several palladium catalysts were used in these studies. Variations in product composition for any one metal were less than the precision of our analyses ($\pm 1\%$) except occasionally when large excesses were used.

Disproportionation Reactions.—These reactions were carried out in the hydrogenation system. The catalyst and solvent were shaken in hydrogen following which the system was evacuated and flushed three or four times with nitrogen or helium. The sample of dialkylcyclohexene was then injected through the serum cap on the side arm and the reaction carried out with continuous agitation.

There was no change in the gas volume of the system (*i.e.*, no hydrogen escaped to the gas phase) and, in experiments carried to completion, the arene/cyclohexane ratio did not vary greatly from the stoichiometric 1:2 although it was usually a little larger. The catalysts were found to be in the order Pd \gg Pt $>$ Rh in effectiveness for the disproportionation reaction.

Registry No.—Rhodium, 7440-16-6; platinum, 7440-06-4; 1,4-diethylcyclohexene, 3454-04-4.

(8) F. Hartog and P. Zwietering, *J. Catal.*, **2**, 79 (1963); S. Siegel, V. Ku, and W. Halpern, *ibid.*, **2**, 348 (1963); S. Siegel and V. Ku, *Proc. Intern. Congr. Catal., 3rd, Amsterdam, 1964*, **2**, 1199; F. Hartog, J. H. Tebben, and C. A. M. Wetering, *ibid.*, **2**, 1210.

(9) S. Siegel, *Advan. Catal.*, **16**, 138 (1966).