EXPERIMENTAL

Materials. The anhydrous hydrogen fluoride and carbon monoxide were obtained from the Matheson Co. and the pure grade paraffins and cycloparaffins, except decalin and 1,4-dimethylcyclohexane, from Phillips. Eastman decalin was washed with 96% sulfuric acid, water, and alkali; fractionation yielded 99% pure *cis*- and *trans*-decalin. Hydrogenation of *p*-xylene (99%) over a platinum-alumina catalyst afforded a 30:70 mixture of *cis*- and *trans*-1,4-dimethylcyclohexane.

Condensation reaction. The requisite amount of hydrogen fluoride was charged into the evacuated 2-l. stainless steel Magne-dash[25] autoclave. Carbon monoxide was then pressured into the autoclave, a bath placed around the autoclave, and the stirring was started. The olefin feed was slowly pressured into the stirred autoclave from a blowcase. Stirring was continued for a short period, after which the contents of the autoclave were discharged into a train consisting of a polyethylene bottle containing a weighed amount of ice and water, a water scrubber, drier, cold (−80°) trap, and a wet testmeter. Carbon monoxide absorption was measured by weight gain. When a solvent was employed in the condensation, it was added from a blowcase or pressure vessel usually prior to addition of carbon monoxide. The contents in the polyethylene bottle was stabilized by warming to 30°. The organic layer was separated, washed with ice water, and stabilized at about 60° to recover additional condensible gases, *e.g.* propane or 2-methylpropane.

The aqueous and wash layers were combined, saturated with sodium sulfate, and extracted with pentane to recover water-soluble organic acids. The pentane extract and organic layer were combined and stirred with warm alkali until the acyl fluorides were completely hydrolyzed (disappearance of infrared band at approximately 5.5 μ). The alkali-insoluble layer, if any, was separated and the soap solution extracted with pentane to remove traces of neutral oil. Acidification of the soap solution with hydrochloric acid yielded a layer of organic acids. The acidulated aqueous layer was saturated with sodium sulfate and extracted several times with pentane to recover water-soluble organic acids. Distillation afforded the acids described in Table IV.

Identification of products. In general the products were characterized by comparing boiling points, melting points, refractive indices, infrared and mass spectra (for hydrocarbons), and gas liquid chromatograms with that of known standards.

Harvey, Ill.

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[25] Autoclave Engineers, Inc., Erie, Pa.

[Contribution from Kedzie Chemical Laboratory of Michigan State University]

Effects of Temperature and Catalyst Variation upon the Stereochemistry of Hydrogenation of Disubstituted Benzenes[1]

ROBERT D. SCHUETZ and LYMAN R. CASWELL

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The hydrogenation of the three xylenes on platinum oxide gave appreciable yields of *trans*-dimethylcyclohexanes in the order *para* > *meta* > *ortho*. The yield of *trans* isomers increased with temperature, but did not appear to be greatly affected by pressure changes within the pressure ranges used. The yields of the *trans* isomers from the hydrogenation of the xylenes on Raney nickel were in the order *meta* > *ortho* > *para*. Hydrogenation of diethyl phthalate on nickel gave significant amounts of the *trans* product, in contrast to hydrogenation on platinum oxide. Attempts to isomerize *cis*-disubstituted cyclohexanes on either catalyst did not give sufficient amounts of the *trans* isomers to account for the *trans* products of hydrogenation. It is concluded that the *trans* products must be formed during the hydrogenation process, and that the stereochemical course of this process is determined mainly by the nature and positions of the substituents and by the catalyst.

Early studies of the stereochemistry of the catalytic hydrogenation of aromatic compounds led to the formulation of the von Auwers-Skita rules[2,3] which states that *cis* isomers are produced by hydrogenation on platinum in acidic media and *trans* isomers are produced by hydrogenation on platinum in basic media or on nickel in the vapor phase. These generalizations do not allow for the possibility of isomerization process.

Horiuti and Polanyi[4] have proposed that the mechanism of catalytic hydrogenation involves dissociation and chemisorption of hydrogen on the catalyst surface and chemisorption of the substrate, followed by addition of hydrogen to the substrate one atom at a time, the addition of each atom of hydrogen being accompanied by desorption at the point to which the hydrogen was added. All steps are reversible.

The hydrogenation of a large number of polynuclear aromatic compounds on Adams' platinum oxide catalyst in glacial acetic acid at room temperature gave stereochemical results which suggested to Linstead and his co-workers[5] that a single aromatic ring must be hydrogenated in a single period of adsorption, with all of the hydrogen being added from the same side of the ring to produce a *cis* product. Such a process requires that the aromatic ring be adsorbed parallel to the catalyst surface. Some kinetic studies,[6] however, have made it necessary to consider the possibility, in mononuclear systems at least, of other orientations of the adsorbed ring.

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[1] Taken in part from the Doctoral dissertation of L. R. Caswell, Michigan State University, 1956.

[2] A. Skita, *Ann.*, **413**, 1 (1923).

[3] K. von Auwers, *Ann.*, **420**, 84 (1925).

[4] I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[5] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985 (1942).

[6] H. A. Smith and H. T. Meriwether, *J. Am. Chem. Soc.*, **71**, 413 (1949).

Siegel and Dunkel[7] have found that in the hydrogenation of the xylenes on platinum oxide in glacial acetic acid at room temperature and a hydrogen pressure of 35 p.s.i., the yields of *cis*-dimethylcyclohexanes are obtained in the order *ortho* > *meta* > *para*, and the presence of *trans* isomers in the products could not be accounted for by isomerization. In a later study, Siegel and McCaleb[8] found that neither dimethyl phthalate nor dimethyl 1-cyclohexene-1,2-dicarboxylate yield *trans* products when hydrogenated on platinum oxide at room temperature, while dimethyl 2-cyclohexene-1,2-dicarboxylate gave some *trans* product at high hydrogen pressures.

Because knowledge of the temperature effect upon the stereochemistry of hydrogenation is yet lacking, the results of studies of this process at a series of temperatures are here reported for the hydrogenation of the xylenes and of diethyl phthalate. The stereochemistry of the hydrogenation of these compounds on Raney nickel has also been investigated.

EXPERIMENTAL

Apparatus. The hydrogenation apparatus used for the hydrogenation studies have already been described.[9]

Reagents. Matheson *o*-, *m*-, and *p*-xylenes were each refluxed 24 hr. over Raney nickel and fractionally distilled with a 20-plate column. The middle third of the distillate was refluxed 24 hr. over sodium metal, again fractionated and the middle third of the distillate taken for experimental use. The refractive indices, n_D^{25}, of these purified xylenes compared with those reported by the American Petroleum Institute[10] were:

o-xylene	observed, 1.5010	reported, 1.50295
m-xylene	" 1.4948	" 1.49464
p-xylene	" 1.4929	" 1.49325

Eastman "White Label" diethyl phthalate was used without further purification.

Hydrogen obtained from the Ohio Chemical and Surgical Co. was used without any intermediary purification.

Solvents. Baker's "Analyzed" glacial acetic acid served as the solvent for all hydrogenations on platinum oxide. All samples were taken from the same bottle.

Commercial Solvents absolute alcohol was rendered anhydrous by the method of Lund and Bjerrum[11] and used as solvent for all hydrogenations with Raney nickel.

Catalysts. Adams' platinum-oxide catalyst was obtained from the American Platinum Works. All hydrogenations on platinum were carried out with samples from the same batch.

Raney nickel catalyst was prepared from the nickel-aluminum alloy by the method of Pavlic and Adkins,[12] and all hydrogenations on nickel made use of samples from the same batch.

Dimethylcyclohexanes. The stereoisomeric dimethylcyclohexanes were prepared as reference standards by hydrogenation of 20 g. of each xylene in 25 g. of 95% alcohol on 10 g. of Universal Oil Products nickel-kieselguhr catalyst at 140°–160° and 1700–1900 p.s.i. The reaction mixtures were filtered, extracted three times with water, using 50 ml. of water each time, and dried over anhydrous magnesium sulfate. The dried products were fractionated with a 90-plate Podbielniak HC 701 Hypercal high temperature fractional distillation apparatus at the rate of 2 ml. per hour, and collected in 1-ml. fractions. The fractions which had boiling points within 1° of the reported[13] boiling points of the pure stereoisomers were combined and refractionated under the same conditions. The boiling points and refractive indices of the samples accepted as pure are compared with the reported values in Table I.

TABLE I

BOILING POINTS AND REFRACTIVE INDICES FOR THE DIMETHYLCYCLOHEXANES

	Boiling Point at 760 Mm.		n_D^{25}	
Isomer	Observed	Reported	Observed	Reported
trans-1,2-Dimethylcyclohexane	122.9	123.419	1.4243	1.42470
cis-1,2-Dimethylcyclohexane	129.4	129.728	1.4333	1.43358
trans-1,3-Dimethylcyclohexane	123.6	124.450	1.4282	1.42843
cis-1,3-Dimethylcyclohexane	120.1	120.088	1.4206	1.42063
trans-1,4-Dimethylcyclohexane	119.3	119.351	1.4183	1.4153
cis-1,4-Dimethylcyclohexane	124.4	124.321	1.4270	1.42731

Diethyl cis-1,2-cyclohexanedicarboxylate. A mixture of 100 g. (0.45 mole) of diethyl phthalate, 2.5 g. of platinum oxide and 100 ml. of glacial acetic acid was quantitatively hydrogenated at room temperature with an initial pressure of 50 p.s.i. The reaction mixture was filtered, extracted with 500 ml. of 6% sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The crude product was fractionated under reduced pressure with a 20-plate column, giving 74.4 g., (72%) of a clear, colorless oil which boiled at 4 mm. at 119.0–119.1°; n_D^{25}, 1.4508. Cope and Herrick[14] found n_D^{25} was 1.4510 for diethyl *cis*-1,2-cyclohexanedicarboxylate.

Diethyl trans-1,2-cyclohexanedicarboxylate. One hundred grams of diethyl phthalate was reduced in a Parr high-pressure hydrogenation apparatus at 150° without solvent, using 10 g. of U.O.P. catalyst and 1800 p.s.i. initial pressure. The crude product was isomerized by the method of Hückel and Goth,[15] using 22 g. of sodium metal and 500 ml. of absolute alcohol. After 4 hr. of refluxing, the reaction mixture was decomposed with 1 l. of 1*M* ammonium chloride and extracted with three 100-ml. portions of ether and benzene

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(7) S. Siegel and M. Dunkel, *Advances in Catalysis*, Vol. IX, A. Farkas, ed., Academic Press, New York, 1957, p. 15.

(8) S. Siegel and G. S. McCaleb, *J. Am. Chem. Soc.*, **81**, 3655 (1959).

(9) R. D. Schuetz, L. R. Caswell, and J. C. Sternberg, *J. Org. Chem.*, **24**, 1080 (1959).

(10) American Petroleum Institute Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Table 5a, Oct. 31, 1950.

(11) L. F. Fieser, *Experiments in Organic Chemistry*, 2nd ed., D. C. Heath, 1941, p. 359.

(12) A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).

(13) American Petroleum Institute Research Project 44, *op. cit.*, Table 7a, October 31, 1952.

(14) A. C. Cope and E. C. Herrick, *J. Am. Chem. Soc.*, **72**, 983 (1950).

(15) S. Hückel and E. Goth, *Ber.*, **58B**, 447 (1925).

in the ratio 2:1. After evaporation of the solvent, the product was distilled under reduced pressure, giving 27 g. (27%) of a colorless oil boiling (3 mm.) at 111.0°; n^{20}_{D}, 1.4493. Price and Schwarcz[16] give 1.4498 as n^{20}_{D} for diethyl *trans*-1,2-cyclohexanedicarboxylate.

Hydrogenations. All low-pressure hydrogenations were carried out in a modified Parr low-pressure hydrogenation apparatus which has already been described,[9] using the 4.6 liter void. Each low-pressure run used 10.0 ml. of glacial acetic acid, 0.2 g. of platinum oxide, 0.04 mole of a xylene or 0.03 mole of diethyl phthalate, and an initial average hydrogen pressure of 270 cm. Each substrate was hydrogenated at 35, 45, 55 and 65° and the usual duration of a run was 1 hr.

High-pressure hydrogenations on platinum[17] were run in a 50-ml. bomb in an Aminco high-pressure hydrogenation apparatus, with an initial gage pressure of 1200 p.s.i., and at 55, 65, 75, and 85°. The quantities of substrate, catalyst and solvent were exactly one-half those used in the low-pressure hydrogenations.

Hydrogenations on nickel were carried in the same apparatus that was used for high-pressure hydrogenations on platinum, and used the same amounts of the substrates. Each run used 5 ml. of a suspension of nickel in ethanol, containing 1 to 2 g. of nickel. The temperature was 198–200°. The duration of each hydrogenation on nickel was 6 hr.

Determination of trans isomers. The acetic acid or alcohol in each reaction mixture was removed in the manner described in a previous paper,[9] and the residual hydrocarbon mixture was dried 24 hr. over Drierite. One milliliter of each of the dimethylcyclohexane mixtures, or 0.1 g. of each of the diethyl 1,2-cyclohexanedicarboxylate mixtures, was diluted to 10 ml. with Merck carbon disulfide. The absorbance of each solution was determined at the appropriate *trans* isomer absorption band with a Perkin-Elmer double-beam infrared spectrophotometer. These absorption bands were: diethyl *trans*-1,2-cyclohexanedicarboxylate, 7.60 μ; *trans*-1,2-dimethylcyclohexane, 10.34 μ; *trans*-1,3-dimethylcyclohexane, 11.92 μ; and *trans*-1,4-dimethylcyclohexane, 9.72 μ.[18] In each case the percentage of the *trans* isomer was determined from the absorbance by the baseline method. The results of these analyses were presented in Tables II and III.

Attempted catalytic isomerizations. To determine if yields of *trans* isomers resulted from catalytic isomerization, 2.5 ml. of each *cis* isomer in 5.0 ml. of glacial acetic acid was subjected to hydrogenation conditions in the presence of 100 mg. of platinum oxide at 85 and 1200 p.s.i. for 1 hr. Similar experiments were made with the same amount of *cis* isomers and 5 ml. of nickel–alcohol suspension at 200° and 1200 p.s.i. The amount of *trans* isomers found in the resulting mixtures are reported in Table IV.

TABLE II

Content of *trans*-Isomers in Products of Hydrogenation on Platinum-Oxide Catalyst

Temp.	Initial Pressure, Cm.	Total Time, Min.	% *trans*-Isomer
	a. Hydrogenation of *o*-Xylene		
35.1	279.6	115	5.5
46.3	278.6	110	7.5
53.	6271.	45	13.3
53.3	279.9	60	15.6
64.8	283.7	13.5[a]	9.2
64.8	278.8	40	13.6
65.0	284.6	60	11.8
75.	6348.	40	11.3
85.	6295.	45	12.7
	b. Hydrogenation of *m*-Xylene		
34.9	279.4	60	14.4
45.4	282.1	60	13.2
46.4	280.5	50	15.1
54.	6218.	30	15.8
55.0	285.4	60	16.1
55.1	279.8	38	15.5
63.8	283.4	11.5[a]	14.9
64.	6316.	22.	16.1
64.5	284.2	60	14.8
68.1	279.8	22	17.1
84.	6320.	60	19.0
	c. Hydrogenation of *p*-Xylene		
36.2	281.8	60	24.5
46.2	281.1	60	27.7
54.	6201.	60	30.0
64.8	278.4	60	32.6
65.	6177.	60	30.4
76.	6259.	60	29.1
85.	6311.	60	33.4
	d. Hydrogenation of Diethyl Phthalate		
35.6	281.4	180	0
45.0	281.6	100	0
55	6272.	60	trace
55.5	279.2	75	0
64.6	281.4	60	0
65	6321.	60	trace
75	6182.	60	0
85.5	6219.	60	0

[a] 50% reduction.

TABLE III

Content of *trans*-Isomers in Products of Hydrogenation on Raney Nickel Catalyst

Substrate	Temp.	Initial Pressure, Cm.	Total Time, Min.	% *trans*-Isomer
o-Xylene	200.	6544	720	11
m-Xylene	199.	6564	720	21
p-Xylene	198.	6683	720	5
Diethyl phthalate	150.5	6332	210	10
Diethyl phthalate	199.	7004	720	21

DISCUSSION

Hydrogenation on platinum-oxide. The hydrogenations of the three xylenes on platinum oxide gave stereochemical results (Table II) in excellent agreement with those by Siegel and Dunkel,[7] and the failure of diethyl phthalate to yield a *trans* product is in agreement with the findings of Siegel and McCaleb[8] for dimethyl phthalate. The relative absence of catalytic isomerization of *cis* isomers under hydrogenation conditions (Table IV) has been confirmed. For all xylenes, an increase in temperature resulted in an increase in the amount of *trans* isomer in the product. It must be concluded that the formation of *trans* isomers occurs as the result of one or more of several possible routes for

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(16) C. C. Price and M. Schwarcz, *J. Am. Chem. Soc.*, 62, 2891 (1950).

(17) R. H. Baker and R. D. Schuetz, *J. Am. Chem. Soc.*, 69, 1250 (1947).

(18) American Petroleum Institute Research Project 44, *Catalog of Infra-Red Spectral Data*, Carnegie Institute of Technology, Serial Nos. 299-304, Sept. 30, 1945.

TABLE IV

CATALYTIC ISOMERIZATION OF THE *cis*-DISUBSTITUTE

Catalyst	Temp.	% *trans*-Isomer
a. *cis*-1,2-Dimethylcyclohexane		
Pt	58.6	0.
Ni	200.	4
b. *cis*-1,3-Dimethylcyclohexane		
Pt	85.	0.
Ni	200.	trace
c. *cis*-1,4-Dimethylcyclohexane		
Pt	85.	3
Ni	200.	trace
d. Diethyl *cis*-1,2-cyclohexanedicarboxylate		
Ni	198.	trace

the hydrogenation process, and that the routes leading to the *trans* product are favored by an increase in temperature.

It is of interest to compare these results with the findings recently reported[19,20] for the hydrogenation of a number of dimethylcyclohexenes. Under the most comparable reaction conditions, all xylenes yield significantly smaller amounts of *trans* products than are obtained from the corresponding dimethylcyclohexenes. Siegel[21] has observed that at pressures below four atmospheres, that the amounts of *trans* isomers obtained by hydrogenation of the xylenes at 25° are those which would be predicted if all of the saturated products are formed *via* desorbed dimethylcycloalkenes. At higher pressures, the amounts of *cis* products increase, suggesting that increased pressure favors hydrogenation in a single period of adsorption according to the Linstead hypothesis. Both pressure ranges considered in this study are high enough for the Linstead path to occur with a significant portion of the molecules. In accord with this view, slightly higher amounts of *trans* isomer were obtained from *o*- and *p*-xylene at the lower pressure than at the higher pressure, at the same temperature; but any such differences with the *m*-xylene must be smaller than the experimental error.

If the assumption is made that *all* of the *trans* products have been formed *via* desorbed dimethylcyclohexenes substituted at the unsaturated carbons, then it is possible to make a rough estimate of the percentage of the xylenes hydrogenated by this route, using the data for the steric results of the hydrogenations of xylenes and of dimethylcyclohexenes under the most nearly comparable conditions. This assumes that cyclohexenes not substituted at the double bond as well as the single adsorption path yield only *cis*-products. This estimation gives about 25–35% of *o*-xylene being hydrogenated through 1,2- and 2,3-dimethyl-1-cyclohexene, about 60% of the *m*-xylene through 1,3- and 2,4-dimethyl-1-cyclohexene, and about 60% of the *p*-xylene through 1,4-dimethyl-1-cyclohexene. In view of the finding[19] that 1,2-dimethyl-1-cyclohexene is the least readily hydrogenated and most easily desorbed of the dimethylcyclohexenes, the low percentage of the *o*-xylene apparently hydrogenated *via* this isomer is unexpected. However, definite conclusions cannot be drawn without a knowledge of the stereochemistry of the dimethylcyclohexenes at the temperatures here considered.

In the case of diethyl phthalate, one explanation for the absence of *trans* hydrogenation products not previously considered lies in the possibility that the ester groups are adsorbed as well as the ring. Such adsorption would make the desorption of partially hydrogenated states more difficult, and would require greater energies, than in the cases of the xylenes.

Hydrogenations on Raney nickel. The amounts of *trans* products obtained by hydrogenations on Raney nickel (Table III), were considerably less than would be expected on the basis of the von Auwers-Skita rules. In fact, *p*-xylene gave slightly less *trans* product than it did on platinum oxide. A possible explanation for this result may be found in Siegel's observation that the amount of *cis*-hydrogenation of 1,2-dimethyl-1-cyclohexene increases markedly with pressure. However, this or any other hypothesis based on hydrogenation *via* desorbed cycloalkenes must await a study of the stereochemistry of the hydrogenation of these cycloalkenes on nickel at elevated temperatures and pressures, in order to have any real significance.

The fact that a 50° temperature increase doubled the amount of *trans* product from the hydrogenation of diethyl phthalate is not inconsistent with the idea that adsorption of the ester groupings may occur.

In all cases, the amount of catalytic isomerization of *cis* isomers on nickel was insufficient to account for the amounts of *trans* products of hydrogenation. It therefore appears that the appearance of *trans* products from the hydrogenations on nickel must result from alternate hydrogenation routes.

The kinetics of the hydrogenations of the three xylenes and the three diethyl phthalates, determined for the same conditions used in this work, will be considered in a subsequent paper, together with a comparison of the kinetic and stereochemical results.

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[19] S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082 (1960).

[20] J. F. Sauvage, R. H. Baker, and A. S. Hussey, *J. Am. Chem. Soc.*, **82**, 6090 (1960).

[21] S. Siegel, G. V. Smith, B. Dmuchowsky, D. Dubbell, and W. Halpren, Abstracts of Papers, 140th Meeting, American Chemical Society, 1961, p. 12S.