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Heterogeneous catalytic hydrogenation of aromatic compounds: I. Deuteration and hydrogen exchange of mono- and polyalkylbenzenes, II. Selectivity in the reduction of diarylalkanes, III. Competitive hydrogenolysis of arylmethanols

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by

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Dean of Graduate College

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PART I. DEUTERATION AND HYDROGEN EXCHANGE OF MONO- AND POLYALKYLBENZENES

INTRODUCTION

The study of the deuteration of the mono- and polyalkylbenzenes was initiated after the report of the hydrogen-deuterium exchange reactions of dimethylcyclopentane (1). The perdeutero isomer predominates in the reaction mixture; complete hydrogen-deuterium exchange was achieved on a palladium catalyst at 60°C. Epimerization of the trans isomer to the cis isomer was also observed. The mechanism by which complete exchange occurs and by which epimerization is achieved is not understood.

It has been shown that the reduction of the benzene nucleus in acetic acid catalyzed by platinum proceeds through an adsorbed cyclohexene intermediate (2). The hydrogenation in acetic acid is nonstereoselective; the reduction produces a mixture of cis- and trans-dialkylcyclohexanes. Various intermediates are proposed to account for the nonstereoselectivity but none of the intermediates completely explains the experimental observations accumulated over the years.

The deuteration of the mono- and polyalkylbenzenes was studied to determine the extent of deuterium incorporation into the cyclohexane product through deuteration and hydrogen-deuterium exchange.

The reductions of the alkylbenzenes were carried out to determine: a) the effectiveness of acetic acid-d_1 as a

source of deuterium and the possible synthetic utilization of the acid as a deuterium source, b) the role played by a carbon alpha to the benzene or cyclohexane nucleus in the exchange process, and c) the mechanistic implications derived from information concerning an α-adsorbed complex.

The polyalkylbenzenes were hydrogenated to determine: a) the role played by the ring carbons in the exchange process, b) the effect of the extent of alkyl substitution on the amount of deuterium incorporation, c) the effect of the alkyl substitution pattern on the amount of deuterium incorporation, d) the extent of deuterium incorporation into cis- and trans-dialkylcyclohexanes, and e) the mechanistic implications derived from information concerning the formation of σ-complexes at the ring carbons and the nature of the intermediate leading to the cis- and trans-dialkylcyclohexanes.

A few half-hydrogenation experiments were performed and the aromatic and aliphatic hydrocarbons separated and analyzed for deuterium incorporation. This limited study was carried out to determine the extent of deuterium exchange in the aromatic compound prior to hydrogenation.

The study was carried out to gain information about the mechanism of the hydrogenation and exchange reactions of aromatic hydrocarbons, the nature of the intermediate in the reduction, especially the intermediate which leads

to cis-trans isomerization of the dialkylcyclohexanes and the mechanism of cycloalkene isomerization and exchange.

LITERATURE REVIEW

Hydrogenations of Alkylbenzenes

Early reports concerning the hydrogenation of benzene and alkylbenzenes were made by Willstatter and Waldschmidt-Leitz (3), Skita and Meyer (4), Skita and Schneck (5), and Adams and Marshall (6). Willstatter and Waldschmidt-Leitz used platinum black and acetic acid at room temperature and atmospheric pressure. Skita, Meyer, and Schneck used colloidal platinum in glacial acetic acid at three atmospheres and 80°C and Adams and Marshall used reduced platinum oxide in acetic acid at three atmospheres and room temperature.

Kuhn and Winterstern studied the hydrogenation of 1,n-diphenylconjugated polyenes and found acetic acid to be the solvent of choice when the fully saturated product was desired (7).

Smith reviewed the catalytic hydrogenation of aromatic hydrocarbons with an emphasis on kinetics and stereochemistry (8). In kinetic work considerable attention must be given to reproducibility of the catalyst, purity of the aromatic compound, temperature control, and a balance between catalyst weight and agitation conditions so that equilibrium conditions are maintained. These conditions are required so the reaction rate rather than the diffusion rate is studied.

The kinetics of the hydrogenations carried out in acetic acid using platinum oxide generally are first-order in the pressure of hydrogen and zero-order in the concentration of the aromatic compound. Zero-order indicates that the organic materials are strongly adsorbed to the catalytic surface. The rates of the hydrogenations are generally observed by following the pressure decrease in a constant volume system.

The rates of the hydrogenations of alkylbenzenes catalyzed by platinum oxide in acetic acid at temperatures below 80°C and pressures below 4 atmospheres are proportional to the pH of the system, the amount of catalyst when the catalyst was present in low concentrations, and the agitation rate when the concentration of the catalyst was high. In alkylbenzene reductions it was observed that the reaction course and the nature of the products are influenced by substituents which prevent the flatwise adsorption of the aromatic ring onto the catalytic surface. The rate of hydrogenation decreased with an increase in the number of substituents and the symmetry of substitution had an influence on the reaction rate. Generally, the more symmetrical the substitution pattern on the benzene nucleus, the greater the rate of hydrogenation, even when the symmetrical substitution leads to a greater degree of substitution. p-Xylene reacted faster than toluene, mesitylene was hydrogenated

faster than either o- or m-xylene and 1,2,4,5-tetramethylbenzene was reduced faster than 1,2,3-trimethylbenzene.

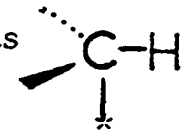
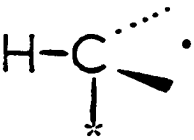
Bond interprets the trends of the alkylbenzene rates in terms of either an increase in the adsorption strength of the reactant through the electron releasing effects of the alkyl groups, or a lower concentration of the aromatic in the adsorbed layer due to steric effects (9).

Much of the mechanistic information concerning the hydrogenation of the alkylbenzenes has come from studies of the stereochemistry of the process. Dialkylcyclohexanes can exist as cis and trans isomers. The cis isomer predominates in the hydrogenation product of the dialkylbenzenes and dialkylcyclohexenes even though it is generally the less thermodynamically stable form. Cis formation is attributed to the flat adsorption of the aromatic compound on the catalytic surface.

Siegel and Dunkel investigated the stereochemistry of the hydrogenation of the three xylenes, and eight dimethylcyclohexenes at 25°C and 35 psi catalyzed by reduced platinum oxide in acetic acid (2). Each olefin yields a mixture richer in the cis isomer. If the hydrogenation consisted solely of the one-sided addition of hydrogen to a double bond, then pure cis-substituted cyclohexane would be produced. This stereoselectivity is not observed. They conceive that the olefin might isomerize to one in which the

groups are trans or to an olefin which can yield the trans isomer by the one-sided addition of hydrogen. The process which produces the trans isomer must occur at an intermediate stage in the reaction.

This lack of stereoselectivity may be due to either a desorbed olefin or a free radical such as  .

The formation of the radical could be the initiation step in a rapid hydrogen transfer chain reaction of a half-hydrogenated state such as  or  . This type of process would be favored when the catalyst is covered mainly by chemisorbed olefin and half-hydrogenated states. Increasing the pressure should decrease the length of the chain process and increasing the pressure from 3 to 150 atmospheres decreased the amount of trans isomer produced in the hydrogenation of 1,2-dimethylcyclohexene.

The composition of the mixtures produced in the hydrogenation of the three xylenes resembles the pattern set by the isomeric olefins. The percentage of the cis isomer decreased in the series ortho> meta> para (95%, 86%, and 74%, respectively).

The hydrogenation proceeds through stages, the latter steps in the sequence coincide with those in the reduction of the corresponding olefin (2). The nonstereoselectivity

of the hydrogenation is due to the reactions of the half-hydrogenated state. They refute the suggestion by Linstead and coworkers that the hydrogenation of the aromatic nucleus proceeds through a single stage (10).

Evidence linking the cycloalkene to the reduction of the xylenes comes from the study of the hydrogenation of 1,2-dimethylcyclohexene and 2,3-dimethylcyclohexene over platinum (11) and palladium (12). Small amounts of o-xylene are formed during the reduction of the cyclohexenes. Isolation of o-xylene demonstrates the existence of a reaction path joining o-xylene to 1,2-dimethylcyclohexene and the saturated isomers.

Additional evidence which links the cyclohexenes to the reduction of the dialkylbenzenes was obtained in the hydrogenation of p-t-butyltoluene and the isomeric xylenes in acetic acid over reduced platinum oxide (13). Comparison of the results obtained for 4-t-butyl-1-methylcyclohexene with those of the aromatic derivative (14) again suggests a common pathway between the reduction of the cyclohexene and the dialkylbenzene.

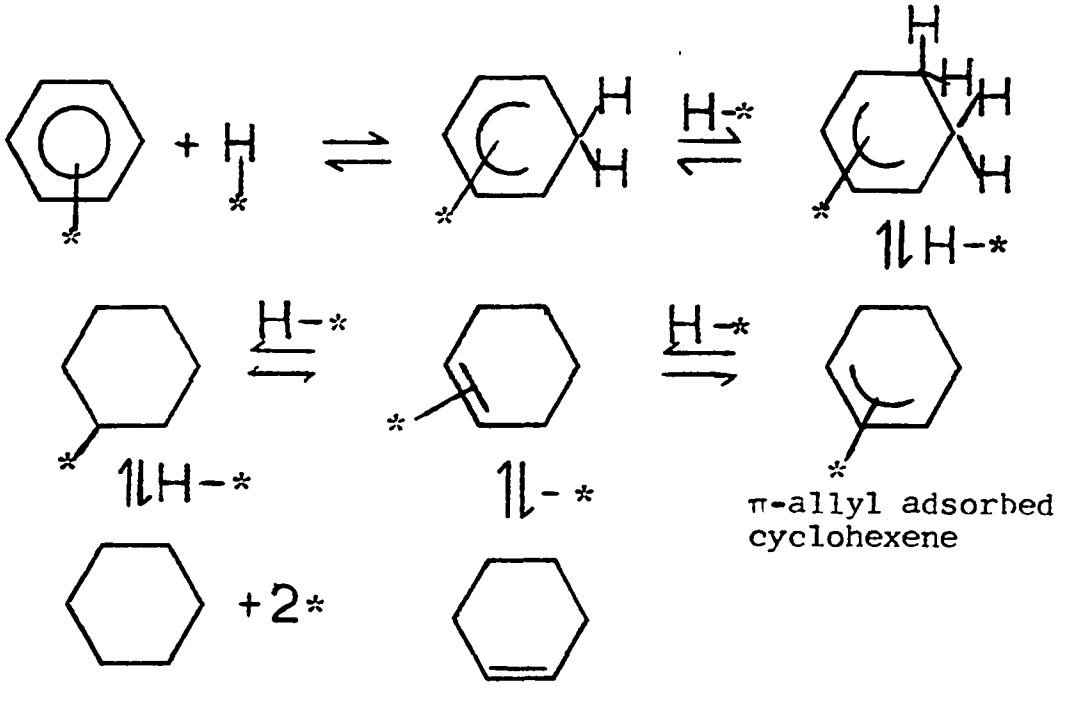
Using gas chromatography, the isolation and identification of cyclohexene intermediates in the hydrogenation of the three xylenes has been reported (15, 16). The results of the hydrogenations of the xylenes and their tetrahydro derivatives suggest that the cycloalkenes result from the

cis addition of four atoms of hydrogen to the adsorbed xylene. The cycloalkene is then released from the catalytic surface before final readsorption and reduction.

Hartog and Zwietering observed the formation of 1,2-dimethylcyclohexene in the hydrogenation of o-xylene over ruthenium, rhodium, and nickel but on platinum the intermediate was hydrogenated faster than the aromatic compound (17). The authors suggest that about 10% of the aromatic compound leaves the surface as the alkene during the hydrogenation.

Before discussing the implications of the stereochemical observations of the hydrogenation reactions, it is necessary to discuss the mechanism of the hydrogenation process. Unsaturated hydrocarbons are thought to adsorb on the metal surface by means of a π-complex in which there is a net charge transfer from the aromatic to the metal. It is represented by:  or  . In the π-complex, the plane of the adsorbed aromatic ring is parallel to the catalytic surface. Bond and Wells reviewed the π-complex hydrogenation mechanism, Scheme 1 (18). The hydrogenation can be visualized by proceeding from the π-complexed aromatic system through a series of intermediates until a π-adsorbed cyclohexene is formed. The extent to which this π-adsorbed olefin or the corresponding σ-1,2-diadsorbed analog is common to the hydro-

genation of both dialkylbenzenes and dialkylcyclohexenes will determine the stereochemistry of the resulting dialkylcyclohexanes (18). The σ-1,2-diadsorbed complex differs from the π-complex in that upon formation of the π-complex, groups attached to the former double bond must assume a cis configuration and the ring probably exists in the chair conformation. The groups attached to the former double bond assume a position directed away from the surface. When the olefin is symmetrically substituted, only the cis configuration is possible because both sides of the ring are equivalent. In 2,3-dimethylcyclohexene, the two sides of the ring are not equivalent and formation of a σ-1,2-diadsorbed-2,3-dimethylcyclohexane can produce both the cis and trans

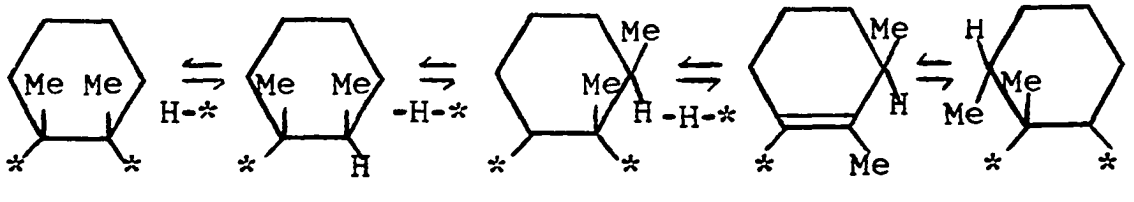


Scheme 1. π-Complex hydrogenation mechanism

methyl configurations depending upon the direction in which the 3-methyl is positioned relative to the catalytic surface. Since 1,2-dimethylcyclohexene and o-xylene do not produce the pure cis isomer on hydrogenation (2), some special mechanism must be invoked to explain this nonstereoselectivity.

The lack of stereoselectivity in the hydrogenation of the dialkylbenzenes can be attributed to the reactions of the dialkylcyclohexenes formed as intermediates. The formation of the trans-dialkylcyclohexane has been attributed to the formation of a "dissociatively adsorbed olefin" (19), a desorbed olefin (11), a σ-allylic complex (20), and a trans-1,2-diadsorbed intermediate (21). A "roll over" mechanism has also been proposed to explain the formation of the trans isomer (22).

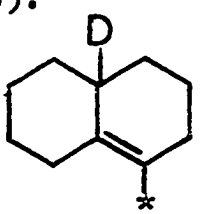
The "dissociatively adsorbed olefin", proposed by Burwell and coworkers (19) has been used to explain the stereochemical observations of a number of hydrogenation and exchange reactions, Scheme 2 (20, 23, 24).



Scheme 2. Dissociatively adsorbed olefin mechanism

The dissociatively adsorbed olefin can lead to the formation of the trans-σ-diadsorbed complex simply by rotating about the ring-catalyst bond and readsorbing.

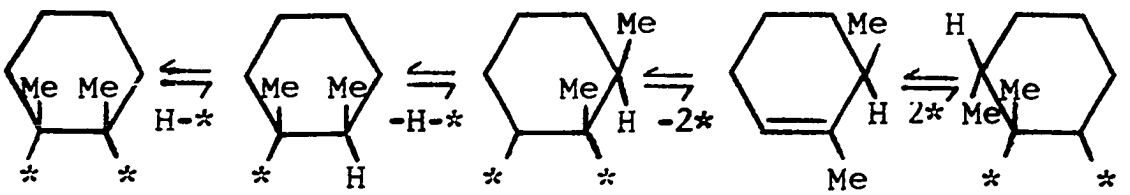
The deuteration of $\Delta^{9,10}$-octalin produced 61% cis- and 39% trans-decalin containing nearly three deuterium atoms per molecule. The $\Delta^{1,9}$-octalin gave less of the cis isomer (54%) than the $\Delta^{9,10}$-isomer and the decalin contained about two deuterium atoms per molecule. Most of the cis- and all of the trans-decalin produced from the $\Delta^{9,10}$-isomer was derived from a common intermediate in which three hydrogen atoms were equilibrated. Such an intermediate could be $\Delta^{1,9}$-octalin-10d and it could be formed from a dissociatively adsorbed olefin (20).



A "dissociatively adsorbed olefin" intermediate has been proposed to explain the high percentage of trans isomer produced in the hydrogenation of 4-methylisopropylidenecyclohexane over reduced platinum oxide in acetic acid (23). The intervention of this type of intermediate is important, over platinum, only with tetrasubstituted alkenes.

A desorption mechanism has been proposed by Siegel and coworkers to explain the formation of trans-dialkylcyclo-

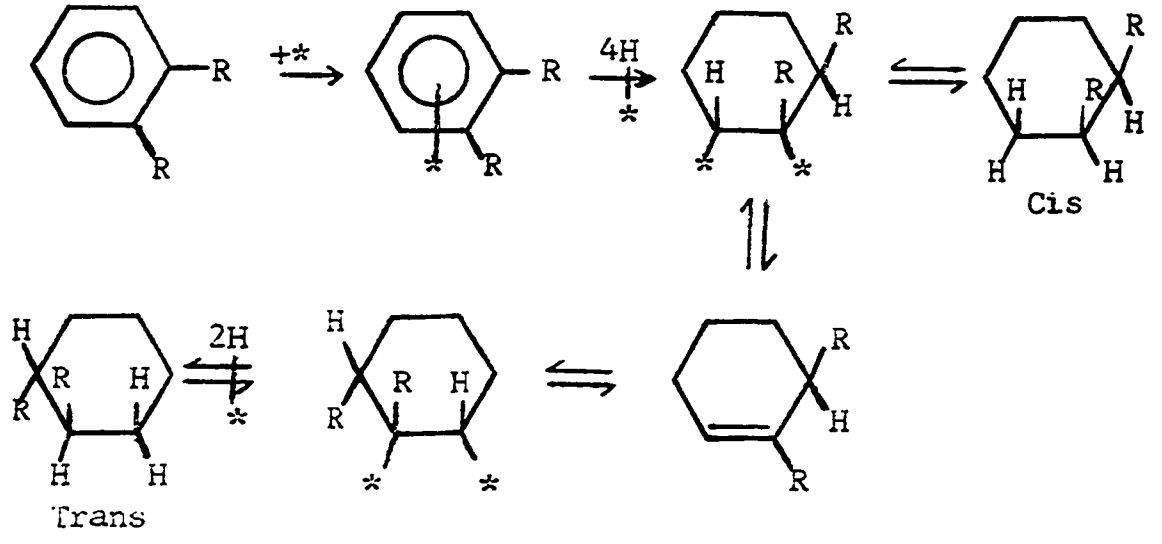
hexanes from the dimethylcyclohexenes and the xylenes (11, 13, 15, 16, 25). The nonstereoselectivity of the process is due to isomerization and desorption. Consider 1,2-dimethylcyclohexene in Scheme 3. 1,2-Dimethylcyclohexene



Scheme 3. The desorption mechanism of Siegel

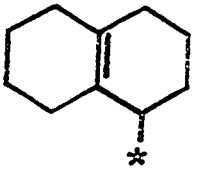
adsorbs to form a cis-σ-1,2-diadsorbed-1,2-dimethylcyclohexane. Isomerization of the 1,2-diadsorbed sigma complex to the σ-1,2-diadsorbed-2,3-dimethylcyclohexane occurs by means of a reversible hydrogenation step. Addition of an adsorbed hydrogen to the 1,2-dimethyl derivative produces a σ-monoadsorbed half-hydrogenated state; hydrogen addition produces a σ-1-monoadsorbed-cis-1,2-dimethylcyclohexane. Reversal of this step but with removal of the other alpha hydrogen atom generates a σ-1,2-diadsorbed-cis-2,3-dimethylcyclohexane which subsequently desorbs from the catalyst. Readsorption of the isomerized olefin in which the two sides of the ring are no longer equivalent can produce both the cis and the trans methyl configurations. Siegel, Thomas, and Holt have shown that 1,2-dimethylcyclohexene can isomerize to 2,3-dimethylcyclohexene and they propose that most of the

trans product arises from the reduction of the 2,3-dimethylcyclohexene (26). The stereochemistry of the reduction of cyclopentenes over reduced platinum oxide has been explained by this mechanism (27). The application of this mechanism to the stereochemistry of the dimethylbenzene reductions is illustrated in Scheme 4 (13).



Scheme 4. Desorption mechanism applied to the aromatic hydrogenation

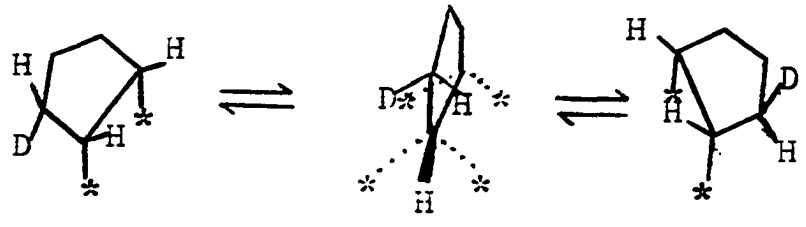
Another possible explanation of the deuteration of $\Delta^{9,10}$-octalin and $\Delta^{1,9}$-octalin, discussed under the dissociatively adsorbed olefin section, is that a σ-allylic complex is involved (20). The intermediate $\Delta^{1,9}$-octalin-10d can be produced from a 1-adsorbed $\Delta^{9,10}$-octalin.



It is conceivable that a type of allylic complex may explain the stereochemistry of the xylene reductions. Yamamoto and coworkers have shown that the selectivity of trans formation parallels the ability of the transition metal to form π-allylic complexes in the case of the hydrogenation of o- and p-xylene (28).

Hussey, Baker, and Keulks proposed that a cycloalkene which forms cis and trans products chemisorbs irreversibly to give the cis-adsorbed and the trans-adsorbed alkene (21). The two adsorbed forms interconvert by way of a symmetrical intermediate on the surface; cis-trans isomerism occurs on the catalytic surface without desorption and the trans-alkane is formed from the trans-diadsorbed alkene. Speculation into the nature of the symmetrical intermediate was not made.

A "roll over" mechanism has been postulated by Schrage and Burwell to explain the hydrogen-deuterium exchange of cycloalkanes observed over palladium (22). This mechanism is proposed to explain the transfer of adsorption from one side of the cycloalkane ring to the other; the intermediacy of a five coordinate carbon is proposed. (Scheme 5)



Scheme 5. "Roll over" mechanism of Schrage and Burwell

The "roll over" mechanism explains the formation of cyclopentane-$\underline{d}_8$ but has not been envoked to explain other observations.

It is apparent that the reduction of the benzene nucleus occurs by the rapid addition of four hydrogen atoms forming an adsorbed cyclohexene intermediate. The fate of the dialkylcyclohexene intermediates has been the subject of much debate and has not been resolved.

Hydrogen-Deuterium Exchange Reactions

Olefinic systems

Olefinic exchange, double bond migration, and cis-trans isomerization are all thought to involve the half-hydrogenated state (18). With ethene the half-hydrogenated state leads to hydrogen-deuterium exchange as illustrated in Scheme 6.

$$CH_2(*)=CH_2 \text{ or } \underset{*}{CH_2}-\underset{*}{CH_2} \overset{D-*}{\rightleftharpoons} \underset{*}{CH_2}-CH_2D \rightleftharpoons CH_2(*)=CHD + H-*$$

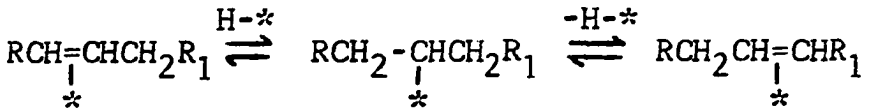
Scheme 6. Exchange involving a half-hydrogenated state

Propene is thought to exchange *via* a π-allyl intermediate, Scheme 7.

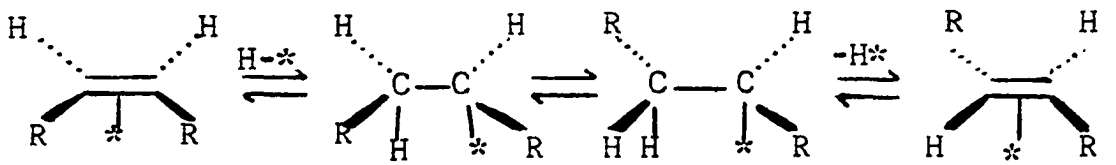
$$CH_3CH(*)=CH_2 - H-* \longrightarrow \underset{*}{CH_2CHCH_2} \xrightarrow{D-*} CH_2D-CH(*)=CH_2$$

Scheme 7. Exchange involving a π-allyl intermediate

In each case subsequent steps would lead to further incorporation of deuterium. Double bond migration and cis-trans isomerization are illustrated in Scheme 8 and 9, respectively. With the smaller cyclic olefins cis-trans isomerization cannot occur in this manner because the carbon is not free to rotate as in the open chain compounds.



Scheme 8. Double bond migration involving a half-hydrogenated state



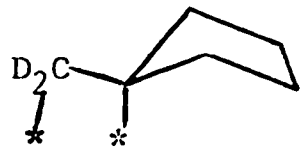
Scheme 9. Cis-trans isomerization involving a half-hydrogenated state

The nature of the diadsorbed intermediate in the exchange process comes from a study carried out by Schrage and Burwell (22, 29) and reviewed by Burwell (1). Adsorption occurs <u>via</u> a σ-1,2-diadsorbed alkane not <u>via</u> a π-complex and the conformation of the diadsorbed intermediate must be eclipsed and not staggered. This is indicated by the exchange reaction of adamantane which exchanges only one deuterium atom per period of residence on the catalytic surface. Any 1,2-diadsorbed adamantane would have to be staggered; since only

one deuterium is added, diadsorption must be in an eclipsed conformation, a conformation not allowed in adamantane. Further evidence for the eclipsed conformation comes from bicyclo[2.2.1]heptene which exchanges two deuterium atoms. If the staggered conformation were favored, further exchange would occur *via* the formation of a diadsorbed intermediate involving the bridgehead carbon, which is staggered relative to an adsorbed olefin.

Based upon the results of the deuterium exchange reactions of bicyclo[3.3.1]nonane, the diadsorbed complex is the more probable intermediate in the exchange process. Exchange involves the bridgehead and both trimethylene units. A bridgehead olefin would be required by the π-complex theory, and such an olefin, while possible, would be a rather high energy intermediate and not as likely as a σ-1,2-diadsorbed complex.

Exchange reactions of cyclopentane *via* the formation of mono- and diadsorbed complexes leads to the formation of the d_5 isomer as the maximally exchanged species. An additional factor causes exchange on both sides of the ring to give d_{10}. The exchange pattern of *trans*-1,2-dimethylcyclopentane indicates that each methyl group exchanges with the set of hydrogens on the other side of the ring *via* a diadsorbed intermediate.



Epimerization forms the cis-1,2-dimethylcyclopentane which is almost completely perdeutero. The mechanism by which more than five hydrogens are exchanged in cyclopentane and by which cis- and trans-dimethylcyclopentane are interconverted is not clearly defined. The "roll over" mechanism is proposed to explain the formation of cyclopentane-$\underline{d}_8$.

Aromatic systems

Aromatic hydrogen-deuterium exchange has been extensively reviewed (8, 9, 18, 25, 30, 31, 32). The dissociative mechanism indicates that exchange and hydrogenation occur by two unrelated mechanisms (33, 34, 35). Hydrogenation involves the simultaneous addition of two hydrogen atoms to an adsorbed hydrocarbon, while exchange with deuterium requires the prior dissociation of the hydrocarbon on the catalyst forming a σ-phenyl complex and a hydrogen atom. The σ-phenyl complex then combines with a deuterium atom and the benzene-$\underline{d}_1$ desorbs (25), Scheme 10. The associative mechanism (36) indicates that a common intermediate is involved in the exchange and hydrogenation steps. (Scheme 11)

exchange:

$D_2 + 2* \rightleftharpoons 2D-*$

$C_6H_6 + 2* \rightleftharpoons C_6H_5-* + H-*$

σ-complex

$C_6H_5-* + D-* \rightleftharpoons C_6H_5D + 2*$

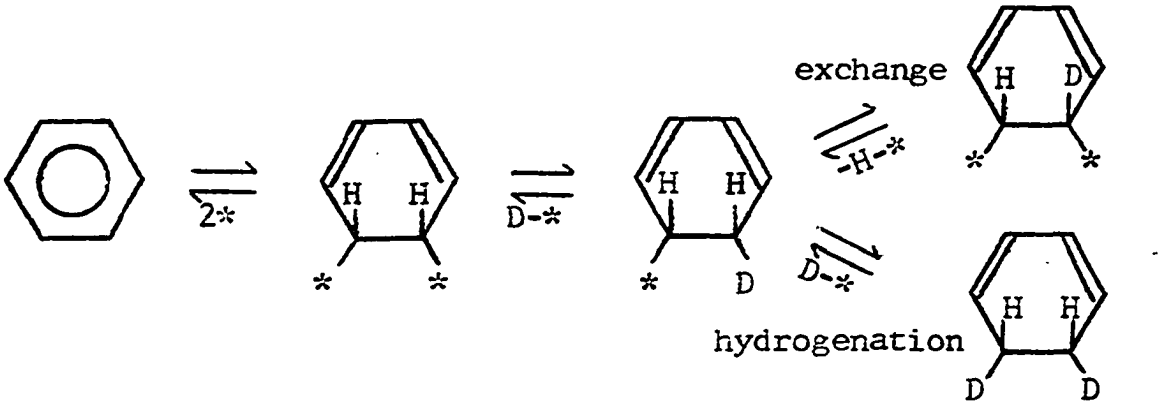
hydrogenation:

$H_2 + 2* \rightleftharpoons 2H-*$

$C_6H_6 + * \rightleftharpoons C_6H_6-*$

$C_6H_6-* + 2H-* \rightleftharpoons C_6H_8-* \xrightarrow{\text{fast}} C_6H_{12} + *$

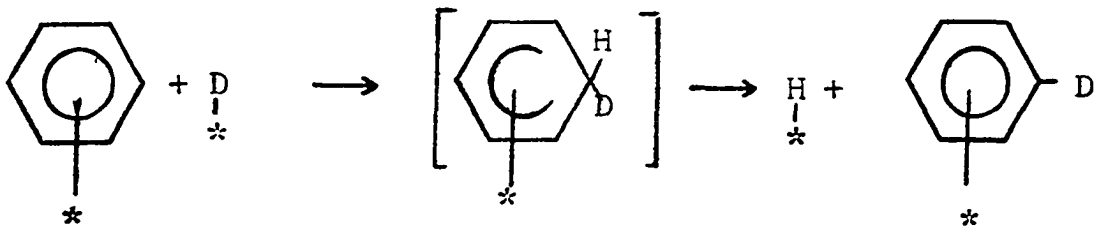
Scheme 10. Dissociative mechanism of Farkas and Farkas



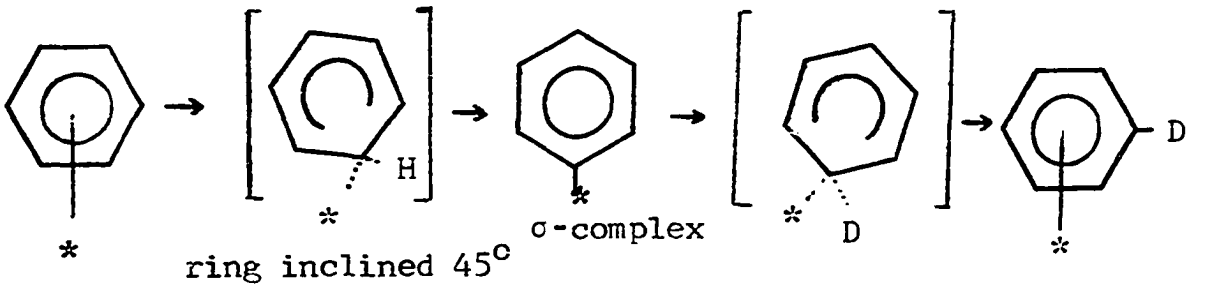
Scheme 11. Associative mechanism of Horiuti and Polanyi

Inconsistencies in the two mechanisms led to the development of a new adsorption theory which deals with the π-complex. The associative and dissociative mechanisms are expressed in terms of the π-complex. The new mechanisms differ from the classical mechanisms in that the dissociative

π-complex mechanism (Scheme 13) involves π-electrons in the dissociation and opening of a double bond is not involved in the new associative mechanism. (Scheme 12)



Scheme 12. The associative π-complex substitution mechanism



Scheme 13. The dissociative π-complex substitution mechanism

When inclined at 45°, the critical stage in the transition state has been reached, the C-H bond has been weakened, and the Pt-H bond is beginning to form. (Scheme 13)

The dissociative π-complex mechanism is of greater importance in exchange reactions of aromatic hydrocarbons with heavy water (30). This mechanism may play a major role when deuterium gas is used. The rapid deuterium exchange between deuterated benzene and polyphenyl compounds confirms the importance of the dissociative π-complex substitution

mechanism (37). The observation of the rapid randomization of normal benzene with deuterated benzene leads to the same conclusion.

Weitkamp investigated the deuteration of naphthalene and its octalin derivatives over a variety of catalysts (38). Exchange on an aromatic ring or about a double bond is largely by the dissociative π-complex mechanism when catalyzed by platinum.

The "ortho deactivation effect" indicates the importance of the dissociative π-complex mechanism (30). The ortho deactivation effect occurs when a hydrogen is ortho to a large inert group or is flanked by two methyl groups. Such a hydrogen is not subject to the exchange process; some loss in exchange tendency is observed when the hydrogen is ortho to a single methyl group. This effect is not explained by the associative π-complex mechanism and is easily explained by the dissociative π-complex mechanism. In going from the π-bonded form to the σ-complex, the molecule rotates through a 90^{o} angle with respect to the catalyst. The ortho group may hinder or prevent σ-complex formation.

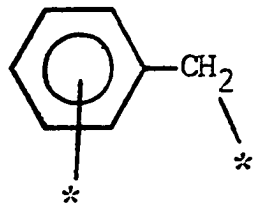
Lauer and Stedman have shown that steric factors are not important in electrophilic aromatic hydrogen isotope substitution reactions carried out in a trifluoroacetic acid-deuterium oxide system (39, 40, 41). Since the associative π-complex substitution mechanism involves an

intermediate sterically similar to the intermediate in the electrophilic aromatic substitution, the ortho deactivation effect is due to steric hindrance in the formation of the σ-complex.

Harper, Siegel, and Kemball observed the relative reactivity of the hydrogens toward exchange in t-butylbenzene to be m, p > CH_3 > o (42). Hydrogens on carbons β to the aromatic ring with no possibility of interacting with the adsorbed nucleus are more reactive toward exchange than are the ortho hydrogens. The reaction, catalyzed by metal films, illustrates the ortho deactivation effect.

Garnett and Sollich observed the ortho deactivation effect when hydrogen-deuterium exchange was carried out over platinum with deuterium oxide (43). Their results are similar to those of Harper and coworkers (42) except that side group exchange was not observed for t-butylbenzene.

Alkyl hydrogen exchange has been observed in other studies. Harper and Kemball studied the exchange and deuteration of p-xylene over platinum foil and observed a substantial amount of side group exchange during deuteration (44). Some exchange of the ring hydrogens also occurs but not to the extent of the methyl groups. This exchange occurs via an intermediate in which the ring is π-bonded and the side chain is σ-bonded to the catalyst. This type of complex has been used to explain exchange reactions over nickel (45).



Horrex and Moyes studied the exchange and deuteration of toluene over platinum foil (46). Exchange first occurred at the methyl group, then at the meta and para positions, with the methyl group exchanging faster than the deuteration was occurring.

The exchange reactions of aromatic hydrocarbons are generally carried out by the use of either deuterium and an evaporated metal film, deuterium oxide and an "active" platinum catalyst, or by the use of other deuterated aromatic hydrocarbons. The application of the theories proposed for the conditions cited in the literature to the liquid phase is not known.

The only report of the reduction of aromatic hydrocarbons in acetic acid-$\underline{d}_1$ is that of Price and Beard (47). About 3% hydrogen-deuterium exchange occurred in the hydrogenation of methyl benzoate-$\underline{d}_5$ in acetic acid catalyzed by 5% platinum on alumina. The mass spectrum of the cyclohexanecarboxylate product showed the $\underline{d}_5$ isomer to be the dominant peak in the molecular ion. The use of platinum

oxide increased the exchange to about 15%; rhodium on alumina catalyzed about 5% exchange. Deuteration of methyl benzoate in acetic acid-$\underline{d}_1$ over 5% rhodium on alumina produced only 2% exchange. This catalyst was used because platinum on alumina resulted in low deuterium incorporation. The predominant peak in the molecular ion was the $\underline{d}_6$ isomer. About 5% exchange was observed in the deuteration of methyl 4-$\underline{t}$-butylbenzoate in acetic acid-$\underline{d}_1$ with a rhodium on alumina catalyst (47). These results contradict the observations of Smith and Burwell (20) who found the same overall pattern in the deuteration of olefins in either the vapor or liquid phases. The observations of Price and Beard also contradict the results of Philipson and Burwell (48) who studied the deuteration of cycloalkenes in acetic acid-$\underline{d}_1$ catalyzed by platinum on alumina. The isotopic distributions of the cycloalkanes produced by deuteration and exchange of the cycloalkene closely resemble those found in the exchange of the cycloalkane in the vapor phase with deuterium on platinum. This observation indicates that the exchange of alkanes and the hydrogenation of alkenes are closely interlinked mechanistically. Philipson and Burwell indicate that deuterations in acetic acid-$\underline{d}_1$ result in the incorporation of more deuterium than is observed for methanol-$\underline{d}_1$ and $\underline{t}$-butanol-$\underline{d}_1$.

RESULTS AND DISCUSSION

General Observations

The time required to completely hydrogenate the aromatic nucleus was recorded for each reduction (see Experimental Section). The time required to reduce each hydrocarbon varied greatly and the variation was not due to impurity in the hydrocarbon, catalyst, or solvent used since the chemicals were taken from the same source. This variation in time required to complete the reduction prevents the formulation of a general statement concerning the reactivity of a particular hydrocarbon in comparison to a series of such compounds. The observation of the time variance provides additional support for the statements made by Smith (8) concerning the amount of care which must be exercised to obtain meaningful results for the kinetics of aromatic hydrocarbon reductions. The times recorded for the hydrogenations and the trends one can draw from them do not contradict the general statements discussed by Smith, i.e., the rate of the hydrogenation decreased as the number of substituents increased and, in general, the more symmetrical the substitution pattern on the benzene nucleus the greater the hydrogenation rate even when this leads to a greater degree of substitution. It is probable that this reduction tendency is a result of the ability of the benzene nucleus to complex with the catalyst. Increased substitution

and substitution by sterically bulky groups hinder complexation with the catalyst. This is illustrated by the very long reduction times observed for 1,2,3-trimethylbenzene, 1,3,5-trisopropylbenzene, and durene. Additional support for steric hindrance to complexation comes from the non-reactive nature of 1,3,5-tri-t-butylbenzene under the reaction conditions. The p-di-t-butyl derivative was reduced fairly rapidly; therefore, the three bulky t-butyl groups prevent interaction between the catalyst and the benzene nucleus thereby preventing complexation with the catalyst. The same proposal has been offered to explain the difficulty encountered in the preparation of the chromium-tricarbonyl complex of tri-t-butylbenzene (49).

The observation that naphthalene did not undergo hydrogenation was unexpected, especially when tetralin was reduced without difficulty. The platinum catalyzed reduction of naphthalene has been reported by a number of workers (50, 51, 38). A comparison of the time required to hydrogenate benzene, naphthalene, and tetralin in acetic acid at 25°C and 2000 psi has been reported (50). Benzene was hydrogenated in 15 minutes, naphthalene in 95 minutes, and tetralin was reduced in 90 minutes. The reduction of naphthalene at 40°C and 2.5 atm in acetic acid over reduced platinum oxide has been reported but complete details are not available (51). Weitkamp observed the slow deuteration

of naphthalene over platinum-charcoal at 30°C and 440 psi (38).

The time required to reduce naphthalene and tetralin at elevated pressures is nearly the same, this indicates that the degree of difficulty for the reduction of the two hydrocarbons at high pressure is nearly the same. Since tetralin was reduced at one atmosphere without difficulty and naphthalene was not reduced, the nonreactivity of naphthalene under the mild conditions of this study is not due to steric inhibition of complexation. A factor which may account for the nonreactivity of naphthalene is the strength of its adsorption on the catalyst. Garnett and Sollich-Baumgartner (30) discussed trends in π-complex adsorption strengths observed in competitive exchange reactions. Naphthalene is more strongly adsorbed on catalytic surfaces through π-complex formation than benzene, biphenyl, anthracene, phenanthrene, and other polycyclic aromatic hydrocarbons. In a study of the platinum catalyzed exchange reactions between normal and deuterated hydrocarbons, naphthalene poisons the catalyst by strong but reversible π-complex adsorption (37). Naphthalene can be deuterated by reagents which are more strongly adsorbed on the catalyst than deuterium oxide. Ethanol is a useful reagent for exchange reactions involving naphthalene. The use of acetic acid in a number of deuterium and tritium exchange reactions is due to the stronger adsorption of acetic

acid as compared to water (37, 52, 53).

The nonreactivity of naphthalene in this study could be due to the strong adsorption of the hydrocarbon on the catalytic surface. This strong adsorption poisons the catalytic surface and prevents the catalysis of the hydrogenation. The strong adsorption of acetic acid on the catalyst is beneficial to the exchange process but not to the hydrogenation process.

Deuteration Results

Acetic acid-$\underline{d}_1$ as a deuterium source

The initial point to be established was the effectiveness of acetic acid-$\underline{d}_1$ as a deuterium source. The reduction of three alkylbenzenes was carried out in acetic acid-$\underline{d}_1$ using hydrogen and deuterium gas. The results are listed in Tables 1 and 2.

Table 1. Comparison of the number of deuterium atoms per mole of alkylcyclohexane produced in acetic acid-$\underline{d}_1$ using hydrogen and deuterium gas

Alkyl group	D/mole, Hydrogen gas		D/mole, Deuterium gas	
	mass spec	nmr	mass spec	nmr
CH_3	5.3	6.2	6.5	7.7
$\underline{i}$-C_3H_8	5.1	5.7	6.3	6.6
$\underline{t}$-C_4H_9	4.6	5.9	5.7	6.2

Table 2. Comparison of the corrected normalized values of the deuterated species in the partial mass spectra of alkylcyclohexanes produced in[a] acetic acid-$\underline{d}_1$ using hydrogen and deuterium gas

Alkyl group	gas	d_3	d_4	d_5	d_6	d_7	d_8	d_9
Methyl	H_2	10.2	18.5	22.1	18.1	12.0	7.5	3.8
	D_2	3.3	10.0	19.2	21.8	16.0	12.7	8.7
Isopropyl	H_2	10.1	21.0	26.5	21.1	10.4	3.9	1.6
	D_2	2.3	8.6	19.6	27.4	22.0	11.4	4.8
$\underline{t}$-Butyl	H_2	13.5	25.2	26.4	17.5	5.9	1.9	1.0
	D_2	3.4	11.6	26.7	31.2	16.1	6.0	2.0

[a]The exchange patterns of the cyclohexane derivatives listed in this and subsequent tables indicate that an exchanged hydrogen atom of the hydrocarbon is being incorporated into other molecules of the product. The hydrogen atom liberated in the exchange of the aromatic hydrocarbon is apparently not exchanging with the solvent but is remaining on the catalyst and is then incorporated into another product molecule. This observation was not expected because of the tremendous excess of sources of deuterium in the reaction mixture. The reductions were generally carried out on one millimole of hydrocarbon (three millimoles of exchangeable hydrogen) using a gas buret containing four millimoles of deuterium and five milliliters (82 millimoles) of acetic acid-$\underline{d}_1$. This tremendous excess of deuterium should flood the catalytic surface with adsorbed deuterium and should result in exchange of a liberated hydrogen atom with the solvent. The results indicate that the liberated hydrogen atoms are incorporated into other product molecules and are not exchanged with the solvent. This suggests that the liberated hydrogen is complexed to the catalyst at a site not in direct contact with the solvent.

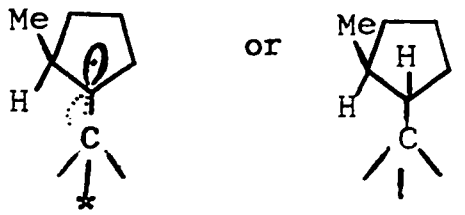
The deuterium per mole value, the average number of deuterium atoms incorporated into a cyclohexane molecule, indicates the deuterium incorporation into the cyclohexane

derivative has increased by about one deuterium atom per mole when deuterium gas is used in place of hydrogen gas (Table 1). The distribution pattern of the deuterated isomers, $\underline{d}_n$, was shifted by one unit when deuterium gas was used in place of hydrogen gas (Table 2). The most prominent peak in the mass spectrum of methylcyclohexane is $\underline{d}_5$ when hydrogen gas was used and $\underline{d}_6$ when deuterium gas was used; comparable shifts are observed for other peak intensities in the mass spectra of methylcyclohexane. The most prominent peak in the mass spectra of isopropylcyclohexane and $\underline{t}$-butylcyclohexane is $\underline{d}_5$ when hydrogen was used and $\underline{d}_6$ when deuterium was used. Thus, acetic acid-$\underline{d}_1$ is a very effective source of deuterium for the deuteration of the aromatic nucleus through hydrogenation and hydrogen-deuterium exchange. This observation confirms a prediction based upon the results of Eidinoff and coworkers (54) who found that the deuteration of olefins in acetic acid over platinum resulted in about 1% deuterium incorporation. The carboxyl hydrogen is the hydrogen atom incorporated into the olefin during the reduction. Isotopic exchange between dissolved hydrogen and carboxyl hydrogen is rapid relative to the reduction steps and the large excess of solvent floods the catalytic surface with adsorbed hydrogen atoms resulting in low deuterium incorporation. When the situation is reversed, i.e., hydrogen gas and acetic acid-$\underline{d}_1$, one would expect to find extensive

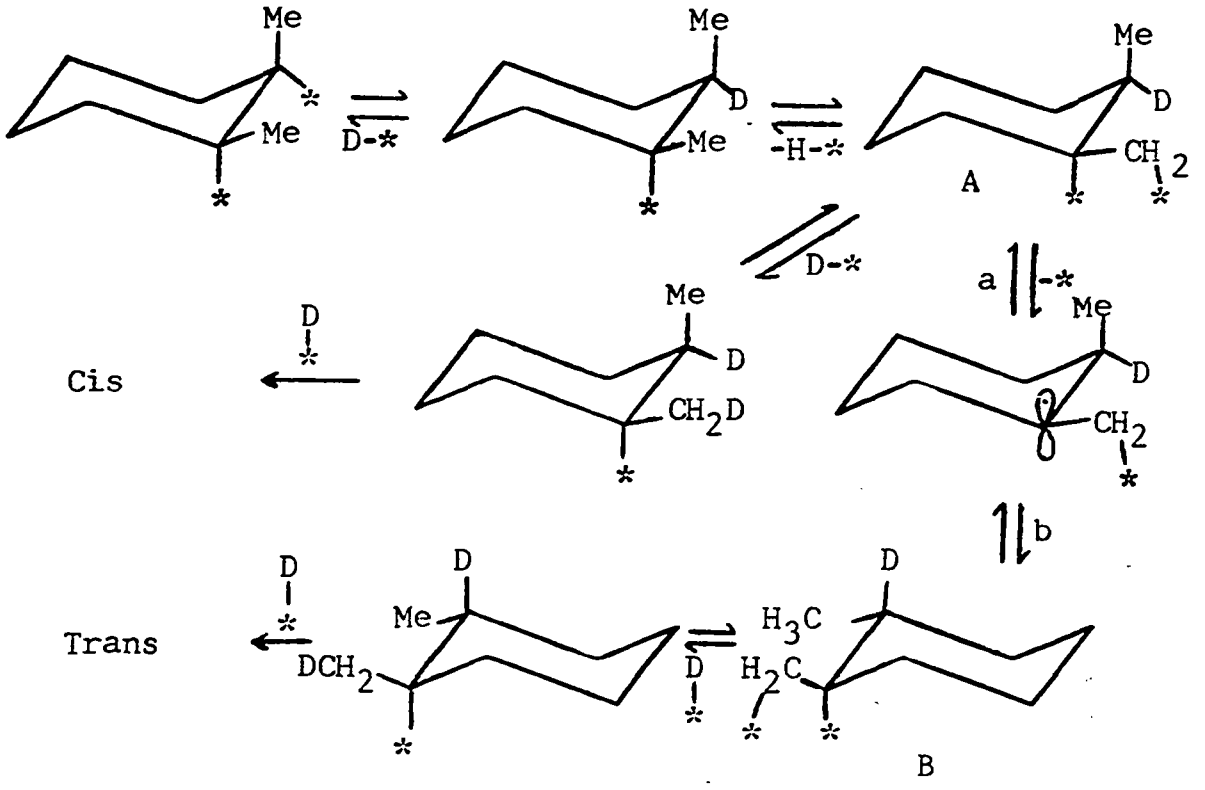
incorporation of deuterium due to the predominance of adsorbed deuterium atoms on the catalyst. Philipson and Burwell studied the reduction of cyclic olefins in the liquid phase using deuterium gas in acetic acid-$\underline{d}_1$ and a number of $\underline{d}_1$-alcohols (48). The use of acetic acid-$\underline{d}_1$ resulted in the most incorporation of deuterium through reduction and exchange; acetic acid-$\underline{d}_1$ exhibited the highest rate of exchange between solvent hydrogen atoms and adsorbed hydrogen atoms. The observations for the cycloalkenes and alkylbenzenes compliment one another and illustrate that acetic acid-$\underline{d}_1$ is an effective deuterating agent. Both studies illustrate that exchange accompanies hydrogenation over platinum. The extensive hydrogen-deuterium exchange observed over reduced platinum oxide precludes the use of this system for the synthesis of the $\underline{d}_6$ isomer and is directly contradictory to the results of Price and Beard (47).

Deuterium incorporation into monoalkylbenzenes

A possible mechanism for the epimerization of trans-1,2-dimethylcyclopentane in hydrogen-deuterium exchange experiments (1) and the lack of stereoselectivity in the hydrogenation of the xylenes and dimethylcyclohexenes involves the formation of an α-monoadsorbed radical or an α-monoadsorbed complex, a half-hydrogenated state.



An intermediate of this type, especially the radical type, could readsorb to the catalyst in two different manners (Scheme 14).



Scheme 14. Cis-trans isomerization during cycloalkene reduction

Scheme 14 depicts the hydrogenation of a cis-1,2-diadsorbed-1,2-dimethylcyclohexane followed by a reverse hydro-

genation step forming an α,1-diadsorbed complex, complex A. The subsequent formation of an α-monoadsorbed radical would provide a path for the conversion of the cis-α,1-diadsorbed complex to the trans-α,1-diadsorbed complex, complex B. Upon formation, the α-monoadsorbed radical could return to the catalyst in two ways; complexation with the catalyst via path a would simply be a reverse of the radical formation reforming the cis-complex. The return to the catalyst via path b would produce the trans-α,1-diadsorbed complex. The formation of the α-monoadsorbed complex provides a pathway by which the adsorption of the ring can be "flipped" from one side to the other. Such a flipping of the ring would allow the complete exchange of all of the ring hydrogens and would also account for methyl group exchange. Complete ring hydrogen-deuterium exchange would be achieved by exchange of all of the hydrogens trans to the methyl groups in the cis-complex, followed by a ring flip and the exchange of all of the hydrogens which had been cis to the methyl groups.

The series benzene, toluene, ethylbenzene, isopropylbenzene, and t-butylbenzene, was chosen to test the extent to which a "flipping" mechanism was operating in acetic acid-d_1. The results are shown in Tables 3 and 4. The number of deuterium atoms incorporated into the cyclohexane molecule and its alkyl derivatives is about 5.0; deuterium incorporation is approximately the same, even in those

molecules which could undergo a ring flip by the formation of the α-monoadsorbed complex. It is apparent that the flipping mechanism involving this type of complex is not important in acetic acid-$\underline{d}_1$.

Table 3. The number of deuterium atoms per mole of alkylcyclohexane produced with hydrogen and acetic acid-$\underline{d}_1$

Alkyl group	D/mole	
	mass spec	nmr
H	4.9	5.8
CH_3	5.3	6.2
C_2H_5	5.4	5.5
$\underline{i}$-C_3H_8	5.1	5.7
$\underline{t}$-C_4H_9	4.6	5.2

Table 4. Corrected normalized values of the deuterated species in the partial mass spectra of alkylcyclohexanes produced in acetic acid-$\underline{d}_1$ using hydrogen gas

Alkyl group	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Hydrogen	6.2	15.0	22.6	22.3	14.7	7.3	4.3
Methyl	3.9	10.2	18.5	22.1	18.1	12.0	7.5
Ethyl	3.3	9.4	18.4	23.4	20.2	12.6	6.4
Isopropyl	3.3	10.1	21.0	26.5	21.1	10.4	3.9
$\underline{t}$-Butyl	5.3	13.5	25.2	26.4	17.5	5.9	1.9

The distribution patterns of the deuterated isomers of cyclohexane and t-butylcyclohexane are slightly different from the pattern produced by the derivatives containing alpha hydrogen atoms (Table 4). The spectra of methyl-, ethyl-, and isopropylcyclohexane have the d_5 isomer as the most prominent peak while the spectra of cyclohexane and t-butylcyclohexane show the d_4 and d_5 isomers to be of nearly equal intensity and to be the most prominent peaks. Some difference in deuterium incorporation into the two sets of hydrocarbons is to be expected because the benzene and t-butylbenzene do not have alpha hydrogen atoms and cannot undergo alpha exchange, while the other alkylbenzenes may do so during their reduction. More deuterium incorporation is expected for the hydrocarbons which can exchange at the alpha position.

Perdeuterocyclohexane and perdeuteromethylcyclohexane are produced in small amounts indicating that the extent of total exchange is small. The nuclear magnetic resonance spectra of methyl-, ethyl-, or isopropylcyclohexane indicate that some deuterium is incorporated into the alkyl groups. The methyl signal of the three alkyl groups shows some splitting of a hydrogen atom by an alpha deuterium atom. The alpha deuterium splitting indicates that there is some tendency of the alkylbenzenes or their hydrogenated derivatives to complex at the alpha carbon. It is apparent that this

complexing is not required and does not lead to increased exchange in the molecule *via* the flipping mechanism.

The observation of deuterium in the methyl signal of ethyl- and isopropylcyclohexane indicates that deuterium is incorporated into a position beta to the ring. This beta exchange must result from an α-monoadsorbed complex which can in a reverse hydrogenation step form the α,1-diadsorbed complex or an α,β-diadsorbed complex. Reduction of the α,B-diadsorbed complex would result in incorporation of deuterium into the β position.

Deuterium is incorporated into positions alpha to the ring *via* alpha adsorption. Alpha adsorption does not lead to a ring flip and therefore, must occur prior to or during the early stages of the reduction. The hydrogen on a carbon alpha to the benzene nucleus is benzylic and may be more prone to exchange as a benzylic hydrogen than as a hydrogen on a carbon alpha to a cyclohexane ring. If alpha exchange occurred prior to reduction, deuterium incorporation would occur at the alpha carbon but would give no clues as to whether an alpha monoadsorbed complex formed during the reduction. The deuteration and hydrogen-deuterium exchange reactions of p-xylene over platinum films has been studied and the rate of methyl group exchange is about 4 times faster than deuteration (44). This report and the failure to observe a flipping mechanism lead to the conclusion that α-deuteration

occurs prior to the reduction of the aromatic nucleus.

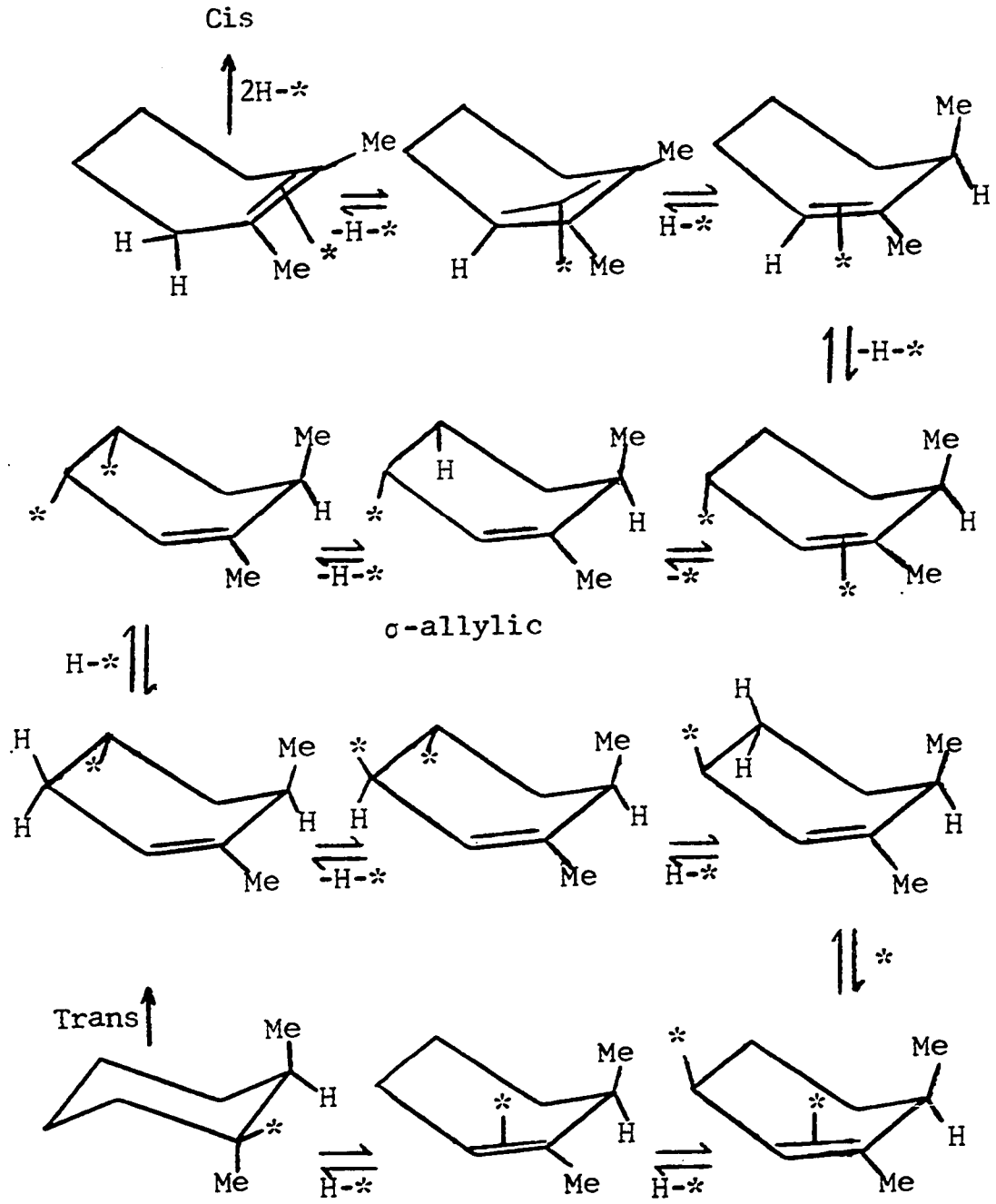
In summary, the results of the deuteration of the monoalkylbenzenes indicate that the formation of the perdeuterocyclohexane derivative and the average deuterium content of the cyclohexane derivatives does not require the formation of an α-monoadsorbed complex which could effect the ring flip illustrated in Scheme 14. Slight differences in the deuterated species distribution pattern are noted between the cyclohexane derivatives which have alpha hydrogen atoms and those which do not. Deuterium is incorporated into alpha positions via alpha adsorption but since the alpha adsorption does not lead to a ring flip, it is proposed that alpha deuteration occurs prior to reduction of the aromatic nucleus.

Deuterium incorporation into polyalkylbenzenes

Since the formation of an α-monoadsorbed complex did not explain the deuterium incorporation into the monoalkylbenzenes, an alternative explanation was sought to explain the extensive amount of exchange observed in these reductions. Such an explanation may involve the intermediate proposed to explain the lack of stereoselectivity in the reduction of the xylenes and dialkylcyclohexenes. The ring carbons may be involved in the process by which the adsorption of one side of the ring is transferred to the other side of the ring. The role played by the ring hydrogen and carbon could

involve the formation of the "dissociatively adsorbed olefin", Scheme 2, page 12 (19), or isomerization *via* a typical σ-1,2-diadsorbed complex proposed for the olefins with the subsequent desorption of an isomeric olefin, Scheme 3, page 14 (11). The role of the ring hydrogen and carbon may be to act as an allylic site forming either a σ-allylic (20) or π-allylic complex with the catalyst. The σ-allylic intermediate was postulated for the octalin system (20). A *trans*-diadsorbed alkene has also been proposed to explain the lack of stereoselectivity in the xylene reductions (21). By combining these two postulates, one may formulate an allylic mechanism which accounts for the lack of stereoselectivity in the xylene reductions. The allylic mechanism is illustrated in Scheme 15 using 1,2-dimethylcyclohexene as an example.

Isomerization to the adsorbed 2,3-dimethylcyclohexene occurs by the formation of a π-allylic intermediate. Adsorption at the new allylic site, in a reverse hydrogenation step, followed by desorption of the olefinic bond results in the formation of a σ-allylic complex. Alternation between mono- and diadsorbed complexes transfers the adsorption to other parts of the ring. Alternation between axial-equatorial diadsorbed complexes retains adsorption on one side of the ring. The formation of an equatorial-equatorial diadsorbed complex, a *trans*-diadsorbed complex, would convert



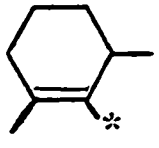
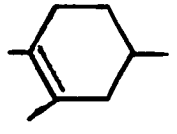
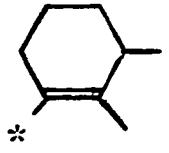
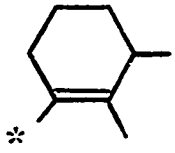
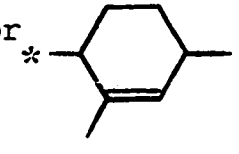
Scheme 15. The allylic-trans-diadsorbed complex mechanism

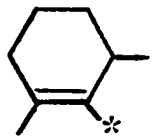
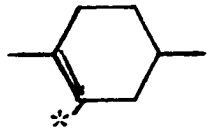
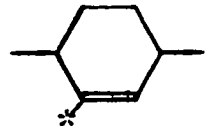
the adsorption from one side of the ring to the other and would result in hydrogen-deuterium exchange on both sides of the ring. The formation of the trans complex would also explain the lack of stereoselectivity in the xylene reductions.

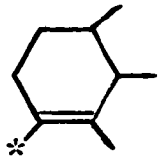
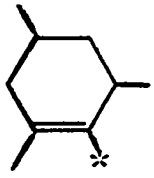
Three different mechanisms, formation of a dissociatively adsorbed olefin, isomerized olefin desorption, or allylic-trans-diadsorbed complex formation may be proposed to explain the lack of stereoselectivity in the xylene reductions and the deuterium incorporation into the monoalkylbenzenes. A relationship between deuterium incorporation and trans-dialkylcyclohexane formation has been postulated (44). The proportion of the trans compound should increase with the extent of ring exchange during deuteration.

The series of o-, m-, and p-xylene; tetralin; naphthalene; 1,4-di-t-butylbenzene; 1,2,3- and 1,3,5-trimethylbenzene; 1,3,5-triisopropyl and 1,3,5-tri-t-butylbenzene; and durene was chosen to determine the role played by the ring carbon in the course of the deuteration and hydrogen-deuterium exchange reactions. This series should also provide information concerning the possibility of exchange of ring hydrogens prior to reduction. Certain members of this series would be expected to differ in the extent to which hydrogen-deuterium exchange occurs on the ring because of the ortho deactivation effect discussed by Garnett and Sollich-

Baumgartner (30). A hydrogen ortho to a large alkyl group or ortho to two methyl groups should be less susceptible to exchange in the aromatic hydrocarbon. This decreased exchange tendency should be observable in the deuterium content of the saturated product.

The results of this series should provide a means for differentiating between the isomerization mechanism involving desorption and the mechanism involving the dissociatively adsorbed olefin. The deuterium incorporation into this series of hydrocarbons should also provide a means for differentiating between the allylic trans-diadsorbed complex mechanism and the dissociatively adsorbed olefin. The formation of the dissociatively adsorbed olefin should be influenced by the alkyl substitution pattern of the cycloalkene intermediate. Isomerization and dissociatively adsorbed olefin formation from an adsorbed 1,3-dimethylcyclohexene would produce two nonequivalent complexes,  and  , whereas, 1,2-dimethylcyclohexane would have two equivalent complexes of the structure  . The formation of complexes of the structure  or  would be more favorable over the

formation of  because of steric factors and one would expect to see more deuterium incorporated into the 1,2-dimethylcyclohexane because of the greater probability for formation of the dissociatively adsorbed olefin. The 1,4-dimethylcyclohexane would be expected to incorporate about the same amount of deuterium as the 1,2-dimethylcyclohexane because all intermediate structures would be of comparable energy, i.e.,  and  .

Another example of the influence of substitution on dissociatively adsorbed olefin formation would be expected from 1,2,3-trimethylcyclohexene and 1,3,5-trimethylcyclohexene. Intermediate structures are  and  . One would expect more deuterium incorporation into the 1,2,3-dimethylcyclohexane because of the more probable ease of formation of the dissociatively adsorbed olefinic complex.

The isomerization and desorption mechanism would be insensitive to the substitution pattern of the cycloalkene intermediates and a comparable extent of deuterium incorporation into the cyclohexane product would be expected for the various dialkylcyclohexenes. Allylic complex for-

mation should be slightly dependent upon the dialkyl-substitution pattern because the allylic intermediates possible for the 1,3-dialkyl isomer are not of comparable stability. The possible allylic intermediates are of comparable stability for the 1,2- and 1,4- isomers. A slightly smaller amount of deuterium should be incorporated into 1,3-dialkylcyclohexane than is observed for the other dialkyl isomers. If an allylic intermediate is involved, slightly more deuterium should be incorporated into the 1,2,3-trimethylcyclohexane than is observed for the 1,3,5-trimethyl isomer.

The deuterium incorporation into the polyalkylcyclohexanes is listed in Tables 5 and 6. The average number of deuterium atoms incorporated per molecule of dimethylcyclohexane, D/mole, is almost exactly the same for the three dimethylcyclohexanes. The number of deuterium atoms per mole incorporated into the two trimethylcyclohexanes is approximately the same, indicating that deuterium incorporation into the polyalkylcyclohexanes is not sensitive to the substitution pattern of the alkyl groups.

The distribution patterns of the deuterated isomers, $\underline{d}_n$, of 1,2- and 1,4-dimethylcyclohexane are very similar to one another; the pattern for the 1,3- isomer is slightly different. The deuterated species distribution patterns of the trimethylcyclohexanes show some differences; more

exchange is observed in the 1,3,5-trimethylcyclohexane. A comparison of the deuterium incorporation into 1,3,5-trimethylcyclohexane and 1,3,5-triisopropylcyclohexane indicates that the deuterium per mole value of the isopropyl compound is slightly less than in the methyl compound. This was also observed in the monoalkyl series. The deuterated

Table 5. The number of deuterium atoms per mole of polyalkylcyclohexane produced with deuterium and acetic acid-$\underline{d}_1$

Polyalkyl groups	D/mole	
	mass spec	nmr
1,2-Dimethyl	7.4	6.8
1,3-Dimethyl	7.5	8.6
1,4-Dimethyl	7.4	8.0
1,2-Tetramethylene	8.4	8.9
1,4-di-t-Butyl	4.7	6.8
1,2,3-Trimethyl	8.6	9.5
1,3,5-Trimethyl	9.0	10.7
1,3,5-Triisopropyl	8.4	6.6
1,2,4,5-Tetramethyl	9.7	10.6

species distribution, $\underline{d}_n$, indicates that more exchange has occurred in the isopropyl compound where the most intense peaks are $\underline{d}_8$ and $\underline{d}_9$; the methyl compound has the $\underline{d}_7$ and $\underline{d}_8$ peaks as the most intense.

The deuterium incorporation into the polyalkylcyclo-

hexanes is not sensitive to the substitution pattern of the alkyl groups. The incorporation of deuterium into the polyalkylcyclohexanes *via* a dissociatively adsorbed olefin should be sensitive to the alkyl group substitution pattern. Therefore, the dissociatively adsorbed olefin is not the intermediate in the deuteration and hydrogen-deuterium exchange reactions of the polyalkylbenzenes or their cyclohexane derivatives in acetic acid-$\underline{d}_1$. The olefin desorption mechanism

Table 6. Corrected normalized values of the deuterated species in the partial mass spectra of polyalkylcyclohexanes produced in acetic acid-$\underline{d}_1$ using deuterium gas

Polyalkyl group	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}
1,2-Dimethyl	2.4	7.8	15.1	17.1	14.0	12.2	10.5	8.0	6.0
1,3-Dimethyl	2.5	6.7	12.4	15.2	14.6	13.6	12.0	9.4	6.9
1,4-Dimethyl	2.4	7.4	14.6	17.2	14.0	12.3	10.4	8.2	6.5
1,2-Tetramethylene	0.4	1.6	3.8	7.4	13.2	20.6	23.4	17.3	7.9
1,4-di-t-Butyl	14.4	22.0	25.4	15.7	11.4	2.3	0.6	0.3	0.1
1,2,3-Trimethyl	1.4	4.0	8.2	11.4	11.8	12.6	12.4	11.4	9.8
1,3,5-Trimethyl	0.7	2.8	6.6	11.2	13.2	13.4	12.0	9.5	9.0
1,3,5-Triisopropyl	1.5	1.5	2.3	7.6	11.6	16.1	16.2	12.3	8.9
1,2,4,5-Tetramethyl	0.6	2.4	5.8	9.2	10.4	11.8	11.8	11.0	8.2

and the mechanism involving the allylic intermediates are basically insensitive to the alkyl group substitution pattern. The desorption mechanism and the allylic mechanism predict that the incorporation of deuterium into the various isomers would be essentially the same. Thus, the results listed in Tables 5 and 6 for the dimethyl- and trimethylcyclohexanes do not allow one to distinguish between the two mechanisms.

The basic difference between the desorption mechanism and the σ-allylic mechanism is that the σ-allylic mechanism does not involve desorption from the catalytic surface; the intermediates in the σ-allylic-complex mechanism are always complexed to the catalyst. The presence of isomerized cyclohexenes in the reaction mixture is explained in the σ-allylic mechanism by proposing that in the alternation around the ring, there is a possibility that a monoadsorbed cyclohexene would be hydrogenated at the point of attachment producing the desorbed cyclohexene. Since only 0.002 mole percent of isomerized olefin has been isolated, the intermediacy of this olefin in the main reaction path has not been definitely established; the reduction of an isomerized monoadsorbed cyclohexene is a definite possibility. To explain the amount of the trans isomer in 1,3- and 1,4-dimethylcyclohexane approximately 14% and 25% of olefin must desorb from the catalytic surface (2). The deuteration and

exchange reactions of benzene over platinum indicate that only 1% of the benzene which is reduced leaves the surface as a cyclohexene intermediate (55). Hartog and Zwietering suggest that only about 10% of o-xylene reduced on other metals leaves the surface as a cyclohexene intermediate (17).

An analysis of the steps involved in the desorption mechanism indicates the amount of deuterium incorporated into the cis isomer should be less than the deuterium incorporated into the trans isomer. Cis formation can occur *via* the hydrogenation of the half-hydrogenated state. The trans isomer is formed *via* isomerization, desorption, readsorption, and reduction. Hydrogen-deuterium exchange on one side of the ring should occur in the adsorbed intermediate which leads to the *cis*-cyclohexane derivative and to the isomerized desorbed olefin. Readsorption to the intermediate which leads to the *trans*-dialkylcyclohexane opens a route for hydrogen-deuterium exchange on the other side of the ring.

The allylic mechanism accounts for the formation of the *cis*- and *trans*-dialkylcyclohexanes during one period of residence on the catalytic surface. A common intermediate is involved in cis and trans product formation and the deuterium incorporation into the cis and trans isomers should be nearly the same if the hydrogenation proceeds *via* the allylic mechanism.

The deuteration of m- and p-xylene and the isolation of the pure cis isomer was carried out to determine the relative importance of the desorption and σ-allylic mechanisms. The results of the study are listed in Tables 7 and 8 and the percentage of the cis-dialkylcyclohexane produced from the three xylenes is shown in Table 9.

Table 7. The number of deuterium atoms per mole of cis- and cis- and trans-dimethylcyclohexane produced with deuterium gas and acetic acid-d_1

Dimethyl groups	D/mole
Cis- and trans-1,3-	7.4
Cis-1,3-	7.3
Cis- and trans-1,4-	7.6
Cis-1,4-	7.5

Table 8. Corrected normalized values of the deuterated species in the partial mass spectra of the cis- and cis- and trans-dimethylcyclohexanes produced in acetic acid-d_1 using deuterium gas

Dimethyl groups	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}
Cis- and trans-1,3-	6.7	12.4	15.2	14.6	13.6	12.0	9.4	6.9
Cis-1,3-	7.5	13.5	16.4	14.9	13.7	11.5	9.0	6.0
Cis- and trans-1,4-	7.4	14.6	17.2	14.0	12.3	10.4	8.2	6.5
Cis-1,4-	7.0	13.8	16.6	13.4	12.8	11.6	8.9	7.4

Table 9. The percentage of cis-dialkylcyclohexane produced from dimethylbenzene

Dimethyl group	% Cis
1,2-	90.4
1,3-	76.8
1,4-	73.8

The average amount of deuterium per mole incorporated into the pure cis-1,3- and 1,4-dimethylcyclohexane is not significantly different from the deuterium incorporated into the mixture of cis and trans products. The distribution pattern of the deuterated species of the cis isomer is very similar to the pattern of the cis-trans mixture. Thus, the cis and trans isomers incorporate approximately the same amount of deuterium indicating that a common intermediate is involved in their formation. This observation is consistent with the allylic mechanism and indicates that the allylic mechanism probably best describes the cis-trans isomerization and the deuterium incorporation into the dialkylcyclohexanes. The desorption mechanism is not disproven by these observations but the observations do favor the allylic mechanism.

Support for allylic complex formation and its importance in the reduction of the dialkylcyclohexenes and the xylenes comes from the work of Yamamoto and coworkers (28). The observations of Smith and Swoap indicate that π-allylic

complex formation occurs in the deuteration of cyclohexene over reduced platinum oxide (56). Hydrogen-deuterium exchange occurs at both the allylic and olefinic positions. These observations are not explained by mono- or diadsorbed complexes but can be explained by postulating a π-allylic intermediate.

Aromatic exchange prior to hydrogenation

It was noted earlier that the study of the incorporation of deuterium into the polyalkylbenzenes should provide information concerning the exchange of aromatic hydrogens prior to reduction. Certain compounds in this series should illustrate the ortho deactivation effect if aromatic exchange is important. The results listed in Tables 5 and 6 do not allow the direct comparison of the deuterium incorporation values except for the three dialkyl- and two trialkylcyclohexanes. The ortho deactivation effect predicts that the amount of aromatic exchange in m-xylene would be less than in o- or p-xylene. The hydrogen-deuterium exchange in 1,3,5-trimethylbenzene should be much less than for the 1,2,3-trimethyl derivative. The ortho deactivation effect is not observed and aromatic exchange prior to reduction is not important because the deuterium incorporation into the three dimethylcyclohexanes is almost exactly the same and the deuterium incorporation into the two trimethylcyclohexanes is approximately the same. Comparison of the other compounds

can be made by dividing the deuterium per mole values of the cyclohexane products by the number of exchangeable hydrogens in the cyclohexane product. From this one obtains the average number of deuterium atoms incorporated per exchangeable hydrogen. Comparisons are made between these values, Table 10.

Table 10. The average number of deuterium atoms incorporated per exchangeable hydrogen atom in the alkylcyclohexanes produced with deuterium and acetic acid-$\underline{d}_1$

Alkyl group	Av D/H
Methyl	0.46
1,4-Dimethyl	0.46
1,3,5-Trimethyl	0.50
1,2,4,5-Tetramethyl	0.49
t-Butyl	0.52
1,4-di-t-Butyl	0.47
i-Propyl	0.35
1,3,5-Trisopropyl	0.28
1,2-Tetramethylene	0.47

Comparisons of the methyl-, polymethylcyclohexanes and decalin indicates that about 0.5 deuterium atom is incorporated per hydrogen atom irrespective of the number of alkyl groups or their substitution pattern. Comparison of t-butylcyclohexane with 1,4-di-t-butylcyclohexane leads to the same conclusion

as does a comparison between 1,4-dimethyl- and 1,4-di-t-butylcyclohexane. Since comparable deuterium incorporation per hydrogen values are observed, exchange of aromatic hydrogens does not occur prior to reduction. A comparison of the two isopropyl derivatives is consistent with this conclusion but a comparison of the methyl- and isopropylcyclohexane values indicates that the isopropyl group is hindering aromatic exchange because of the low deuterium per hydrogen value. It is felt that this low value is a result of the inclusion of the six β methyl hydrogens as exchangeable hydrogens. Probably not all of these hydrogens are subject to exchange during one period of residence on the catalytic surface.

The conclusion that aromatic hydrogen exchange does not occur prior to reduction to any important extent was based upon a calculation. To be sure of this conclusion, benzene, toluene, and p-xylene were half-hydrogenated, the products and starting materials separated by gas chromotagraphy, and analyzed for deuterium incorporation by mass spectroscopy, Table 11. Benzene did not incorporate enough deuterium to explain the distribution pattern of the cyclohexane deuterated species. This was also true for toluene and p-xylene, thus, aromatic hydrogen-deuterium exchange prior to reduction is not an important process and cannot explain the deuterium incorporation into cyclo-

hexane and its derivatives.

Table 11. The corrected normalized values of the deuterated species in the mass spectra and the number of deuterium atoms per mole of hydrocarbon produced in acetic acid-$\underline{d}_1$

	D/mole	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7
Benzene[a]	0.3	83.2	10.9	2.9	1.4	0.9	0.7		
Cyclo-hexane[a]	4.5	0.3	1.8	7.2	17.2	26.2	24.5	12.7	4.8
Cyclo-hexane[b]	1.9	18.6	31.2	24.2	11.1	7.3	4.0	2.2	1.0
Toluene[a]	0.6	64.3	20.7	9.1	4.8	0.9	0.2		
Methyl-cyclohexane[a]	5.7	0.0	0.5	1.9	7.0	16.3	23.7	22.6	14.0
p-Xylene[a]	0.8	69.2	12.2	5.2	4.2	2.6	3.0	3.4	0.2
1,4-Di-methylcyclohexane[a]	6.2	0.0	0.2	1.1	4.8	13.1	22.9	21.3	12.8

[a]Half-hydrogenation.

[b]From cyclohexene.

It has been proposed that hydrogen-deuterium exchange occurs on the ring *via* a cyclohexene intermediate and its allylic analogue or *via* desorption-readsorption. To determine that cyclohexene could undergo exchange during its reduction in acetic acid-$\underline{d}_1$, the compound was hydrogenated in acetic acid-$\underline{d}_1$ and the mass spectrum of the cyclohexane was compared to the cyclohexane produced by the reduction

of benzene, Table 11. Much exchange is noted in the cyclohexene reduction product; thus, the premise that ring exchange occurs *via* the cyclohexene intermediate is valid.

The observation that aromatic exchange is not an important process is consistent with the observations of Kemball and coworkers (31, 44). The deuteration of benzene over metal films involved the addition of deuterium with very little exchange (31). The rate of ring exchange was about two-thirds the rate of hydrogenation for *p*-xylene (44). In the deuteration of benzene over supported platinum catalysts in the vapor phase, the reduction of the benzene nucleus was found to proceed faster than the exchange of the aromatic hydrogens (55).

The exchange reactions of aromatic hydrocarbons are generally carried out over metal films in the gaseous phase and, therefore, the relationship of the theories developed for this system to the liquid phase in an acetic acid-d_1 solvent is not known. Smith and Burwell have observed the same overall pattern in the deuteration of olefins in either the vapor or liquid phases (20). The experiments performed on *p*-xylene by Harper and Kemball provides a basis for comparison of metal films and the vapor phase with reduced platinum oxide in acetic acid-d_1 (44). The mass spectrum obtained on recovered *p*-xylene after 10% of the material had reacted gave a deuterium per mole value of 1.92. The

deuterium per mole value of the 1,4-dimethylcyclohexane was 7.4. The liquid phase reaction resulted in the incorporation of 0.8 deuterium atoms per mole in the p-xylene recovered after ca. 50% of the material had reacted; the cyclohexane derivative also incorporated 7.4 deuterium atoms per mole in the liquid phase. Thus, some hydrogen-deuterium exchange is occurring in the aromatic hydrocarbon in the liquid phase, but not to the extent as is observed over metal films in the vapor phase. This exchange is probably occurring at the alpha positions for the most part as was observed in the vapor phase. Therefore, the theories presented in the discussion of aromatic exchange in the literature review apply to the acetic acid-d_1 system but not to as great an extent as do the theories postulated for olefinic exchange and the lack of stereoselectivity in the reduction of the cyclohexene intermediates.

Deuterium incorporation into methyl cyclohexanecarboxylate

The results of the hydrogenation or deuteration of the mono- and polyalkylbenzenes in acetic acid-d_1 is accompanied by an extensive amount of exchange; the formation of small amounts of the perdeutero species is observed in the deuterations of some alkylbenzenes. These results, while consistent with the results obtained in the vapor phase over metal films (31, 44, 55) are contradictory to the results of Price and Beard (47). The reduction of methyl benzoate-d_5

in acetic acid was accompanied by about 3% hydrogen-deuterium exchange over platinum on alumina, 15% exchange over reduced platinum oxide and 5% exchange over rhodium on alumina. Deuteration of the ester over rhodium on alumina in acetic acid-$\underline{d}_1$ resulted in only 2% exchange (47). Since the results were contradictory, methyl benzoate was reduced over reduced platinum oxide using hydrogen and deuterium gas and 5% rhodium on alumina in acetic acid-$\underline{d}_1$ using deuterium gas. The results of the reductions are listed in Tables 12 and 13.

Table 12. The number of deuterium atoms per mole of monosubstituted cyclohexane produced in acetic acid-$\underline{d}_1$

Group	Gas	Catalyst	D/mole
$\underline{t}$-Butyl	H_2	Pt	4.6
$\underline{t}$-Butyl	D_2	Pt	5.7
Carbomethoxy	H_2	Pt	3.7
Carbomethoxy	D_2	Pt	4.5
Carbomethoxy	D_2	Rh/Al_2O_3	5.3

The results for $\underline{t}$-butylcyclohexane are included for reference to the alkylbenzene reductions. The deuterium per mole values indicate that the use of deuterium gas in place of hydrogen gas results in the incorporation of about one more deuterium atom per mole of the methyl cyclohexane-

carboxylate. The distribution pattern of the deuterated species, $\underline{d}_n$, has shifted by one unit when the pattern obtained for the saturated ester produced by use of deuterium is compared to the pattern of the ester produced with hydrogen gas. These results are the same as was observed for the alkylbenzene reductions. The use of rhodium on alumina also resulted in randomization of the deuterium through exchange. More deuterium was incorporated into the saturated ester upon use of the supported rhodium but the deuterium incorporation observed is not at all similar to that previously reported (47). Price and Beard observed the dominant peak in the mass spectrum of methyl cyclohexanecarboxylate to be the $\underline{d}_6$ species when 5% rhodium on alumina was used as the catalyst. The results are contradictory.

Table 13. Corrected normalized value of the deuterated species produced by the reduction of a monosubstituted benzene in acetic acid-$\underline{d}_1$

Group	Gas	Catalyst	d_2	d_3	d_4	d_5	d_6	d_7
t-Butyl	H_2	Pt	5.3	13.5	25.2	26.4	17.5	5.9
t-Butyl	D_2	Pt	1.3	3.4	11.6	26.7	31.2	16.1
Carbomethoxy	H_2	Pt	14.3	23.8	25.4	27.6	8.0	2.8
Carbomethoxy	D_2	Pt	6.7	16.2	24.6	24.8	15.1	6.6
Carbomethoxy	D_2	Rh/Al_2O_3	1.4	6.1	17.1	30.0	26.0	10.7

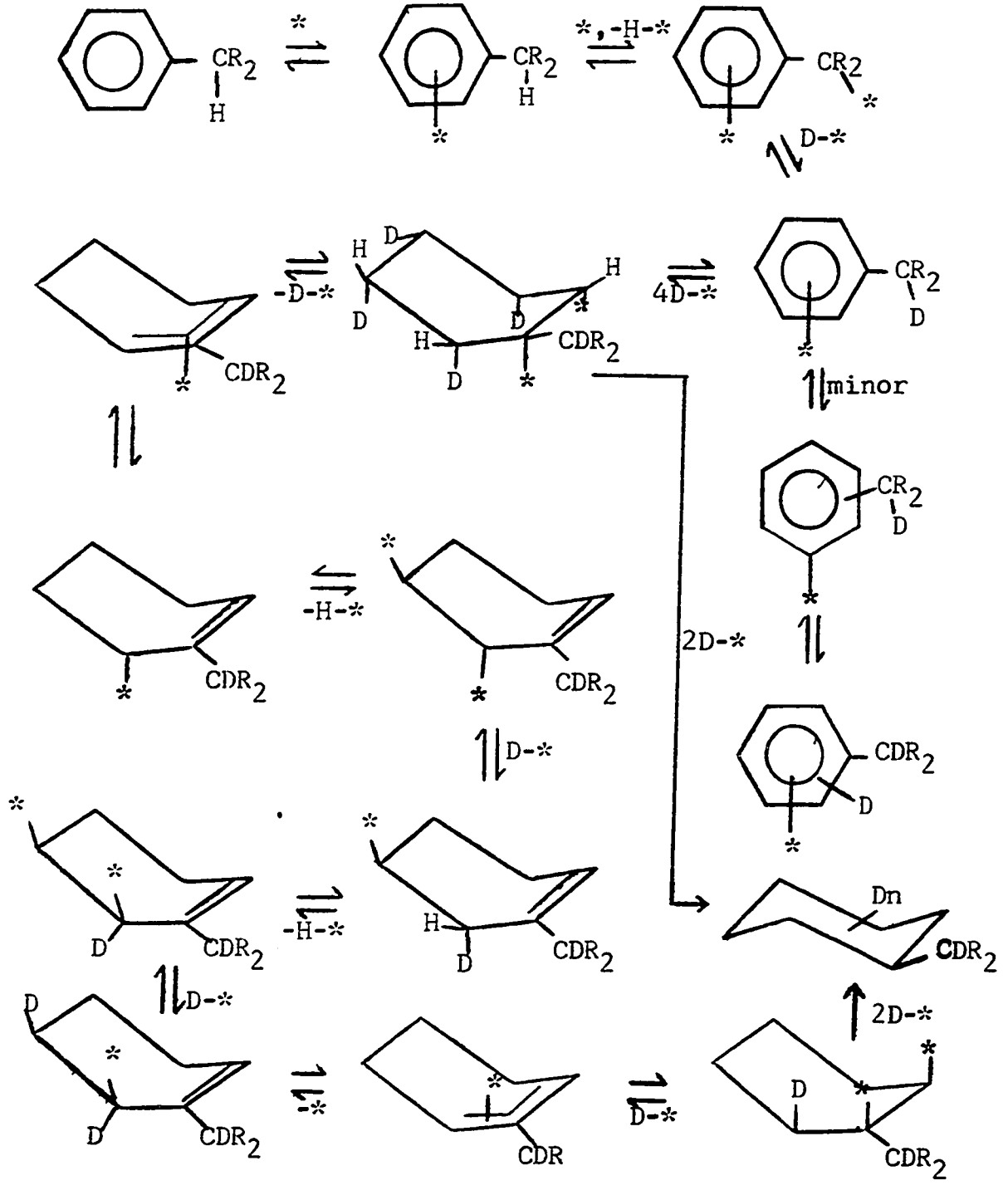
Price and Beard published the nmr spectrum of methyl cyclohexanecarboxylate-$\underline{d}_6$. The cyclohexyl hydrogens gave two broad peaks at δ 1.3 and 1.7 which integrate for 4.6 hydrogens relative to the methoxy group. The nmr spectrum of the methyl cyclohexanecarboxylate produced by use of deuterium and reduced platinum oxide was measured. The cyclohexyl hydrogens gave two broad peaks at δ 1.33 and 1.75 and integrated relative to the methoxy group for 6.4 hydrogen atoms. The two spectra are very similar, indicating that each reduction has produced methyl cyclohexanecarboxylate but the extent of deuterium incorporation is very different.

The results listed in Table 13 are consistent with the results of the deuteration of the mono- and polyalkylbenzenes, which are consistent with the vapor phase reactions. This consistency would be predicted from the observations of Smith and Burwell (20). This consistency leads one to conclude that extensive hydrogen-deuterium exchange accompanies the reduction of methyl benzoate over platinum and rhodium catalysts.

Mechanism for the deuteration of mono- and polyalkylbenzenes

From the results of this study involving the deuteration of mono- and polyalkylbenzenes in acetic acid-$\underline{d}_1$ and the other studies cited in the literature, it is proposed that the incorporation of deuterium into the cyclo-

hexane product results *via* the following process (Scheme 16). The benzene nucleus forms a π-complex with the catalyst. While π-complexed on the catalytic surface, hydrogen-deuterium exchange at carbons alpha to the ring occurs *via* the formation of a diadsorbed complex involving both π-complexation and σ-complexation at the α-carbon. Exchange of the aromatic ring hydrogens may occur *via* the dissociative π-complex substitution mechanism but only to a minor extent. Four deuterium atoms are added to the benzene nucleus producing an adsorbed cyclohexene intermediate which undergoes hydrogen-deuterium exchange *via* alternation between mono- and diadsorbed complexes formed from an allylic complex. Formation of a *trans*-diadsorbed complex allows for exchange on both sides of the ring with the formation of the perdeutero isomer in measurable amounts. Trans complex formation also accounts for the formation of *trans*-cyclohexane products where cis-trans isomerism is possible. All of these steps are reversible, thereby allowing for the formation of a perdeutero isomer of cis stereochemistry. The exchange process ultimately leads back to a diadsorbed olefin which is subsequently reduced to the cyclohexane product.



Scheme 16. The deuteration mechanism of mono- and polyalkylbenzenes

EXPERIMENTAL

Equipment

Nuclear magnetic resonance (nmr) spectra were measured on a Varian A-60 spectrometer. Gas liquid partition chromatography (glpc) separations were performed on a Varian Aerograph Model 200 instrument fitted with dual thermal conductivity detectors. Two columns were used. One as a 6' by ¼" column packed with 15% SE-30 on Chromosorb W. The second column was a 6' by ¼" column packed with 10% QF-1 on Chromosorb P.

The mass spectra of the cyclohexane derivatives were measured on an Atlas CH4 spectrometer with an electron energy of 20 ev. The peak intensities were corrected for natural isotope abundances after the method of Trahanovsky and coworkers (57). These corrections were performed at the Iowa State University computer center using a program written by W. S. Trahanovsky. The program written in Fortran IV is detailed below.

```
C      N = NUMBER OF HYDROGENS PLUS ONE
C      AONE = FRACTION OF P ADDED TO P + 1
C      ATWO = FRACTION OF P ADDED TO P + 2
       DIMENSION A(20),B(20),BNOR(20),BSUM(20),NUM(20),TITLE(20)
     5 READ (1,10, END=100)TITLE,N, AONE, ATWO, (A(I),I=1,N
    10 FORMAT (20A4/I10,2F10.5/(8F10.1))
       B(1)=A(1)
       B(2)=A(2)-AONE*B(1)
       DO 20 J=3,N
    20 B(J) = A(J)-AONE*B(J-1)-ATWO*B(J-2)
       SUM =0.0
       DO 30 K = 1,N
```

```
 30 SUM = SUM + B(K)
    DO 40 L = 1,N
 40 BNOR(L) = B(L)*100./SUM
    BSUM(1) =BNOR(1)
    DO 50 M = 2,N
 50 BSUM(M) = BSUM(M-1) + BNOR(M)
    DEUT =0.0
    DO 60 I = 1,N
    AI =I
 60 DEUT = DEUT + BNOR(I)*(AI-1.0)*0.01
    DO 65 I =1,N
 65 NUM(I)=I-1
    WRITE(3,67) TITLE
 67 FORMAT('1',20A4)
    WRITE (3,70)
 70 FORMAT('ODEUTERATED  RAW   CORRECTED NORMALIZED PERCENT
         '/'  SPECIE
   1S   DATA       DATA       DATA       SUM')
    WRITE (3,80) (NUM(I),A(I),B(I),BNOR(I),BSUM(I),I=1,N)
 80 FORMAT (I6,2F10.1,2F10.2,'%')
    WRITE (3,90) DEUT
 90 FORMAT ('ONUMBER OF DEUTERIUMS = 'F5.2)
    WRITE (3,95) N, AONE, ATWO
 95 FORMAT ('ON = 'I2'   AONE = 'F7.5'   ATWO = 'F7.5)
    GO TO 5
100 STOP
    END
```

Hydrogenation apparatus

All hydrogenations were carried out using an atmospheric pressure hydrogenation apparatus which consists of three gas burets, capacities of 10 ml, 50 ml, and 100 ml, connected to a U-tube manometer, and a removable 50 ml erlenmeyer flask fitted with an addition side-arm. The burets are also connected to an external leveling bulb. One arm of the manometer is open to the atmosphere.

Materials

The hydrocarbons used in the hydrogenations are commerically available and were used without further purification, with the exception of tetralin which was fractionally distilled and naphthalene which was recrystallized. The purity of the hydrocarbons was established by nuclear magnetic resonance.

The deuterium gas (99.65 atom %) used in the hydrogenations was obtained from Bio-Rad Laboratories, Richmond, California.

The deuterium per mole values determined by nuclear magnetic resonance were calculated from the intensity of the nmr signal of naphthalene, an internal standard.

All numerical values reported in data tables have been averaged.

Boron triacetate

Boron triacetate was prepared after the method of Cook and coworkers (58) using 20 g (0.3 mole) of boric acid and 120 g (1.2 mole) of acetic anhydride. A yield of 52 g (94%) of white crystals was obtained: mp 146-148°, lit (58) mp 124°.

Acetic acid-d_1

A mixture of 32 g (2.6 mole) of deuterium oxide and 153 g (1.5 mole) of acetic anhydride was refluxed in a 250 ml

round-bottomed flask. The course of the reaction was followed by periodically obtaining the nuclear magnetic resonance spectrum of the solution. When the acetic anhydride peak had disappeared (ca. 2 hours), 54 g (0.3 mole) of boron triacetate was added to the mixture after cooling to ca. 30°. The mixture was then distilled, 197 g of acetic acid-d_1, boiling between 114-115.8° was collected (104% yield). The nuclear magnetic resonance spectrum of acetic acid-d_1 indicated the presence of 1.3% of acetic acid.

Hydrogenation procedure

Three milliliters of acetic acid and 0.020 g of platinum oxide were added to a side-armed flask connected to a hydrogenation apparatus. The system was flushed with hydrogen, filled with hydrogen at atmospheric pressure, and the catalyst prereduced. About 1 millimole of the hydrocarbon and 2 ml of acetic acid were added to the flask through the side-arm and the mixture stirred mechanically. Periodically, the pressure of the hydrogen was adjusted to atmospheric pressure. When the hydrogenation was completed, the solution was decanted from the catalyst, 10 ml of ethyl ether and 10 ml of water were added to the solution and the water layer drawn off. The etheral layer was treated with two 10 ml-portions of saturated sodium chloride solution, two 10 ml-portions of saturated sodium hydrogen carbonate solu-

tion and dried over anhydrous magnesium sulfate. The ether was partially removed by distillation through a 30 cm vacuum jacketed fractionating column. The residue was separated using a SE-30 glpc column and the product collected.

About two millimoles of benzene, toluene, and p-xylene were subjected to a half-hydrogenation and the half-hydrogenation products were separated on a QF-1 glpc column and the products collected.

One deuteration of methyl benzoate was carried out using the general procedure but catalyzed by 0.020 g of 5% rhodium on alumina.

The compounds used in the study of the hydrogenation of aromatic hydrocarbons in acetic acid-$\underline{d}_1$ are listed in Table 14.

The results for the hydrogenation of ethylbenzene are included to provide an example of the steps involved in product isolation and the spectral measurements carried out on the ethylcyclohexane. After concentrating the etheral solution of ethylcyclohexane, 0.2 ml of the ether solution was injected into the gas chromatograph and the ethylcyclohexane collected in a collection tube cooled by a dry ice-acetone bath. The procedure was repeated until about seventy milligrams of product was collected. Approximately twenty milligrams of product were submitted for mass spectral

Table 14. Hydrocarbons hydrogenated in acetic acid-$\underline{d}_1$

Compound	No. of hydrogenations	time range min.
Benzene	14	40-123
Toluene	11	53-107
Ethylbenzene	7	58-210
Isopropylbenzene	7	71-163
t-Butylbenzene	7	120-261
p-Xylene	5	70-240
m-Xylene	3	92-162
o-Xylene	3	185-495
Mesitylene	11	50-291
Naphthalene	2	no reaction
Tetralin	4	139-600
1,2,3-Trimethylbenzene	4	542-1420
p-di-t-Butylbenzene	4	110-210
1,3,5-tri-t-Butylbenzene	2	no reaction
1,3,5-Triisopropylbenzene	2	470-1700
Durene	2	480-1350
Cyclohexene	1	13
Methyl benzoate	2	111-161
Methyl benzoate over Rh/Al_2O_3	1	254

analysis. Peak heights were measured by use of a caliper and the peak heights were set relative to the base peak in the molecular ion. The peak heights set relative to the base peaks, were key punched onto IBM cards and are called the raw data heights. The raw data and values of the natural isotope abundance that the parent ion adds to the parent plus one and parent plus two peaks, key punched onto cards, were submitted with the program to the computer center. The computer print out supplied corrected data (peak heights corrected for natural isotope abundance), normalized data, the percent sum (sum of the normalized data) and the number of deuterium atoms per mole. (Table 15)

Table 15. Mass spectral data for ethylcyclohexane

M/e	peak ht.	rel to base raw data	corrected data	normalized data	percent sum
112	4.5	2.6	2.6	0.64	0.64
113	6.9	4.0	3.8	0.93	1.56
114	24.5	14.2	13.9	3.40	4.97
115	70.0	40.6	39.4	9.66	14.63
116	131.7	76.4	72.8	17.89	32.52
117	172.4	100.0	93.4	22.93	55.44
118	154.5	89.6	81.0	19.89	75.34
119	102.0	59.2	51.6	12.68	88.01
120	53.8	31.2	26.3	6.45	94.47
121	25.0	14.5	12.0	2.94	97.40
122	11.9	6.9	5.7	1.41	98.81
123	5.6	3.2	2.6	0.65	99.46
124	2.8	1.6	1.3	0.33	99.79
125	1.7	1.0	0.9	0.21	100.00

Number of deuteriums = 5.37

The nmr sample was prepared by first determining the mass of an empty nmr tube, followed by the addition of 0.0237 g (1.85 mmole) of naphthalene and 0.0300 g (2.67 mmoles) of collected ethylcyclohexane. The sample was dissolved in carbon tetrachloride and the spectrum recorded. The deuterium per mole value was calculated from the integral of the naphthalene resonance and the integral of the ethylcyclohexane resonance. The naphthalene integral was 95.8 units or 11.9 units per hydrogen. The ethylcyclohexane integral was 178.3 units. The integral of the ethylcyclohexane was calculated from the naphthalene integral after this formula:

$$\text{number of hydrogens} \times \frac{\text{naphthalene integral}}{\text{naphthalene hydrogens}} \times \frac{\text{mole hydrocarbon}}{\text{mole naphthalene}}$$

i.e.,

$$\text{integral} = 16 \times 11.9 \times \frac{2.67}{1.85} = 275 \text{ units or } \frac{17.2 \text{ units}}{\text{hydrogen}}$$

The deuterium per mole value is calculated after this formula:

$$\frac{\text{calculated integral - observed integral}}{\frac{\text{integral units of hydrocarbon calculated}}{\text{hydrogen}}}$$

i.e.,

$$\text{D/mole} = \frac{275 - 178.3}{17.2} = 5.6$$

The nmr spectrum of ethylcyclohexane is shown in Figure 1. The corrected deuterated species distributions of the cyclohexane derivatives are listed in Table 16 and the sources of the compounds used are listed in Table 17.

Figure 1. The nmr spectrum of ethylcyclohexane and naphthalene in carbon tetrachloride

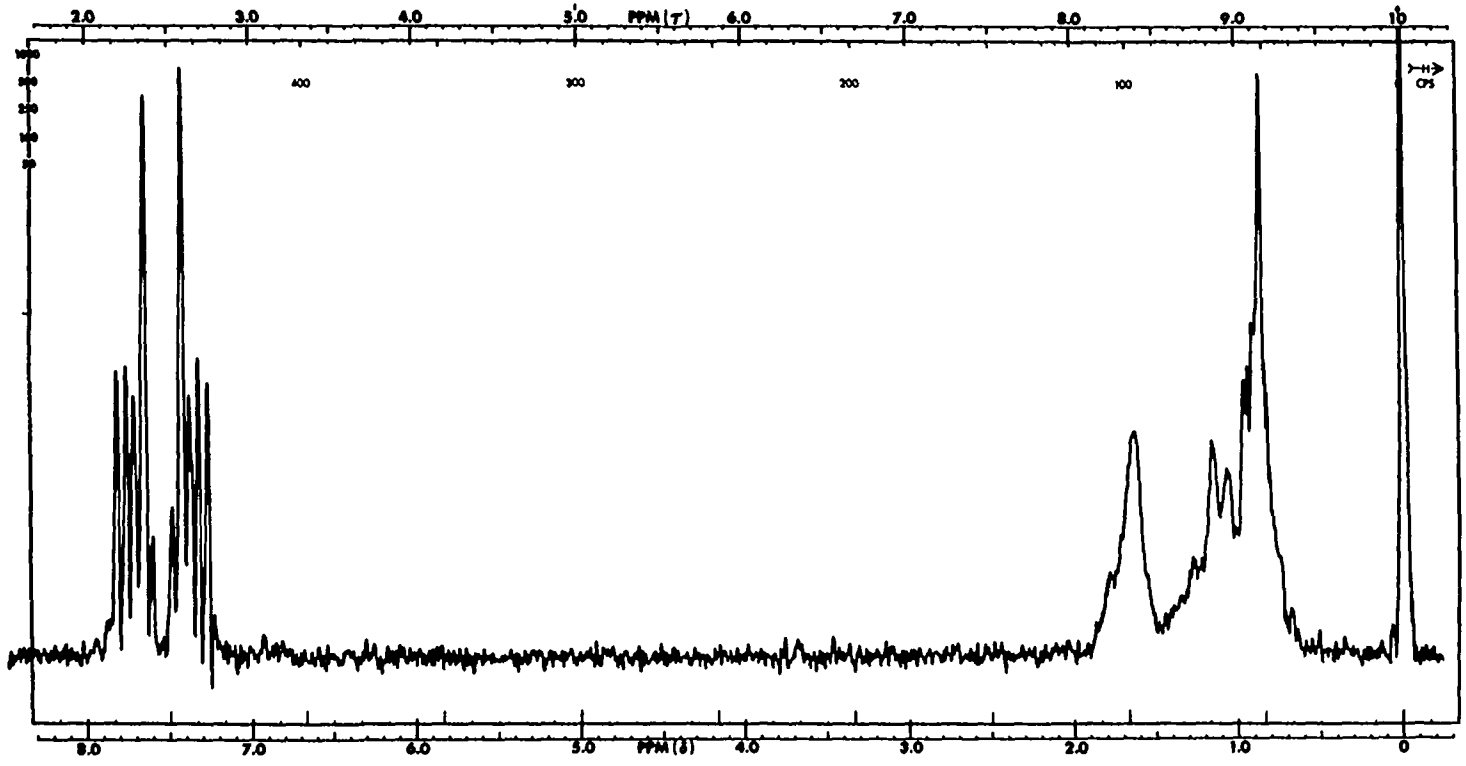

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
1 H
CPS
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Table 16. Corrected normalized values of the deuterated species in the mass spectra of cyclohexane derivatives produced in acetic acid-$\underline{d}_1$

Cyclohexane	Gas	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
	H_2	0.4	1.8	6.2	15.0	22.6	22.3	14.7	7.3	4.3
Methyl	H_2	0.1	1.1	3.9	10.2	18.5	22.1	18.1	12.0	7.5
	D_2	0.1	0.1	0.7	3.3	10.0	19.2	21.8	16.0	12.7
Ethyl	H_2	0.6	0.7	3.3	9.4	18.4	23.4	20.2	12.6	6.4
Isopropyl	H_2	0.2	0.8	3.3	10.1	21.0	26.5	21.1	10.4	3.9
	D_2	0.0	0.0	0.5	2.3	8.6	19.6	27.4	22.0	11.4
<u>t</u>-Butyl	H_2	1.4	1.6	5.3	13.5	25.2	26.4	17.5	5.9	1.9
	D_2	0.6	0.5	1.3	3.4	11.6	26.7	31.2	16.1	6.0
1,2-Dimethyl	D_2	0.0	0.0	0.6	2.4	7.8	15.1	17.1	14.0	12.2
1,3-Dimethyl	D_2	0.2	0.1	0.6	2.5	6.7	12.4	15.2	14.6	13.6
<u>Cis</u>-	D_2	0.0	0.2	0.6	2.7	7.5	13.5	16.4	14.9	13.7
1,4-Dimethyl	D_2	0.0	0.2	0.5	2.4	7.4	14.6	17.2	14.0	12.3
<u>Cis</u>-	D_2	0.0	0.0	0.4	2.2	7.0	13.8	16.6	13.4	12.8
1,2-Tetramethylene	D_2	0.4	0.1	0.3	0.4	1.6	3.8	7.4	13.2	20.6
1,4-di-<u>t</u>-Butyl	D_2	0.2	1.4	6.2	14.4	22.0	25.4	15.7	11.4	2.3

Table 16. (Continued)

Cyclohexane †	Gas†	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
1,2,3-Trimethyl	D_2	0.1	0.1	0.2	1.4	4.0	8.2	11.4	11.8	12.6
1,3,5-Trimethyl	D_2	0.0	0.0	0.1	0.7	2.8	6.6	11.2	13.2	13.4
1,3,5-Triisopropyl	D_2	0.0	5.0	2.7	1.5	1.5	2.3	7.6	11.6	16.1
1,2,4,5-Tetra-methyl	D_2	0.0	0.0	0.4	0.6	2.4	5.8	9.2	10.4	11.8
Carbomethoxy	H_2	1.2	5.5	14.3	23.8	25.4	17.6	8.0	2.8	0.8
	D_2	0.5	1.8	6.7	16.2	24.6	24.8	15.1	6.6	2.3
	D_2[a]	0.0	0.2	1.4	6.1	17.1	30.0	26.0	10.7	5.1
Benzene[b]	H_2	83.2	10.9	2.9	1.4	0.9	0.7			
Cyclohexane[c]	H_2	0.3	1.8	7.2	17.2	26.2	24.5	12.7	4.8	2.4
Cyclohexane[d]	H_2	18.6	31.2	24.2	11.1	7.3	4.0	2.2	1.0	0.4
Toluene[b]	H_2	64.3	20.7	9.1	4.8	0.9	0.2			
Methylcyclo-hexane[c]	H_2	0.0	0.5	1.9	7.0	16.3	23.7	22.6	14.0	7.2
p-Xylene[b]	D_2	69.2	12.2	5.2	4.2	2.6	3.0	3.4	0.2	
1,4-Dimethyl-cyclohexane[c]	D_2	0.0	0.2	1.1	4.8	13.1	22.9	21.3	12.8	9.7

†Footnotes are described on p. 76.

Table 16. (Continued)

Cyclohexane	Gas	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}
	H_2	2.7	1.7	0.8	0.2						
Methyl	H_2	3.8	1.7	0.6	0.1	0.1	0.2				
	D_2	8.7	4.0	2.0	0.8	0.4	0.2				
Ethyl	H_2	2.6	1.4	0.6	0.3	0.1					
Isopropyl	H_2	1.6	0.7	0.4							
	D_2	4.8	2.0	0.8	0.4	0.1	0.1				
t-Butyl	H_2	1.0	0.3								
	D_2	2.0	0.4	0.2							
1,2-Dimethyl	D_2	10.5	8.0	6.0	3.7	1.8	0.6	0.2			
1,3-Dimethyl	D_2	12.0	9.4	6.9	4.0	1.3	0.4	0.1			
Cis-	D_2	11.5	9.0	6.0	2.9	0.9	0.2				
1,4-Dimethyl	D_2	10.4	8.2	6.5	3.9	1.5	0.6	0.2	0.1		
Cis-	D_2	11.6	8.9	7.4	3.9	1.3	0.4	0.3			
1,2-Tetramethylene	D_2	23.4	17.3	7.9	2.6	0.8	0.2				
1,4-di-t-Butyl	D_2	0.6	0.3	0.1							
1,2,3-Trimethyl	D_2	12.4	11.4	9.8	7.2	4.8	2.8	1.3	0.4	0.1	

Table 16. (Continued)

Cyclohexane	Gas	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}
1,3,5-Trimethyl	D_2	12.0	9.5	9.0	7.7	6.6	5.0	2.0	0.2		
1,3,5-Triisopropyl	D_2	16.2	12.3	8.9	5.7	3.9	2.5	1.6	0.6		
1,2,4,5-Tetramethyl	D_2	11.8	11.0	8.2	7.4	5.8	4.9	4.0	3.3	2.2	0.7
Carbomethoxy	H_2	0.3	0.2								
	D_2	0.9	0.4								
	D_2[a]	2.4	0.9	0.2							
Cyclohexane[c]	H_2	1.5	0.9	0.4	0.1						
Methylcyclohexane[c]	H_2	3.9	1.6	0.7	0.4	0.2					
1,4-Dimethylcyclohexane[c]	D_2	6.6	3.5	2.2	1.3	0.4	0.1				

[a]Rhodium on alumina catalyst was used.

[b]Recovered starting material in a half-hydrogenation.

[c]Saturated product in a half-hydrogenation.

[d]Saturated product of the hydrogenation of cyclohexene.

Table 17. Commercial chemicals

Compound	Source
Acetic acid	Baker
Acetic anhydride	Matheson, Coleman & Bell
Benzene	Baker
Boric acid	Baker and Adamson
t-Butylbenzene	Phillips
Cumene	Matheson, Coleman & Bell
Cyclohexene	Mallinckrodt
p-di-t-Butylbenzene	Eastman
Durene	Eastman
Ethylbenzene	Eastman
Magnesium sulfate	Mallinckrodt
Mesitylene	Matheson, Coleman & Bell
Methyl benzoate	Matheson, Coleman & Bell
Naphthalene	Eastman
Platinum oxide	Sargent
Rhodium on alumina	Matheson, Coleman & Bell
Sodium chloride	Mallinckrodt
Sodium hydrogen carbonate	Mallinckrodt
Tetralin	Mallinckrodt
Toluene	Baker
1,3,5-tri-t-Butylbenzene	Group chemicals
1,2,3-Trimethylbenzene	Baker
1,3,5-Triisopropylbenzene	Aldrich
o-Xylene	Eastman
m-Xylene	Eastman
p-Xylene	Eastman

Part II. SELECTIVITY IN THE REDUCTION OF DIARYLALKANES

INTRODUCTION

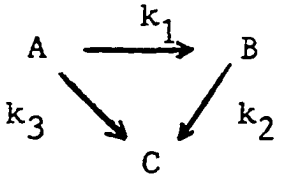
While studying the incorporation of deuterium into the alkylbenzenes it was observed that deuterium was incorporated into the benzylic position; hydrogen-deuterium exchange was occurring at the position alpha to the benzene nucleus. It was postulated that the adsorption of one phenyl group in a diphenyl compound could be transferred to the second phenyl group via the formation of an α-monoadsorbed intermediate formed from a π-complexed benzene nucleus. The process envisioned, using diphenylmethane as an example, would involve the formation of a π-complex with one phenyl group, the hydrogenation of the complexed ring with the subsequent formation of an α-monoadsorbed cyclohexylphenylmethane, and formation of the π-complexed cyclohexylphenylmethane from the α-monoadsorbed complex. Such a process would involve the selective formation of the disaturated cyclohexyl derivative from the diphenyl compound.

Selectivity in the hydrogenation of diolefins and acetylenes has been extensively studied over the years (59). In contrast to the aliphatic systems, there are few reports concerning the selectivity in the hydrogenation of diaryl compounds (60, 61, 62, 63).

Accordingly, a study of the hydrogenation of a series of 1,n-diarylalkanes was undertaken. The hydrogenations

were carried out in either glacial acetic acid or in an acetic acid-hydrocarbon cosolvent system at room temperature and atmospheric pressure. The hydrogenations were carried out to determine: a) if there is selectivity in the formation of the half-saturated product, B, or in the completely saturated product, C, b) if selectivity in product formation was dependent upon the chain length separating the two aryl groups, c) the effect of nuclear substitution upon the selectivity of product formation, d) if the selectivity in product formation was dependent upon the nature of the solvent system employed and, if so, whether this selectivity was dependent upon the amount of acid present and upon the steric bulk of the solvent, e) the effect of catalytic poisons and competitive reactions upon product selectivity, and f) the mechanism for the formation of the disaturated product, C.

Two mechanisms for the reduction can be envisioned, a sequential-parallel mechanism of the form



or a sequential mechanism of the form

where A is the diaryl compound, B the aryl-saturated inter-

mediate, and C is the disaturated product.

The selectivity in C formation is represented by the ratio k_1/k_3, and k_1/k_2 represents the selectivity in the formation of B. If selectivity in C formation is observed, indicated by a low numerical value for k_1/k_3, the sequential-parallel mechanism would be operating. The absence of selectivity in C formation indicates the sequential mechanism is the only mechanism of importance. Selectivity in B formation is indicated by a k_1/k_2 value of greater than 2.0. The value of 2.0 comes from the statistical reactivities of a diaryl and a monoaryl compound. If the aryl group in a diaryl compound is of equal reactivity to an aryl group in a monoaryl compound, then $k_1=2k_2$. When k_1/k_2 is greater than 2.0, B is less reactive than A for some reason and B is formed in preference to its reduction.

LITERATURE REVIEW

There are few reports in the literature concerning the selectivity in the hydrogenation of diarylalkanes.

Smith and coworkers (60) found that the hydrogenation curve shows no discontinuity at the half-hydrogenation point when diphenyl compounds were hydrogenated in acetic acid on reduced platinum oxide at 64 psi. This might be due to: a) once the compound is adsorbed on the catalyst, both rings are reduced before desorption occurs, or b) the reaction proceeds by steps, the diphenyl compound is hydrogenated to a phenylcyclohexyl intermediate which subsequently is hydrogenated to the fully reduced product. In the latter case, the lack of a break in the hydrogenation curve could be explained only if the rates of hydrogenation of the diphenyl compound and the intermediate were the same.

Smith and coworkers measured the rates of reduction of diphenyl compounds and their phenylcyclohexyl derivatives (Table 18). All of the hydrogenations were zero-order in hydrocarbon concentration and first-order in hydrogen pressure.

The substitution of a benzene nucleus into a molecule already containing one such nucleus causes a considerable decrease in the rate of hydrogenation. This retarding influence is reduced as the phenyl groups are separated by

increasing the methylene chain length, i.e., 1,6-diphenylhexane. The substitution of a cyclohexyl group for a phenyl group has essentially no influence on the rate of hydrogenation.

Table 18. Smith's rate constants for phenyl hydrogenations

Diphenyl cpd	$k_p x10^{-2}$	Cyclohexyl cpd	$k_c x10^{-2}$	k_p/k_c
Biphenyl	5.41	Phenylcyclohexane	6.14	0.88
Diphenylmethane	6.29	Phenylcyclohexylmethane	6.65	0.95
Diphenylacetic acid	1.82	Phenylcyclohexylacetic acid	1.91	0.95
Benzilic acid	1.46	Phenylcyclohexylglycolic acid	1.63	0.90
1,2-Diphenylethane	8.06			
1,6-Diphenylhexane	11.43			

They proposed that one phenyl group is adsorbed on the catalyst and that the remaining nucleus decreases the rate due to steric factors. An increase in the number of benzene nuclei would cause a decrease in the hydrogenation rate and the substitution of the cyclohexyl group for the phenyl group would have little additional influence.

Rate measurements can give no evidence as to whether these compounds are hydrogenated completely before they are desorbed from the catalyst, or, whether one phenyl is hydro-

genated, the compound desorbed, subsequently readsorbed, and reduced (60). In order to investigate the hydrogenation mechanism of the diphenyl compounds, they carried out half-hydrogenations of these compounds.

The half-hydrogenation products of biphenyl contained about 60% phenylcyclohexane, diphenylmethane gave essentially pure phenylcyclohexylmethane, 1,2-diphenylethane gave an inseparable mixture, diphenylacetic acid gave a minimum of 90% phenylcyclohexylacetic acid, and benzilic acid gave 65% phenylcyclohexylglycolic acid, 17.5% of the saturated product and 17.5% of the starting material.

From these results it would appear that the diphenyl compound must desorb after one ring is saturated, and the original diphenyl compound is adsorbed in preference to the half-saturated material even though the rates of hydrogenation of the two compounds are the same. If the differences in the adsorption tendencies are sufficiently great, one may obtain the practically pure half-saturated compound.

Since the product composition of the partial hydrogenation of a diphenyl compound was determined by the adsorption characteristics, Smith and coworkers developed a calculation of the relative adsorption tendencies on reduced platinum oxide for the sequential mechanism (61).

If the reactions were homogeneous, the composition of the reaction mixture at any time would be dependent upon the

relative magnitudes of k_1 and k_2. In the heterogeneous system, the product composition depends upon the relative adsorption tendencies T_A and T_B of A and B on the platinum. T_C is assumed to be zero. The ratio of T_A/T_B is calculated by the following method.

An equilibrium is assumed to exist on the catalytic surface; $A_{ads} + B \rightleftharpoons B_{ads} + A$. Since the hydrogenations are zero-order in A and B, it is assumed that all of the catalytic sites are covered by A and B throughout the reaction. Furthermore, it is assumed that the same total number of sites are available to either A or B and the rate constants are the same for the hydrogenation of either compound.

The equilibrium constant for adsorption is; $K = \frac{\sigma_B C_A}{\sigma_A C_B}$ (1)

where C_A is the concentration of A, and σ_A and σ_B are the fraction of catalytic sites occupied by A and B respectively.

The rate of consumption of A is; $$\frac{-dC_A}{dt} = k\sigma_A pH_2 \qquad (2)$$

The rate of production of B is; $$\frac{dC_B}{dt} = k(\sigma_A - \sigma_B)pH_2 \qquad (3)$$

The rate of change of B relative to A is;

$$\frac{dC_B}{dC_A} = -\frac{k(\sigma_A - \sigma_B)pH_2}{k\sigma_A pH_2} = \frac{\sigma_B}{\sigma_A} - 1 \qquad (4)$$

$$\frac{dC_B}{dC_A} = \frac{KC_B}{C_A} - 1 \qquad (5)$$

Integration of equation 5 gives equation 6.

$$\log\frac{C_A}{C_A o} = \frac{\log\left[1-(K-1)\frac{C_B}{C_A}\right]}{(K-1)} \qquad (6)$$

Smith and coworkers calculated a K = 0.22 and T_A/T_B = 4.6 for benzilic acid. Thus, benzilic acid is 4.6 times more readily adsorbed on the catalyst than the phenylcyclohexylglycolic acid.

Selectivity in the hydrogenation of biphenyl and diphenylmethane was reported by Rylander and Steele (62) and discussed by Rylander (63). The study was carried out over various platinum metal catalysts. The half-hydrogenation of biphenyl was carried out at 100°, 1000 psi using 5 to 10 grams of substrate, 25 ml of acetic acid or cyclohexane as the solvent, and 600 mg of catalyst. The maximum yield of cyclohexylbenzene bears no relationship to the values of the rate constants for the hydrogenation of biphenyl and phenylcyclohexane. The product composition depends upon the relative strength of the adsorption of biphenyl and phenylcyclohexane and upon the amount of dicyclohexyl formed directly from the biphenyl without the formation of free cyclohexylbenzene.

The partial hydrogenation of 10 ml of diphenylmethane at 1000 psi in 25 ml of acetic acid was carried out over 600 mg of 5% Pt/C, and 200 mg of reduced platinum oxide

(Table 19).

Table 19. Rylander's experimental conditions and results

Cat	T	$\%Ph_2CH_2$	$\%PhCH_2Cy$	$\%Cy_2CH_2$	H_2moles
600 mg Pt/C	102°	18	62	20	3.06
200 mg PtO_2	32°	34	47	19	2.55

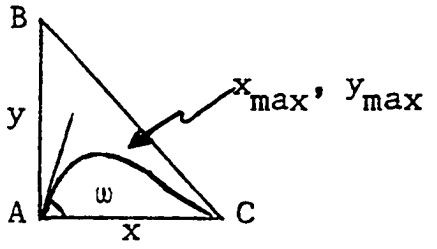
These results do not show the high selectivity in phenylcyclohexane formation that was reported by Smith (60). Rylander analyzed the product mixtures by gas chromatography and this may explain the difference in the observations.

In a recent book, Thomas and Thomas (64) discussed an empirical and a kinetic method of estimating the selectivity in consecutive reactions. An empirical method of determining the most favored conditions for the production of a desired product B from reactant A at the expense of undesired product C was formulated by Weber (65) and discussed by Waterman and coworkers (66). If y is the fraction of A converted to B and x is the fraction of A converted to C, then a single empirical equation

$$y = \frac{x(1-x)}{a + bx} \qquad (7)$$

in which a and b are constants, describes the level of conversion in a series of selective catalytic reactions in which only one reaction parameter is varied. A right isosceles triangle in which y is the vertical axis and x is

the horizontal axis is a convenient way of representing the experimental points (x,y).



If the reaction parameter that is varied is contact time, then for every value of contact time there will be a corresponding conversion, y and x. A typical plot is shown above.

The kinetic method of estimating selectivity was developed by Van Der Borg (67). The kinetic scheme describes the data as well as the empirical equation and was developed for the sequential-parallel mechanism. This allows the selectivity of C formation to be introduced, k_1/k_3. It is assumed that each reaction is first-order; the rate equations for conversion of A into B and C are (x and y retain the meaning defined for the empirical method).

$$\frac{-d(1-x-y)}{dt} = (k_1 + k_3)(1-x-y) \tag{8}$$

$$\frac{dy}{dt} = k_1(1-x-y)-k_2y \tag{9}$$

$$\frac{dx}{dt} = k_3(1-x-y) + k_2y \tag{10}$$

The initial conditions are y=0, x=0, therefore, equation 8 gives

$$\frac{d(1-x-y)}{(1-x-y)} = - (k_1 + k_3)dt \tag{11}$$

and

$$\ln(1-x-y) = -(k_1 + k_3)t \tag{12}$$

or

$$(1-x-y) = e^{-(k_1 + k_3)t} \tag{13}$$

substitution of 13 and 9 gives

$$\frac{dy}{dt} + k_2 y = k_1 e^{-(k_1 + k_3)t} \tag{14}$$

solution of equation 14 with the initial conditions of y=0, x=0, one obtains

$$y = \frac{k_1}{k_2 - (k_1 + k_3)}\left[e^{-(k_1 + k_3)t} - e^{-k_2 t}\right] \tag{15}$$

From equations 15 and 13 one obtains

$$(1-x-y)^{\frac{k_2/k_1}{1 + k_3/k_1}} = 1-x-\left(\frac{k_2}{k_1} - \frac{k_3}{k_1}\right)y \tag{16}$$

The ratio k_1/k_2 represents the selectivity in B formation, (σ_2), and k_1/k_3 represents the selectivity in C formation, (σ_3). The values of σ_2 and σ_3 are obtained by plotting the experimental data in a right angle isosceles triangle as represented earlier. The values of σ_3 and σ_2 are obtained in the following way; dividing equation 9 by equation 10, the maximum values of y and x are

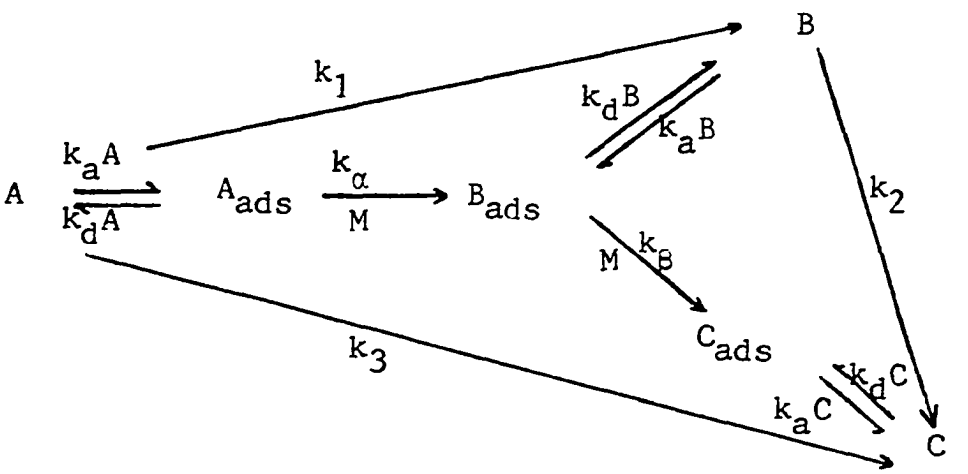
$$\frac{dy}{dx} = 0 = \frac{k_1(1-x_{max}-y_{max}) - k_2 y_{max}}{k_3(1-x_{max}-y_{max}) + k_2 y_{max}} \tag{17}$$

$$\sigma_2 = \frac{k_1}{k_2} = \frac{y_{max}}{1-x_{max}-y_{max}} \tag{18}$$

The slope of the curve at the origin (y=0, x=0) from the triangle plot and equations 9 and 10 is

$$\frac{dy}{dx} = \frac{k_1}{k_3} = \sigma_3 = \tan \omega \qquad (19)$$

The kinetics of the selective formation of an intermediate product in consecutive heterogeneous reactions have been developed by De Boer and Van Der Borg (68) and discussed by Thomas and Thomas (64). Assuming the rates of consumption of **A** and production of B and C to be pseudo first-order, one may develop a general scheme detailing the elementary reactions involved. (Scheme 17)



Scheme 17. Elementary reactions in the reduction of a diunsaturated compound

k_a = Rate constant for adsorption

k_d = Rate constant for desorption

k_α = Rate constant for conversion of A_{ads} to B_{ads}

k_β = Rate constant for conversion of B_{ads} to C_{ads}

A, B, and C retain the meaning proposed earlier

Analysis of this general scheme indicates that selective formation of C is basically dependent upon the tendency of B_{ads} to desorb relative to its tendency to undergo the second hydrogenation. The selectivity of C formation is dependent upon the magnitude of k_dB and k_β.

Different conditions are discussed with respect to this scheme and product selectivity.

The establishment of the adsorption-desorption equilibrium is fast with respect to the slow surface reaction. All steps but k_α and k_β are fast and once B_{ads} is formed it is rapidly desorbed from the catalytic surface. In this case, the ordinary sequential mechanism is operating and selectivity in C formation is not observed, $k_3 \longrightarrow 0$. A kinetic selectivity factor for B formation, in terms of the elementary reactions is

$$\sigma_2 = \frac{k_1}{k_2} = \frac{k_a A k_d B k_\alpha}{k_d A k_a B k_\beta} \qquad (20)$$

A high selectivity of B formation is observed when A is more strongly adsorbed than B, even when $k_\alpha = k_\beta$.

Adsorption and desorption of B are of the same order of magnitude as k_α and k_β, but the adsorption and desorption of A is rapid. The concentration of A on the catalyst is governed by k_aA and k_dA while the concentration of B on the

catalyst is governed by k_aB, k_dB, and k_α and k_β. Selectivity in C formation is governed by k_dB and k_β, i.e., equation 21.

$$\sigma_3 = \frac{k_1}{k_3} = \frac{k_dB}{k_\beta} \tag{21}$$

The selectivity in B formation is

$$\sigma_2 = \frac{k_1}{k_2} = \frac{k_aAk_dBk_\alpha}{(k_\alpha + k_dA)k_aBk_\beta} \tag{22}$$

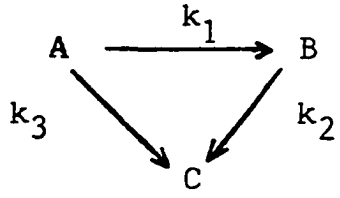
Selectivity in C formation is dependent upon the tendency of B to desorb and its tendency to undergo hydrogenation.

From these conditions it can be seen that the overall rate constant, k_3, is important if the adsorption and desorption rates of B are comparable to the rates of hydrogenation, and selectivity of C formation is favored by a greater rate of hydrogenation relative to the rate of desorption of B.

RESULTS AND DISCUSSION

The derivation of equation 6 by Smith and coworkers (61) involved many assumptions some of which may not be valid. One assumption of questionable validity is that the rate constants are the same for the reduction of the diaryl compound and its half-saturated derivative. If this assumption cannot be made, the derivation of an equation similar to equation 6 for the sequential-parallel mechanism becomes very complex and difficult to solve. The empirical method of estimating the selectivity in product formation in consecutive reactions is ideally suited to the study of the selectivity in the hydrogenation of diarylalkanes (64). The use of the empirical method would give estimates of values for the selectivity in the formation of both the half-saturated product, B, and the fully saturated product, C.

The sequential-parallel mechanism readily accommodates selectivity in C formation. Selectivity in C formation implies that A is converted directly to C bypassing the desorbed half-saturated product, product B.



When selectivity in C formation is observed, k_3 is favored over k_1. The ratio of k_1/k_3, the representation for the

selectivity of C formation, should be small when selectivity is observed and will approach zero as selectivity in C formation becomes more pronounced.

The sequential mechanism cannot account for selectivity in C formation, only selectivity in B formation can be accommodated by this mechanism. The sequential mechanism involves the formation of the half-saturated product as a desorbed intermediate in the formation of the disaturated product.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The study of the selectivities of B and C formation from diarylalkanes should allow one to make basic conclusions concerning the mechanism of the reduction. The results of a series of hydrogenations of 1,n-diarylalkanes catalyzed by reduced platinum oxide in acetic acid and represented graphically after the empirical method are listed in Tables 20 through 26. The selectivities in B and C formation observed in glacial acetic acid are listed in Table 20. The ratio k_1/k_3 represents the selectivity in the formation of the saturated product; the ratio $k_1/2k_2$ represents the selectivity in the formation of the half-saturated product. The k_1/k_3 values shown in Table 20 are all large, thus, the degree of selectivity in C formation is very low. A low selectivity in C formation indicates that k_3 is much smaller than k_1 and k_3 is unimportant relative to k_1. This observation has

important mechanistic implications for the hydrogenation process. An insignificant k_3 value indicates that the sequential mechanism is the mechanism of major importance and the sequential-parallel mechanism is not involved in the diarylalkane reduction.

Table 20. Selectivities in the formation of the half-saturated and saturated products observed in acetic acid

Compound	Run #	$k_1/2k_2$	k_1/k_3
Biphenyl	4	1.37	7.2
Diphenylmethane	10	1.54	14.7
1,2-Diphenylethane	3	0.88	9.3
1,3-Diphenylpropane	4	0.79	15.7
1,4-Diphenylbutane	25	0.70	14.3
1,6-Diphenylhexane	2	0.67	13.7
1,6-Bis(4-methylphenyl)hexane	1	0.80	6.6
1,8-Diphenyloctane	2	0.64	17.0
1,10-Diphenyldecane	1,2	0.60	9.6

A regular trend is not observed in the manner in which the k_1/k_3 ratio varies with the length of the alkane chain separating the two aryl groups (Table 20). Since the selectivity in C formation is very low and unimportant, a rationalization for this variance will not be proposed.

The ratio $k_1/2k_2$, the selectivity in the formation of

B, is independent of the mechanism under consideration and represents the reactivity of B relative to starting material A. In a completely random process, where the reactivity of a benzene nucleus is independent of the presence of a second aryl group, the reactivity of A would be expected to be twice that of B, $k_1=2k_2$ and $k_1/2k_2=1.0$.

The $k_1/2k_2$ values listed in Table 20 indicate that the selectivities in the formation of the half-saturated product are dependent upon the length of the alkane chain separating the two aryl groups. The $k_1/2k_2$ values for biphenyl and diphenylmethane are greater than 1.0 while the values for the other homologs are less than 1.0 indicating that the first two members of this homologous series are significantly different from the other members in terms of selectivity in the formation of the half-saturated product. In biphenyl, which does not have an alkane chain separating the two aryl groups, and diphenylmethane, in which the two aryl groups are separated by one methylene unit, selectivity in the formation of the half-saturated product is observed. It is proposed that the observed selectivity in the formation of B is due to the favored reactivity of the diaryl compound over that of its half-saturated product due to steric factors, in biphenyl and diphenylmethane. The adsorption of one phenyl group does not aid in the adsorption of the second phenyl group because when one benzene nucleus is adsorbed to the catalyst, the

second phenyl group is not in a sterically favorable position to complex with the catalyst. Thus, the adsorbed ring is hydrogenated and desorbed from the catalyst forming the desorbed half-saturated product. It is further proposed that the selectivity in the formation of the half-saturated product is a result of the preferential adsorption of the diphenyl compound on the catalyst over that of the half-saturated product. The preferential adsorption of the diphenyl compound may be due to differences in the solvation of the half-saturated product and the diphenyl compound or to steric hindrance to complexation of the half-saturated product. The adsorption of B could be sterically retarded by the presence of a cyclohexyl group in very close proximity to the phenyl group. This steric effect most likely does not explain the observed selectivity in B formation for the steric hindrance of a phenyl group should be about the same as that of a cyclohexyl group (60).

The selectivity in the formation of the half-saturated product in the reduction of biphenyl and diphenylmethane is most likely due to differences in the solvation of the diphenyl compound and its half-saturated product. The conversion of a benzene nucleus into a cyclohexane ring may result in a different type of solvation in the half-saturated product. The remaining benzene nucleus may be more highly solvated in the half-saturated product than it was in the

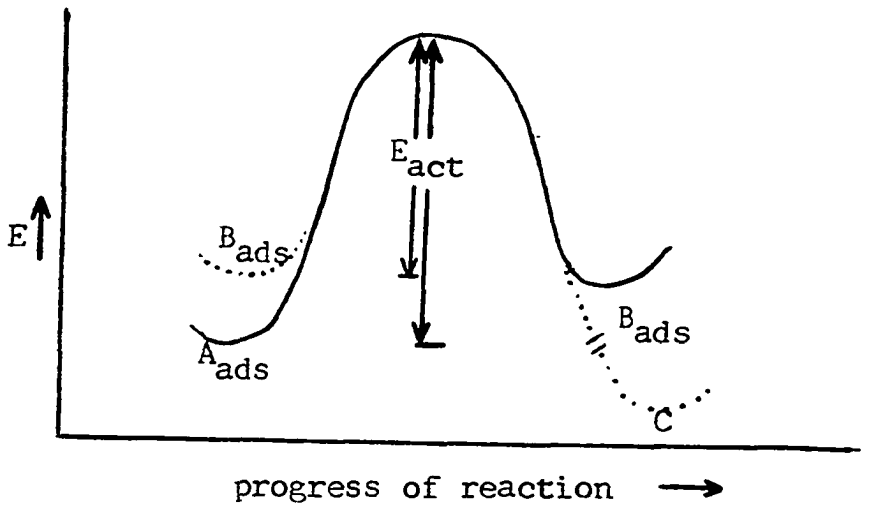
diphenyl compound. The greater degree of solvation of the phenyl group in B should make interaction with the catalyst more difficult, thus complexation with the catalyst is retarded.

As the length of the alkane chain separating the two aryl groups is increased from one methylene group to two methylene groups, diphenylmethane to 1,2-diphenylethane, a marked decrease in the selectivity in the formation of the half-saturated product is noted. This decrease continues as the alkane chain is increased to ten methylene units, 1,10-diphenyldecane, but the extent of this decrease is not as great as that observed between the methane and ethane derivatives. The $k_1/2k_2$ values for the ethane derivative through the 1,10-diphenyldecane are less than 1.0 indicating that the reactivity of the half-saturated product is greater than that of the diaryl compound.

The favored reduction of the half-saturated product over that of the 1,n-diarylalkane, where n is varied from 2 to 10, is explained by the formation of a diadsorbed or chelated diaryl complex on the catalytic surface. The formation and reactivity of this diadsorbed complex relative to the mono-adsorbed half-saturated product molecule can be discussed in terms of the transition state energies and energies of activation for the reductions of the two complexes. The favored reduction of the half-saturated product can be explained in

two ways depending upon initial assumptions made concerning transition state energies and energies of activation for the reduction of the two complexes. In one case, it is assumed that the transition state energies for the reduction of the mono- and diadsorbed complexes are the same. In the other case it is assumed that the transition state energy for the reduction of the monoadsorbed B complex is lower than that for the reduction of the diadsorbed A complex.

If it is assumed that the transition state energies for the reduction of the monoadsorbed B complex and the diadsorbed A complex are the same, then the preferential reduction of B is explained by proposing that the diadsorbed A complex is of lower energy than the monoadsorbed B complex.



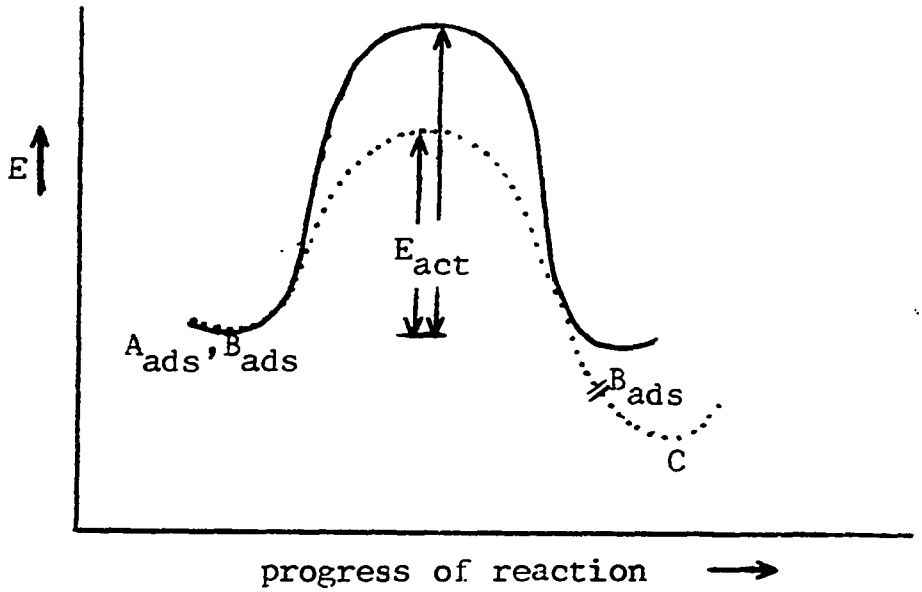
Since the transition state energies are the same for the reduction of either complex, the energy of activation for the reduction of the diadsorbed A complex is higher than

for the monoadsorbed B complex and the half-saturated product is preferentially reduced. Adsorbed B is the product of the reduction of the diadsorbed A molecule and the B molecule then desorbs from the catalyst prior to its reduction to the disaturated product, product C. This desorption is indicated by the lack of selectivity in C formation in which A is converted to C during one period of residence on the catalytic surface. The conversion of diadsorbed A to adsorbed B to C would involve direct conversion of A to C during one adsorption and this is not observed.

The second way the preferred reactivity of the half-saturated product can be explained in terms of a diadsorbed diarylalkane complex involves the assumption that the transition state energy for the reduction of the monoadsorbed B complex is lower than the transition state energy for the reduction of the diadsorbed A complex. If the diadsorbed A complex is of lower energy than the monoadsorbed B complex, the preferential reduction of B is expected because the energy of activation for the reduction of adsorbed B is lower than that for the reduction of diadsorbed A.

The preferential reduction of B is also expected, if the diadsorbed A complex and monoadsorbed B complex are of comparable energies because the transition state energies for the reduction of diadsorbed A is greater than for the reduc-

tion of monoadsorbed B. If monoadsorbed B is of lower energy than the diadsorbed A complex, the preferential reactivity of B is still expected until the energy of activation for the reduction of B is greater than that for the reduction of A.



The effect of the diadsorption increases with an increase in the length of the alkane chain separating the two aryl groups (Table 20). The selectivity in the formation of the half-saturated product continues to decrease with an increase in the length of the alkane chain between the two benzene nuclei. It should be possible to increase the length of the alkane chain to a point where the adsorption of one benzene nucleus does not influence the adsorption of the second nucleus, i.e., it should be possible to prevent diadsorption of the A molecule by separating the two aryl

groups by a long alkane chain. If diadsorption can be prevented, k_1 should equal $2k_2$ and the ratio $k_1/2k_2$ should equal 1.0. 1,20-Diphenyleicosane was obtained but was not soluble in acetic acid. Therefore, a cosolvent system of acetic acid-cyclohexane was used to study the hydrogenation of the eicosane derivative. Other representative 1,n-diarylalkanes were reduced in the cosolvent system to allow a comparison of the diphenyleicosane results to the results obtained in pure acetic acid. The cosolvent reductions may also provide information concerning the solvation effects of the diarylalkane and the half-saturated product discussed earlier. The selectivities of B and C formation obtained in a 50:50 mixture by volume of cyclohexane and acetic acid are listed in Table 21.

Table 21. Selectivities in the formation of the half-saturated and saturated product observed in 5 ml acetic acid and 5 ml cyclohexane

Compound	Run #	$k_1/2k_2$	k_1/k_3
Diphenylmethane	11,12	2.14	15.0
1,4-Diphenylbutane	27	1.30	8.6
1,6-Bis(4-methylphenyl)hexane	2	1.40	8.3
1,10-Diphenyldecane	3	1.29	12.5
1,20-Diphenyleicosane	1	1.32	4.7

A comparison between Table 20 and Table 21 indicates that the addition of cyclohexane to the hydrogenation solvent has a marked effect upon the selectivity in B formation, $k_1/2k_2$, while the effect upon the selectivity in C formation is small and variable. The k_1/k_3 values are high and indicate that k_3 is an unimportant process in either solvent system.

The 1,20-diphenyleicosane follows the trend set by its butane and decane homologs in the cosolvent system. The selectivities in B and C formation which could not be observed for diphenyleicosane in pure acetic acid can now be estimated by a comparison between the butane and the decane derivatives in pure acetic acid and the cosolvent system. The $k_1/2k_2$ value predicted for diphenyleicosane in acetic acid is less than one, in the region of 0.6 as is observed for the butane and decane. The results for the eicosane derivative indicate that the adsorption of one phenyl group influences the adsorption of a second phenyl group. A further increase in the length of the alkane chain separating the two aryl groups probably would not give a random hydrogenation ($k_1=2k_2$).

The $k_1/2k_2$ values have increased upon the addition of cyclohexane to the solvent. In the cosolvent system, k_1 is favored over k_2 and selectivity in B formation is now observed since $k_1/2k_2$ is greater than 1.0. The preferential

one stage reduction of the diaryl compound to its half-saturated product is the greatest for diphenylmethane. The other diarylalkanes show selectivities in B formation which are less than that of the diphenylmethane but are comparable to one another. Methylation of the benzene nucleus has had little additional effect upon the selectivity in B formation as shown by 1,6-bis(4-methylphenyl)hexane. This change in selectivity upon addition of a cosolvent gives credence to the proposal that the preferential adsorption of diphenylmethane over that of cyclohexylphenylmethane is a result of differences in solvation of the two compounds in acetic acid.

The 50:50 acetic acid-cyclohexane cosolvent system produced a marked change in the selectivities of B formation. Further changes in the solvent system were made and the results are listed in Tables 22 and 23.

Table 22. Selectivities in the formation of the half-saturated and saturated product observed in 1 ml acetic acid and 9 ml cyclohexane

Compound	Run #	$k_1/2k_2$	k_1/k_3
Diphenylmethane	13	3.20	10.9
1,4-Diphenylbutane	28	1.92	6.4

The values listed in Table 22 indicate that a 90:10 cyclohexane to acetic acid solvent system has had an additional marked effect upon the product mixture and the selectivity

in B formation. Further attempts to exploit these observations by decreasing the acid concentration to a trace amount are shown in Table 23. The results listed in Table 23 indicate that the 90:10 solvent mixture gave the largest selectivity in B formation. The selectivity values obtained for the weakly acidic solutions are in the same range as the 90:10 solvent mixture.

Table 23. Selectivities in the formation of the half-saturated and saturated product and acid concentration dependence

1,4-Diphenylbutane Run #	Acetic acid	Cyclohexane	$k_1/2k_2$	k_1/k_3
25	10 ml	0	0.70	14.3
27	5 ml	5 ml	1.30	8.6
28	1 ml	9 ml	1.92	6.4
31	0.2 ml	5 ml	1.65	12.5
32	0.4 ml	5 ml	1.68	7.6
33	0.04 ml	10 ml	1.74	7.8

It is proposed that the change in the selectivity in B formation upon the addition of cyclohexane is a result of the greater ability of this nonpolar cosolvent to solvate the diarylalkane and its half-saturated product. The preferential formation of B upon the addition of cyclohexane could be the result of changing the tendency of A to diadsorb and changing the adsorption equilibrium of B. A diadsorbed A complex has

been proposed to explain the preferential reduction of B in pure acetic acid. A greater solvation of the diaryl compound by cyclohexane could prevent the formation of the diadsorbed A complex. If the diaryl compound formed a monoadsorbed complex, the reduction of the monoadsorbed A complex would produce desorbed B molecules much in the same manner as is proposed for the reductions of diphenylmethane and biphenyl. As the amount of cyclohexane in the solvent was increased, the tendency for the formation of the diadsorbed complex would decrease due to the greater solvation of the diaryl compound. The hydrogenation should occur in a random fashion, i.e., $k_1=2k_2$ or $k_1/2k_2=1.0$ when A forms only a monoadsorbed complex. Values of $k_1/2k_2$ are greater than 1.0 for all concentrations of cyclohexane studied. This is explained by a comparison between the solvation of a phenylcyclohexyl compound and a diphenyl compound by cyclohexane. This comparison indicates that a cyclohexyl compound should be more highly solvated by cyclohexane than would a phenyl compound. This greater solvation of the B molecule should result in a decreased tendency of B to adsorb to the catalyst; preferential adsorption and reduction of A relative to B should be observed. The preferential solvation of B could lead to an increase in the rate of desorption of B from the catalytic surface and a decrease in the rate at which it adsorbs. It is proposed that both effects, prevention of diadsorption of

the diaryl compound and inhibition of complexation by the half-saturated product are necessary to explain the solvent effect.

The proposal that both effects, inhibition of B complexation and the monocomplexation of A, is consistent with Scheme 17 and the equations developed from the elementary reactions detailed in the scheme. Equations 20 and 21 (page 91) break k_1, k_2, and k_3 down into their fundamental components. The ratio k_1/k_3 is dependent upon the rate at which B desorbs from the catalyst relative to the rate at which adsorbed B molecules are reduced. The k_1/k_3 values are high and selectivity in C formation is not observed because of the much greater tendency of B_{ads} to desorb from the catalyst upon formation rather than to undergo reduction. The ratio k_1/k_2 is dependent upon the adsorption and desorption rates of A and B and the rates of hydrogenation of adsorbed A and B. The solvent should not alter the hydrogenation rates; therefore, the adsorption equilibrium of A and the adsorption equilibrium of B must explain the effect of the cosolvent on the k_1/k_2 ratio. Scheme 17 does not allow one to separate the effects of each equilibrium on k_1/k_2 but the experimental results do not demand such a separation.

The observation that the addition of cyclohexane to acetic acid resulted in a change in the selectivity of B formation and the explanation of this change of selectivity

in terms of adsorption effects, led to experiments in which the adsorption characteristics of the reactants might be changed. The effect of the steric bulk of the solvent upon the selectivity in B formation was determined and the results are listed in Table 24.

Table 24. Selectivities in the formation of the half-saturated and saturated product observed in various cosolvents

1,4-Diphenylbutane Run #	Acetic acid	Cosolvent	$k_1/2k_2$	k_1/k_3
28	1 ml	9 ml cyclo-hexane	1.92	6.4
39	1 ml	9 ml decalin	1.72	8.3
40	1 ml	9 ml bicyclo-hexyl	2.01	9.9

The effect of methyl substitution on the benzene nucleus was determined and the results are listed in Table 25.

Table 25. Selectivities in the formation of the half-saturated and saturated product - aryl substitution dependence

Compound	Run #	$k_1/2k_2$	k_1/k_3
1,6-Diphenylhexane	2	0.67	13.7
1,6-Bis(4-methylphenyl)hexane	1	0.80	6.6

The results of the experiments indicate that selectivity in

B formation is not sensitive to the steric bulk of the solvent nor to substitution of a methyl group onto the benzene nucleus. The solvent effect is due to the nonpolar nature of the solvent; the reactivities of A and B are influenced by the nonpolar solvent. Substitution of a methyl group onto the benzene nucleus increases the electron density of the π-cloud of the ring and increases the steric hindrance to complexation. An increase in the electron density of the π-cloud should increase the adsorption tendency of the π-cloud. Steric hindrance should decrease the adsorption tendencies. It appears that the combined effect of the two factors produced no change in the selective formation of B.

Experiments in the presence of benzene and naphthalene were carried out to prevent the diadsorption of 1,4-diphenylbutane on the catalytic surface. In the presence of excess benzene, there should be competition between benzene and 1,4-diphenylbutane for catalytic sites. This competition should prevent the diadsorption of the diarylalkane because the adjacent sites required for diadsorption would not be available for complexation, benzene would occupy these sites. Experiments were carried out in the presence of naphthalene to determine that the diadsorption of 1,4-diphenylbutane was the process that was being prevented in the benzene inhibited reductions. Naphthalene is known to be very strongly adsorbed to the catalytic surface (30) and was found not to undergo

deuteration in the study of the deuterium incorporation into the mono- and polyalkylbenzenes. Naphthalene was added to the hydrogenation solvent to poison some catalytic sites by adsorption at these sites and thereby preventing diadsorption. The results of these studies are listed in Table 26.

Table 26. Selectivities in the formation of the half-saturated and saturated product obtained in the presence of inhibitors in acetic acid

1,4-Diphenylbutane Run #	Inhibitor	$k_1/2k_2$	k_1/k_3
34	10 mg naphthalene	0.96	15.6
35	1 ml benzene	1.04	19.2
38	10 mg naphthalene (1 ml acetic acid 9 ml cyclohexane)	1.76	12.5

The selectivity in the formation of the half-saturated product in the presence of catalytic inhibitors was about 1.0. Thus, when diadsorption is prevented, the hydrogenation of a diarylalkane proceeds in a random manner, i.e., $k_1=2k_2$, the value predicted from the number of aryl groups in the two molecules. The preferential reduction of the half-saturated product in pure acetic acid is due to the formation of the diadsorbed A complex which is of a lower reactivity than a monoadsorbed B molecule. The diadsorption of A is not responsible for the solvent effect as shown by the reduction of 1,4-diphenylbutane in the cosolvent system in the presence

of naphthalene. The selectivity in B formation is the same whether naphthalene is present or not (Tables 22 and 26). Thus, the solvent effect is due to the inhibition of the diadsorption of the diarylalkane and the decreased tendency of the desorbed half-saturated product to readsorb to the catalyst.

To summarize, this study has shown that the reduction of diarylalkanes proceeds via the sequential mechanism in which the desorbed half-saturated product is formed as an intermediate in the reduction. Selectivity in the formation of the disaturated product is not observed in the reductions. Selectivity in the formation of the half-saturated product is observed with biphenyl and diphenylmethane in all cases and with other compounds when a cosolvent system is employed. The selectivity in the formation of the half-saturated product is sensitive to the length of the alkane chain separating the two aryl groups only for biphenyl and diphenylmethane. The cosolvent effect is not sensitive to the steric bulk of the solvent nor to the concentration of acid in the system. The selectivity in B formation is not sensitive to methyl substitution on the benzene nucleus.

In the reduction of 1,n-diarylalkanes, when n is varied from 2 to 10, the preferential reduction of the half-saturated product is observed in acetic acid. Experiments involving the use of benzene and naphthalene as catalytic

inhibitors showed that the decreased reactivity of A was due to the formation of a diadsorbed A complex.

Selectivity in B formation for diphenylmethane and biphenyl is a result of the monoadsorption of the diarylalkane and the decreased tendency for the readsorption of B due to solvation effects. Selectivity in B formation is noted for the other diarylalkanes in a cosolvent system, and is a result of the inability of A to form the diadsorbed complex because of greater solvation effects in the cosolvent system. The monoadsorption of the A molecule should give a selectivity in B formation of 1.0 as shown by benzene and naphthalene inhibition studies. The observed selectivity in the cosolvent system is greater than 1.0 and the additional selectivity is a result of the decreased tendency of B to readsorb to the catalyst because of the increased solvation of the half-saturated product.

EXPERIMENTAL

Equipment

Nuclear magnetic resonance (nmr) spectra were measured on a Varian A-60 spectrometer. Chemical shifts are reported as δ-values in parts per million (ppm) from tetramethylsilane (TMS), an internal standard.

Gas liquid partition chromatography (glpc) analyses were performed on a Varian-Aerograph Model 200 instrument fitted with dual thermal conductivity detectors. Two columns were used, one was a 6' by ¼" column packed with 10% Carbowax 20 M on chromosorb P, the other column was a 6' by ¼" column packed with 10% QF-1 on chromosorb P. Mass spectra were measured on an Atlas CH4 spectrometer.

Materials

Diphenylmethane, biphenyl, and 1,2-diphenylethane are commercially available, the former was purified by distillation at reduced pressure and the latter two were purified by recrystallization from ethanol-water and dried overnight in a vacuum desiccator. Purity of the compounds was established by nmr and glpc.

1,4-Diphenylbutane

A mixture of 0.200 g of platinum oxide, 2.063 g (0.100 mole) of 1,4-diphenyl-1,3-butadiene and 60 ml of ethyl acetate was hydrogenated at room temperature and atmospheric

pressure in a 125 ml flask. When the hydrogenation was complete, the solution was decanted from the platinum, the solvent removed on a rotovac, the product recrystallized from ethanol-water and dried overnight in a vacuum desicator; mp 51.0-52.0°; lit (69), mp 52°; nmr (CCl_4) δ 1.6 (multiplet, 4), 2.6 (multiplet, 4), and 7.1 (s, 10).

1,3-Diphenylpropane

Zinc amalgam was prepared after the method of Vogel (70) using 10 g of granular zinc, 0.75 g of mercury(II) chloride, 13 ml of concentrated hydrochloric acid and 25 ml of water. A solution of 6.4 g (0.03 mole) of 1,3-diphenyl-2-propanone in 50 ml of 95% ethanol was added to the zinc amalgam and the mixture refluxed for 2 days. The course of the reaction was followed by periodically removing a sample of the reaction mixture and observing the nuclear magnetic resonance spectrum. Twelve 2.5-ml portions of concentrated hydrochloric acid were periodically added to the refluxing mixture. The mixture was cooled, the solution decanted from the zinc amalgam, extracted with two 50-ml portions of ether, the ether washed with two 30-ml portions of saturated sodium chloride solution, a 30-ml portion of saturated sodium hydrogen carbonate solution, and the solution dried over anhydrous magnesium sulfate. The ether was removed by distillation and the product distilled at reduced pressure, boiling range 165-175°. The nuclear magnetic resonance spectrum indicated

that about 25% of the starting material remained.

To remove the starting material, the above procedure was repeated, the refluxing continued for 24 hours and the product extracted into pentane. Two fractions were collected from a distillation at 2 mm, 128-131° and 131-134°.

The two fractions were purified by collection from a QF-1 glpc column and also from a Carbonwax 20-M glpc column.

1,6-Diphenylhexane

A mixture of 1.00 g (4.30 mmole) of 1,6-diphenyl-1,3,5-hexatriene and 60 mg of platinum oxide in 75 ml of benzene was hydrogenated at 25° and one atmosphere. The catalyst was removed by filtration, the solvent removed on a rotovac and the product purified by collection from a QF-1 glpc column; lit (71a), bp 206-208° (20 mm); nmr (CCl_4), δ 1.45 (broad, 8), 2.54 (broad, 4), 7.05 (s, 10).

1,8-Diphenyloctane

A mixture of 1.00 g (3.87 mmole) of 1,8-diphenyl-1,3,5,7-octatetraene, 50 mg of platinum oxide, and 70 ml of methanol was treated as described above; lit (71a), bp 208-210° (8mm); nmr (CCl_4), δ 1.45 (broad, 12), 2.47 (broad, 4), 7.03 (s, 10).

1,10-Diphenyldecane and 1,20-diphenyleicosane

1,10-Diphenyldecane and 1,20-diphenyleicosane were prepared after the method of Van Alphen (71b) using 10.0 g (0.43 mole) of sodium, 32 g (0.20 mole) of bromobenzene, 25 g

(0.083 mole) of 1,10-dibromodecane, and 50 ml of anhydrous ethyl ether.

The 1,10-diphenyldecane was obtained in a fraction distilling in the range of 150-160° at 0.1 mm. The impure material was purified by collection from a QF-1 glpc column; nmr (CCl_4) δ 1.3 (broad, 16), 2.6 (t, 4, J=7.0 Hz), and 7.2 (s, 10).

The 1,20-diphenyleicosane was recovered from the distillation residue and was recrystallized from ethanol: mp 53.0-53.5°; nmr (CCl_4), δ 1.3 (s, and multiplet, 37) 2.6 (t, 4, J=7.0 Hz), and 7.2 (s, 9).

Anal. Calculated for $C_{32}H_{50}$: C, 88.41; H, 11.59; Found: C, 88.20; H, 12.37.

The mass spectrum of the eicosane gave m/e of 92 as the base peak. Other principal peaks, greater than 10% of the base peak were, the molecular ion 434, 42.8%; 435, 16.1%; 436, 3.6%; 105, 15.7%; 104, 12.5%; 91, 83.9%. The molecular ion region percentages relative to the molecular ion were: M+ (434), 100% M + 1 (435), 37.5%; M + 2 (436), 8.3%.

1,6-Bis(4-methylphenyl)hexane

1,6-Bis(4-methylphenyl)hexane was prepared after the method of Van Alphen (71) using 10.0 g of sodium, 34.2 g (0.2 mole) 4-bromotoluene, 24.4 g (0.10 mole) of 1,6-dibromohexane, and 50 ml of anhydrous ether. The product was iso-

lated as a distillation fraction collected over a range from 150-165° (1 mm) which subsequently crystallized. The product was recrystallized from ethanol: mp 48-49°; nmr (CCl_4) δ 1.5 (broad multiplet, 8), 2.3 (s, 6), 2.5 (t, 4, J=7.0 Hz), and 6.9 (s, 8).

Anal. Calculated for $C_{20}H_{26}$: C, 89.49; H, 10.51. Found: C, 89.65; H, 10.05.

Hydrogenation Procedure

The diarylalkane, platinum oxide, and acetic acid were mixed in a 50 ml side-armed erlenmeyer flask. The side-arm of the flask was covered with a red-rubber septum, a teflon coated stir bar was added to the flask and the flask connected to an atmospheric pressure hydrogenation apparatus. The system was flushed and filled with hydrogen, and the stirring begun. Periodically, 0.1 ml aliquots of the reaction mixture were withdrawn by inserting the needle of a 1 ml syringe through the septum. The aliquot was added to 5 ml of pentane and the pentane solution washed with two 10-ml portions of saturated sodium hydrogen carbonate solution and dried with anhydrous magnesium sulfate. The pentane solution was then analyzed by gas-liquid partition chromatography using a QF-1 column. Peak areas were determined by cutting and weighing photocopies of the chromatogram.

The compounds hydrogenated and the hydrogenation con-

ditions are listed in Table 27. Following Table 27 are representative graphs illustrating the plots of the percentage of the half-saturated product B versus the percentage of the disaturated product C, produced in the hydrogenation of some of the compounds listed in Table 27.

Table 27. Diarylalkanes hydrogenated and calculations from the glpc traces of the product mixtures

mg cpd	mg cat	solvent	%A	%B	%C
Biphenyl					
308	40	10 ml HOAc	19.2	52.6	28.2
Diphenylmethane					
360	40	10 ml HOAc	18.4	56.6	25.0
168	20	5 ml HOAc 5 ml cyclohexane	14.1	60.7	25.2
186	20	5 ml HOAc 5 ml cyclohexane	14.3	60.7	25.0
170	20	1 ml HOAc 9 ml cyclohexane	10.8	68.8	20.4
1,2-Diphenylethane					
364	40	10 ml HOAc	26.3	46.2	27.5
1,3-Diphenylpropane					
233	20	5 ml HOAc	28.2	44.8	27.0
1,4-Diphenylbutane					
420	40	10 ml HOAc	29.3	45.2	25.5
210	20	5 ml HOAc 5 ml cyclohexane	20.5	53.2	26.3
210	20	1 ml HOAc 9 ml cyclohexane	15.2	59.6	25.2

Table 27. (Continued)

mg cpd	mg cat	solvent	%A	%B	%C
210	20	0.2 ml HOAc 5 ml cyclohexane	17.6	58.1	24.3
210	20	0.4 ml HOAc 5 ml cyclohexane	17.6	59.1	23.3
210	20	40μ l HOAc[a] 10 ml cyclohexane	16.9	58.6	24.5
210	20	10 ml HOAc 10 mg naphthalene	25.0	47.8	27.2
210	20	10 ml HOAc 0.874 g benzene	24.0	50.2	25.8
210	20	1 ml HOAc 9 ml cyclohexane 10 mg naphthalene	16.8	59.0	24.2
210	20	1 ml HOAc 9 ml decalin	16.4	56.8	26.8
210	20	1 ml HOAc 9 ml bicyclohexyl	14.1	56.9	29.0
1,6-Diphenylhexane					
252	20	5 ml HOAc	31.6	42.6	25.8
1,6-Bis(4-methylphenyl)hexane					
266	20	10 ml HOAc	27.9	44.6	27.5
266	20	5 ml HOAc 5 ml cyclohexane	18.6	52.1	29.3
1,8-Diphenyloctane					
287	20	5 ml HOAc	32.0	41.0	27.0
1,10-Diphenyldecane					
340	20	5 ml HOAc	30.0	40.0	30.0
310	20	10 ml HOAc	36.3	38.5	25.2

[a]1.00 ml Acetic acid in 250 ml cyclohexane solution.

Table 27. (Continued)

mg cpd	mg cat	solvent	%A	%B	%C
321	20	5 ml HOAc 5 ml cyclohexane	19.5	50.2	30.3
1,20-Diphenyleicosane					
200	20	5 ml HOAc 5 ml cyclohexane	19.3	51.4	29.3

Key to symbols

mg cpd - The initial amount of 1,n-diarylalkane.

mg cat - The amount of PtO_2 used.

%A - Percentage of 1,n-diarylalkane observed in the glpc trace.

%B - Percentage of 1,aryl-n-saturatedalkane observed in the glpc trace.

%C - Percentage of 1,n-disaturatedalkane observed in the glpc trace. Percentages listed in the % product columns is the product mixture composition at which the %B is a maximum.

The sources of the chemicals available commercially are listed in Table 28.

Figure 2. Plots of the percentage of the half-saturated product against the percentage of the saturated product of the hydrogenation of diphenylalkanes in acetic acid

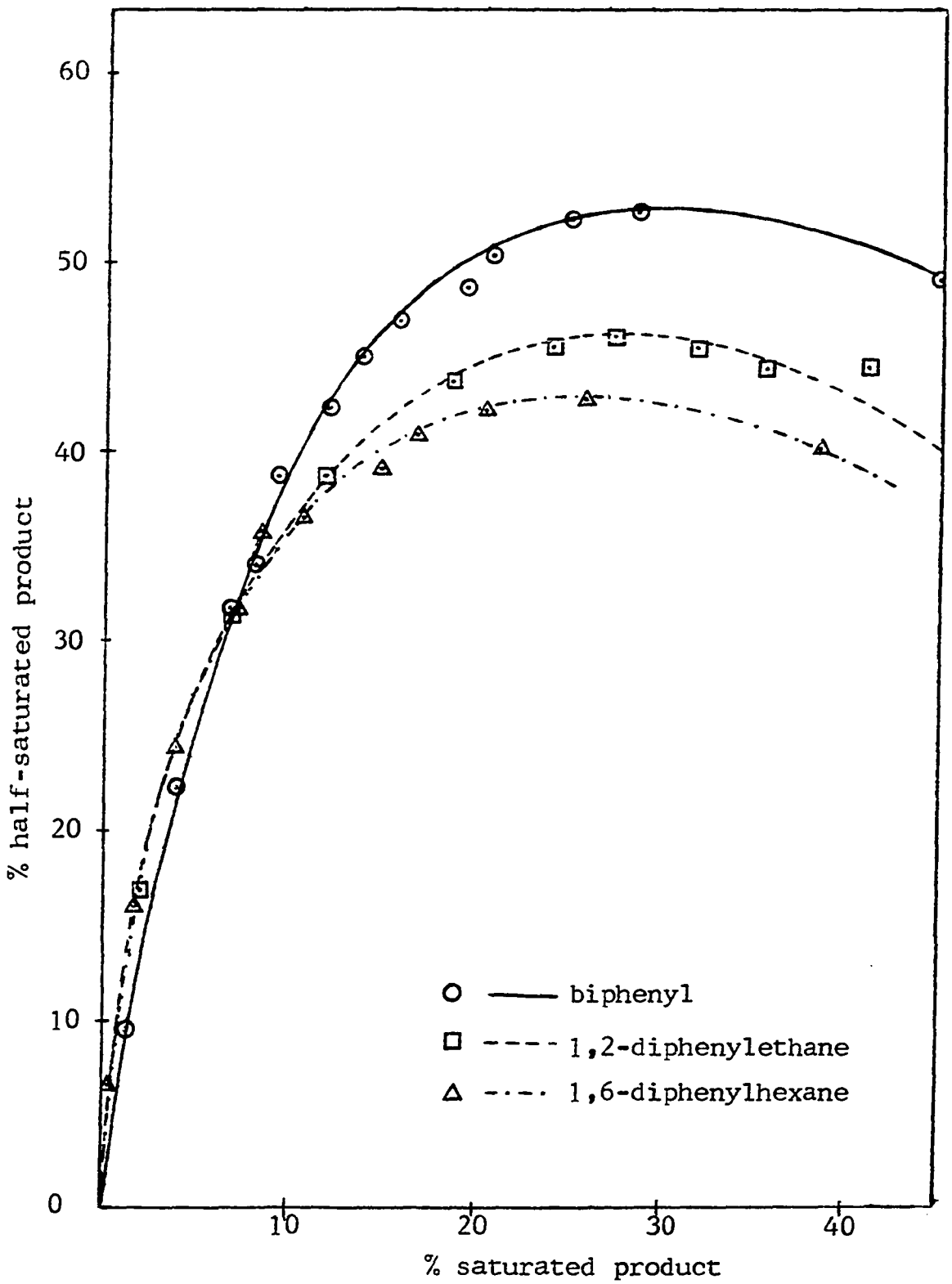

60
50
40
30
20
10
0
% half-saturated product
10
20
30
40
% saturated product
biphenyl
1,2-diphenylethane
1,6-diphenylhexane

Figure 3. Plots of the percentage of the half-saturated product against the percentage of the saturated product of the hydrogenation of diphenylalkanes - solvent comparisons

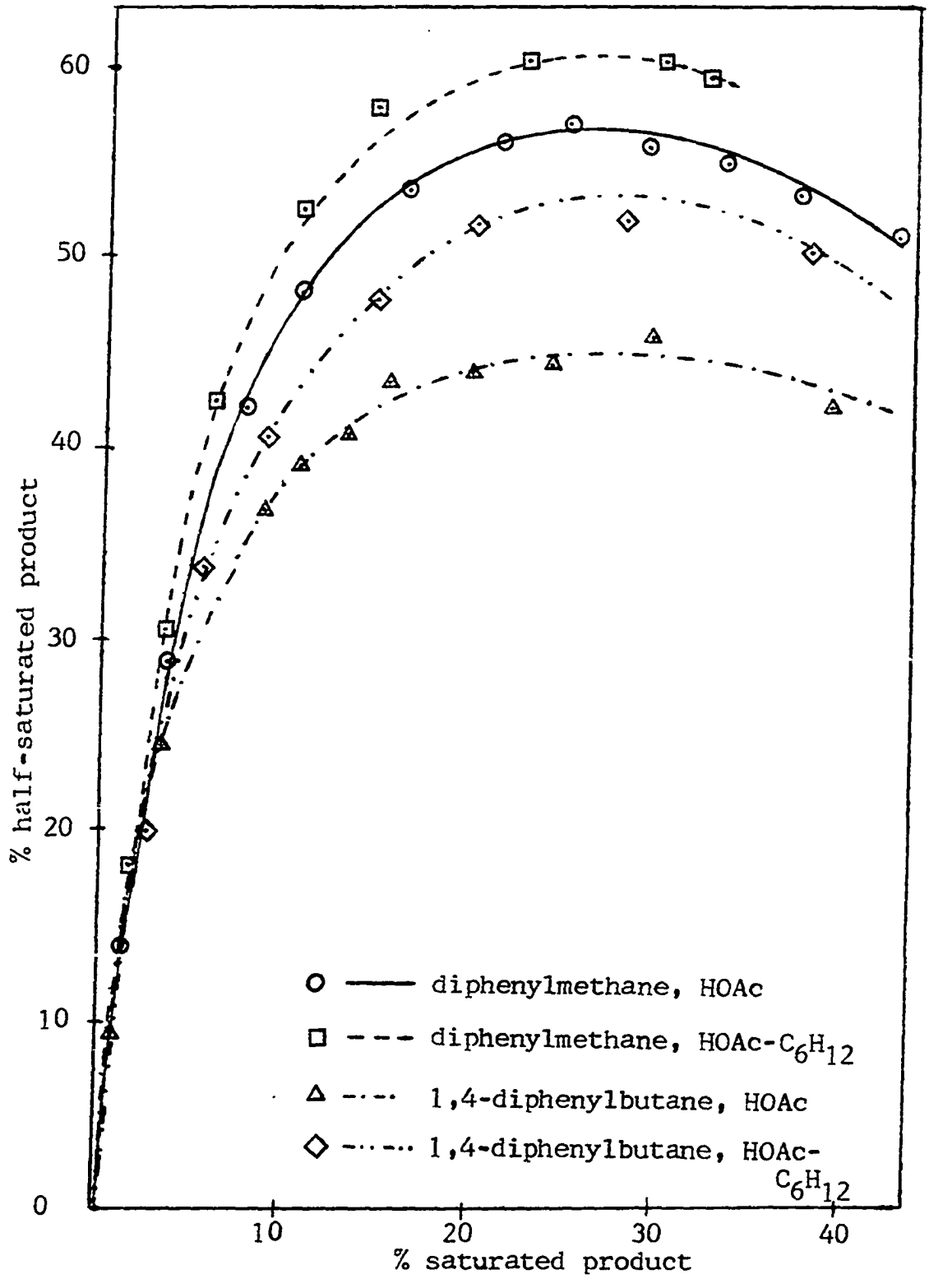

60
50
40
30
20
10
0
% half-saturated product
10
20
30
40
% saturated product
diphenylmethane, HOAc
diphenylmethane, HOAc-C6H12
1,4-diphenylbutane, HOAc
1,4-diphenylbutane, HOAc-C6H12

Figure 4. Plots of the percentage of the half-saturated product against the percentage of the saturated product of the hydrogenation of diphenylbutane

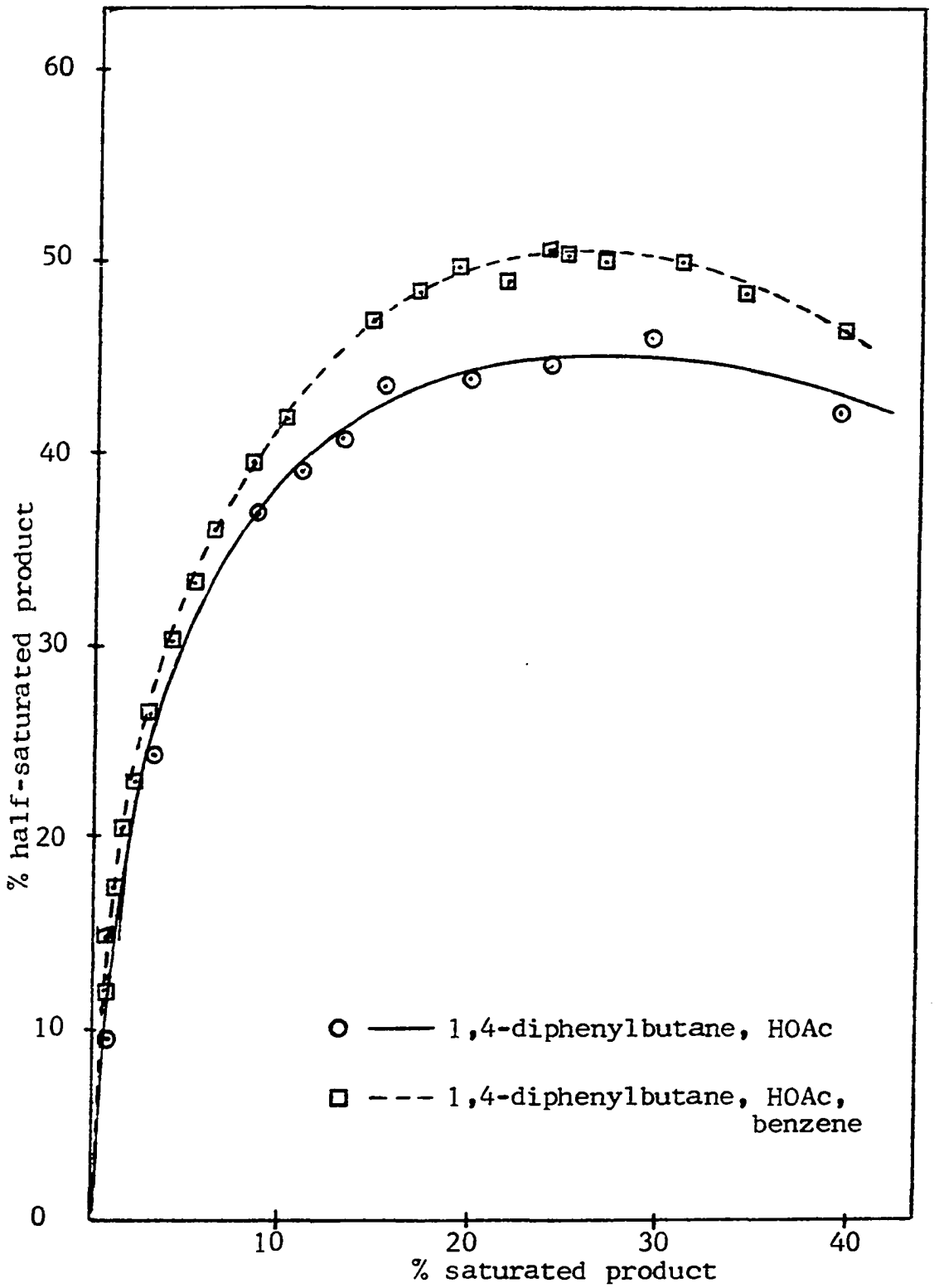

60
50
40
30
20
10
0
% half-saturated product
10
20
30
40
% saturated product
1,4-diphenylbutane, HOAc
1,4-diphenylbutane, HOAc, benzene

Table 28. Commercial chemicals

Compound	Source
Acetic acid	Baker
Benzene	Baker
Biphenyl	Eastman
Bromobenzene	Baker
4-Bromotoluene	Eastman
Cyclohexane	Baker
Decalin	Baker
1,10-Dibromodecane	Aldrich
1,6-Dibromohexane	Aldrich
Dicyclohexyl	Aldrich
1,4-Diphenyl-1,3-butadiene	Aldrich
1,2-Diphenylethane	Aldrich
1,6-Diphenyl-1,3,5-hexatriene	Aldrich
Diphenylmethane	Matheson, Coleman & Bell
1,8-Diphenyl-1,3,5,7-octatetraene	Aldrich
1,3-Diphenyl-2-propanone	Eastman
Ethyl acetate	Baker
Ethyl ether	Baker
Hydrochloric acid	Baker & Adamson
Mercury(II) chloride	Baker
Methanol	Baker
Platinum oxide	Sargent
Zinc	Fisher

Part III. COMPETITIVE HYDROGENOLYSIS OF ARYLMETHANOLS

INTRODUCTION

Various mechanisms have been proposed for the catalytic hydrogenolysis of benzyl-oxygen bonds in a variety of alcohols, esters, and ethers (72, 73, 74, 75, 76). Differences in the electron density at the benzylic carbon have been proposed to explain the stereochemical observations of the hydrogenolyses (75). Differing types of intermediates involving adsorbed phenyl groups are proposed (73, 74, 77).

Systematic studies of the effect of a phenyl substituent on the hydrogenolysis and a substituent effect correlated by a Hammett $\sigma\rho$ treatment have not been made. There have been two reports involving a substituent effect in benzylic hydrogenolyses. One report (78) concerns the opening of the oxirane ring in arylethylene oxides over platinum and another report (79) involves the reaction of synthesis gas ($2H_2$:1CO) with nuclear substituted benzyl alcohols over a cobalt catalyst.

This study was made because of the lack of information concerning a substituent effect in benzylic hydrogenolyses over common hydrogenation catalysts. The competitive hydrogenolyses between benzyl alcohol and a series of nuclear substituted benzyl alcohols were carried out in slightly acidic ethanol catalyzed by 10% palladium on charcoal. Adsorption effects of the aryl group were studied by the

competitive hydrogenolyses of benzyl alcohol with other arylmethanols. This study was carried out to determine: a) if the hydrogenolysis of the series of benzyl alcohols was sensitive to the electronic effect of the nuclear substituents and, if so, was this electronic effect correlated by the Hammett treatment, b) if the hydrogenolysis of the series of benzyl alcohols required phenyl adsorption on the catalyst and, if so, was the hydrogenolysis sensitive to the steric nature of the nuclear substituents, c) if steric hindrance toward complexation was observed, was this complexation sensitive to the number and kinds of nuclear substituents, d) if the hydrogenolysis was sensitive to the number of substituents, was complexation sensitive to the substitution pattern of these substituents, e) if adsorption was required for catalysis, are arylmethanols in which the aryl groups are more strongly adsorbed on the catalyst than phenyl, more reactive than benzyl alcohol, and f) the mechanistic implications of the results of the competitive hydrogenolyses.

After this study was completed, a study of substituent effects in the hydrogenolysis of benzyl alcohol derivatives over palladium was reported (80). Competitive reductions were not carried out; the reactions were followed and compared by measuring the uptake of hydrogen in a constant volume system. A rho of -0.37 was observed for the hydrogenolysis of the benzyl alcohols.

LITERATURE REVIEW

The hydrogenolysis of the benzyl-heteroatom bond is well known and the catalytic hydrogenolysis of benzyl groups attached to oxygen, nitrogen, and sulfur has been reviewed (81). In cases of benzyl-oxygen bond cleavage, palladium is the catalyst of choice, especially when the hydrogenation of the benzene nucleus is to be avoided (63, 81). Benzyl-oxygen bonds are readily broken in the presence of palladium under acidic conditions. It is likely that protonation of the oxygen is the opening step in the reduction (82). Benzyl alcohol is rapidly and quantitatively reduced to toluene over palladium on charcoal in ethanol at room temperature and three atmospheres. Nuclear-substituted benzyl alcohols and α-substituted benzyl alcohols behave similarly.

The hydrogenolysis of benzyl ethers and esters proceed smoothly in good yields when catalyzed by palladium-charcoal at one and three atmospheres in acetic acid or ethanol. Aldehydes and ketones may be reduced to alcohols and those carbonyl compounds which upon reduction form substituted benzyl alcohols form the corresponding hydrocarbon upon hydrogenolysis (81).

A solvent study was made for the hydrogenolysis of benzyl alcohol and benzyl acetate (83). Acetic acid is an excellent solvent for the palladium catalyzed hydrogenolysis of benzyl compounds.

Baltzly and Buck carried out a limited study of the effect of nuclear and α-substitution on the hydrogenolysis of the benzyl-oxygen linkage by comparing the rates for the hydrogenolyses (84). The reactions were catalyzed by palladium-charcoal and were carried out in ethanol at three atmospheres. Numerical values were not given for the rates. An α-alkyl group decreased the reactivity of the benzyl derivative. Branching of the alkyl group continues to decrease the reactivity to the point where 2,2-dimethyl-1-phenyl-1-propanol is not reduced at room temperature; the corresponding ketone is reduced to the alcohol. Introduction of a phenyl group into the α-position has no general effect on the hydrogenolysis rate; an α-hydroxymethyl group has about the same effect as an α-methyl group and the α-carboxyl or carbamido group completely prevent hydrogenolysis.

The hydrogenation of a series of nuclear substituted propiophenones catalyzed by palladium-charcoal produced the propylbenzenes (85). The effect of the nuclear substitution of a hydroxy or methoxy group on the hydrogenation rate was determined by comparing the rates of hydrogen consumption. Nuclear substitution decreased the rate of hydrogenation.

Information concerning the mechanism of hydrogenolyses at the benzylic position comes from a study of the reduction of phenylcarbonyl compounds (86). The palladium-charcoal catalyzed hydrogenation of propiophenone and benzaldehyde

involves a two-step process, ketone reduction followed by alcohol reduction. The reduction of the alcohol is inhibited by the presence of the hydrocarbon product. A progressive decrease in the rate of alcohol reduction occurred upon the addition of two, three, and five equivalents of the hydrocarbon product per equivalent of alcohol. Other phenylcarbonyl compounds exhibit this phenomenon. The mechanism proposed to explain the inhibitory effect involves the formation of a catalyst-hydrocarbon complex which ties up the active sites on the catalyst that are required for hydrogenolysis catalysis.

Mechanistic information also comes from adsorption effects which are observed in the hydrogenolyses of a variety of benzylic compounds. Isogai attempted the hydrogenolysis of benzilic acid and its derivatives in ethanol over palladium-charcoal but hydrogenolysis was not observed (87). He explained these results by proposing that groups which are fairly strongly adsorbed to the catalyst, such as phenyl and carboalkoxy, prevent the adsorption of oxygenated leaving groups through steric hindrance. Mitsui and coworkers studied the hydrogenolysis of dibenzylic ethers over palladium-charcoal in ethanol (88). Diphenylmethyl benzyl ether is adsorbed to the catalyst by means of one phenyl of the diphenylmethyl moiety, the phenyl of the benzyl group, and the ether oxygen. The other phenyl of the diphenylmethyl moiety

remains unadsorbed and acts as an electron withdrawing group aiding in the polarization of the benzylic carbon.

Stereochemical studies of the hydrogenolyses of a variety of benzylic compounds has provided other mechanistic information. The hydrogenolyses have been carried out at tertiary centers of known stereochemistry. The stereochemistry of the hydrogenolyses over various catalysts has been determined from the stereochemistry of the product. The observations are explained by proposing the adsorption of groups attached to the tertiary center. Optically active 2-phenyl-2-butanol was subjected to hydrogenolysis over palladium and other metals (89). Net retention of optical activity with inversion of configuration was observed over palladium. Hydrogenolysis of the acid phthalate derivative of the butanol also gave inversion of configuration. Raney nickel catalyzed retention of configuration. Raney nickel, which has a high affinity for oxygen, will adsorb the phenyl, methyl (or ethyl), and hydroxy groups of the butanol and a proton and electrons attack the asymmetric carbon from the catalyst side. The asymmetric carbon has a partial positive charge because of bond polarization brought about by adsorption. Palladium has a low affinity for oxygen and adsorption on palladium must involve phenyl, methyl, and ethyl; a proton and electrons attack the asymmetric carbon from the side of the catalyst with inversion of configuration. The hydro-

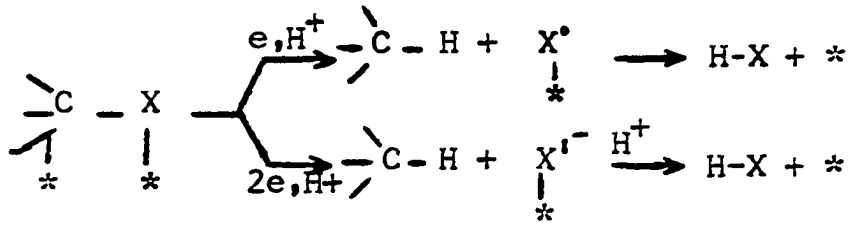
genolysis and adsorption of the acid phthalate proceeds in the same manner because the bulky group cannot adsorb on the catalyst. The inversion of configuration observed in the palladium-charcoal catalyzed hydrogenolysis of 2-aryloxy-2-phenyl-1-propanols is attributed to the adsorption of the phenyl, methyl, and hydroxymethyl groups (90).

Mitsui and Imaizumi (75) classified hydrogenolysis reactions into four groups based upon stereochemical observations and the chemical constitution of the reactants. One classification involves radical cleavage on the catalytic surface. Radical cleavage is an important mechanism for the hydrogenolysis of thioethers; the leaving group has a very strong tendency to be adsorbed on the catalyst.

The second classification is a S_N1 type reaction on the surface of the catalyst. The S_N1 reaction also involves sulfur compounds and the leaving group is the only group adsorbed on the catalyst.

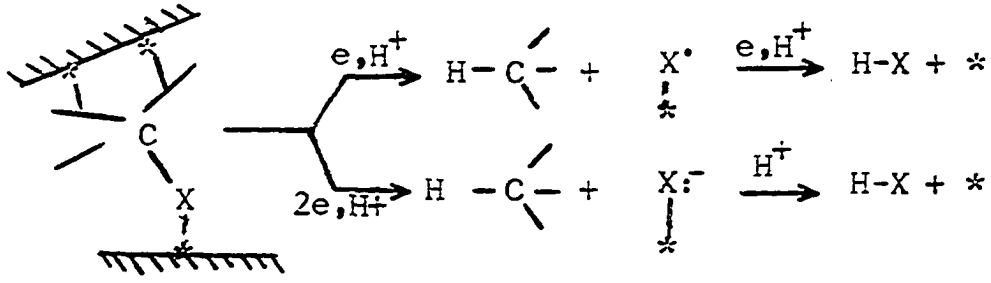
The third and fourth classifications proposed by Mitsui and Imaizumi relate to oxygen compounds. The third classification is a S_Ni type reaction which generates either an adsorbed radical or anion (Equation 23). Adsorption of the leaving group and at least one of the groups attached to the carbon bearing the leaving group is involved. Hydrogen is transferred from the catalytic surface to generate either an adsorbed radical or anion and the desorbed hydro-

genated organic material. Since the leaving group is adsorbed to the catalyst and hydrogen is transferred from the catalytic surface, retention of configuration is observed.



(23)

The fourth classification of surface reactions is a S_N2 type reaction in which the leaving group is adsorbed on one catalytic surface and the groups bonded to the carbon bearing the leaving group are adsorbed on another catalytic surface. This type of diadsorption is important only when the leaving group is large and bulky or has special steric requirements for complexation (Equation 24).

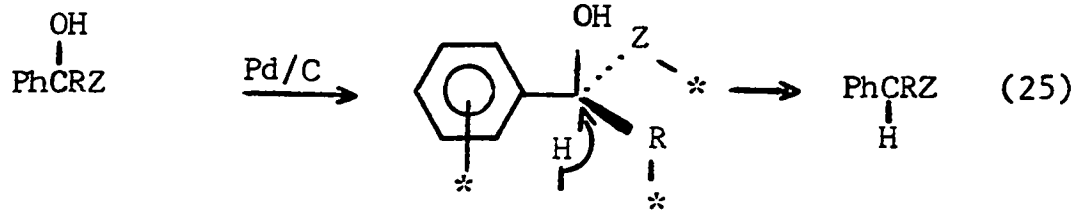


(24)

Hydrogen is transferred from the surface to which the other groups are adsorbed with inversion of configuration at the asymmetric carbon and formation of either an adsorbed radical

or anion and the desorbed organic product.

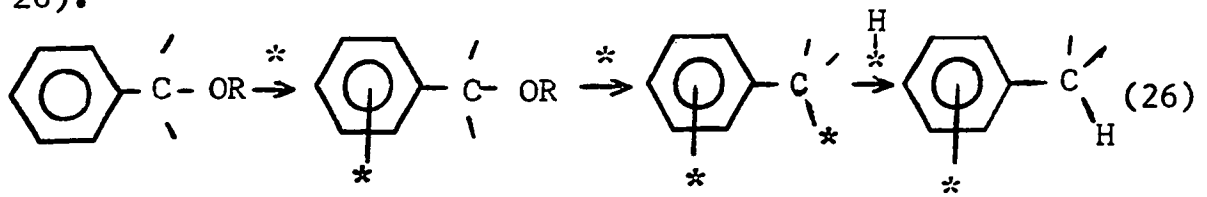
The S_Ni and S_N2 type mechanisms explain the stereochemistry of hydrogenolyses carried out over Raney nickel where retention of configuration is generally observed. The adsorbed state over Raney nickel involves adsorption of the oxygen leaving group and the S_Ni type reaction is observed. With palladium, the adsorbed state does not involve adsorption of the oxygen leaving group, hydrogen transfer occurs from the catalyst side of the molecule displacing the leaving group with inversion of configuration (89, 90, 91, 92) (Equation 25).



(25)

Equation 25 resembles the S_Ni mechanism with the exception that the leaving group is not adsorbed and the displacement of this group results in inversion of configuration.

Mitsui and coworkers subsequently proposed that the inversion of configuration observed in the palladium catalyzed hydrogenolyses was due to a series of reactions involving complexation at the benzylic carbon (77) (Equation 26).



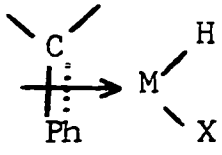
(26)

The hydrogenolysis of 3-hydroxy-3-phenylvaleric acid and its derivatives proceeds with inversion with a high degree of retention of optical activity over palladium-charcoal in ethanol. The results are consistent with the adsorption proposals and the S_Ni mechanism proposed earlier (93). Other adsorption information comes from a study by Smith and coworkers who investigated the hydrogenolysis of the benzyl esters of tartaric, malic (2-hydroxy-1,4-butanedioic), and succinic acids over palladium-charcoal (94). The tartrate and malate hydrogenolyze at the same rate while the succinate undergoes hydrogenolysis much more slowly. This difference is explained by postulating the adsorption of the carbobenzyloxy and the hydroxy group.

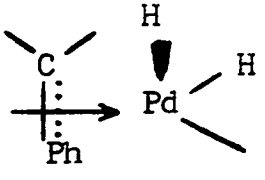
The palladium-charcoal catalyzed hydrogenolyses of atrolactic acid (2-hydroxy-2-phenylpropanoic acid), its acetate and trifluoroacetate indicate that the reactivity of the trifluoroacetate was greater than the acetate which in turn was more reactive than the acid (73, 74). A high degree of inversion of configuration was observed; the phenyl, hydroxy, or carboalkoxy groups may control the stereochemistry because the hydrogenolysis of the phenylcholestanols over palladium-charcoal in ethanol proceeded with complete inversion of configuration.

The hydrogenolysis of a series of 1-phenyl-1-cycloalkanols was also studied (73, 74). The reaction transition

state is reached by a change in hybridization at the benzylic carbon from sp^3 to sp^2 and the formation of a π-benzyl intermediate is proposed.

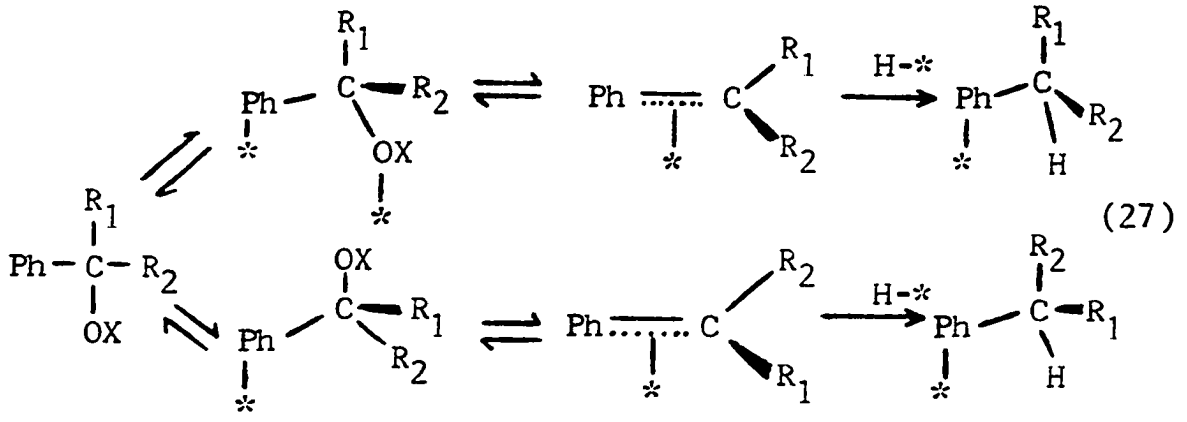


This intermediate could lead to retention or inversion depending upon the polar character of the leaving group. Less polar groups would lead to retention and more polar groups would lead to inversion. Inversion of stereochemistry may involve benzyl coordination at internuclear sites, surface adsorption sites, and transfer of hydrogen from a nuclear site; a site in which coordination occurs by a bond projecting from a surface (73, 74). An intermediate of the form



has a planar π-benzyl intermediate and addition of hydrogen from above the plane of the benzyl group results in inversion of configuration.

Mitsui and coworkers proposed that the stereoselectivity of benzylic hydrogenolyses carried out over palladium is determined by the formation of the π-benzylic complex (76). (Equation 27)



(27)

The reaction will occur with inversion or retention of configuration depending upon the manner in which the π-benzylic complex is formed. If the leaving group complexes with the catalyst, one π-benzylic intermediate will be formed and the reduction of this intermediate will lead to retention of configuration. If the leaving group does not complex with the catalyst, a different π-benzylic complex will be formed and the reduction of this intermediate will lead to inversion of configuration.

Garbisch and coworkers studied the hydrogenolysis of 1-substituted cis- and trans-4-t-butyl-1-phenylcyclohexane over palladium-charcoal in acetic acid at room temperature and three atmospheres (72). The hydrogenolysis of the alcohol was stereoconvergent forming 83% of the cis-alkane. Hydrogenolysis of the acetate proceeded with inversion of configuration. The stereoconvergent hydrogenolyses must proceed

through a common intermediate which may be a monoadsorbed complex that attains configurational equilibrium prior to hydrogenation. The stereospecific inversion of configuration does not pass through the monoadsorbed complex rather the hydrogenolysis proceeds *via* a direct substitution process but the authors did not elaborate on this point.

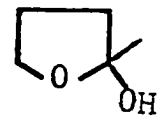
A substituent effect has been noted in the hydrogenolysis of benzyl alcohols carried out over palladium-charcoal in acetic acid in a constant volume system (80). The reactions were followed and compared by measuring the rate of hydrogen consumption. The reaction rate was retarded by electron withdrawing substituents, accelerated by electron donating substituents, and retarded by alpha substituents. Substituent effects are more pronounced for α,α-dialkylbenzyl alcohols than for the primary benzyl alcohols; a rho of -0.37 was observed for the primary benzyl alcohols while a rho of -1.43 was observed for the tertiary benzyl alcohols. The hydrogenolysis of benzyl alcohol was carried out in acetic acid-$\underline{d}_1$ using deuterium gas; the average deuterium content of the toluene product was 1.0 deuterium atoms per mole with 17% of the deuterated species being the $\underline{d}_2$ isomer and 4% of the deuterated species were the $\underline{d}_3$ isomer. The authors propose that a rho of -0.37 implies that the hydrogenolysis of the primary benzyl alcohols proceeds *via* direct displacement of the leaving group by a hydride ion in an S_N2 type reaction.

The deuteration studies indicate that the aromatic ring will be π-bonded to the catalyst and some adsorption occurs at the benzylic carbon.

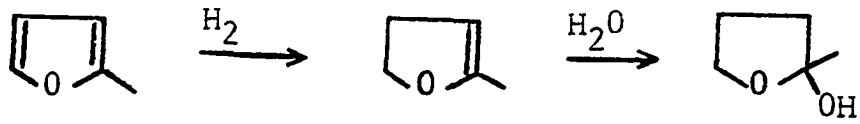
There are few reports in the literature concerning the hydrogenation or hydrogenolysis of furfuryl alcohol over palladium-charcoal. Schujkin and Belskij studied the hydrogenolysis of a series of α-alkyl furfuryl alcohols over palladium-charcoal in the gaseous phase at 275° (95). Yields of 65 to 80% of the alkylfurans were obtained. Weinhaus studied the hydrogenolysis of furfuryl alcohol over palladium catalysts (96). Furfuryl alcohol incorporated 2 moles of hydrogen. Over palladium-charcoal, the reaction stopped after the addition of 1 mole of hydrogen and it was necessary to add fresh catalyst to complete the hydrogenation. The product of the reduction was proposed to be tetrahydrofurfuryl alcohol; a carbon-hydrogen analysis compares quite well with the calculated values. The hydrogenation of 2-methylfuran over palladium charcoal at 275° produced 71% of 2-methyltetrahydrofuran and 29% of 2-pentanone (97). The hydrogenation 2-methylfuran in water produced γ-acetopropyl alcohol in good yield (98).

$$+ H_2 + H_2O \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2OH$$

The ketone is the open form of the cyclic hemiacetal, 2-

hydroxy-2-methyltetrahydrofuran,  which can be

formed as shown below:



RESULTS AND DISCUSSION

The hydrogenolysis of various benzyl-oxygen bonds is thought to involve the adsorption of the phenyl group. Phenyl adsorption is postulated to explain the stereochemistry of the hydrogenolysis of optically active benzylic compounds but the exact role played by the phenyl group adsorption has not been defined (77). The adsorption of the phenyl group is thought to bring about polarization of the benzyl-oxygen bond and the benzylic carbon has a partial positive charge as a result of this polarization (89). The formation of a π-benzyl intermediate is postulated for the hydrogenolysis of benzyl alcohols over palladium (73, 74, 76). The intermediacy of the π-benzylic complex and the proposal involving polarization of the benzyl-oxygen bond as a result of phenyl adsorption are the only reports in the literature in which the role played by the phenyl group is spelled out.

Product inhibition of the hydrogenolysis of benzyl alcohols has been observed and this inhibition is a result of the formation of a catalyst hydrocarbon complex (86). This complex ties up the active sites on the catalyst which are required for hydrogenolysis and are not available for catalysis. Further elaboration as to the nature of this complex was not made. The structural feature common to both

the alcohol and hydrocarbon is the benzene nucleus. Inhibition must involve the formation of a π-complex between palladium and the toluene derivative. If π-complex formation ties up active sites required for hydrogenolysis, then the mechanism for the hydrogenolysis involves π-complex formation prior to rupture of the benzyl carbon-oxygen bond. The formation of a π-complexed benzene nucleus was indicated by deuteration studies (80).

Substituents should display their electronic effect, noted in studies well correlated by the Hammett treatment, in the hydrogenolysis of the benzyl-oxygen bond if the reaction primarily involves the rupture of the carbon-oxygen bond. If strong adsorption of the benzene nucleus is required for catalysis of the hydrogenolysis, either an electronic effect or a steric effect should be observed. An electronic effect could be observed if the substituents alter the electron density of the π-cloud. This change in electron density of the π-cloud may be transferred to the benzylic carbon and the electronic effect of the substituents should alter the rate of the hydrogenolysis.

Changes in the electron density of the π-cloud may result in changes in the adsorption tendencies of the benzene nuclei. This change may or may not be transferred to the alpha carbon. Electron releasing groups will increase the electron density of the π-cloud and should make the π-cloud

more available for complexation with the catalyst. Electron releasing groups may not cause an increase in reactivity of the benzene nucleus relative to the unsubstituted benzyl alcohol but these groups will not inhibit the complexation of the substituted nucleus because of electronic factors. Electron withdrawing groups should decrease the electron density of the π-cloud and should result in the decreased reactivity of the substituted benzene nucleus relative to benzyl alcohol because the benzene nucleus is less available for complexation. The reactivity of the benzyl alcohols substituted with electron releasing groups will indicate whether an electronic effect or a steric effect is being observed. The steric effects of all groups will cause the substituted benzyl alcohols to react more slowly than the unsubstituted benzyl alcohol because of steric hindrance to complexation. Electron releasing groups should cause the substituted alcohol to be more reactive or of equal reactivity to the benzyl alcohol if the electronic effect is the only effect of importance for the reduction.

A series of substituted benzyl alcohols was subjected to competitive hydrogenolysis with benzyl alcohol or another substituted benzyl alcohol to determine the effect of nuclear substitution on the rate of the hydrogenolysis (Table 29). If the hydrogenolysis were sensitive to the electron nature of the substituent, the expected order of reactivity would

be p-OMe> p-Me> p-H > p-Cl > p-CF_3 or by the similar reactivity of benzyl alcohol and its p-methyl and p-methoxy derivatives.

Table 29. Rate constants for the hydrogenolysis of substituted benzyl alcohols relative to the rate constant for benzyl alcohol obtained in 0.03 M HCl in ethanol

Substituent	k_S/k_H
p-Me	0.05
m-Me	0.05
p-OMe	0.06
m-OMe	0.17
p-Cl	0.02
p-CF_3	0.002
m-CF_3	0.006

An electronic effect is not observed in the hydrogenolysis of the substituted benzyl alcohols, rather a steric effect towards complexation is observed. All of the substituted alcohols react less readily than does benzyl alcohol. Benzyl alcohol is preferentially adsorbed on the catalytic surface and is preferentially reduced to toluene. The hydrogenolysis is not sensitive to the electronic nature of the π-cloud but of the steric effects which alter the complexation with the catalyst. Thus, the role of the phenyl group is not to act merely as an electron donor to stabilize the benzylic reaction site but the benzene nucleus must adsorb

to the catalyst prior to the hydrogenolysis of the carbon-oxygen bond.

A Hammett correlation was not attempted because of the large error in the rate constants obtained (see Experimental Section), the small differences in the rate constants, and all of the compounds are less reactive than benzyl alcohol. The relative rate constants decrease in a manner predicted from the electronic nature of the substituents, especially when the meta-substituents or para-substituents are compared, i.e., p-OMe> p-Me> p-Cl > p-CF_3 but the range of values is very small, 0.06 to 0.002.

The results of the competitive hydrogenolyses of the substituted benzyl alcohols are contrasted with the results obtained by measuring the rates of hydrogen consumption in noncompetitive hydrogenolyses of substituted benzyl alcohol (80). An electronic effect is not observed in the competitive study while a small but measurable electronic effect is observed in the noncompetitive study. The competitive hydrogenolyses were carried out on one millimole of each of two substrates and were catalyzed by twenty milligrams of 10% Pd/C, while the noncompetitive reactions were carried out on one millimole of substrate catalyzed by three hundred milligrams of 1% Pd/C. In the latter reactions, the percentage of adsorbed substrate was much greater than the percentage of adsorbed substrate in the competitive reactions.

In the competitive hydrogenolyses, two competitive processes are involved; there is competition between the substrates for adsorption sites and there is competition between the adsorbed substrates for adsorbed hydrogen atoms. The two competitive processes are illustrated in equations 28 and 29 using symbols A and B to represent benzyl alcohols.

$$A \underset{}{\overset{*}{\rightleftharpoons}} A\text{-}* \xrightarrow{H\text{-}*} A\text{-}H + 2* \qquad (28)$$

$$B \underset{}{\overset{*}{\rightleftharpoons}} B\text{-}* \xrightarrow{H\text{-}*} B\text{-}H + 2* \qquad (29)$$

The results of the competitive hydrogenolyses indicate the combined effect of the adsorption competition and the reduction competition. In the noncompetitive reactions most of the substrate is adsorbed to the catalyst and the rate measured is that of the reaction with adsorbed hydrogen atoms. Thus, the differences between the two studies is due to the inclusion of adsorption effects in the competitive study.

The results of the meta- and para-substituted benzyl alcohols indicate that the benzene nucleus is strongly adsorbed to the catalytic surface and this complexation is a necessary condition for the catalysis of the hydrogenolysis. The adsorption of the benzene nucleus determines the reactivity of the benzyl alcohols. Complexation is sensitive to steric hindrance by substituents on the benzene nucleus; the electronic effect of the substituent has very little effect upon the relative reactivity of the benzyl alcohol.

A steric effect towards complexation rather than an electronic effect of a substituent has also been observed in hydrogen-deuterium exchange reactions of aromatic compounds carried out over platinum metals. Fraser and Renaud studied the effect that a substituent has upon exchange at positions ortho, meta, and para to a substituent (99). Fluoro, chloro, methoxy, hydroxy, and other substituents exert a large steric effect in the exchange process but the electronic character of the substituent does not determine the position of exchange. The lack of an electronic effect on the position of exchange has also been noted by Garnett and Sollich-Baumgartner and resulted in the proposal of the ortho deactivation effect which involves steric inhibition to complexation at positions ortho to large bulky groups (30).

The steric hindrance to complexation of the benzene nucleus in the benzyl alcohols was observed for meta- and para-substituted alcohols. These substituents were fairly remote from the hydroxy group; therefore, two ortho substituted benzyl alcohols and α-methylbenzyl alcohol in which the substituent is in close proximity to the hydroxy group, were subjected to competitive hydrogenolysis (Table 30). The ortho substituent has exactly the same effect as a meta or para group; the ortho group also causes steric inhibition to complexation and the effect of the inhibition is the same

as the meta or para substituent. Thus, the presence of a group in a position ortho to the reaction center has no additional effect on the reaction other than steric inhibition to complexation.

Table 30. Rate constants for the hydrogenolysis of ortho-, para-, and alpha-substituted benzyl alcohols relative to the rate constant for benzyl alcohol obtained in 0.03 M HCl in ethanol

Substituent	k_S/k_H
p-Me	0.05
o-Me	0.05
p-Cl	0.02
o-Cl	0.02
α-Me	0.05

The presence of a methyl group in the alpha position has the same effect upon the rate as does a ring methyl substituent. The alpha methyl group should not interfere with aromatic complexation; therefore, the retarding influence of a methyl group alpha to a benzylic position is due to inhibition to complexation at the benzylic carbon. An alpha methyl group causes a decreased reactivity relative to benzyl alcohol by steric inhibition to complexation at the benzylic carbon. Thus, the reaction proceeds via full complexation at the benzylic carbon and this complexation

is as important as complexation of the benzene nucleus.

The observation of complexation at the benzylic carbon led to an experiment in which the extent of deuterium incorporation at the benzylic carbon was determined. The hydrogenolysis of benzyl alcohol was carried out in ethanol-$\underline{d}_1$ using deuterium gas and the toluene product was collected and analyzed for deuterium content by mass spectroscopy. The extent of deuterium incorporation into toluene should indicate whether a rapid reduction of the adsorbed toluene occurs without hydrogen-deuterium exchange forming toluene-$\underline{d}_1$ or the adsorbed hydrocarbon stays on the catalyst long enough to undergo complete exchange at the α-carbon forming the $\underline{d}_3$ isomer. The results of the deuteration study indicate that about three percent of the $\underline{d}_3$ isomer and about ten percent of the $\underline{d}_2$ isomer are produced in the hydrogenolysis (Table 31). The large amount of the $\underline{d}_0$ isomer was not expected and may be due to a large isotope effect in which a small amount of hydrogen on the catalytic surface is preferentially incorporated into the toluene product. Preferential incorporation of hydrogen would result in a much greater amount of the $\underline{d}_0$ isomer than would be predicted from the relative concentrations of hydrogen atoms and deuterium atoms. The deuterated isomer distribution indicates that hydrogen atoms which are removed from adsorbed substrate molecules in the exchange process are incorporated into other substrate mole-

cules. This latter point was also noted in the deuteration studies of the alkylbenzenes (see Part I). The nmr of the toluene indicates that all of the deuterium is located on the carbon alpha to the benzene nucleus.

Table 31. The corrected normalized value of each deuterated species of toluene and benzyl alcohol-$\underline{d}_2$

Compound	d_0	d_1	d_2	d_3	D/mole
Toluene[a]	44.0	42.8	9.6	3.4	0.72
Benzyl alcohol-$\underline{d}_2$	8.7	22.4	62.5	6.3	1.67
Toluene[b]	13.8	33.0	48.9	4.4	1.44

[a]Produced from benzyl alcohol in ethanol-$\underline{d}_1$ and 20 microliters of conc. DCl and deuterium gas.

[b]Produced from benzyl alcohol-$\underline{d}_2$ in 0.03 $\underline{M}$ HCl in ethanol and hydrogen gas.

The observation of toluene-$\underline{d}_3$ indicates that complete exchange of the methyl hydrogens has occurred in a small but measurable amount. Complete methyl group exchange in toluene indicates that the hydrogenolysis proceeds through a diadsorbed intermediate in which the phenyl is π-complexed and the methyl is sigma complexed to the catalyst. This intermediate has a finite lifetime and while adsorbed to the catalyst, exchange of the methyl hydrogens can occur $\underline{via}$ the reversible formation of the monoadsorbed π-complex and the diadsorbed intermediate.

The observation of the preferential incorporation of

hydrogen into the toluene product of the deuteration of benzyl alcohol led to an experiment in which the preferential incorporation of deuterium may be observed. Benzyl alcohol-$\underline{d}_2$ (actual deuterated species distribution is shown in Table 31) was subjected to hydrogenolysis in acidic ethanol using hydrogen gas and the toluene product was collected and analyzed for deuterium content by mass spectroscopy. A comparison of the deuterated species distribution of benzyl alcohol-$\underline{d}_2$ and the toluene produced from it should indicate whether deuterium atoms which are removed from adsorbed substrate molecules in the exchange process are incorporated into other product molecules or are lost to the solvent. If preferential incorporation of liberated deuterium atoms into other product molecules were observed, the percentage of the $\underline{d}_3$ species in the toluene product should be greater than the percentage of the $\underline{d}_3$ species in benzyl alcohol-$\underline{d}_2$. If the deuterium atom liberated in the exchange process is lost to the solvent, the percentage of the $\underline{d}_3$ species of the toluene should be less than the percentage of the $\underline{d}_3$ species of benzyl alcohol-$\underline{d}_2$.

The results of the reduction of benzyl alcohol-$\underline{d}_2$ indicate that hydrogen-deuterium exchange is occurring but the deuterium atoms liberated in the exchange process are lost to the solvent; exchange is occurring but the preferential

incorporation of deuterium into other product molecules is not observed. The results of the reduction of benzyl alcohol-$\underline{d}_2$ indicate that the preferential incorporation of hydrogen into the toluene product of the deuteration of benzyl alcohol is probably due to an isotope effect. The observation of hydrogen-deuterium exchange at the alpha carbon of benzyl alcohol-$\underline{d}_2$ provides additional support for an intermediate in which the benzene nucleus is π-complexed to the catalyst and the alpha carbon is σ-complexed to the catalyst.

Steric hindrance to complexation of the benzene nucleus was noted in the hydrogenolysis of monosubstituted benzyl alcohols. The effect of increased substitution and the

substitution pattern of these substituents was determined by a comparison of two series of polysubstituted benzyl alcohols under conditions of competitive hydrogenolysis (Table 32).

Table 32. Rate constants for the hydrogenolysis of polysubstituted benzyl alcohols relative to the rate constant for benzyl alcohol obtained in 0.03 M HCl in ethanol

Substituents	k_S/k_H
p-Me	0.05
3,5-Dimethyl	0.006
3,4-Dimethyl	0.006
2,3-Dimethyl	0.004
2,4,6-Trimethyl	0.003
p-OMe	0.06
3,5-Dimethoxy	0.007
3,4-Dimethoxy	0.005
2,3-Dimethoxy	0.003

The addition of one methyl or methoxy group to the benzene nucleus decreased the reactivity of the benzyl alcohol by a factor of twenty. The addition of a second substituent decreased the reactivity of the disubstituted benzyl alcohol by a factor of ten when compared to the monosubstituted benzyl alcohol or a factor of two hundred when compared to benzyl alcohol. The addition of a third substituent,

2,4,6-trimethylbenzyl alcohol, resulted in a decrease in reactivity by a factor of two when compared to the dimethyl compound.

The replacement of a hydrogen by a methyl or methoxy group produced a marked decrease in the complexation tendency of the benzene nucleus because of the greater steric hindrance to complexation. Thus, the reactivity decreased by a factor of twenty. Replacement of a hydrogen by a second substituent resulted in a further increase in the steric hindrance but the degree of this increase is not as great as for the first substituent. Thus, the decrease in reactivity was a factor of ten. The addition of a third methyl group does not produce as great a change in steric factors towards complexation as did the second methyl group; therefore, the decreased reactivity of the trimethylbenzyl alcohol relative to the dimethylbenzyl alcohol is only a factor of two.

The reactivity of the benzyl alcohol is decreased as the benzene nucleus becomes more highly substituted because of the increased steric hindrance towards complexation. The substitution pattern of the substituents has little effect upon the reactivity of the alcohol (Table 32). The order of reactivity of the polysubstituted benzyl alcohols is consistent with the observations of Rader and Smith who studied the competitive hydrogenation of benzene, toluene, and the polymethylbenzenes (100). The ease of adsorption decreased

with increased nuclear substitution and the relative ease of adsorption may result from the relative amount of steric strain arising from the flatwise adsorption of the benzene nucleus on the catalyst. They found that the ease of adsorption decreased with an increased symmetry of substitution of the dimethyl- and trimethylbenzenes. This was not observed in the competitive hydrogenolyses and failure to observe this trend may be due to the error in the rate constants or the small differences between the rate constants.

The results listed in Tables 29, 30, and 32 have been explained by the strong adsorption of the benzene nucleus on the catalyst prior to rupture of the carbon-oxygen bond. Phenyl adsorption controls the reactivity of the benzyl alcohol. If an arylmethanol is subjected to competitive hydrogenolysis with benzyl alcohol and the aryl group is more strongly adsorbed to the catalyst than the phenyl group, the arylmethanol should be more reactive than benzyl alcohol. The trends in π-complex adsorption strengths observed in competitive exchange reactions indicate that naphthalene is more strongly adsorbed to the catalyst than benzene, anthracene or the polycyclic aromatic hydrocarbons (30). A series of arylmethanols was subjected to competitive hydrogenolysis and the results are listed in Table 33. The hydrogenolysis of 2-hydroxymethylfuran (furfuryl alcohol) was also attempted but simple hydrogenolysis was not observed.

Table 33. Rate constants for the hydrogenolysis of arylmethanols relative to the rate constant for benzyl alcohol obtained in 0.03 M HCl in ethanol

Compound	k_{Ar}/k_{Ph}
1-Hydroxymethylnaphthalene	14
2-Hydroxymethylnaphthalene	21
9-Hydroxymethylanthracene	56

The results listed in Table 33 illustrate that as π-complex formation of the aromatic system becomes stronger, the reactivity of the arylmethanol increased. This observation confirms the significance of π-complex formation prior to hydrogenolysis. The rate constant for the anthracene derivative would not be expected to be greater than for the naphthalene derivatives on the basis of π-complex formation tendencies. The actual anthracene reaction was very slow; preferential adsorption and reduction of the anthracene derivative with very slow hydrogenolysis was observed. The greater reactivity of the anthracene is probably due to a decrease in the number of available sites for hydrogenolysis. It is proposed that the bulky adsorbed aromatic prevents complexation at active sites in the vicinity to the adsorption site and thereby prevents benzyl alcohol reduction. The apparent increased reactivity of the anthracene is probably the result of partial poisoning of the catalyst to benzyl alcohol reduction because of the bulk of the anthracene.

During the formulation of this study, the hydrogenolysis of various leaving groups was contemplated. If an electronic effect were observed, the effect of the leaving group upon the rho for the reactions would be determined. The significance of the leaving group effect may give information concerning the mechanism of the hydrogenolysis. Preliminary experiments on benzyl acetates were carried out (Table 34).

Table 34. Rate constants for hydrogenolysis of p-substituted benzyl alcohols and acetates relative to the rate constant of the unsubstituted benzyl compound obtained in 0.03 M HCl in ethanol

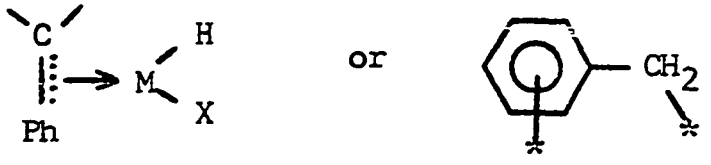
Substituent	k_S/k_H	
	OH	OAc
p-Me	0.05	0.06
p-Cl	0.02	0.03

The results obtained for the acetates are in very good agreement with the results of the alcohols, an electronic effect is not observed in either case. The same effects are involved in the hydrogenolysis of the alcohol or the acetate and the alcohol reactions were studied in more detail. Further studies of the effect of the leaving group were not undertaken.

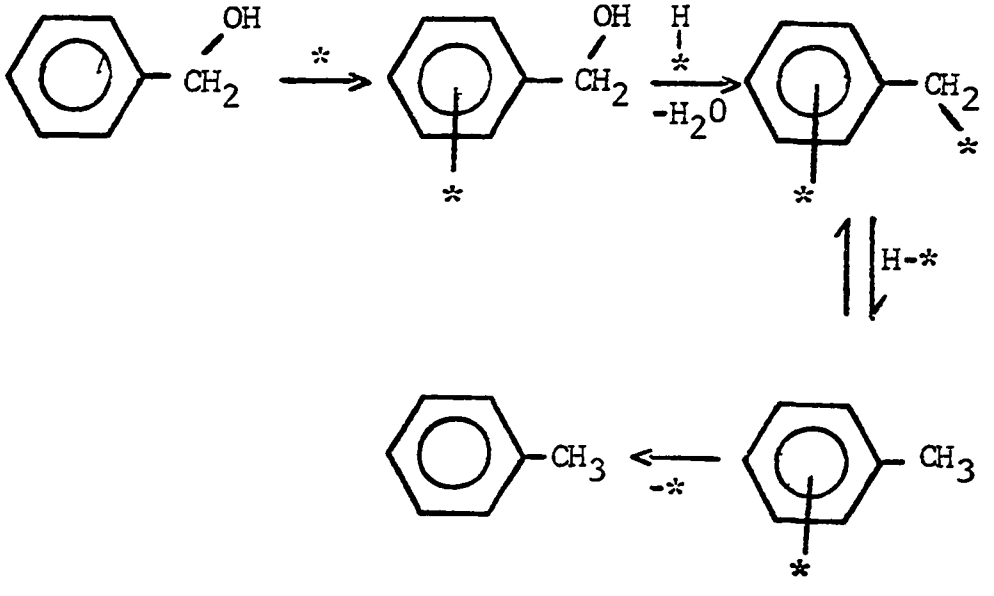
To summarize, this study has shown that the adsorption of the benzene nucleus on the surface of the catalyst is a necessary condition in the catalytic hydrogenolysis of

the benzyl-oxygen bond. The importance of phenyl adsorption in the catalytic process is indicated by the decreased reactivity of substituted benzyl alcohols relative to benzyl alcohol. Factors which inhibit adsorption of the benzene nucleus decrease the rate of hydrogenolysis. Factors which favor complexation increase the rate of hydrogenolysis, i.e., arylmethanols with aryl groups that are more strongly adsorbed than the phenyl group, such as naphthyl, react more readily than benzyl alcohols. The adsorption of the aryl group determines the reactivity of the benzyl derivative and is sensitive to steric hindrance towards complexation with the catalyst. Groups substituted on the benzene nucleus cause steric hindrance towards complexation and the reactivity of the alcohols is sensitive to the steric bulk of the substituent, not its electronic nature. The decreased adsorption of a substituted benzene nucleus is dependent only upon the bulk of the substituent not its position of substitution as shown by a comparison of ortho-, meta-, and para-substituted benzyl alcohols. The adsorption of the benzene nucleus on the catalyst was very dependent upon the number of ring substituents. As the number of substituents was increased, the adsorption of the benzene nucleus and the reactivity of the benzyl alcohol decreased. The reactivity of the polysubstituted benzyl alcohols was not sensitive to the position of substitution.

The very low reactivity of α-methylbenzyl alcohol and the hydrogenolysis of benzyl alcohol in deuterated solvents indicate that complexation at the benzylic carbon is very important in the catalytic process. The intermediate in the hydrogenolysis process may be the π-benzyl intermediate (73, 74) or the α,π-diadsorbed complex, either



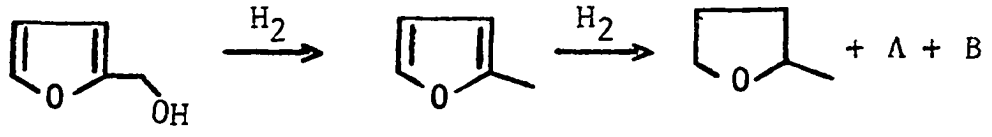
Either of these intermediates refute the suggestion that the palladium catalyzed hydrogenolysis of a benzyl group proceeds <u>via</u> a S_Ni reaction, Equation 23 or a S_N2 reaction, Equation 25 (75). The mechanism that is proposed for the hydrogenolysis of the benzyl-oxygen bond is shown in Scheme 18.



Scheme 18. Benzyl hydrogenolysis mechanism

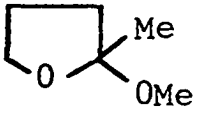
Furfuryl alcohol is somewhat different than the benzyl alcohols, mainly in terms of the nature of the furan ring and the benzene nucleus. The hydrogenolysis of furfuryl alcohol was carried out to determine if the course of this hydrogenolysis paralleled that of the benzyl alcohol hydrogenolyses. The hydrogenation of 2-methylfuran was attempted to determine the stability of the compound under the reaction conditions.

Two moles of hydrogen were adsorbed per mole of furfuryl alcohol. The glpc chromatogram shows the presence of a small amount of 2-methyltetrahydrofuran and the two products with retention times of ca. 12 and 15 minutes with poor separation between the two peaks. The peak with a retention time of 12 minutes is the major product. 2-Methylfuran was not present in the hydrogenolysis product. The hydrogenation of 2-methylfuran resulted in the incorporation of slightly more than one mole of hydrogen per mole of 2-methylfuran. Analysis of the reaction mixture by glpc showed the presence of 2-methyltetrahydrofuran in small amounts and the two products with retention times of ca. 12 and 15 minutes that were noted in the chromatogram of the furfuryl alcohol. The chromatograms of the reduction of furfuryl alcohol and 2-methylfuran are identical; this observation and failure to observe 2-methylfuran in the product mixture of furfuryl alcohol indicates the reaction proceeds via equation 30.

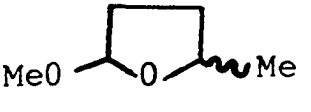


(30)

The structure of compounds A and B were deduced from spectral observations. The nmr of the mixture of A and B produced in ethanol was very complex but indicated incorporation of ethanol into the products. Since the hydrogenation of 2-methylfuran in ethanol appeared to proceed via the incorporation of solvent into the product, the reduction was carried out in 0.02 M HCl in methanol. If methanol were incorporated into the product, the nmr spectrum of the product mixture would be much simpler than the ethanol product. Once again, the adsorption of one mole of hydrogen per mole of 2-methylfuran was noted. Chemical analysis and spectral data indicate that the major component of the hydrogenolysis of 2-methylfuran is 2-methoxy-2-methyltetrahydrofuran.

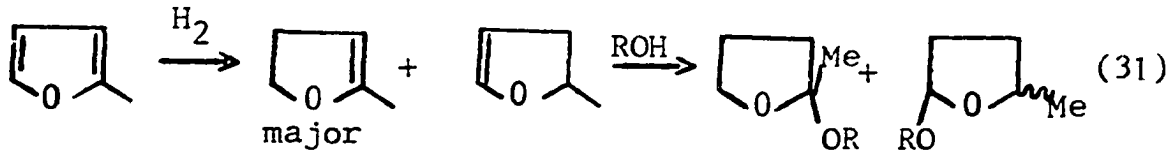


The nmr of the mixture of A and B indicates that the minor product is 4-methyl-2-methoxytetrahydrofuran.



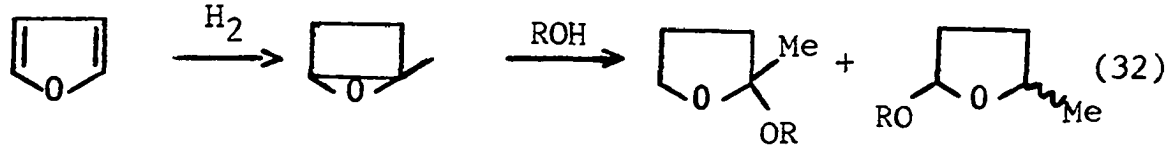
Two sequences can be postulated to explain the formation of the major components of the reduction of 2-methylfuran.

In one sequence the dihydrofuran derivative is formed as an intermediate in the reduction. The intermediate then reacts with solvent to give the observed products. (Equation 31)



(31)

The other sequence involves the formation of an intermediate epoxide which is opened by solvent forming the two tetrahydrofuran derivatives. (Equation 32)



(32)

A series of experiments were carried out in an attempt to determine the relative importance of equations 31 and 32. Cyclopentadiene was subjected to the hydrogenation procedure used for the reduction of furfuryl alcohol and the only product of the reduction was cyclopentane. Equation 32 involves the formation of an epoxide intermediate; if the reaction of cyclopentadiene proceeded in this manner, bicyclo-[2.1.0]pentane should be a product of the reaction because the bicyclic derivative should be stable to the reaction conditions. Since bicyclo[2.1.0]pentane is not a product of the reduction of cyclopentadiene, a reaction sequence similar to equation 32 is not operative for cyclopentadiene. This

result suggests that equation 32 does not explain the formation of solvent incorporated product in the reduction of 2-methylfuran.

The reduction of furan was carried out in 0.02 M hydrochloric acid in methanol; one millimole of hydrogen was adsorbed per millimole of furan and the reduction gave two products. One product was tetrahydrofuran; the other product, the major product, has a glpc retention time comparable to that expected for 2-methoxytetrahydrofuran. The nmr of this product corresponded to that predicted for 2-methoxytetrahydrofuran.

A series of reactions were carried out on 4,5-dihydro-2-methylfuran. One experiment involved the reaction between the dihydrofuran and 0.02 M HCl in methanol, the solvent in which the hydrogenations were carried out. The second reaction involved the mixing of the dihydrofuran, 0.02 M HCl in methanol, and a catalytic amount of 10% Pd/C while the third experiment involved an actual hydrogenation of a reaction mixture comparable to that of reaction two. The gas chromatogram of the dihydrofuran-methanol mixture indicated the presence of one product; the nmr of this product corresponded to that predicted for 2-methoxy-2-methyltetrahydrofuran. The glpc of the second reaction mixture also indicated the presence of one product, 2-methoxy-2-methyltetrahydrofuran and the glpc of the third reaction mixture

indicated the presence of 2-methyltetrahydrofuran and the solvent incorporated product.

The results of the furan reduction and the reaction of 4,5-dihydro-2-methylfuran with methanol indicate that equation 31 most likely explains the formation of the products of the reduction of 2-methylfuran and furfuryl alcohol.

An experiment involving 2-methylfuran and 0.02 M HCl in methanol was carried out and the absence of the solvent incorporated product was noted by glpc analysis. This result indicates that solvent incorporation into the furan nucleus occurs at an intermediate stage in the reaction and coupled with the results of the reactions of 4,5-dihydro-2-methylfuran indicates that equation 31 most likely describes product formation.

EXPERIMENTAL

Equipment

Nuclear magnetic resonance (nmr) spectra were measured on a Varian A-60 spectrometer. Chemical shifts are reported as δ-values in parts per million (ppm) from tetramethylsilane (TMS), an internal standard.

Gas liquid partition chromatography (glpc) analyses were carried out on a Varian Aerograph Model 200 instrument fitted with dual thermal conductivity detectors. The analyses were carried out on a 6' by ¼" column packed with 10% SE-52 on Fluoropack. Mass spectra were measured on an Atlas CH4 spectrometer.

Materials

Benzyl alcohol, p-chlorobenzyl alcohol, 2,3-dimethoxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, furfuryl alcohol, m-methoxybenzyl alcohol, p-methoxybenzyl alcohol, m-methylbenzyl acetate, p-methylbenzyl acetate, p-methylbenzyl alcohol, and 1-phenylethanol are commercially available. Liquids were purified by distillation. o-Chlorobenzyl alcohol, 1-hydroxymethylnaphthalene, and 2,4,6-trimethylbenzyl alcohol were obtained from group chemicals. The purity of all compounds was established by glpc prior to hydrogenolysis.

m-Methylbenzyl alcohol

To 11.2 g (0.200 mole) of potassium hydroxide in 100 ml of 10% ethanol-water was added 10.0 g (0.0667 mole) of m-methylbenzyl acetate and the mixture heated to reflux. An additional 25 ml of ethanol was added to the refluxing mixture to effect homogeneity and the refluxing was continued for four hours. The mixture was cooled and extracted with two 200-ml portions of ethyl ether. The etheral layer was washed with 100 ml of saturated sodium chloride solution, 100 ml of saturated sodium hydrogen carbonate solution, and dried over anhydrous magnesium sulfate. The ether was removed on a rotovac and the product distilled at reduced pressure: bp 108-109° (12 mm); lit (101), bp 215° (740 mm); nmr (CCl_4), δ 2.28 (s, 3), 3.85 (s, 1), 4.40 (s, 2), 7.03 (s, 4).

o-Methylbenzyl alcohol

The procedure described for m-methylbenzyl alcohol was carried out on o-methylbenzyl acetate using equivalent quantities of chemicals. The product was distilled at reduced pressure and crystallized: mp 32-33°; lit (102), mp 34°.

Benzyl acetate

Benzyl acetate, obtained from group chemicals, contained

ca. 10% of benzyl alcohol. To remove this impurity, 7.0 g (0.090 mole) of acetyl chloride was added to 61 g (0.40 mole) of benzyl acetate, and the mixture heated for one and one-half hours. The mixture was cooled, taken up in ether, the ether solution was washed with three 100-ml portions of saturated sodium hydrogen carbonate solution and dried over anhydrous magnesium sulfate. The ether was removed on a rotovac and the product distilled at reduced pressure. Redistillation of the major fraction produced benzyl acetate that was 96% pure (glpc).

p-Chlorobenzyl acetate

A mixture of 3.55 g (0.0250 mole) of p-chlorobenzyl alcohol, 4.0 g (0.050 mole) of acetyl chloride and 10 ml of ethyl acetate was refluxed for one hour, cooled, and poured into 200 ml of ethyl ether. The ether solution was washed with three 50-ml portions of saturated sodium hydrogen carbonate solution and dried over anhydrous magnesium sulfate. The ether was removed on a rotovac and the product distilled at reduced pressure: bp 126-127° (12 mm); lit (103), bp 240°; nmr (CCl_4), δ 2.0 (s, 3), 5.0 (s, 3), 7.3 (s, 4).

n-Heptyl acetate

A mixture of 11.6 g (0.100 mole) of 1-heptanol, 10 g

(0.13 mole) of acetyl chloride, and 50 ml of benzene was slowly heated to reflux and the mixture was then refluxed one hour, cooled, and poured into 50 ml of saturated sodium chloride solution. The benzene layer was washed with two 50-ml portions of saturated sodium hydrogen carbonate solution and dried over anhydrous magnesium sulfate. The benzene was removed on a rotovac and the product distilled at reduced pressure: bp 78-79° (12 mm); lit (104), bp 191.5°; nmr (CCl_4), δ 0.95 (broad), 1.34 (broad) (13), 1.96 (s, 3), 4.0 (t,2, $\underline{J}$ = 6.0 Hz).

m-Methoxybenzyl acetate

The procedure used to synthesize n-heptyl acetate was carried out on 13.8 g (0.100 mole) of m-methoxybenzyl alcohol: bp 137° (12 mm); lit (105), bp 142-144° (15 mm); nmr (CCl_4), δ 2.03 (s, 3), 3.75 (s, 3), 5.0 (s, 2), 7.0 (m, 4).

m-Trifluoromethylbenzyl alcohol

A slurry of 1.42 g (0.038 mole) of lithium aluminum hydride in 50 ml of dry ether was added to a 250 ml three-necked round-bottomed flask fitted with a magnetic stir bar, a dropping funnel, and a reflux condenser. A solution of 9.50 g (0.050 mole) of m-trifluoromethylbenzoic acid in 25 ml of dry ether was added dropwise to the slurry over a period of one hour and the mixture stirred for thirty minutes. The reaction mixture was quenched by addition of

10 ml of ethyl acetate, the mixture stirred for thirty minutes and 3 ml of water, 3 ml of 15% sodium hydroxide solution and 12 ml of water were added in succession. Seventy milliliters of 10% hydrochloric acid solution was added to the quenched mixture, the ether layer separated, and the aqueous layer extracted with two 50-ml portions of ethyl ether. The combined etheral layers were washed with two 100-ml portions of saturated sodium hydrogen carbonate and dried over anhydrous magnesium sulfate. The ether was removed on a rotovac and the product distilled at reduced pressure: bp 99.5° (12 mm); lit (106), bp 68° (2 mm); nmr (CCl_4), δ 4.31 (broad, 1), 4.53 (s, 2), 7.46 (m, 4).

p-Trifluoromethylbenzyl alcohol

The above procedure was carried out on 2.38 g (0.0125 mole) of p-trifluoromethylbenzoic acid using one-fourth of the amount of the chemicals listed except that 50 ml of ether was used: bp 99.0° (12 mm); lit (107), bp 78.5-80° (4 mm); nmr (CCl_4), δ 3.92 (broad, 1), 4.60 (s, 2), 7.45 (m, 4).

3,5-Dimethylbenzyl alcohol

The above procedure was carried out on 7.50 g (0.050 mole) of 3,5-dimethylbenzoic acid, using equivalent quantities of other chemicals except that 75 ml of ether was used: bp 122.5° (12 mm); lit (108), bp 218-221°; nmr (CCl_4), δ 2.2 (s, 6), 3.4 (s, 1), 4.6 (s, 2), 6.8 (s, 3).

3,4-Dimethylbenzyl alcohol

The above procedure was carried out on 7.50 g (0.050 mole) of 3,4-dimethylbenzoic acid using equivalent quantities of other chemicals except that 160 ml of ether was used. The product was recrystallized from ether-pentane: mp 57-58°; lit (109), mp 62.5-63.5°.

2,3-Dimethylbenzyl alcohol

The above procedure was carried out on 3.75 g (0.025 mole) of 2,3-dimethylbenzoic acid using one-half of the chemicals listed except that 150 ml of ether was used. The product was recrystallized from ether-pentane: mp 60-62°; lit (110), bp_{20} 128-130°.

3,5-Dimethoxybenzyl alcohol

The above procedure was carried out on 9.10 g (0.050 mole) of 3,5-dimethoxybenzoic acid using equivalent quantities of chemicals listed except that 200 ml of ether was used. The product was recrystallized from ether-pentane: mp 47-48°; lit (111), mp 48-49°.

2-Hydroxymethylnaphthalene

The above procedure was carried out on 7.80 g (0.050 mole) of 2-naphthaldehyde using 0.50 g (0.013 mole) of lithium aluminum hydride, 150 ml of ether, and quenching the reaction with one-half of the quantities of the materials

listed. The product was recrystallized from ethanol-water and dried overnight in a vacuum desiccator: mp 80.5-81.5°; lit (112), mp 80-80.5°.

9-Hydroxymethylanthracene

9-Hydroxymethylanthracene was synthesized from 10.3 g (0.050 mole) of 9-anthraldehyde after the above procedure using the quantities of chemicals listed under the preparation of 2-hydroxymethylnaphthalene. The product was recrystallized from benzene: mp 164-165°; lit (113), mp 162-164°.

Hydrogenolysis Procedure

A mixture of 0.020 g of 10% Pd/C, ca. 1 millimole each of two benzyl alcohols being compared, ca. 1 millimole of 1-heptanol, a standard for concentration comparison and 10 ml of acidic ethanol (5.00 ml concentrated HCl in 2.000 l of 95% ethanol solution) was prepared in a 50 ml erlenmeyer flask fitted with a side-arm covered by a red rubber septum and a teflon coated stir bar. The flask was connected to an atmospheric pressure hydrogenation apparatus, the system was flushed, and filled with hydrogen. A sample of the reaction mixture was withdrawn by inserting the needle of a 1 ml syringe through the red rubber septum and stirring was initiated. Aliquots were periodically withdrawn from the reaction mixture. The aliquots were dissolved in 5 ml of

ethyl ether, the ether washed with 10 ml of saturated sodium hydrogen carbonate solution and dried over anhydrous magnesium sulfate. The ether solution was separated and analyzed on a SE-52 glpc column. The peak areas of the reactants was determined by cutting and weighing photocopies of the chromatogram.

Competitive hydrogenolyses involving benzyl acetate were carried out after the general procedure using equivalent quantities of the acetates, n-heptyl acetate was used as the standard.

Relative rate constants were calculated after the method of Nave (114) and the rate constants for the hydrogenolyses are listed in Tables 35, 36, and 37. Representative experimental results and rate constants calculated from this data are shown in Table 38.

Hydrogenolysis in deuterated solvents

A mixture of 0.020 g of 10% Pd/C, 0.3056 g (2.830 mmole) of benzyl alcohol, 5 ml of ethanol-$\underline{d}_1$, and 20 microliters of concentrated hydrochloric acid-$\underline{d}_1$ were treated after the general hydrogenolysis procedure except that aliquots were not removed and deuterium gas was used. When the hydrogenolysis was complete the entire mixture was poured into 10 ml of ether and worked up in the usual way. The ether solution was separated and the toluene collected from a SE-30 glpc

column and the toluene analyzed by mass spectroscopy. The deuterium isomer distribution is shown in Table 31 in the Results and Discussion Section.

Hydrogenolysis of furfuryl alcohol and 2-methylfuran

Furfuryl alcohol and 2-methylfuran were subjected to hydrogenation after the usual procedure except that aliquots were not removed and, because of water solubility problems, the catalyst was filtered from the solution and the solution analyzed on a SE-52 glpc column. Three hydrogenations were carried out on ca. 5 millimoles of 2-methylfuran, using equivalent quantities of other materials; two of the hydrogenations were carried out in acidic methanol and the major product of each reduction was collected from a SE-52 glpc column. The nmr of the product of the ethanol reduction was obtained. Chemical analysis and spectra were obtained for the product of the methanol solution. The collected methanol product was purified by collection for a second time from a SE-52 glpc column and chemical analysis and spectra were obtained for the doubly collected product.

Anal. Calculated for $C_6H_{12}O_2$: C, 62.04; H, 10.42 Found, singly collected product: C, 60.96; H, 10.22. Found, doubly collected product: C, 61.78; H, 10.30: nmr (CCl_4) δ 1.18 (d, 0.6, J = 6.0 Hz), 1.35 (s, 2.4), 1.86 (m, 4.0), 3.09 (s), 3.22 (s), 3.34 (s), 3.78 (m), (4.6), 4.82 (broad, 0.4).

ir (CCl_4) 2900 (s), 1713 (w), 1372 (s), 1194 (s), 1150 (s), 1110 (vs), 1095 (vs), 1058 (vs), 1024 (vs) cm^{-1}.

Mass spectra

a. Singly collected product, inlet temperature of 150°, ionization energy 20ev (peaks of intensity greater than 15.0% of base peak). m/e(%); 84(100%), 83(28.8%), 69 (15.5%), 55(28.5%), 44(21.9%), 43(76.4%), 42(16.0%), 41 (16.0%). Nothing with m/e greater than 86.

b. Singly collected product, low inlet temperature, ionization energy of 20ev (peak intensities of greater than 10% of base peak). m/e(%); 101(43.2%), 87(17.3%), 86(32.2%), 85(ca. 240%), 84(100%), 83(13.6%), 61(14.4%), 58(27.3%), 56(14.5%).

c. Doubly collected product, inlet temperature 150° ionization energy, 70ev (peak intensities of greater than 10.0% of base peak). m/e(%); 84(70.5%), 83(31.3%), 69(15.2%), 56(11.6%), 55(43.2%), 54(10.4%), 53(17.5%), 44(15.3%), 43(100.0%), 42(36.4%), 41(41.7%), 39(56.1%).

Cracking of dicyclopentadiene and hydrogenation of cyclopentadiene

About 3 ml of dicyclopentadiene was cracked and the cyclopentadiene distilled by heating dicyclopentadiene at a temperature of ca. 180°. The mixture was separated by distillation through a fractionating column and the cyclo-

pentadiene collected in a dry ice-acetone bath. The hydrogenation was carried out on 0.020 g of 10% Pd/C, 0.250 g (3.80 mmole) of cyclopentadiene and 5 ml of acidic methanol in a 50 ml erlenmeyer flask after the procedure used for 2-methylfuran. When the hydrogenation was complete, the reaction mixture was analyzed by nmr. About 2 moles of hydrogen were adsorbed per mole of cyclopentadiene and the nmr indicated cyclopentane to be the only product.

Hydrogenation of furan

A mixture of 0.020 g of 10% Pd/C, 0.200 g (3.00 mmole) of furan and 5 milliliters of acidic methanol was hydrogenated after the method used for 2-methylfuran. When the hydrogenation was complete, the reaction mixture was analyzed on a SE-52 glpc column. About 1 mole of hydrogen was adsorbed per mole of furan and two products were observed in the chromatogram; one product was shown to be tetrahydrofuran by comparison of retention times with an authentic sample. The other product, with a retention time comparable to that of the solvent incorporated product in the hydrogenation of 2-methylfuran, was collected and analyzed by nmr (CCl_4) δ 1.83 (broad, 4), 3.20 (s, 3), 3.72 (multiplet, 2), 4.85 (broad, 1).

Reactions of 4,5-dihydro-2-methylfuran

A mixture of 0.1880 g (2.238 mmole) of 4,5-dihydro-2-

methylfuran and 5 ml of methanol was stirred in a 50 ml erlenmeyer flask for one hour. The mixture was analyzed on a SE-52 glpc column and one major product was present. The retention time of this product was comparable to that of the solvent incorporated product of the reduction of 2-methylfuran. The product was collected and analyzed by nmr (CCl_4) δ 1.33 (s, 3), 1.83 (broad multiplet, 4), 3.10 (s, 3), 3.78 (multiplet, 2).

A second reaction was carried out on 0.2035 g (2.541 mmole) of 4,5-dihydro-2-methylfuran and 5 ml of methanol in the presence of 0.020 g of 10% Pd/C in a 50 ml erlenmeyer flask. After stirring for one hour, the mixture was analyzed on a SE-52 glpc column. The chromatogram was identical to the chromatogram of the product mixture produced in the absence of the palladium-charcoal.

The third reaction involved the attempted hydrogenation of 4,5-dihydro-2-methylfuran. A mixture of 0.020 g of 10% Pd/C, 0.2150 g (2.560 mmole) of 4,5-dihydro-2-methylfuran and 5 ml of acidic methanol was treated after the method used for 2-methylfuran. About one-half a mole of hydrogen was adsorbed per mole of 4,5-dihydro-2-methylfuran. The reaction mixture was analyzed on a SE-52 glpc column. The reaction mixture contained two products, one product was 2-methyltetrahydrofuran (by analogy to the furan reaction mixture). The solvent incorporated product was the other product.

Reaction of 2-methylfuran with methanol

A mixture of 0.240 g (2.92 mmole) of 2-methylfuran and 5 ml of 0.02 M HCl in methanol (the hydrogenolysis solvent) was stirred in a 50 ml erlenmeyer flask for one hour and then analyzed on a SE-52 glpc column. The chromatogram indicated the presence of only 2-methylfuran; incorporation of solvent into the furan nucleus was not observed.

Hydrogenolysis of benzyl alcohol-d_2

A mixture of 0.020 g of 10% Pd/C, 0.3000 g (2.73 mmole) of benzyl alcohol-d_2 and 5 ml of 0.03 M HCl in ethanol was treated after the general hydrogenolysis procedure except that aliquots were not removed. When the hydrogenolysis was complete, the entire mixture was poured into 10 ml of ether and worked up in the usual way. The ether solution was separated and the toluene collected from a SE-30 glpc column and the toluene analyzed by mass spectroscopy. The deuterium isomer distribution is shown in Table 31 in the Results and Discussion Section.

The sources of the chemicals available commercially are listed in Table 39.

Table 35. Substituted benzyl alcohols subjected to competitive hydrogenolysis and the rate constants obtained for the hydrogenolysis relative to benzyl alcohol obtained in 0.03 M HCl in ethanol

Substituent	k_S/k_H
p-Me	0.05 ± 0.02
m-Me	0.05 ± 0.01
o-Me	0.05 ± 0.02
p-OMe	0.06 ± 0.03 0.02 ± 0.008[a,b]
m-OMe	0.17 ± 0.10[c] 0.01 ± 0.007[a]
p-Cl	0.02 ± 0.009[a]
o-Cl	0.02 ± 0.006[a]
p-CF_3	0.002 ± 0.002[a] 0.001 ± 0.0006[d]
m-CF_3	0.006 ± 0.003[a] 0.02 ± 0.02[c,e]
α-Me	0.05 ± 0.003[a]
3,5-Me_2	0.006 ± 0.003[a]
3,4-Me_2	0.006 ± 0.003[a]
2,3-Me_2	0.004 ± 0.002[a]

[a]Obtained in competition with p-methylbenzyl alcohol.

[b]Obtained in competition with m-methylbenzyl alcohol.

[c]The product of the hydrogenolysis of m-methoxybenzyl alcohol comes at the same place in the glpc as does the benzyl alcohol, thus the rate is less than observed.

[d]Obtained in competition with p-methoxybenzyl alcohol.

[e]Obtained in competition with m-methoxybenzyl alcohol.

Table 35. (Continued)

Substituent	k_S/k_H
$3,5\text{-}(OMe)_2$	$0.007 \pm 0.0006^{d,f}$
$3,4\text{-}(OMe)_2$	$0.005 \pm 0.0006^{d,f}$
$2,3\text{-}(OMe)_2$	$0.003 \pm 0.003^{d,f}$
$2,4,6\text{-}Me_3$	0.003 ± 0.002^{g}

[f]1-Nonanol was used as the standard in the hydrogenolysis.

[g]Obtained in competition with 3,5-dimethylbenzyl alcohol.

Table 36. Arylmethanols subjected to competitive hydrogenolysis and the rate constants obtained for the hydrogenolysis relative to benzyl alcohol obtained in 0.03 M HCl in ethanol

Arylmethanol	k_{Ar}/k_{Ph}
1-Hydroxymethylnaphthalene	14 ± 5
2-Hydroxymethylnaphthalene	21 ± 8
9-Hydroxymethylanthracene	56 ± 11

Table 37. Substituted benzyl acetate subjected to competitive hydrogenolysis and the rate constants obtained for the hydrogenolysis relative to benzyl acetate obtained in 0.03 M HCl in ethanol

Substituent	k_S/k_H
p-CH_3	0.06 ± 0.03
p-Cl	0.03 ± 0.02^{a}

[a]Obtained in competition with p-methylbenzyl acetate.

Table 38. Representative examples of competitive hydrogenolyses carried out in 0.03 M HCl in ethanol

aliquot	Glpc peak areas relative to standard compound 1	compound 2	k_S/k_H
	benzyl alcohol	o-methylbenzyl alcohol	
initial	0.5588	0.9122	-
#1	0.4107	0.9053	0.0280
#3	0.1672	0.8359	0.0721
#4	0.0680	0.8214	0.0496
	benzyl alcohol	2-hydroxynaphthalene	
initial	0.6734	0.8827	-
#1	0.6715	0.5738	15.6
#2	0.6301	0.3098	15.7
#3	0.6128	0.0693	27.0

Table 39. Commercial chemicals

Compound	Source
Acetyl chloride	Baker
9-Anthraldehyde	Aldrich
Benzene	Mallinckrodt
Benzyl alcohol	Baker
p-Chlorobenzyl alcohol	Aldrich
Dicyclopentadiene	Baker
4,5-Dihydro-2-methylfuran	Aldrich
3,5-Dimethoxybenzoic acid	Aldrich
2,3-Dimethoxybenzyl alcohol	Aldrich
3,4-Dimethoxybenzyl alcohol	Aldrich
2,3-Dimethylbenzoic acid	Aldrich
3,4-Dimethylbenzoic acid	Aldrich
3,5-Dimethylbenzoic acid	Aldrich
Ethanol-d_1	Strohler Isotope
Ethyl acetate	Baker
Ethyl ether	Baker
Furan	Baker
Furfuryl alcohol	Aldrich
1-Heptanol	Matheson, Coleman & Bell
Hydrochloric acid	Baker and Adamson
Hydrochloric acid-d_1	Strohler Isotope
Lithium aluminum hydride	Alfa Inorganics

Table 39. (Continued)

Compound	Source
Magnesium sulfate	Mallinckrodt
m-Methoxybenzyl alcohol	Aldrich
p-Methoxybenzyl alcohol	Aldrich
o-Methylbenzyl acetate	Columbia
m-Methylbenzyl acetate	Columbia
p-Methylbenzyl acetate	Columbia
p-Methylbenzyl alcohol	Aldrich
2-Naphthaldehyde	Aldrich
1-Nonanol	Aldrich
Pentane	Baker
1-Phenylethanol	Eastman
Potassium hydroxide	Mallinckrodt
Sodium chloride	Mallinckrodt
Sodium hydrogen carbonate	Mallinckrodt
Sodium hydroxide	Baker
m-Trifluoromethylbenzoic acid	Pierce
p-Trifluoromethylbenzoic acid	Pierce

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