# Heterogeneous Catalytic Deuteration of Substituted Benzenes in Acetic Acid-d_1[1]

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Series of mono- and polyalkylbenzenes and methyl benzoate were reduced in acetic acid-d_1 using hydrogen and deuterium and the amounts and distributions of deuterium incorporated into the cyclohexane derivative were determined. Platinum was used as the catalyst in all cases except one in which rhodium on alumina was used. Extensive hydrogen–deuterium exchange which results in the formation of almost all possible deuterated species of the cyclohexane products is reported. It is concluded that the use of acetic acid-d_1 and hydrogen gas is an effective means of adding deuterium to aromatic hydrocarbons and that the hydrogen–deuterium exchange is relatively insensitive to the presence of α-hydrogen atoms and to the kind, number, and substitution patterns of substituents on the benzene ring.

The benzene nucleus of most aromatic hydrocarbons is readily reduced by hydrogen at low pressures in acetic acid using platinum as a catalyst.[2] In this paper, we report the results of a study of the deuteration of

cis and trans isomers
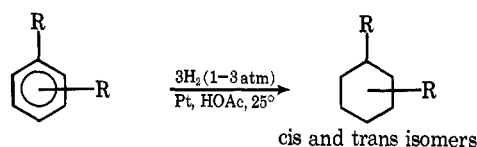
series of mono- and polyalkylbenzenes in acetic acid-d_1 using hydrogen and deuterium. One of our first objectives was to determine the effectiveness of acetic acid-d_1 and hydrogen compared to acetic acid-d_1 and deuterium as a means of introducing deuterium into organic compounds. Other major goals of this study were to determine the effects of the structure of the alkyl groups, the number of α-hydrogen atoms, and the alkyl substitution pattern on the amount and distribution of deuterium incorporation.

The generally accepted mechanism for the catalytic hydrogenation of benzene has been reviewed by Bond and Wells.[3] The initial step involves the reversible formation of a π complex of the benzene with the catalyst surface in some way, possibly with a single catalyst atom. The adsorbed benzene then picks up hydrogen atoms which have been previously united with the catalyst through a series of reversible steps until an adsorbed cyclohexene is formed.[3,4] There is some question as to whether the adsorbed cyclohexene is a π complex or a σ-1,2 dicomplex.[3,5] The olefin complex then picks up a single hydrogen atom to form a monoadsorbed complex. This process can reverse or another

hydrogen atom can be picked up to form the unadsorbed cycloalkane. The reversibility of the formation of the monoadsorbed species accounts for the hydrogen–deuterium exchange reaction of olefins.[3,5,6] This mechanism for the hydrogenation of olefins is the classic Horiuti–Polyanyi mechanism.[7]

Results

About 1 mmol of the aromatic compound in 5 ml of acetic acid at room temperature was hydrogenated at atmospheric pressure using *ca.* 20 mg of platinum oxide in a standard apparatus. The time required to complete the hydrogenation depended on the compound and ranged from 40 to 1700 min except for 1,3,5-tri-*tert*-butylbenzene, which was not reduced.[8] After the hydrogenation, the alkane was extracted with ether and the acetic acid was removed by a normal work-up procedure. Usually most of the ether was removed by distillation and the alkane was purified by glpc and analyzed by nmr and mass spectral analyses. The nmr analysis involved the use of a standard, naphthalene. In general, the total amount of deuterium in the alkanes was found to be higher by nmr analysis than mass spectral analysis, but the numbers were always reasonably close. We attribute the difference between the nmr and mass spectral values to error involved in the integration of the nmr signals.

The initial point to be established was the effectiveness of acetic acid-d_1 and hydrogen gas as a deuterium source. The reduction of three alkylbenzenes was carried out in acetic acid-d_1 using hydrogen or deuterium. The results of these experiments are listed in Tables I and II.

TABLE I

NUMBER OF DEUTERIUM ATOMS PER MOLE OF
ALKYLCYCLOHEXANE PRODUCED IN ACETIC
ACID-d_1 USING HYDROGEN OR DEUTERIUM

Alkyl group	D/mol, hydrogen gas		D/mol, deuterium gas	
	Mass spectrum	Nmr	Mass spectrum	Nmr
Methyl	5.3	6.2	6.5	7.7
Isopropyl	5.1	5.7	6.3	6.6
tert-Butyl	4.6	5.9	5.7	6.2

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(2) (a) R. Willstatter and E. Waldschmidt-Leitz, *Chem. Ber.*, **54**, 113 (1921); (b) A. Skita and W. A. Meyer, *ibid.*, **45**, 3589 (1912); (c) A. Skita and A. Schneck, *ibid.*, **55**, 144 (1922); (d) R. Adams and J. R. Marshall, *J. Amer. Chem. Soc.*, **50**, 1970 (1928).

(3) G. C. Bond and P. B. Wells, *Advan. Catal.*, **15**, 91 (1964).

(4) (a) S. Siegel and M. Dunkel, *ibid.*, **9**, 15 (1957); (b) S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6082 (1960); (c) *ibid.*, **82**, 6087 (1960); (d) S. Siegel, G. V. Smith, B. Dmuchovsky, D. Dubbell, and W. Halpern, *ibid.*, **84**, 3136 (1962); (e) S. Siegel and B. Dmuchovsky, *ibid.*, **84**, 3132 (1962); (f) F. Hartog and P. Zwietering, *J. Catal.*, **2**, 79 (1963); (g) S. Siegel, V. Ku, and W. Halpern, *ibid.*, **2**, 348 (1963); (h) S. Siegel and V. Ku, *Proc. Int. Congr. Catal., 3rd*, **2**, 1199 (1965).

(5) (a) K. Schrage and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **88**, 4555 (1966); (b) R. L. Burwell, Jr., *Chem. Eng. News*, **44**, 56 (August 22, 1966); (c) R. L. Burwell, Jr., *Accounts Chem. Res.*, **2**, 289 (1969), and references cited therein.

(6) J. J. Philipson and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **92**, 6125 (1970).

(7) I. Horiuti and M. Polyanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(8) It is not clear why we failed to hydrogenate 1,3,5-tri-*tert*-butylbenzene, since it is reported to be reduced fairly readily under conditions similar to ours.[9] Possibly the large substituents retarded the rate of complexation of the aromatic nucleus with the catalyst more effectively under our conditions.

(9) H. Van Bekkum, H. M. A. Buurmans, G. Van Minnen-Pathuis, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **88**, 779 (1969).

TABLE II

DEUTERATED SPECIES OF THE ALKYLCYCLOHEXANES PRODUCED IN ACETIC ACID-d_1 USING HYDROGEN OR DEUTERIUM[a]

Alkyl group	Gas	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}
Methyl	H_2	0.1	1.1	3.9	10.2	18.5	22.1	18.1	12.0	7.5	3.8	1.7	0.6	0.1	0.1	0.2
	D_2	0.1	0.1	0.7	3.3	10.0	19.2	21.8	16.0	12.7	8.7	4.0	2.0	0.8	0.4	0.2
Isopropyl	H_2	0.2	0.8	3.3	10.1	21.0	26.5	21.1	10.4	3.9	1.6	0.7	0.4			
	D_2			0.5	2.3	8.6	19.6	27.4	22.0	11.4	4.8	2.0	0.8	0.4	0.1	0.1
tert-Butyl	H_2	1.4	1.6	5.3	13.5	25.2	26.4	17.5	5.9	1.9	1.0	0.3				
	D_2	0.6	0.5	1.3	3.4	11.6	26.7	31.2	16.1	6.0	2.0	0.4	0.2			

[a] The values reported in this and other tables are corrected normalized values obtained from the partial mass spectra of the alkanes.

TABLE III

DEUTERATED SPECIES AND THE NUMBER OF DEUTERIUM ATOMS PER MOLE OF
ALKYLCYCLOHEXANES PRODUCED IN ACETIC ACID-d_1 USING HYDROGEN

Registry no.	Alkyl group	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	D/mol Mass spectrum	Nmr
110-82-7	Hydrogen	0.4	1.8	6.2	15.0	22.6	22.3	14.7	7.3	4.3	2.7	1.7	0.8	0.2			4.9	5.8
108-87-2	Methyl	0.1	1.1	3.9	10.2	18.5	22.1	18.1	12.0	7.5	3.8	1.7	0.6	0.1	0.1	0.2	5.3	6.2
1678-91-7	Ethyl	0.6	0.7	3.3	9.4	18.4	23.4	20.2	12.6	6.4	2.6	1.4	0.6	0.3	0.1		5.4	5.5
696-29-7	Isopropyl	0.2	0.8	3.3	10.1	21.0	26.5	21.1	10.4	3.9	1.6	0.7	0.4				5.1	5.7
3178-22-1	tert-Butyl	1.4	1.6	5.3	13.5	25.2	26.4	17.5	5.9	1.9	1.0	0.3					4.6	5.2

The deuterium per mole values, the average numbers of deuterium atoms incorporated into the cyclohexane molecules, indicate that the deuterium incorporation into a cyclohexane derivative increases by about one deuterium atom per mole when deuterium is used in place of hydrogen (Table I). The distribution pattern of the deuterated isomers, d_n, was shifted by one unit when deuterium was used in place of hydrogen (Table II); e.g., the most prominent peak in the mass spectrum of methyl-, isopropyl-, and tert-butylcyclohexane is d_5 when hydrogen was used and d_6 when deuterium was used. Notice that the amounts of deuterium per mole and the exchange patterns of the cyclohexane derivatives given in Tables I and II (and subsequent tables) indicate that some of the exchanged hydrogen atoms of the hydrocarbon are being incorporated into other molecules of the product. Some of the hydrogen atoms liberated in the exchange of the aromatic hydrocarbon are apparently not exchanging with the solvent but are remaining on the catalyst and are then incorporated into other product molecules. Since only 1 mmol of hydrocarbon was reduced in the presence of 82 mmol (5 ml) of acetic acid-d_1 if all of the liberated hydrogen atoms exchanged with the solvent, one would expect a much larger incorporation of deuterium in the absence of a very large isotope effect for the hydrogenation step. Of course, an alternative explanation for the large amount of incorporation of hydrogen is that complete randomization of hydrogen and deuterium atoms occurs but there is a large isotope effect on the step which transfers hydrogen atoms from the catalyst to the hydrocarbon.

The results of the deuteration of benzene, toluene, ethylbenzene, isopropylbenzene, and tert-butylbenzene are presented in Table III. The nmr spectra of the methyl-, ethyl-, and isopropylcyclohexanes indicate that some deuterium is incorporated into the alkyl groups. The methyl signal of the three alkyl groups shows some splitting by geminal or vicinal deuterium atoms.

The results of the deuteration of polyalkylbenzenes are listed in Table IV. Hydrogenation of the o-, m-,

and p-xylenes give 90, 77, and 74% of the cis-dimethylcyclohexanes, respectively.

To check if aromatic hydrogen exchange prior to reduction was important, benzene, toluene, and p-xylene were half hydrogenated, and the products and starting materials were separated by glpc and analyzed for deuterium incorporation by mass spectroscopy. These results are presented in Table V.

During our study, it was reported that the catalytic deuteration of methyl benzoate in acetic acid-d_1 involved little hydrogen–deuterium exchange.[10] Since this result was surprising considering the extensive exchange that we found with the mono- and polyalkylbenzenes, we reduced methyl benzoate over reduced platinum oxide using hydrogen and deuterium and 5% rhodium on alumina in acetic acid-d_1 using deuterium. The results of these reductions are given in Table VI.

Our results disagree with those reported, since we find extensive exchange similar to that observed with the alkylbenzenes whereas the dominant peak in the mass spectrum of methyl cyclohexanecarboxylate was reported to be that of the d_6 isomer using deuterium and 5% rhodium on alumina. Moreover, hydrogenation of methyl benzoate-d_5 using 5% platinum on alumina and hydrogen in acetic acid was reported to give predominantly methyl cyclohexanecarboxylate-d_5. Again, this result conflicts with our results obtained with platinum, deuterium, and acetic acid-d_1, assuming that the extent of exchange on platinum and platinum on alumina would be similar.

The published nmr spectrum of the material reported to be methyl cyclohexanecarboxylate-d_6 gave two broad peaks at δ 1.3 and 1.7 for the cyclohexyl hydrogen atoms which integrated for 4.6 hydrogen atoms relative to the methoxy group. The nmr spectrum of our methyl cyclohexanecarboxylate produced by use of deuterium and platinum in acetic acid-d_1 also showed two broad peaks at δ 1.33 and 1.75 for the cyclohexyl hydrogen atoms which integrated relative to the methoxy group for 6.4 hydrogen atoms. The two spectra

(10) C. C. Price and C. D. Beard, *J. Amer. Chem. Soc.*, **92**, 5921 (1970).

TABLE IV
DEUTERATED SPECIES AND THE NUMBER OF DEUTERIUM ATOMS PER MOLE OF POLYALKYLCYCLOHEXANES PRODUCED IN ACETIC ACID-d_1 USING DEUTERIUM[a]

Registry no.	Polyalkyl groups	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}	Mass spectrum	Nmr
583-57-3	1,2-Dimethyl			0.6	2.4	7.8	15.1	17.1	14.0	12.2	10.5	8.0	6.0	3.7	1.8	0.6	0.2				7.4	6.8
591-21-9	1,3-Dimethyl		0.1	0.6	2.5	6.7	12.4	15.2	14.6	13.6	12.0	9.4	6.9	4.0	1.3	0.4	0.1				7.5	8.6
589-90-2	1,4-Dimethyl	0.2	0.2	0.5	2.4	7.4	14.6	17.2	14.0	12.3	10.4	8.2	6.5	3.9	1.5	0.6	0.2	0.1			7.4	8.0
1678-97-3	1,2,3-Trimethyl		0.1	0.2	1.4	4.0	8.2	11.4	11.8	12.6	12.4	11.4	9.8	7.2	4.8	2.8	1.3	0.4	0.1		8.6	9.5
1839-63-0	1,3,5-Trimethyl	0.1		0.1	0.7	2.8	6.6	11.2	13.2	13.4	12.0	9.5	9.0	7.7	6.6	5.0	2.0	0.2			9.0	10.7
2090-38-2	1,2,4,5-Tetramethyl			0.4	0.6	2.4	5.8	9.2	10.4	11.8	11.8	11.0	8.2	7.4	5.8	4.9	4.0	3.3	2.2	0.8	9.7	10.6
34386-82-8	1,4-Di-tert-butyl	0.2	1.4	6.2	14.4	22.0	25.4	15.7	11.4	2.3	0.6	0.3	0.1								4.7	6.8
34387-60-5	1,3,5-Triisopropyl		5.0	2.7	1.5	1.5	2.3	7.6	11.6	16.1	16.2	12.3	8.9	5.7	3.9	2.5	1.6	0.6			8.4	6.6
91-17-8	1,2-Tetramethylene	0.4	0.1	0.3	0.4	1.6	3.8	7.4	13.2	20.6	23.4	17.3	7.9	2.6	0.8	0.2					8.4	8.9

ᵃ These data are for the mixtures of stereoisomers that were obtained from the reductions.

are very similar and yet our sample was certainly not predominantly the d_6 species.

Discussion

The times required for the hydrogenation of the various arenes fit the generalizations[11] that the rates of hydrogenation decrease as the number of substituents increase and increase as the symmetry of the substitution pattern of the benzene ring increases, even when the higher symmetry leads to a greater degree of substitution.[8,9]

The results shown in Tables I and II clearly show that acetic acid-d_1 and hydrogen are a very effective means of adding deuterium to aromatic hydrocarbons. Evidently the adsorbed hydrogen exchanges very rapidly with the acidic deuterium atoms of the solvent and so deuterium atoms are incorporated into the hydrocarbon almost to the same extent as when deuterium is used. Our observation is consistent with the results of Eidinoff and coworkers,[12] who found that the deuteration of olefins in acetic acid over platinum resulted in *ca.* 1% deuterium incorporation.

These results suggest that acetic acid-t_1 and hydrogen should be a convenient way to introduce tritium into molecules.

Philipson and Burwell studied the reduction of cyclic olefins in the liquid phase using deuterium in acetic acid-d_1 and a number of d_1 alcohols.[6] The use of acetic acid-d_1 resulted in the most incorporation of deuterium through reduction and exchange; acetic acid-d_1 exhibited the highest rate of exchange between solvent hydrogen atoms and adsorbed hydrogen atoms.

From the results presented in Tables III and IV, it is seen that extensive exchange takes place during the reduction of the benzene ring so that no single deuterated species predominates and, in fact, virtually all possible deuterated species are obtained. Moreover, this hydrogen–deuterium exchange is relatively insensitive to the presence of α-hydrogen atoms or the kind, number, and substitution patterns of alkyl substituents on the benzene ring. The data in Table III show that the number of deuterium atoms incorporated into cyclohexane and its alkyl derivatives is about 5.0 and the distribution of the deuterium is approximately the same, even in those compounds which possess α-hydrogen atoms. The absence of α-hydrogen atoms does not seem to prevent the ring from exchanging hydrogen atoms on both of its sides, since even cyclohexane and *tert*-butylcyclohexane contain species with >6 deuterium atoms. The hydrocarbons which possess α-hydrogen atoms do show a slightly higher fraction of species that contain >6 deuterium atoms, and this is consistent with exchange of the α-hydrogen atoms. The incorporation of deuterium into the α positions of the methyl-, ethyl-, and isopropylcyclohexanes is confirmed by their nmr spectra, and the nmr spectra of the ethyl- and isopropylcyclohexanes indicate that exchange of the β-hydrogen atoms may also have occurred. The lack of deuterium incorporation into the *tert*-butyl group of the *tert*-butylcy-

(11) H. A. Smith in "Catalysis," Vol. V, P. H. Emmett, Ed., Reinhold, New York, N. Y., 1957, pp 175–256.

(12) M. L. Eidinoff, J. E. Knoll, D. K. Fukushima, and T. F. Gallagher, *J. Amer. Chem. Soc.*, **74**, 5280 (1952).

TABLE V

Deuterated Species and the Number of Deuterium Atoms per Mole of Hydrocarbon Produced
in Acetic Acid-d_1 Stopping the Reaction after 50% Reaction

Registry no.	Hydrocarbon	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}	D/mol
71-43-2	Benzene[a]	83.2	10.9	2.9	1.4	0.9	0.7										0.3
	Cyclohexane[a]	0.3	1.8	7.2	17.2	26.2	24.5	12.7	4.8	2.4	1.5	0.9	0.4	0.1			4.5
108-88-3	Toluene[a]	64.3	20.7	9.1	4.8	0.9	0.2										0.6
	Methylcyclohexane[a]	0.0	0.5	1.9	7.0	16.3	23.7	22.6	14.0	7.2	3.9	1.6	0.7	0.4	0.2		5.7
106-42-3	p-Xylene[b]	69.2	12.2	5.2	4.2	2.6	3.0	3.4	0.2								0.8
	1,4-Dimethylcyclohexane[b]	0.0	0.2	1.1	4.8	13.1	22.9	21.3	12.8	9.7	6.6	3.5	2.2	1.3	0.4	0.1	6.2

[a] Hydrogen was used.   [b] Deuterium was used.

TABLE VI

Deuterated Species and the Number of Deuterium Atoms per Mole of the Methyl Cyclohexanecarboxylate
Produced by the Reduction of Methyl Benzoate in Acetic Acid-d_1

Group	Gas	Catalyst	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	D/mol
Methoxycarbonyl	H_2	Pt	1.2	5.5	14.3	23.8	25.4	17.6	8.0	2.8	0.8	0.3	0.2		3.7
Methoxycarbonyl	D_2	Pt	0.5	1.9	6.7	16.3	24.7	24.9	15.2	6.7	2.3	0.8			4.5
Methoxycarbonyl	D_2	Rh/Al_2O_3		0.2	1.4	6.1	17.1	30.0	26.0	10.7	5.1	2.4	0.9	0.2	5.4

clohexane is consistent with the requirement that only 1,2-, not 1,3-diadsorbed species, can form.[5]

From the results presented in Table IV, it is seen that the substitution patterns of dimethyl- and trimethylbenzenes have little effect on the deuterium incorporation. The amount of deuterium incorporated per mole and its distribution are very similar for all three xylenes. The results of the 1,2,3- and 1,3,5-trimethylbenzenes are also very similar. The slight differences which exist show that more deuterium was incorporated into the 1,3,5 compound, the more symmetrical isomer. 1,2,4,5-Tetramethylbenzene leads to the same sort of results obtained with the di- and trimethyl derivatives. There is, in fact, a gradual increase in the total amount of deuterium incorporated in going from the dimethyl (7.4 D/mol) to the trimethyl (8.8 D/mol) to the tetramethyl (9.7 D/mol) compounds, and this is expected since the number of α-hydrogen atoms which can undergo exchange is also increasing in this series.

The 1,4-di-tert-butylbenzene leads to species containing greater than six deuterium atoms and so deuterium atoms must be incorporated on both sides of the ring despite the bulky substituents. 1,3,5-Triisopropylbenzene gives comparable results; however, the interpretation of the results is a little more ambiguous since the α- and β-hydrogen atoms of the isopropyl groups can undergo exchange. 1,2-Tetramethylenebenzene does lead to a greater amount of deuterium incorporation than o-xylene, which is expected since an additional ring is present.

The insensitivity of the hydrogen–deuterium exchange to the kind, number, and substitution patterns of alkyl groups on the benzene ring is further seen from comparison of the numbers of deuterium atoms incorporated per exchangeable hydrogen atom for the various cyclohexanes. These numbers are presented in Table VII for the methyl-, polymethyl-, tert-butyl-, 1,4-di-tert-butyl-, and 1,2-tetramethylenecyclohexanes (decalin) and indicate that ca. 0.5 deuterium atom is

TABLE VII

Average Number of Deuterium Atoms Incorporated per Exchangeable Hydrogen Atom in the Alkylcyclohexanes Produced with Deuterium and Acetic Acid-d_1

Alkyl group	Average D/H
Methyl	0.46
1,4-Dimethyl	0.46
1,3,5-Trimethyl	0.50
1,2,4,5-Tetramethyl	0.49
tert-Butyl	0.52
1,4-Di-tert-butyl	0.47
Isopropyl	0.35
1,3,5-Triisopropyl	0.28
1,2-Tetramethylene	0.47

incorporated per hydrogen atom irrespective of the kind, number, and substitution patterns of the alkyl groups.

Both isopropyl derivatives show slightly lower numbers of deuterium atoms incorporated per exchangeable hydrogen atom than the other compounds, but these low values are probably a result of the inclusion of the six hydrogen atoms on the β-methyl groups as exchangeable hydrogens. Probably not all of these hydrogens are subject to exchange during one period of residence on the catalytic surface.

The extensive hydrogen–deuterium exchange which is reported in this study demands that hydrogen exchange can occur on both sides of the ring of a given molecule. Several published results also demand exchange on both sides of the ring. For example, the hydrogenation of the xylenes and 1,2-dimethylcyclohexane leads to a considerable amount of the trans-dimethylcyclohexanes.[4,13] Also, extensive hydrogen–deuterium exchange occurs during the reduction of some cycloalkenes[6] and the hydrogen–deuterium exchange of some cycloalkanes.[5] Moreover, trans-1,2-dimethylcyclopentane is partially converted to its cis isomer.

(13) S. Siegel, *Advan. Catal.*, **16**, 123 (1966).

during the hydrogen–deuterium exchange reactions.[5,14]

One possible explanation for the extensive hydrogen–deuterium exchange observed in this study, and its relative insensitivity to the presence of α-hydrogen atoms or the kind, number, or substitution patterns of substituents, is that exchange of the hydrogen atoms of the starting arene occurs. The results shown in Table V indicate that some exchange of the hydrogen atoms had occurred after 50% deuteration. This explanation requires that the rate of prior exchange relative to the rate of reduction of a given arene is relatively insensitive to substituents, which is not an expected condition, but not an impossible one.

Another mechanism which accounts for the data in Tables III and IV involves the intermediate formation of a trans 1,2-diadsorbed complex. The essential point in this mechanism is that the ring can be flipped by going through a trans 1,2-diadsorbed state without ever leaving the catalyst surface. The ring could, of course, still contain unsaturation. The insensitivity of the hydrogen–deuterium exchange reaction to the kind, number, and substitution patterns of alkyl groups on the benzene ring is readily explained if the monoadsorbed complex can go to either a cis or trans 1,2-diadsorbed complex with comparable ease and with ring substituents having very little effect on this process.

cis 1,2-diadsorbed
complex

trans 1,2-diadsorbed
complex
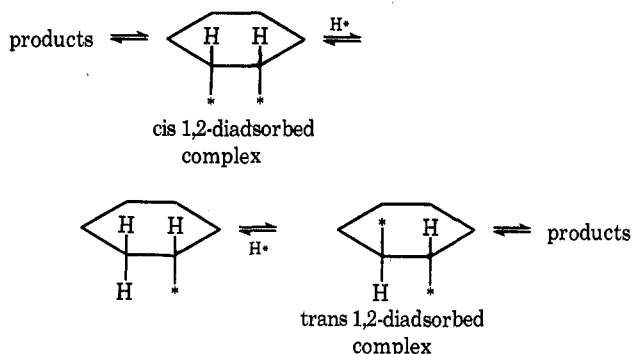
A trans 1,2-diadsorbed alkene has been postulated to explain the trans products from the reduction of xylenes,[15] but is not a readily acceptable mechanism since exchange experiments indicate that olefins are either π adsorbed to the catalyst or if diadsorbed by 1,2 σ bonds, the σ bonds prefer to be eclipsed.[5,6,16] However, evidence that the hydrocarbon–catalyst bonds of the 1,2-diadsorbed complex must be eclipsed comes mainly from hydrogen–deuterium exchange experiments with adamantane, bicyclo[2.2.1]heptane, and cyclopentane.[5,6] With these systems, it is difficult or impossible for hydrocarbon–catalyst bonds of a trans 1,2-diadsorbed complex to have a dihedral angle of <60°. From the inspection of Dreiding models, one can see that the flexibility of the cyclohexane ring permits the dihedral angle between 1,2-trans carbon–hydrogen bonds to be as low as ca. 30°. Thus, we feel that trans 1,2-diadsorbed complexes of cyclohexane rings are not out of the question and we are unaware of any evidence which rigorously excludes their existence.

The extensive hydrogen–deuterium exchange found in the substituted cyclohexanes could also result from the desorption of a cyclohexene intermediate followed by readsorption of the cyclohexene, on either side of the ring, and reduction to give the cyclohexane. The desorption mechanism has been proposed to explain the formation of trans-dialkylcyclohexanes from the dimethylcyclohexenes and xylenes,[4,9,13,17] and cyclohexenes have been produced during the reduction of aromatic compounds[4,9,18] but in most cases they have been isolated in only low yields. Arguments have been presented that indicate that cyclohexene formation is only a side reaction.[14,19]

No support is obtained from the results in Table IV for mechanisms of hydrogen–deuterium exchange which go through "dissociatively adsorbed olefins" (σ-bonded olefins),[19,20] or involve "rolling over" of the cycloalkane from one side to the other.[5a,c] The deuterium incorporation by either one of these mechanisms would be expected to be quite sensitive to the substitution patterns of the polyalkylbenzenes.

The results presented in Table VI clearly show that the same sort of hydrogen–deuterium exchange occurs during the reduction of a benzene ring that contains a methoxycarbonyl group as occurs during the reduction of alkyl-substituted benzene rings. The report[10] that the deuteration of methyl benzoate gave exclusively the d_6 isomer and the hydrogenation of methyl benzoate-d_5 gave exclusively the d_5 isomer is difficult to explain considering our results. Possibly subtle differences in the catalyst or reaction conditions account for the disagreement of our results.

Experimental Section

Methods and Materials.—Most equipment has been previously described.[21] For glpc analysis, a 6 ft × 0.25 in. 15% SE-30 on Chromosorb W and a 6 ft × 0.25 in. 10% QF-1 on Chromosorb P column were used. The mass spectra of the cyclohexane derivatives were measured with an ionization voltage of 20 eV. The calculations needed to correct the peak intensities for natural isotope abundance were carried out on the Iowa State University IBM Series 360 Model 65 computer.

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

The hydrocarbons used in the hydrogenations were commercially available and were used without further purification, with the exception of tetralin, which was fractionally distilled. The purity of the hydrocarbons was established.

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

The deuterium per mole values determined by nmr were calculated from the relative intensities of the nmr signals of the hydrocarbon compared to those of naphthalene, an internal standard.

All numerical values reported in data tables have been averaged.

Acetic acid-d_1 was prepared by refluxing a mixture of 2.6 mol

(14) R. L. Burwell, Jr., and K. Schrage, *Discuss. Faraday Soc.*, **41**, 215 (1966).

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

(16) K. Schrage and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **88**, 4549 (1966).

(17) A. W. Weitkamp, *Advan. Catal.*, **18**, 2 (1968).

(18) F. Hartog, J. H. Tebben, and C. A. M. Weterings, *Proc. Int. Congr. Catal., 3rd*, **2**, 1210 (1965).

(19) (a) J. F. Sauvage, R. H. Baker, and A. S. Hussey, *J. Amer. Chem. Soc.*, **82**, 6090 (1960); (b) *ibid.*, **83**, 3874 (1961); (c) G. V. Smith and R. L. Burwell, Jr., *ibid.*, **84**, 925 (1962).

(20) R. L. Burwell, Jr., B. K. C. Shim, and H. C. Rowlin, *ibid.*, **79**, 5142 (1957).

(21) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

of deuterium oxide and 1.5 mol of acetic anhydride for 2 hr. After the mixture was allowed to cool, 0.3 mol of boron triacetate, which was prepared by the method of Cook, *et al.*,[22] was added to it. The mixture was distilled to give a 104% yield of a colorless liquid, bp 114–115.8°. The nmr spectrum indicated the presence of 1.3% light acetic acid.

Hydrogenation Procedure.—To a flask which possessed a side arm containing a stopcock was added a magnetic stirring bar, 3 ml of acetic acid, and 20 mg of platinum oxide (Sargent). The flask was connected to the hydrogenation apparatus, the system was flushed with hydrogen and filled with hydrogen at atmospheric pressure, and the catalyst was prereduced by vigorous stirring. The stirring was stopped, *ca.* 1 mmol of the benzene derivative and 2 ml of acetic acid were added to the flask through the side-arm, and the stirring was resumed. Peri-

(22) H. G. Cook, J. D. Ilett, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 3125 (1950).

odically, 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 was drawn off. The ethereal layer was treated with two 10-ml portions of saturated sodium chloride solution and two 10-ml portions of saturated sodium hydrogen carbonate solution and dried (MgSO₄). The ether was partially removed by distillation and the residue was purified by glpc.

One deuteration of methyl benzoate was carried out in the same fashion except that 20 mg of 5% rhodium on alumina (Matheson Coleman and Bell) was used as the catalyst.

# *Notes*

Dineoalkyl Ethers. A General Synthesis of the Symmetrical Ethers

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A method for the synthesis of dineoalkyl ethers has never been reported, although this type of structure should be of potential interest because of the ether functionality combined with the stability characteristics imparted by the neighboring neoalkyl groups. The di- and polypentaerythritols (obtained indirectly by the Tollens reaction of acetaldehyde with formaldehyde) are the only reported examples of this structure type excepting the parent compound itself, dineopentyl ether, which was recently prepared[1] by hydrogenolysis of neopentyl alcohol. The direct synthesis of several new members of this structure type, particularly those with tetrahydroxyl functionality as well as alicyclic β substitution, is reported.

Consideration of trimethylolethane as a starting material suggested the use of a suitable blocking group to mask two of the hydroxyl groups allowing its reaction as a monool. This was achieved by its conversion to 2,2,5-trimethyl-5-*m*-dioxanemethanol (2) in high
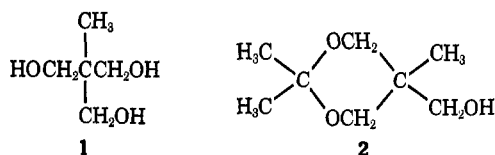
yield which should be stable to basic or neutral conditions but easily cleaved by acid to regenerate the methylol groups.

(1) H. Pines and P. Steingaszner, *J. Catal.*, **10**, 60 (1968).

Alkaline condensation of tosylate (3) with 2 gave the desired 5,5'-(oxydimethylene)bis(2,2,5-trimethyl-*m*-dioxane) (4) in conversions ranging up to 64% depending upon solvent, base, and reaction time. Although a precipitate of tosylate salt can usually be detected early as an opalescence, the formation of this dineoalkyl ether (4) requires a minimum of 48 hr to obtain good yields of product. The mesylate 5 was also prepared and used in the alkaline condensation but offered no advantages over the tosylate. Mild acid hydrolysis of 4 gave the desired 2,2'-(oxydimethylene)bis(2-methyl-1,3-propanediol) (6) quantitatively (eq 1). Mass
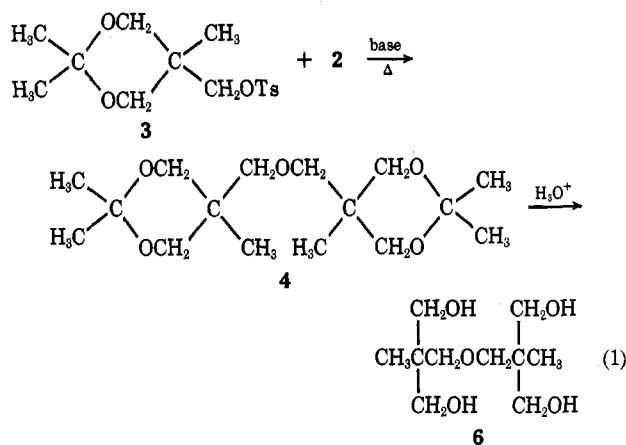
spectrographic examination of 4 showed no molecular ion species but a major peak at 287 corresponding to initial loss of a methyl group. The failure to observe a molecular ion is apparently characteristic of a 2-methyl-1,3-dioxanyl-type structure. This was confirmed by the synthesis[2] of 2,2,5,5-tetramethyl-1,3-dioxane (7). The mass spectrum of this structurally related compound showed no molecular ion but a major peak at 129 from loss of a methyl group.

Although the above analytical data on both the intermediate (4) and product (6) dineoalkyl ethers were not

(2) C. S. Rondestvedt, Jr., *J. Org. Chem.*, **26**, 2247 (1961).