to decrease rapidly as the pH is increased above 7. The addition of bromide on the one hand decreases the rate of reaction in acid solution, owing to tribromide formation, but on the other hand it shifts the decrease with increasing pH to higher pH values. From these results it is concluded that molecular bromine is a more rapid oxidizing agent for ether than either tribromide or hypobromous acid.[21] All this is very much in line with the present findings. The fact that in this case k_{Br_2} obviously does *not* increase significantly with increasing pH is easily understood when we remember that ethers cannot be expected to form anions. These results thus constitute an indirect confirmation of our suggestion.

It might be added that to our knowledge only oxalic acid and oxalates exhibit a completely different behavior,[10,22] being oxidized by hypobromous acid much more rapidly than by bromine.

Acknowledgment. B. P.-H. wishes to thank Dr. I. Pecht, Max Planck Institut für physikalische Chemie, Göttingen, for helpful discussion during the revision of this paper.

(22) R. O. Griffith, A. McKeown, and A. G. Winn, *Trans. Faraday Soc.*, 28, 107 (1932); H. A. Liebhafsky and B. Makower, *ibid.*, **29**, 597 (1933).

Hydrogenations of Cycloalkenes Using Tris(triphenylphosphine)chlororhodium(I)

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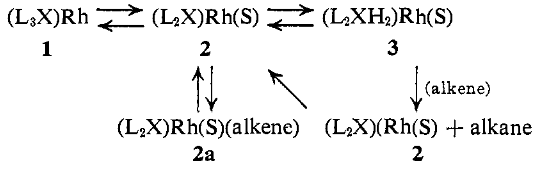
Abstract: The homogeneous hydrogenations of 1-methylcyclohexene (**4**), 1,4-dimethylcyclohexene (**5**), 1-methyl-4-isopropylcyclohexene (**6**), and 4-methylmethylenecyclohexane (**7**) in benzene and benzene–ethanol solution at 25.0 ± 0.1° under 1 atm of hydrogen using tris(triphenylphosphine)chlororhodium(I) are reported. The three trisubstituted alkenes are hydrogenated very slowly relative to cyclohexene and **7** (15 to 100 times slower). The products formed from **5**, **6**, and **7** are 50.0, 29.9, and 66.6% *cis* isomer, respectively. When deuterium at 1 atm is used, rather extensive exchange is observed in the products from **5** and **6** and the exchange patterns are different in the *cis* and *trans* products while the isomeric products from **7** are very slightly exchanged. The implications of these results relative to the mechanistic details of this reaction are discussed.

The homogeneous catalytic hydrogenation of alkenes using tris(triphenylphosphine)chlororhodium(I) and related complexes as catalysts is currently of considerable interest.[1,2] The most generally satisfactory mechanism is that proposed by Wilkinson[1a] which is summarized in Scheme I. According to this view, the rate-limiting step is the displacement of coordinated solvent (S) from the *cis*-dihydrido species **3** by alkene. The resulting complex is viewed then to progress to product by a fast, *simultaneous* transfer of both hydrogens from the metal atom to the coordinated alkene.[1a] The rate of this reaction is influenced by the nature of the ligand L,[1c,2f] the halogen X,[1a,b] the solvent S,[1a,b] and the alkene[1a,b,2a–d] and conforms to the rate expression[1a]

Scheme I



$$\text{rate} = \frac{k[H_2][\text{alkene}][\text{catalyst}]}{1 + K_1[H_2] + K_2[\text{alkene}]}$$

It has been reported that trisubstituted double bonds are not hydrogenated by this procedure.[2a–d] However, it has since been shown that trisubstituted alkenes are indeed hydrogenated under these conditions, albeit very slowly.[1b] We have also found that trisubstituted alkenes undergo hydrogenation using these catalysts and we report here the results of our studies of the hydrogenation and the deuteration of 1-methyl- (**4**), 1,4-dimethyl- (**5**), and 1-methyl-4-isopropylcyclohexene (**6**), and 4-methylmethylenecyclohexane (**7**), using this procedure. The exchange patterns observed when these substrates are reduced in deuterium reveal some very interesting details concerning the several steps of the over-all process.

Results

Initial rates of hydrogenation of the several cycloalkenes were obtained from plots of hydrogen absorption *vs.* time from experiments which were all carried out under the same arbitrary set of experimental conditions in an apparatus we have developed for rate

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(1) (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966); (b) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *ibid.*, 1574 (1967); (c) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *ibid.*, 1054 (1968); (d) F. H. Jardine and G. Wilkinson, *J. Chem. Soc., C*, 270 (1967).

(2) (a) A. J. Birch and K. A. M. Walker, *ibid.*, 1894 (1966); (b) J. F. Biellmann and H. Liesenfelt, *Bull. Soc. Chim. Fr.*, 4029 (1966); (c) C. Djerassi and J. Gutzwiller, *J. Amer. Chem. Soc.*, 88, 4537 (1966); (d) A. J. Birch and K. A. M. Walker, *Tetrahedron Lett.*, 4939 (1966); 1935 (1967); (e) A. L. Odell, J. B. Richardson, and W. R. Roper, *J. Catal.*, 8, 393 (1967); (f) R. Stern, Y. Chevallier, and L. Sajus, *C. R. Acad. Sci., Paris, Ser. C.*, **264**, 1740 (1967); (g) J. F. Biellmann and M. J. Jung, *J. Amer Chem. Soc.*, **90**, 1673 (1968).

studies using heterogeneous catalysts.[3] Under these particular conditions ([catalyst] = 2.4 ± 0.1 mM; [alkene] > 0.6 M; solvent, 3:1 benzene–alcohol; 25.0 ± 0.1°; 760 ± 1 mm), hydrogen absorption rates were linear for the first several minutes of the reactions even with cyclohexene and 4-methylmethylenecyclohexane (**7**). Hence the initial rates summarized in Table I are for the pseudo-first-order reaction which follows the rate law

$$\text{rate} = k'[\text{catalyst}]$$

The values for the corresponding specific reaction rates (k', min^{-1}) are also included in Table I along with the product isomer compositions.

Table I. Initial Rates and Rate Constants for the Hydrogenation of Cycloalkenes Using Tris(triphenylphosphine)chlororhodium(I)[a]

Substrate[b]	[Alkene], M	Initial rate $\times 10^6$ mol min^{-1}	k' min^{-1}	% *cis*[c]
C_6	1.10	180	17	...
1-MeC_6 (**4**)	0.94	5.3	0.49	...
1,4-Me_2C_6 (**5**)	0.82	1.7	0.16	50.0
1-Me-4-*i*-PrC_6 (**6**)	0.67	2.7	0.25	29.9
4-MeMethC_6 (**7**)	0.81	78	7.2	66.6

[a] In 3.00 ml of benzene and 1.00 ml of ethanol at 25.0° (760 mm); substrate, 0.50 ml; [catalyst], 2.4 mM. [b] C_6 is cyclohexane, 4-MemethC_6 is 4-methylmethylenecyclohexane, etc. [c] Standard deviation, ±0.1%.

several samples were subjected to mass spectrometric analysis. The rather surprising results are summarized in Table II along with the results from similar experiments using **6** (benzene only in experiment 2).

Notice that not only are the product isomers appreciably exchanged but also that the exchange patterns are quite different in the one *vs.* the other. The ratios of *cis*-d_0:*trans*-d_0 and *cis*-d_1:*trans*-d_1 are unity, within experimental error, and the deuterium which is missing in these species can be accounted for as cycloalkene-d_1 and the d_4 products. Mass spectrometric analysis of the residual gas phase showed it to contain HD. Some deuterium (~0.3–0.4%) was also found in the solvent as C_2H_5OD, but there was no deuterium in the benzene. The question whether ethanol contributes to the exchange patterns is not moot, however, because *when benzene alone* was used as the solvent, the exchange patterns remained the same and an amount of HD equivalent to the d_3 plus d_4 species was also found in the gas phase. We conclude that the exchange observed in the ethanol is incidental.

In any event, it is clear that the rate of transfer of the deuterium atoms from the central metal atom to the more highly substituted double bond carbons is so slow (Table I) that the exchange reactions, hence the *stepwise* transfer of H or D, become easily observable. In order to understand the nature of these exchange processes, we have also investigated the addition of deuterium to **4** and **7** (Table I) under the same conditions. These results are summarized in Table III.

Table II. Deuterium Addition to 1,4-Dimethyl- and 1-Methyl-4-isopropylcyclohexenes Using Tris(triphenylphosphine)chlororhodium(I)

	cis-1,4-Me_2[a,b]		*trans*-1,4-Me_2[a,b]		*cis*-1-Me-4-*i*-Pr[c,d]		*trans*-1-Me-4-*i*-Pr[c,d]	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
d_0	1.9	0.8	1.5	1.6	0.6	0.5	0.4	0.2
d_1	5.3	3.9	5.3	3.4	2.9	1.9	2.2	0.9
d_2	84.4	88.0	92.5	93.7	90.1	92.2	96.7	98.2
d_3	7.8	7.0	0.8	1.1	5.4	4.9	0.4	0.4
d_4	0.4	0.3	0.0	0.2	1.0	0.5	0.3	0.2
d_5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
d_{av}	1.99[e]	2.02[e]	1.93[e]	1.95[e]	2.03[f]	2.03[f]	1.98[f]	1.99[f]

[a] At 10.7% reduction in benzene–ethanol. [b] Product is 50.0% *cis* isomer. [c] At 12.0% reduction; (1) in benzene–ethanol; (2) in benzene alone. [d] Product is 29.9 ± 0.1% *cis* isomer in 3:1 benzene–ethanol but 33.0 ± 0.2% *cis* isomer in benzene alone. [e] The recovered alkene contained 0.6 and 0.7% d_1 species, respectively. [f] The recovered alkene from both experiments contained 0.6% d_1 species.

While the rates of hydrogenation of trisubstituted alkenes are too slow to make this a very practical hydrogenation procedure,[4] at least for ordinary hydrogenations at low pressure, the high specificity of this reaction for furnishing product in which *only two* deuterium atoms have been introduced[1a,b,2b] led us to investigate the addition of deuterium to 1,4-dimethylcyclohexene (**5**) under these same conditions. The reaction mixture was carefully separated into *cis*- and *trans*-1,4-dimethylcyclohexanes and unreacted **5** and the

Table III. Deuterium Addition to 4-Methylmethylenecyclohexane and 1-Methylcyclohexene Using Tris(triphenylphosphine) chlororhodium(I)

	cis-1,4-Me_2[a]	*trans*-1,4-Me_2[a]	1-Me[b]
d_0	0.3	1.0	2.1
d_1	1.6	2.0	1.5
d_2	98.1	96.9	86.7
d_3	0.0	0.1	8.6
d_4		0.0	1.1
d_{av}	1.98[c]	1.95[c]	2.05[d]

[a] At 10.0% reduction; the product is 66.6 ± 0.1% *cis* isomer. [b] At 10.0% reduction. [c] The recovered alkene contained 0.3% d_1 species. [d] The recovered alkene contained 0.3% d_1 species.

Discussion

The exchange patterns observed in the data of Table II would seem to require, contrary to Scheme I, a

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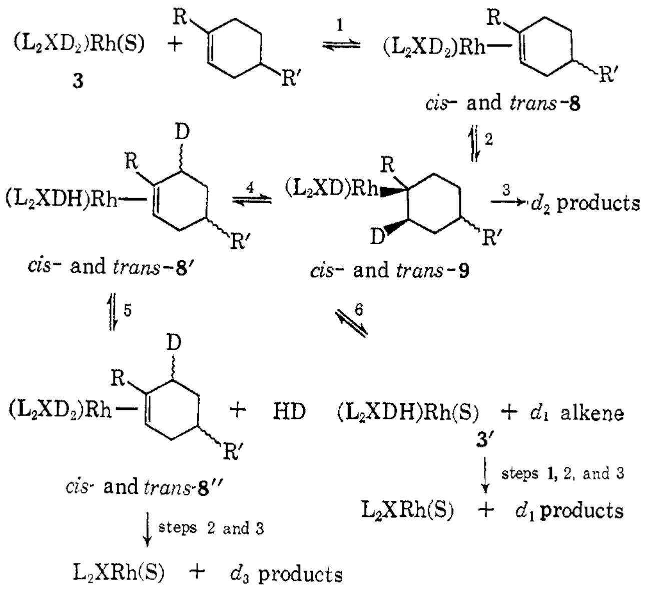
(3) A. S. Hussey, G. W. Keulks, G. P. Nowack, and R. H. Baker, *J. Org. Chem.*, 33, 610 (1968); A. S. Hussey, G. W. Keulks and R. H. Baker, *J. Catal.*, 10, 258 (1968).

(4) A number of other solvents were tried. Cyclohexanone, acetophenone, and nitrobenzene were fairly effective but an increase in rate was observed only in acetophenone, and this was very small. In benzene alone, the rates are about one-half those in 3:1 benzene–alcohol.

Scheme II[a]

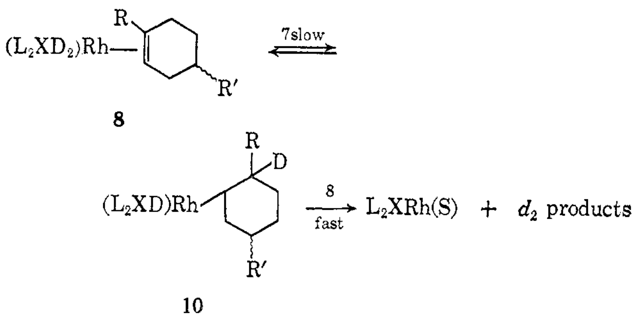


[a] Cycloalkene + **3′**, through the sequence steps 1, 2, 4, and 6, leads to $L_2XH_2Rh(S)$ (**3″**), whence d_0 product is formed *via* steps 1, 2, and 3.

reversible formation of the complex of alkene with **3** and also a reversible formation of an alkylrhodium intermediate. A recent communication[2g] reports the intervention of isomerization in the hydrogenation of a semicyclic alkene when this hydrogenation procedure was used, and a second[2e] demonstrates that tritium exchange accompanies the reduction of cyclohexene at 60°. This exchange is very much reduced at 30°. While all of these facts clearly establish the *stepwise* nature of the transfer of the two hydrogen atoms from the central metal atom, for most mono- and disubstituted double bond systems near room temperature the transfer can nevertheless be regarded to be simultaneous *in a practical sense*,[1a,b,2b] as in Scheme I.

Likewise, exchange in the recovered dialkylcyclohexenes is small (Table II, footnote *e*) and, within the precision of the data, it is equal to the sum of d_0 plus d_1 less d_4 products; hence the rate of dissociation of the complexes of these trisubstituted alkenes with **3**, while finite, must be small relative to the rate of the addition reactions. Again, for less highly substituted alkenes near room temperature, the formation of their complexes with **3** can also properly be considered to be irreversible *in a practical sense*. It is necessary however to modify Scheme I for trisubstituted alkenes to accommodate the exchange we observe. Such a sequence of steps which accommodates the formation of the exchanged product species is presented in Scheme II. If **3′** follows an analogous sequence of steps, d_0, d_1, and d_2 product species finally result, but the formation of the d_4 product we observed probably requires a recycling of some exchanged cycloalkene-d_1. This scheme is consistent with the appearance in the gas phase of HD equal to d_3 plus d_4 products as well as with the equality between the deuterium which is missing from the d_0 and d_1 products with that which is found as cycloalkene-d_1 plus the d_4 products. However, one is then confronted by the question why so little *trans*-**9** is diverted through steps 4, 5, and 6 (*i.e.*, why k_{4c}[*cis*-**9**], and hence k_{-2c}[*cis*-**9**], appear to be so much larger than k_{4t}[*trans*-**9**] and k_{-2t}[*trans*-**9**], respectively). We believe this comes about because of two interrelated factors: first, k_{2c} is larger than k_{2t} and, for both **5** *and* **6**, [*cis*-**9**] is larger than [*trans*-**9**]; second, most of the *trans*-**8** (but a smaller fraction of *cis*-**8**) proceeds to product *via* an alternate set of steps, as in Scheme III. Notice that Scheme III implies that only d_2 species will be found in the product; hence considerable *cis*-**8** (as well as some *trans*-**8**) must follow the steps of Scheme II. Support for the existence of such an alternate pathway is furnished by the data summarized in Table III.

Scheme III



Here it is seen that appreciably more *cis* product is formed from **7** than from **5** but the exchange pattern shows that *cis*-**9** is a barely significant intermediate in the over-all process for the addition of deuterium to **7**. That is to say, a pathway involving the *reverse* order of addition of deuterium atoms (*first* to tertiary carbon, *then* to primary carbon) must be followed by almost all of *cis*-**8** from **7**. Accordingly, the steps of Scheme III should also be available as an alternative pathway for **8** from **5** and **6**.

A consideration of the energy states of the several intermediates supplies a rationale for the fraction of **8** which follows each pathway. Consider **5** for which the rates of formation of *cis* and *trans* product are the same. When heterogeneous platinum and rhodium catalysts are used,[5] this substrate furnishes nearly the same amount of *cis* and *trans* products; hence the 4-methyl group must not exert much influence upon the mode of chemisorption on these metal surfaces.[3,5] It is thus reasonable to expect k_{1c} and k_{1t} for the reaction of **3** with **5** to be nearly equal and, hence, that the rates of formation of *cis*-**8** and *trans*-**8** from **5** are closely the same. But a consideration of the conformations of the corresponding **9** species of Scheme II and the **10** species of Scheme III makes it obvious that *cis*-**9** (a) and *trans*-**10** (d) are of lower energy than *trans*-**9** (b) and *cis*-**10** (c), respectively, as in Figure 1. It is then only necessary that the corresponding transition states resemble **9** and **10** in order that k_{2c} be larger than k_{2t} and that k_{7t} be larger than k_{7c}. It follows that [*cis*-**9**] from **5** is greater than [*trans*-**9**] in Scheme II but [*trans*-**10**] greater than [*cis*-**10**] in Scheme III, and the greater exchange observed in the *cis* product comes about because k_{4c}[*cis*-**9**] is larger than k_{4t}[*trans*-**9**], not because the rate constants for the exchange steps differ appreciably.

The process *trans*-**9** to *trans* product, as compared to

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(5) A. S. Hussey, T. A. Schenach, and R. H. Baker, *J. Org. Chem.*, 33, 3258 (1968).

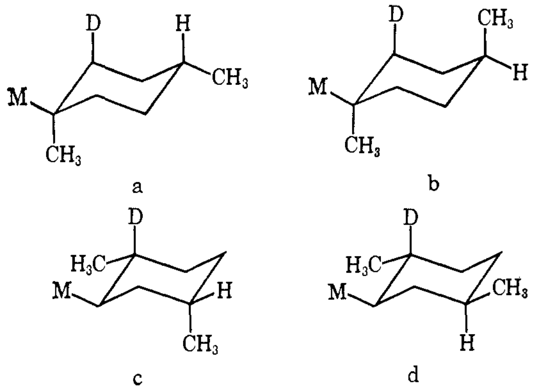

Figure 1. Conformations of the dimethylcyclohexylrhodium intermediates of Scheme II (a, *cis*-**9**; b, *trans*-**9**) and Scheme III (c, *cis*-**10**; d, *trans*-**10**).

cis-**9** to *cis* product, is one from a higher energy intermediate to a lower energy product. Therefore, k_{3t} (Scheme II) is probably considerably larger than k_{3c} and the less favorable $k_{4t}:k_{3t}$ ratio further decreases the diversion of *trans*-**9** through the exchange steps 4, 5, and 6. Similar logic leads one to the conclusion that [*cis*-**9**] > [*trans*-**9**] also when **6** is reduced because *trans*-**9** from **6** is even higher in energy relative to alternative intermediate *trans*-**10** of Scheme III. The exchange pattern for **4** (Table III) shows that an appreciable fraction of this substrate also proceeds to product *via* the steps of Scheme II, in the course of which the 1-methyl-1-cyclohexylrhodium intermediate is diverted through the exchange steps much to the same extent as is its *cis*-1,4-dimethyl-1-cyclohexylrhodium counterpart (*cis*-**9**). This implies that at least 50% of **4** proceeds to product *via* the steps of Scheme III.

Experimental Section

Hydrogenation Apparatus. The hydrogenation apparatus used in these studies was similar to that developed for studies using platinum catalysts.[3] The system was made more compact, however, in order to reduce the total volume which had to be flushed with relatively expensive deuterium. For the same reason, the jacketted gas ballast and butyl phthalate manometer were omitted, and the pressure was monitored instead by a more sensitive capacitance relay system at the open-end mercury manometer where the differential internal *vs.* external pressure was also measured.[3]

Catalyst. The catalyst was prepared as described.[1a] Its preparation was straightforward and its properties, including elemental composition, were closely in agreement with those reported.

Substrates and Solvents. Cyclohexene, 1-methylcyclohexene (**4**), 1,4-dimethylcyclohexene (**5**), 1-methyl-4-isopropylcyclohexene (**6**), and 4-methylmethylenecyclohexane (**7**) were very carefully purified as in our rate studies using heterogeneous platinum catalysts,[3] as were the solvents. However, the homogeneous catalyst used in these studies appears not to be nearly as susceptible to incidental poisons as platinum metal catalysts; hence the final purification immediately before use[3] could be eliminated.

Rate Measurements. In a typical experiment, 10.0 ± 0.2 mg (1.08×10^{-2} mmol) of tris(triphenylphosphine)chlororhodium(I)[1a] was added to the reaction flask and the hydrogenation system was alternately evacuated and flushed with hydrogen five times. With the hydrogen pressure set near 1 atm, 3.00 ± 0.01 ml of benzene and 1.00 ± 0.01 ml of ethanol were added through the side-arm entry port to the reaction flask. The reaction flask was then vigorously agitated[3] for 60 min, at which time 0.50 ± 0.01 ml (3.8 mmol) of 1,4-dimethylcyclohexene (**5**) was added. The pressure was quickly adjusted close to 760 mm, and the agitation was begun anew. The volume of hydrogen in the gas buret was read to the nearest 0.1 ml at 30-sec intervals. The slope of a plot of STP milliliters of hydrogen absorbed *vs.* time was linear, at least to 50% reduction, and gave a rate of reaction of 1.72×10^{-6} mol min^{-1} for **5** under these conditions. Analysis of the reaction mixtures at various stages between 10 and 80% hydrogenation gave ratios of 1.000 ± 0.002 for the *cis* and *trans* products (glpc, using Dow Corning Silicone No. 200 on 110–120 mesh C-22 Firebrick) as in Table I.

Identical experiments using 10.0 ± 0.2 mg of catalyst, 3.00 ± 0.01 ml of benzene, 1.00 ± 0.01 ml of ethanol, and 0.50 ± 0.1 ml of cyclohexene, **4**, **6**, or **7** were also carried out. Similar experiments with **4** were also carried out using other solvents. The rates observed ($\times 10^6$ mol min^{-1} as in Table I) were methylene chloride (0.87), chloroform (0.00), ethylene chloride (1.1), chlorobenzene (0.04), cyclohexanone (3.8), acetophenone (5.5), nitrobenzene (4.4), and benzonitrile (0.00) as compared to 5.3 in benzene–ethanol.

Deuteration Studies. In experiments identical with the above, **4**, **5**, **6**, and **7** were reduced in benzene–ethanol under deuterium at 1 atm. The rate of deuterium addition is very slightly faster than hydrogen addition, as observed before.[1a] The reductions were interrupted when the reactions were about 10% complete and the reaction mixtures were separated into product (as separate isomers for **5**, **6**, and **7**), unreduced substrate, and solvent by glpc procedures. The *cis*:*trans* product ratios for **5**, **6**, and **7** were the same with deuterium as with hydrogen (Table I) as were the rates of reaction. The deuteriumated products (along with the recovered unreduced substrate, the ethanol and benzene solvents, and the residual gas phase) were then subjected to analysis for isotopic hydrogen using a CEC 21-104 mass spectrometer.

The deuterium distribution in the products are given in Tables II and III. The amount of deuterium in the unreduced substrates was small (see footnotes to Tables II and III) and the cycloalkene-d_1 plus d_4 products were equal to the sum of d_0 and d_1 product within experimental error. Some deuterium was also found in the solvent as C_2H_5OD (but none in the benzene) and considerable HD was found in the gas phase.

When benzene alone was used as the solvent [Table II, 0.80 ml (4.8 mmol) of 1-methyl-4-isopropylcyclohexene (**6**), experiment 2], the exchange pattern in the products from **6** was the same as when benzene–ethanol was the solvent, no deuterium could be found in the benzene, and the HD content of the gas phase was equal (within the precision of measurement of so small a per cent) to the excess deuterium which was found in the d_3 and d_4 products (125 ml of residual isotopic hydrogen enriched by 0.3 ± 0.1% HD, equivalent to 1.5×10^{-2} mmol; the d_3 and d_4 products at 12.0% reduction of 4.8 mmol of **6** (Table I) are equivalent[6] to 1.4×10^{-2} mol).

Acknowledgment. We gratefully acknowledge financial assistance from the National Science Foundation (GP 4656) and from Teijin, Ltd. (Tokyo, Japan).

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(6) In benzene, **6** furnishes 33.0 ± 0.2% *cis*-1-methyl-4-isopropylcyclohexane but in 3:1 benzene–ethanol, 29.9 ± 0.1% (Table II). This difference in *cis*:*trans* is real but such a change is not observed with **5** in benzene alone (rate in benzene, 1.4×10^{-6} mol min^{-1}).