

Steric Factors in the Exchange with Deuterium of Some Cyclic Hydrocarbons Catalyzed by Palladium

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The exchange with deuterium of bicyclo[3.3.1]nonane(I), *endo*-3-methylbicyclo[3.3.1]nonane(II), *exo*-3-methylbicyclo[3.3.1]nonane(III), *trans*-2,3-dimethylbicyclo[2.2.1]heptane(IV), and bicyclo[3.2.2]octane(V), catalyzed by palladium has been investigated. The results confirm that repeated roll-over of intermediate olefins propagates the exchange reaction from one face of a ring to another in cycloalkanes. Severe steric hindrance of nonbonded groups with the surface of the catalyst is also important in reactions of these compounds.

INTRODUCTION

The results from reactions of *endo,endo*-2,3-trimethylenenorbornane(VI), *exo,exo*-2,3-trimethylenenorbornane(VII), bicyclo[3.3.0]octane(VIII) and 1-methylbicyclo[3.3.0]octane(IX) with deuterium on palladium catalysts (1) strongly indicated that the mechanism which propagates exchange from one face of a ring to another in cycloalkanes is repeated roll-over of intermediate olefins (2), with or without desorption from the surface. The intentions of the present work were to study reactions of additional model compounds in order to confirm this mechanism, and to explore further the influence of steric hindrance with the surface on the reactivity of adsorbed species. The structures of such rather rigid compounds of this type (1) are advantageous for this purpose.

EXPERIMENTAL METHODS

Hydrocarbons. The preparation of I has been previously described (1). II was obtained as follows: bicyclo[3.3.1]non-6-ene-*endo*-3-carboxylic acid (3) was hydrogenated (Adams Pt; 1 atm) and treated with LiAlH₄ in ether giving *endo*-3-hydroxy-

methylbicyclo[3.3.1]nonane. The product was treated with tosylchloride and the resulting tosylate (4) reduced by LiAlH₄ in ether to a mixture of II and *endo*-3-hydroxymethylbicyclo[3.3.1]nonane which were separated by chromatography on activated alumina. II was converted into III in 98% yield by passing in hydrogen over a 2% wt Pd/SiO₂ catalyst at 250°C. IV was prepared by the method of Alder and Roth (5).

Bicyclo[3.2.2]non-6-ene obtained as a gift from Dr. A. Penrose was converted to V by gas phase hydrogenation using a 5% wt Pt/SiO₂ catalyst at 50°C.

All the compounds were purified to >99% by preparative glc as previously described (1).

Catalysts and reaction systems. For most experiments a 2% wt Pd/SiO₂ catalyst and a flow system were employed. The reaction conditions, catalyst preparation, and procedure for examining the products for deuterium content and isomerization were previously described (1). Films (10 mg) prepared as before (1) were used as catalysts for reactions of IV in a static system with an 8:1 mixture of deuterium to hydro-

TABLE I
 SOME DISTRIBUTIONS FOR EXCHANGE OF I, II AND III

Compound:	I	I	I	II	II	III	III
$T(^{\circ}\text{C})$:	70	117	136	117	165	104	127
Conversion (%) of d_0 :	3.25	2.29	6.6	6.3	11.5	4.0	18.0
d_1	13.8	12.8	20.1	19.8	18.8	35.0	29.8
d_2	13.2	9.9	7.5	23.0	14.6	32.5	19.2
d_3	2.3	2.9	2.3	3.0	4.4	12.5	14.3
d_4	2.7	3.6	2.1	1.6	3.0	8.0	11.6
d_5	4.3	4.4	3.0	2.1	2.5	5.75	9.8
d_6	3.4	4.0	2.3	2.4	2.4	5.0	8.1
d_7	4.9	5.4	3.7	4.8	3.7	5.25	8.7
d_8	21.8	14.9	8.8	7.1	5.7		
d_9	2.2	4.3	4.6	7.0	6.1		
d_{10}	19.4	18.3	15.7	9.8	8.6		
d_{11}	1.4	3.0	5.6	9.7	10.3		
d_{12}	9.5	15.2	23.0	6.2	7.8		
d_{13}	0.9	1.0	2.2	5.2	9.0		
d_{14}				0.2	1.9		
d_{15}					1.0		

carbon at a total pressure of 45 mm of Hg. The static system was coupled via a capillary leak to a Metropolitan Vickers M.S.2 instrument and initial distributions of deuterioisomer obtained as previously described (6). For all the compounds parent ions with appropriate corrections for fragmentation and naturally occurring isotopes were used to estimate the abundances of the products.

RESULTS

Some typical results for the exchange of **I**, **II** and **III** are given in Table 1. The distributions for **I** which had pronounced maxima in the d_3 , d_{10} and d_{12} isomers closely agreed with those obtained before by Schrage and Burwell (7) using a Pd/Al₂O₃ catalyst. Thirteen hydrogens were readily exchanged in **II** with slight maxima appearing in d_{11} and d_{13} isomers as the temperature increased. Isomers d_{14} and d_{15} only became significant at temperatures where isomerization of **II** to **III** commenced. Thus at 165°C after 11.5% conversion of the d_0 isomer ~3% of **III** was detected in the products. Because of the difficulty encountered in separating **II** and **III** on the glc column when both also consisted of mixtures of their deuterioisomers, separate experiments in hydrogen were carried out and showed selective conversions of **II** to **III** of

15 and 89% at 162 and 200°C, respectively. Only 7 hydrogens in descending distributions were exchanged in **III** with negligible amounts of higher isomers even at 18% conversion of d_0 .

Only two hydrogens were initially exchanged in **IV** (column 2, Table 2). After the d_0 isomer had decreased to 12% at 80°C the reaction was quenched by chilling and the products isolated for glc analysis which showed that isomerization had not occurred.

 TABLE 2
 INITIAL AND OTHER DISTRIBUTIONS FOR
 EXCHANGE OF IV WITH DEUTERIUM
 ON PALLADIUM FILMS

$T(^{\circ}\text{C})$:	80	80	140	140
d_0		30.7	14.9	3.8
d_1	22.9	11.1	12.6	4.6
d_2	75.3	37.8	27.6	10.0
d_3	1.8	18.7	23.0	13.0
d_4		1.7	6.9	10.7
d_5			2.3	7.4
d_6			—	4.8
d_7			—	5.5
d_8			0.9	8.5
d_9			4.4	9.2
d_{10}			4.4	10.0
s_{11}			2.3	13.4
d_{12}			0.7	6.2
d_{13}				3.1

TABLE 3
 SOME DISTRIBUTIONS FOR EXCHANGE OF V

$T(^{\circ}\text{C})$	Conversion (%)										
	of d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}
70	2.1	10	79	10							
112	44.0	17	35	11	14	7	5	3	3	2	1

The experiment was repeated at 80°C until the d_0 isomer had diminished to 30.7% (column 3, Table 2) and the temperature rapidly raised to 140°C with the appearance of d_8 to d_{12} isomers (column 4, Table 2). The reaction was maintained at 140°C until substantial quantities of these higher isomers had formed (column 5, Table 2) then quenched and analyzed as before. Conversion of **IV** to **4** and 2% of the corresponding *exo-exo*-2,3-dimethyl and *endo-endo*-2,3-dimethyl isomers, respectively, was now detected.

At low conversions there was a pronounced maximum in the d_2 isomer in the products from **V** (Table 3), and at extensive conversions an additional maximum in the d_4 isomer with diminishing quantities of higher isomers.

DISCUSSION

The interconversion of monoadsorbed alkyl and 1,2-diadsorbed species ($\alpha\beta$ process) is responsible for multiple exchange with deuterium of alkanes and cycloalkanes on Pd catalysts. This process is limited to *cis*-elimination and addition of hydrogen and/or deuterium atoms. A previous study of exchange with deuterium of **VI**, **VII**, **VIII** and **IX** on Pd catalysts (1) supported the view that initial replacement of hydrogens on both faces of rings in cycloalkanes such as cyclopentane (8) is due to repeated roll-over of 1,2-diadsorbed species. The evidence is against an alternative mechanism of *trans*-elimination and addition during interconversion of π -bonded alkenes and alkenyls (9).

Burwell (10) believes that the 1,2-diadsorbed species is eclipsed 1,2-diadsorbed alkane with carbon-metal σ -bonds. The ease of forming such a species is therefore akin to the ease of obtaining eclipsed conformations in the free alkanes. An alterna-

tive which we prefer is that the 1,2-diadsorbed species is an alkene π -bonded to one metal atom (11).



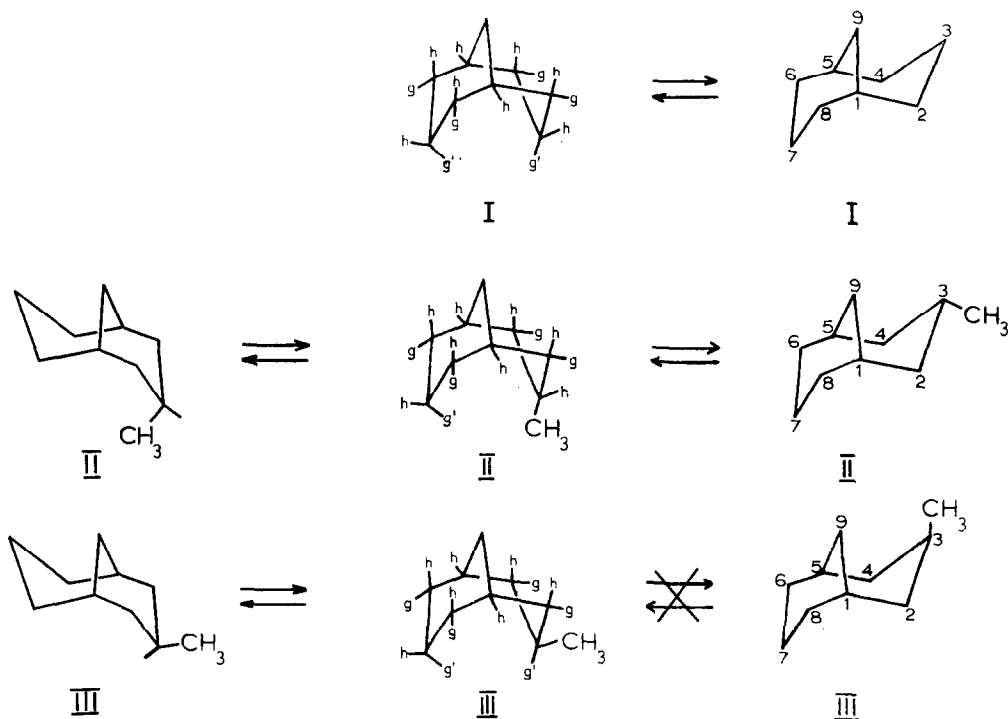
Burwell's major criticism of this model is that certain essential olefinic intermediates have too high a strain energy to be responsible for the facile multiple exchange observed for some compounds. For example, there is rapid propagation of exchange through the bridgehead positions in **I** (7), yet bicyclo[3.3.1]non-1-ene has a strain energy of ~ 12 kcal mole $^{-1}$ (12). We are not convinced by such arguments. Both Roth, Geller and Burwell (2) and ourselves (1) agree that Δ 1,5-bicyclo[3.3.0]octene, with considerable strain energy, is readily formed in exchange of bicyclo[3.3.0]octane on Pd. Also, olefins complexed to zero-valent metals such as Pd have considerable bond lengthening and deviation from planarity at the unsaturated centers due essentially to $d\pi-p\pi^*$ back-donation. This relieves strain. Strained olefins therefore should and do form stronger π -complexes. Conformations of π -bonded alkenes on metal surfaces are therefore not directly related to conformations of the corresponding free alkanes or alkenes. However, it is possible that an approach towards an eclipsed conformation is required in the transition state during conversion of alkyl to π -bonded alkene, but there is no relevant information on this point from a homogeneous analogue. Another example that arguments based on strain energy are not conclusive is the facile exchange on Pd of all the hydrogens in 2,3-dimethyl butane (13). Burwell's model requires the unfavored eclipsed 2,3-diadsorbed alkane, whereas nonbonded repul-

sions between the methyl groups are much less severe in π -bonded tetramethylethylene. [This detailed consideration is essential because a referee has argued that we cannot ignore Burwell's mechanism because the interpretation of some of the present results depends on which model is chosen. We believe that eclipsing is not in itself an essential condition for multiple exchange but that a reasonable possibility of forming an olefinic complex is. Conformation and conformational flexibility can then be considered as factors in determining the ease of formation of the latter. In the subsequent discussion we will therefore interpret the results on the basis of our mechanism but will refer to the implications of Burwell's model when it leads to different conclusions.]

The simplest view of roll-over of the 1,2-diadsorbed species is that transient desorption of π -bonded olefin occurs. Since we are dealing with a kinetic and not a thermodynamic situation this step depends on the energy required to break the π -bond and not on the enthalpy of dehydrogenation (14). Burwell (10) believes that during

roll-over of eclipsed 1,2-diadsorbed alkane the intermediate is still attached to the surface. He has to invoke both side-bonded roll-over and end-bonded roll-over to explain results, when those for bicyclo[3.3.0]octane are included (2). But in either case the intermediate is effectively an alkene with slight residual bonding to the surface.

The chair-chair conformation of **I** is preferred but the C_3 - C_7 interaction causes flattening of the C_6 rings which favors both eclipsing and double bond formation. The chair-chair conformation of **II** is not preferred because of the severe interaction of C_3 methyl with C_7 . The chair-boat conformation must be important and more so than the boat-chair where the C_3 -methyl is axial to C_6 and C_8 . The situation is quite different for **III** where the chair-boat conformation is least stable because of the severe interaction of C_3 -methyl with C_9 . The chair-chair conformation is obviously preferred to the boat-chair. There are also a variety of other conformations some of which will be discussed later. Certainly there is no doubt that the presence of a methyl substituent makes **II** and **III** less flexible than **I**.



The structure of **II** is such that its exchange behavior should provide a decisive test of the roll-over mechanism and the π -allylic mechanism. According to Burwell (10) the d_8 maximum for **I** corresponds to completion of exchange of the h -set of atoms by the $\alpha\beta$ process, and the d_{10} and d_{12} maxima to additional exchange of the g -atoms in one and both of the trimethylene units.

Burwell attributes the absence of initial exchange of the g^1 -atoms to (a) the difficulty of having a $C_1C_2C_3$ - π -allylic (and equivalent) systems with consequent *trans*-addition of a D atom at C_3 or C_7 ; forbidden, or (b) roll-overs of bicyclo[3.3.1]non-1-ene are essential to allow the $\alpha\beta$ process to replace the g^1 -atoms and obviously this is not possible. The trimethylene units in **I** are therefore isolated with regard to two-set exchange, as first observed in 1,1,3,3-tetramethylcyclohexane where 5 and not 6 hydrogens are initially replaced (11).

In **II** a g^1 -atom is replaced by a methyl group providing a tertiary center which may invert to give the more stable isomer **III**. Since the results for **I** indicate that the tertiary C_3 in **II** cannot be a terminal atom in a π -allylic complex, the π -allylic mechanism predicts that inversion cannot occur even though 15 hydrogens in **II**, corresponding to 12 in **I**, may undergo initial exchange. On the other hand if roll-over of olefin is responsible for two-set exchange **II** should isomerize to **III**. The d_{11} maximum for **II** (Table 1) is due to replacement of the 8 hydrogens of the h -set plus the three of the methyl group. Additional exchange of the 2 g -atoms (C_6 and C_8) is responsible for the appearance of d_{12} and d_{13} . The exchange of the other 2 g -atoms (C_2 and C_4) is more difficult but when d_{14} and d_{15} isomers are observed at higher temperatures isomerization is detected. The latter can only be explained by roll-over of either 3-methyl-*endo*-bicyclo[3.3.1]nonane or 3-methylbicyclo[3.3.1]non-2-ene. Models show that roll-over of these olefins leaving C_9 oriented away from the surface is sterically more difficult than roll-over of *endo*-3-methylbicyclo[3.3.1]non-6-ene, thus explaining the easier replacement of the C_6 and C_8 g -atoms. The d_{14} and d_{15} isomers are probably

present in the products as **III** and their real abundances are higher than shown in Table 1 since fragmentation of **III** is sixfold that of **II** in the mass spectrometer under the conditions used.

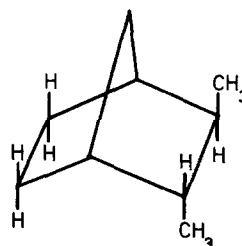
Substantial and sometimes approximately equal quantities of d_1 and d_2 isomers are observed in the distributions for **I**, **II** and **III**. [A referee has argued as follows that this supports Burwell's picture of the $\alpha\beta$ process. An eclipsed C_1C_2 (and equivalent positions) is obtained when one of the C_6 rings in **I** adopts a boat conformation whereas, for C_2C_3 (and equivalent positions), eclipsing requires a double twist boat or chair-skew boat conformation. Thus with C_1C_2 eclipsing easier than C_2C_3 eclipsing there would be an impediment to propagation of the $\alpha\beta$ process from C_2 to C_3 .] If this argument is correct the $\alpha\beta$ process should propagate over C_2 , C_1 and C_8 (eclipsed C_1C_2 and C_1C_8 are identical) giving possibly less d_3 than d_2 but substantially more than d_4 , and this is not so. Besides, our results are in accord with all those reported for **I** (10) in that a very slight but definite maximum in d_5 is observed. This is entirely contrary to expectation on the basis of Burwell's model but is readily explained by our mechanism. The d_5 maximum indicates that some exchange begins in, and is confined to, a trimethylene unit (5H exchangeable) because π -bonded bicyclo[3.3.1]non-2-ene is more easily formed than π -bonded[3.3.1]non-1-ene. There is therefore some difficulty in propagating the exchange through the bridgehead positions. The above feature concerning d_2 is not unique to bicyclo[3.3.1]nonanes since, using supported Pd in flow systems, substantial amounts and often maxima in d_2 isomers are observed in the exchange of many cycloalkanes, e.g., cyclopentane and methylcyclopentane (10), where the hydrogens are already eclipsed. An explanation is that intermediate olefins are formed and migrate to sites which cannot propagate the exchange but can only add two D atoms.

The exchange of only 7 hydrogens and the decreasing amounts of isomers from d_1 to d_7 for **III** (Table 1) is an interesting problem. These must be either the 7 in the h -set or the 5 h plus 2 g -atoms in the un-

substituted C₆-ring. Since Burwell's mechanism requires the very unlikely chair-boat conformation it precludes exchange of the 2 *h*-atoms at C₂ and C₄. In order to replace these 2 *h*-atoms our mechanism requires formation of π -bonded Δ -1,2(4,5)-*exo*-3-methylbicyclo[3.3.1]nonenes. There is probably some steric hindrance to its formation but models indicate that it is possible. The exchange of the 2 *g*-atoms at C₆ and C₈ by Burwell's mechanism requires roll-over of the eclipsed C₆C₇ (C₇C₈)-diadsorbed species and as we have seen this can only occur with either the extremely unlikely double twist boat or the skew-boat-chair conformations. Steric repulsion by the surface renders equally improbable roll-over in the latter conformation, or in our terms read-sorption of *exo*-3-methylbicyclo[3.3.1]non-7-ene with C₉ directed away from the surface. We therefore believe that the exchangeable hydrogens are in the *h*-set. Finally we note that because of decreasing flexibility from **I** to **II** to **III**, and increasing steric repulsions to roll-over of bicyclo[3.3.1]non-2-ene, *endo*-3-methylbicyclo[3.3.1]non-7-ene and *exo*-3-methylbicyclo[3.3.1]non-7-ene the ease of multiple exchange and especially two-set exchange decreases from **I** to **II** to **III**. This is clearly reflected by the substantial amounts of light isomers and falling distributions for **III**.

Kemball (15) noted that the exchange of the tertiary hydrogen occurred more readily than the primary hydrogens in isobutane on nickel. Also, Hilaire, Maire and Gault (16) found that the exchange of *cis*-1,2-dimethylcyclobutane was about one hundredfold faster than of the corresponding *trans*-isomer on palladium although the rates were about the same on platinum. Since the tertiary hydrogens in the *trans*-isomer are sterically hindered tertiary C-H bonds must be more readily broken than primary or secondary bonds on palladium. Our results for **IV** (Table 2) provide a very interesting example of steric effects of this kind.

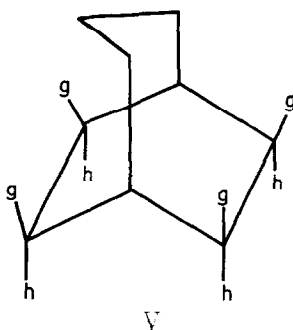
At 80°C only hydrogens in the dimethylene unit are replaced giving an initial maximum in the *d*₂ isomer so that this compound is very similar in behavior to



IV

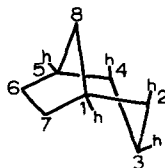
bicyclo[2.2.1]heptane itself (13). The only distinction is that at substantial conversion at 80°C there is very little of the *d*₄ isomer. This is due to the severe steric hindrance to attack of one *endo*-hydrogen by the *endo*-methyl group. Exchange of the hydrogens in the -(CH₃)CH-CH(CH₃)- unit only commences at 140°C, with isomerization. Restriction to attack of the fourth hydrogen in the dimethylene unit is removed in the *exo,exo*-isomer. The tertiary hydrogens are sterically hindered in **IV** but the primary hydrogens are not, and thus secondary C-H bonds are more reactive than the primary bonds. The order of ease of attack is therefore tertiary > secondary > primary bonds on palladium and the previously reported results for reaction of **VI** (1) also agree with this sequence.

Roth, Geller and Burwell (2) found that initial exchange of bicyclo[3.2.1]octane on palladium was largely confined to the trimethylene with some reaction of the dimethylene unit. Multiple exchange was not extensive, the trimethylene unit being associated with a slight maximum in the *d*₅ isomer, and propagation of the reaction from one unit to the other did not take place. On the other hand multiple exchange of bicyclo[3.3.1]nonane (**I**) is very extensive and there is facile propagation of exchange past the bridgehead carbon atoms. Reactions of **V** were examined to compare with the above results. The most stable conformation of **V** has the C₆-ring in the twist-boat conformation exposing the *h*-atoms to attack. However, we thought that there might be exchange of 5 hydrogens in the trimethylene unit with possible extension through the bridgeheads to the dimethylene units. The results (Table 3) show that



exchange is apparently largely confined to the dimethylene units giving initially a maximum in the d_2 isomer, and in the d_2 and d_4 isomers at substantial conversion. Models suggest that the 4 h -atoms of the C_6 -ring are those readily replaced and that chemisorption at the common faces between the dimethylene and trimethylene units is sterically hindered so that attack of the hydrogens in the trimethylene unit and the g -sets is inhibited. Compound **V** therefore does not resemble those with a methylene bridge, e.g., bicyclo[3.2.1]octane and bicyclo[3.3.1]nonane.

Since h_1 and h_2 -atoms (h_4 and h_5) are virtually eclipsed, with the C_6 -ring in the boat conformation, in bicyclo[3.2.1]octane, and the trimethylene unit is sterically simi-



Bicyclo[3.2.1]Octane

lar to that in **I**, an initial maximum in d_7 in addition to that in d_5 might have been expected if Burwell's theory (10) is correct.

The simplest explanation is that the exchange cannot propagate from the trimethylene unit because the anti-Bredt olefin Δ -1,2-bicyclo[3.2.1]octene is much more difficult to form than bicyclo[3.3.1]-non-1-ene.

We have now found that heptacyclo-[9,3,0^{1,11},0^{2,6},0^{3,10},0^{4,8},0^{7,14},0^{9,13}]-tetradecane only undergoes simple stepwise exchange on Pd catalysts (17) in spite of the fact that it contains 4 separate pairs of

perfectly eclipsed, adjacent, tertiary hydrogens out of a total of 16. Since it is extremely unlikely that this cage compound could form a π -complexed olefin the absence of multiple exchange confirms our arguments about the nature of the 1,2-diadsorbed species and the $\alpha\beta$ process.

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