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Exchange with Deuterium of some Cyclic Hydrocarbons Catalyzed by Palladium

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The exchange with deuterium of endo,endo-2,3-trimethylenenorbornane, exo,exo-2,3-trimethylenenorbornane, bicyclo[3.3.0]octane and 1-methylbicyclo[3.3.0]octane catalyzed by palladium has been investigated. These compounds were chosen because their structural features can distinguish the mechanism which propagates the exchange reaction from one face of a ring to another in cycloalkanes. The results clearly indicate that roll-over of intermediate olefins is responsible and not *trans*-addition of deuterium to π-allyl intermediates or suprafacial 1,3 shifts of hydrogen via transient allylic complexes.

INTRODUCTION

Many investigations of isotopic exchange between deuterium and paraffins catalyzed by transition metals have been carried out in order to elucidate mechanisms of reactions between hydrocarbons and hydrogen on such catalysts. Reactions of cycloalkanes on palladium are particularly interesting, because initial distributions of deuteroisomers show pronounced multiple exchange with clearly defined maxima corresponding to certain sets of hydrogen atoms in a given compound (*1*, *2*). For example, the initial distributions for exchange of cyclopentane have major maxima in the d_5 and d_{10} isomers (*3*). Clearly, there is a process which is limited to replacement of hydrogen atoms on one face of the ring, a feature generally observed from the initial distributions of a variety of cycloalkanes. This process (the $\alpha\beta$ process (*4*)) is the interconversion of adsorbed alkyl and alkene and is confined to *cis*-elimination and addition of hydrogen and/or deuterium.

The mechanism of initial exchange on both faces of rings, or multiset exchange (*5*), is still controversial. It does not occur on palladium via $\alpha\alpha$, $\alpha\alpha\beta$ or $\alpha\alpha\beta\beta$-adsorbed species as observed with other metal catalysts, especially rhodium (*1*). Studies of a variety of model compounds on palladium have narrowed the possibilities to two alternatives, both of which satisfactorily explain all the published results (*6*). The resolution of this problem is obviously pertinent to an understanding of metal-catalyzed epimerization of certain paraffins and many hydrogenations, e.g. 1,2-disubstituted cycloalkenes and benzenes to both *trans* and *cis* isomers of the corresponding cycloalkanes.

Process A

Repeated roll-over of intermediate olefins with (*7*) or without (*2*, *6*) desorption presents the other faces of rings to the surface so that the $\alpha\beta$-process can propagate the exchange from one side of the molecule to the other.

Process B

Reorientation of adsorbed species does not occur but *trans*-elimination and addition of hydrogen and/or deuterium occur via interconversion of adsorbed olefin and π-allylic complexes (*1*).

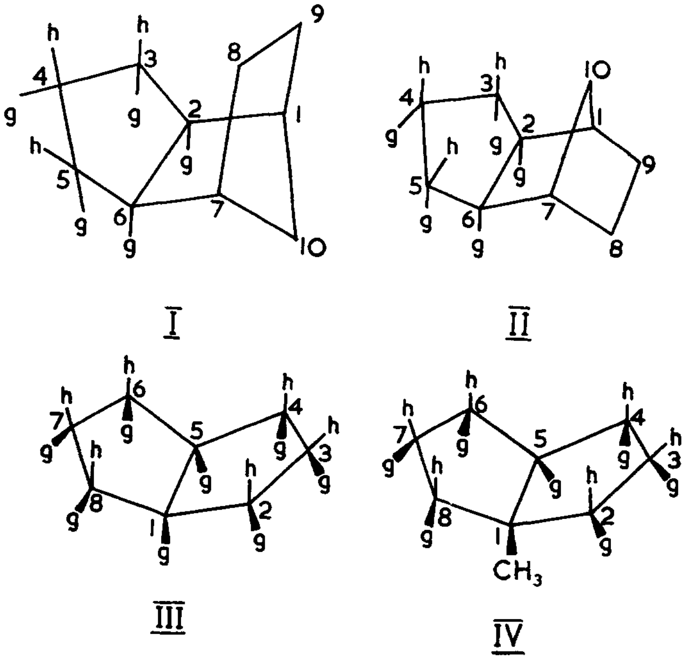
In order to decide the correct mechanism, the endo, endo and exo, exo isomers of 2,3-trimethylenenorbornane were chosen for study. These compounds are substituted bicyclo[3.3.0]octanes, and because of strain only *cis*-geometry is allowed for ring junction at the C_2 and C_6 positions of (I) and (II). This feature restricts to some extent the ease of operation of both processes, so the results might give a clear-cut distinction. In addition, the possibility of simultaneous endo–exo isomerization could also be examined. During the course of this work Burwell *et al.* (*6*) published results which revealed that all 14 hydrogens are readily exchanged initially in bicyclo[3.3.0]octane itself on palladium. They showed that this could only arise by Process A if bicyclo[3.3.0]oct-Δ1,5-ene rolls over on the surface. Process B also explains this result provided π-allylic species including one of the tertiary carbon atoms is possible. They suggested that 1-methylbicyclo[3.3.0]octane would be worth investigating as the Δ1,5-alkene would not now be possible (Fig. 1), so only 11 hydrogens could be replaced by Process A. On the other hand, Process B with π-allylic complexes including the tertiary carbon atom C_5 should still be possible, so if the latter is responsible, 13 hydrogens should be readily exchanged initially.

In this paper we report the preparation and details of reaction of endo,endo-2,3-trimethylenenorbornane (I), exo,exo-2-3-trimethylenenorbornane (II), bicyclo[3.3.0]-octane (III), and 1-methylbicyclo[3.3.0]-octane (IV), with deuterium on palladium catalysts. The structures and different sets of exchangeable hydrogens in these compounds are shown in Fig. 1.

EXPERIMENTAL

Hydrocarbons

(I) was obtained by hydrogenating cyclopentadiene dimer. (II) was prepared by stirring (I) in concentrated sulphuric acid for 15 hr at 20°C, then neutralizing the acid and extracting the product (*8*). (III), cyclooct-1,5-diene, was refluxed



I

II

III

IV

FIG. 1. Detailed structures of compounds (I)–(IV).

with potassium (*8*) to give bicyclo[3.3.0]oct-2-ene which was then hydrogenated over Adams platinum. (IV), bicyclo[3.3.0]oct-2-ene, was treated with a solution of formic acid in concentrated sulphuric acid at 20°C giving a mixture of carboxylic acids which were finally isolated as their methyl esters. The latter mixture was reduced by lithium aluminum hydride to a mixture of alcohols, the tosylates of which were further reduced by lithium-aluminum hydride to a mixture of paraffins and a 20% residue of alcohols.

The paraffins, which were each isolated by preparative G.L.C. consisted of 40% bicyclo[3.3.1]nonane, 40% 1-methylbicyclo[3.3.0]octane, 10% *trans*-bicyclo[4.3.0]-nonane, and 10% of an unidentified isomer. The molecular weight and structure of each product were determined by M.S. and NMR analyses. The structural assignment of the unexpected bicyclo-[3.3.1] nonane was confirmed, as it was identical with an authentic sample obtained by hydrogenating bicyclo[3.3.1]-non-2-ene (available as a gift from Dr. A. Penrose of the New University of Ulster). Furthermore, experiments on exchange of bicyclo[3.3.1]nonane, synthesized as above, with deuterium over a Pd/Al$_2$O$_3$ catalyst gave results identical with those reported for similar experiments on this compound by Schrage and Burwell (*2*). The skeletal rearrangement which obviously occurred during this synthesis is now being investigated in detail.

Samples of (I) to (IV) were purified to >99% using a Perkin-Elmer F-21 instrument with an 8 ft column of 20% w/w Apiezon L on Chromosorb P at 160°C.

Catalysts

Both supported palladium and palladium films were used. Two percent w/w Pd/silica (a) (Whatmans S.G. 40 grade silica, 60–85 mesh) and 2% w/w Pd/Γ-alumina (b) (Merck) were prepared by impregnating the supports with palladium chloride, drying and reducing in hydrogen. Immediately prior to use, each sample of catalyst was treated with hydrogen at 300°C for 2 hr, cooled to reaction temperature and deuterium passed for 5 min. Palladium films (c) were prepared as previously described (*9*).

Palladium chloride and palladium wire (spectroscopically standardized quality) were obtained from Johnson, Matthey and Co. Ltd., and deuterium (Cambrian Chemicals Ltd.) was purified by passage through a palladium thimble.

Reaction Systems

The supported catalysts were used in a flow system at atmospheric pressure with a 12/1 ratio of deuterium to paraffin. Flow rates were between 5 and 15 ml/min, and catalyst samples between 50 and 150 mg, depending on the reaction temperature desired. Products were trapped in liquid nitrogen and, where applicable, tested for isomerization using a Perkin–Elmer F 11 GLC unit with a 20 m capillary column containing Apiezon L.

Reactions on films were carried out in a static system with an 8/1 mixture of deuterium to paraffin at a total pressure of 45 mm of Hg. In all cases, parent ions with appropriate corrections for fragmentation and naturally occurring isotopes were used to obtain distributions of deuteroisomers. The static system was coupled via a capillary leak to a Metropolitan Vickers M.S. 2 instrument and initial distributions obtained as previously described (*9*). Products from the flow system were analyzed either by the above instrument or an A.E.I. M.S. 902.

Results

Some typical results for exchange of (I) and (II) on supported catalysts are given in Table 1. In all experiments, even with a substantial percent exchange, only 5 hydrogens were replaced by deuterium in (I). Although (II) behaved similarly with a maximum in the d_5 isomer, smaller but significant quantities of d_6 and d_7 isomers with a slight maximum in the latter also appeared at low conversion.

Initial distributions for (III) and (IV) using 80 mg films at 30°C are reported

TABLE 1

Some Distributions for Exchange of (I) and (II) with Deuterium on Supported Palladium Catalysts

Hydrocarbon	(I)	(I)	(II)	(II)
Temperature (°C)	90	74	80	123
Catalyst	b	a	b	a
% Exchange	8.2	22.6	7.0	10.0
d_1	3.44	7.95	2.80	3.98
d_2	1.12	2.58	1.60	2.36
d_3	0.73	3.24	0.36	0.71
d_4	1.12	3.80	0.65	1.05
d_5	2.48	4.76	1.04	1.14
d_6		0.25	0.20	0.34
d_7			0.31	0.40

in Table 2. Rates of exchange of (III) and (IV) were virtually the same. Large maxima in d_8 and d_7 isomers respectively appeared but, whereas significant quantities of all isomers from d_9 to d_{14} were also observed for (III), there was no initial exchange beyond 11 hydrogens in (IV). Some distributions for (IV) obtained at higher temperatures are compared with a distribution for (III) in Table 3. At the higher temperatures the d_7 maximum disappeared, but there was a substantial maximum at the d_{11} isomer, with only minor quantities of d_{12} and d_{13} isomers.

TABLE 2

Initial Distributions for Exchange of III and IV at 30°C on Palladium Films

Hydrocarbon	(III)	(IV)
d_1	10.8	4.0
d_2	1.7	2.6
d_3	1.3	5.9
d_4	1.2	6.4
d_5	1.0	7.2
d_6	2.4	13.7
d_7	9.8	32.2
d_8	47.6	6.9
d_9	3.7	7.0
d_{10}	4.8	7.5
d_{11}	2.3	6.6
d_{12}	2.7	—
d_{13}	4.6	—
d_{14}	5.9	—

Discussion

Metal films are much more active than the supported catalysts, and heavy films were deliberately used in order to obtain distributions of deuteroisomers at low temperatures, where two-set exchange is less favored (*3*). However, at comparable temperatures in the higher range, the same significant features in the distributions were always observed for each compound, irrespective of catalyst type.

TABLE 3

Some Distributions for Exchange of III and IV with Deuterium on Palladium Catalysts

Hydrocarbon	(III)	(IV)	(IV)
Temperature (°C)	30	120	90
Catalyst	c	b	c
% Exchange	22.0	7.9	27.7
d_1	1.44	0.67	1.88
d_2	0.68	0.50	1.05
d_3	0.30	0.34	0.67
d_4	0.27	0.41	0.87
d_5	0.27	0.48	1.15
d_6	0.39	0.64	1.59
d_7	2.15	0.64	1.70
d_8	10.84	0.66	2.15
d_9	0.78	0.69	3.95
d_{10}	1.16	0.71	5.00
d_{11}	0.53	1.21	6.45
d_{12}	0.55	0.33	0.74
d_{13}	0.97	0.07	0.54
d_{14}	1.26	—	—

In the exchange of (III) at 68°C on a supported palladium catalyst, Burwell *et al.* (*6*) observed comparable maxima in the d_8 and d_{14} isomers. Our results for (III) at lower temperatures (Tables 2 and 3) show similar maxima although d_8 is greater than d_{14}. The d_8 maximum arises from exchange of one set of hydrogens, the *g*-set, while the d_{14} maximum from exchange of both *h* and *g*-sets (Fig. 1). The mechanism of replacement of the *g*-set is the $\alpha\beta$-process, whereas initial exchange of both sets is explicable by either Process A or B. Burwell has shown that to obtain a d_{14} maximum by Process A, bicyclo[3.3.0]oct-Δ1,5-ene must roll over. Propagation of exchange via roll-over of the Δ1,2-ene is improbable as this would give a *trans* ring junction, while several roll-overs of the Δ2,3-ene would only give initial exchange of 12 hydrogens, since the *h*-atoms at C_3 and C_7 could not be replaced. Substitution of the 1-methyl group as in (IV) eliminates the possibility of a Δ1,5-ene and hence initial exchange by Process A cannot include the *h*-atoms at C_3 and C_7 (Fig. 1). To obtain a d_{14} maximum in (III) by Process B π-allylic species involving carbon atoms (1,2,3) ≡ (3,4,5), etc., and (2,3,4) ≡ (6,7,8) must be postulated. The 1-methyl group in IV should not diminish the possibility of π-allylic species at carbons (2,3,4) or (3,4,5) etc. (Fig. 1), so a d_{13} maximum is expected for (IV), analogous to the d_{14} maximum for (III), if Process B is responsible. Since the results in Tables 2 and 3 show that only 11 hydrogens are initially replaced in (IV), direct topside addition of deuterium to π-allylic complexes is ruled out.

We have not yet considered the possibility of topside 1,3-hydrogen shifts via transient allylic complexes as proposed by Smith *(10)* and discussed theoretically by Mango *(11)*, but in fact these are already ruled out by the geometry of (III), where the d_{14} maximum necessitates suprafacial shift of hydrogen in the *h*-set (Fig. 1) from C_3 to C_1 or C_5, imposing a *trans*-ring junction, highly strained in this molecule. However, our results do not rule out this mechanism for compounds where the molecular geometry permits it.

There is clear evidence from the studies of Gault *et al.* *(12)* on the relative rates of exchange of *cis* and *trans*-1,2-dimethylcyclobutane and from our own work on the exchange of *trans*-2,3-dimethylbicyclo[2.2.1]heptane *(13)* that palladium reacts with C–H bonds in paraffins in the order tertiary > secondary > primary. Thus the d_5 maximum for (I) (Table 1) represents exchange of the 5 atoms of the *g*-set (Fig. 1), attack being initiated at the tertiary positions. Initial exchange of hydrogens in the dimethylene unit (C_8 and C_9) does not occur since there is no maximum in the d_2 isomer, as observed previously for bicyclo[2.2.1]heptane *(14)*. The major feature of interest here is the absence of two-set exchange, so roll-over of the Δ2,6-olefin (cf. roll-over of bicyclo[3.3.0]oct-Δ1,5-ene) is not occurring because it would give initial exchange of all 8 hydrogens in the *h* and *g*-sets and isomerization of (I) to (II). Such isomerization is not observed but occurs at appreciable rates at much higher temperatures (~200°C). The formation of a double bond in the 2–6 position and subsequent readsorption of the olefin, inverted with respect to the surface, is severely sterically hindered. The mechanism of the isomerization under more drastic conditions on palladium is considered elsewhere *(15)*.

Another important feature is the absence of d_6 and d_7 isomers of (I) so exchange does not propagate to the *h*-set (Fig. 1). Hence roll-over of the 3 or 4 olefin is not occurring, and inspection of models reveals that this would also be greatly hindered by the dimethylene unit (C_8 and C_9). A π-allyl complex involving carbons (3,4,5) and Process B should give exchange of 7 but not 8 hydrogens, either by topside addition or suprafacial 1,3-shifts. Although one might postulate some steric hindrance from endo protons on C_8 and C_9 this would scarcely be strong enough to prevent these processes occurring.

The results for the exo isomer (II) can be explained in similar fashion, with the maximum in the d_5 isomer corresponding to the *g*-set (Fig. 1). Again the absence of exchange of 8 hydrogens shows that roll-over of the Δ2,6-olefin does not occur. Roll-over of the olefins at positions 3 and 4 accounts for the d_6 and d_7 isomers, with exchange both in the *g* and *h*-set. We discount the possibility that d_6 and d_7 isomers arise from initial exchange of both the *g*-set and the 2 endo hydrogens in the dimethylene unit (C_8 and C_9) since this would require a simultaneous αγ-exchange process, which only occurs with great difficulty on palladium and would hardly give a maximum at the d_7 isomer *(1)*.

In general the weight of evidence supports Process A and is against Process B. The degree of steric hindrance to roll-over of the olefins (V) to (VII) (Fig. 2) increases in the order (V) < (VI) < (VII), so that while two-set exchange occurs readily in (III) and (IV), it is absent for (I) and is limited in (II).

Burwell *et al.* *(6)* favor roll-over while

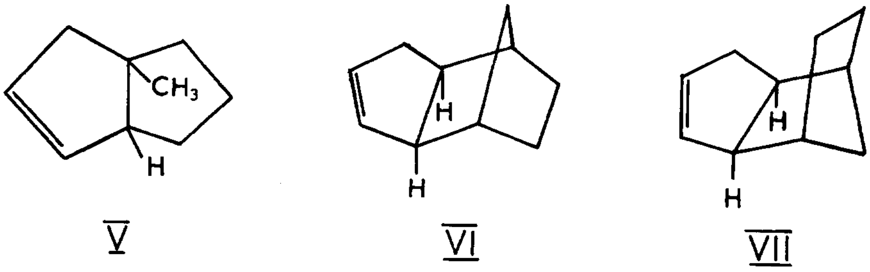


Fig. 2. Structures of some key olefins.

the olefinic intermediates are still chemisorbed, and as they point out, while a parallel orientation of the olefin to the surface during roll-over is one possibility (e.g., Δ2,3-bicyclo[3.3.0]octene), only perpendicular orientation of olefins such as Δ1,5-bicyclo[3.3.0]octene is possible. At present we have no data which would decide whether the chemical bond of the olefin to the surface is completely broken before roll-over takes place or not. If the former is true, then Burwell's speculation about parallel and perpendicular bonding of intermediates is redundant.

Mobility of olefins on the surface even starting with paraffins in a large excess of deuterium at temperatures as low as 0°C (*3*) on palladium surfaces accords with the highly selective character of this metal in hydrogenating dienes and acetylenes to olefins (*16*) and also the good hydrocracking ability of Pd/Y-zeolite and Pd/silica-alumina catalysts where migration of olefin from metal to acid sites is required.

Although the present results rule out Process B, the issue of whether allyl complexes are formed in such reactions is still not settled. It is possible that olefin mobility might be partly due to π-allyl complexes interconverting with σ-allyl intermediates. *Cis*-addition of hydrogen and/or deuterium to the latter would immediately release olefinic intermediates to the gas phase.

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