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Deuteration Isomerization and Exchange of Cycloolefins over Palladium Catalysts

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The deuteration, exchange, and isomerization of cyclopentene and of several disubstituted cycloolefins with four- and five-membered rings are studied over palladium films and over palladium-pumice catalysts at very low conversions.

The *cis-trans* distribution and the deuterium content of the saturated products depend mostly upon the size of the ring. *Cis*-dimethylcyclobutanes, poorly exchanged, and *trans*-dimethylcyclopentanes with a high content of deuterium are the main saturated products obtained from dimethylcyclobutenes and cyclopentenes, respectively.

On the other hand, most of the isomerized and exchanged cycloolefins contain no or one deuterium atom. No correlation may be derived then between the deuterium distributions of the olefins and of the saturated hydrocarbons, when the calculations are based on the Horiuti-Polanyi model or any similar model.

It is, therefore, believed that the deuteration does not proceed by the same mechanism as the double-bond migration and the olefin exchange. While the interconversion between diadsorbed species and π-allylic species determine the nature of the saturated products, double-bond migration and olefin exchange involve entirely different intermediaries.

INTRODUCTION

The mechanism of the catalytic hydrogenation of olefins on metals has been investigated for many years. Both tracer techniques and stereochemical studies suggest that each metal acts differently. The hydrogenation of the cycloolefins over palladium for example, (*1–5*) differs in many ways from the hydrogenation over other classical metal catalysts platinum, (*6–11*, *3*, *4*) nickel, (*12*) rhodium (*13*).

1. An extensive double-bond shift takes place simultaneously over palladium, while it is of little importance over nickel, rhodium, and platinum.
2. When hydrogen is replaced by deuterium, the saturated hydrocarbons obtained are extensively exchanged over palladium. Over nickel and platinum, less deuterated molecules are obtained (*12*).
3. In the hydrogenation of the cycloolefins with five or six-membered rings disubstituted on two vicinal carbon atoms, the more stable saturated isomer, the *trans* 1,2-dimethylcycloalkane, is predominant over palladium. The *cis trans* ratio is practically independent of the position of the double bond in the reacting olefin (*3*). On the contrary, stereoselectivity depends upon the cycloolefin which reacts over nickel (*12*) and platinum (*4*, *6*); the less stable isomer is in general predominant or at least obtained in much larger amount than over palladium.

Three mechanisms have been proposed so far to explain the contact reactions of 1,2 disubstituted cycloolefins over palladium.

Siegel and Smith (*1*, *3*, *6*, *14*) explained all their stereochemical results on the basis of a simple Horiuti–Polanyi mechanism (*15*) (interconversion between mono and diadsorbed species). The different stages of this mechanism take place with a retention of configuration at the adsorbed carbon atoms. Therefore, in the case of the 1,2-dimethylcyclohexene or cyclopentene, only a *cis* addition of hydrogen is allowed during a single sojourn of the molecule over the catalyst. The formation of the *trans* isomer is explained by supposing that the 1,2-dimethylcycloalkene is first isomerized to the 2,3-dimethylcycloalkene; this olefin is then readsorbed on the other face of the ring and rapidly hydrogenated to the *trans* saturated products (*8, 14*).

In their explanation, Hussey *et al.* (*2, 11*) replaced the intermediate olefin of Siegel by a symmetrical adsorbed intermediate on the surface. This symmetrical species can lead to two different adsorbed olefins and by hydrogenation either to the *cis* or to the *trans* saturated product. They explain in this way the formation of the *trans* from the 1,2-dimethylcycloalkene, even the desorption of the olefin is almost negligible as it happens over platinum (*11*).

A last explanation of the hydrogenation of the 1,2-dimethylcycloalkene involves the π-allylic species which were shown to play an important role in the exchange of the saturated cyclic hydrocarbons (*16–19*). The explanation is suggested in early papers introducing this new type of intermediate (*16, 17*). The π-allylic species are assumed to interconvert with the diadsorbed species in two different ways, either by adding an adsorbed hydrogen from one side of the ring, or by reacting with molecular hydrogen on the other side of the ring (attack from the bottom or from the top). Therefore, a number of interconversions between diadsorbed and π-allylic species determine a number of inversions of the carbon atoms, and the probability of the *cis* or the *trans* configuration of the saturated hydrocarbon should be very similar to that of the equilibrium one. At the same time, if hydrogen is replaced by deuterium, both saturated isomers are expected to be highly exchanged. Such an extensive exchange was first observed in the deuteration products of cyclohexene and cyclopentene over iron (*20*).

Similar distributions were also observed in the deuteration of 1,2-dimethylcyclopentene over palladium. On the other hand, 90% *cis*-1,2-dimethylcyclopentane is formed with a very low number of deuterium atoms per molecule (*12*) over nickel, which is known to be a poor metal to form π-allylic species at low temperatures.

To choose between the possible explanations, three series of experiments have been carried out and are presented in this paper. First, we have compared the *cis-trans* distribution and the deuterium content of the saturated hydrocarbons obtained by deuteration of various cycloolefins with a five-membered ring and with a four-membered ring, disubstituted on two vicinal carbon atoms. From the study of catalytic exchange and of *cis-trans* isomerization of saturated hydrocarbons, it was deduced that over palladium the π-allylic species can be formed easily from cyclopentanes and cyclohexanes, but only with much difficulty from cyclobutanes (*18, 19*). For example, while all fourteen hydrogens of the *cis*-1,2-dimethylcyclopentane are exchanged at 20°C and a rapid epimerization occurs, only ten of the twelve hydrogens of the *cis*-1,2-dimethylcyclobutane are exchanged initially, and the *cis-trans* isomerization is not detectable (*19*). Therefore if, as we believe, the π-allylic species intervenes in the hydrogenation process in determining the *cis-trans* selectivity, one should observe striking differences in the *cis-trans* ratio and in the exchange patterns of the hydrocarbons obtained in the deuteration of cyclopentenes and cyclobutenes.

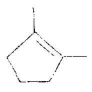
The second series of experiments was performed to check in the case of a simple model compound, cyclopentene, the possibility of a simple Horiuti–Polanyi mechanism, with desorption and readsorption of an intermediate olefin (*14*). According to such a mechanism, when the reactions take place in the presence of deuterium, there should exist a relationship between the deuterium distribution of the cycloolefins and of the saturated products.

The last series of experiments was carried out to test another consequence of the classical mechanism. In the hydrogenation of 1,2-dimethylcyclopentenes, the amounts of *trans* should depend upon the relative rates of isomerization and hydrogenation. Several experiments were then effected over the same palladium catalyst with various ratios of the rates of hydrogenation and isomerization.

EXPERIMENTAL

Materials

A mixture (85/15) of 1,2-dimethylcyclopentene (I) and 2,3-dimethylcyclopentene (III) was prepared by adding 2-methylcyclopentanone to methylmagnesium iodide, hydrolyzing the adduct and dehydrating the tertiary alcohol which was obtained. Both olefins were then separated by preparative VPC on a silicone oil column. A mixture of 1,2-dimethylcyclopentanes *cis* (VI) and *trans* (VII) was obtained by hydrogenation of the mixture of olefins over a Pt–Al_2O_3 catalyst, and the separation of the stereoisomers was effected by VPC. 1-methyl-2-methylene-cyclopentane (III) was prepared according to Wittig by adding triphenylmethylenephosphine to 2-methylcyclopentanone (*21*).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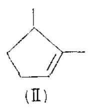
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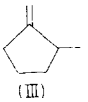
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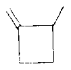
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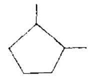
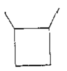

cis trans
(VI) (VII)


cis trans
(VIII) (IX)


(X)


(XI)

Photolysis of 2,3-dimethylbutadiene (*22*), obtained by dehydration of pinacol, yielded 1,2-dimethylcyclobutene (IV). Purification of this compound was made by chromatography at 40° on a dimethylsulfolan column. 1-methyl-2-methylene-cyclobutane (V) was prepared in 9 steps from 1,3-butane-diol according to a method of preparation devised by Conia and Gore (*23*). The preparation of 1,2-dimethylcyclobutane *cis* (VIII) and *trans* (IX), by hydrogenation of 1-methyl-2-methylene-cyclobutane, has been described elsewhere (*19*). The stereoisomers were separated by VPC. The configuration *cis* was assigned to the high-boiling isomer, according to Kazanskii and Lukina (*24*). This assignment was then confirmed unequivocally by the stereoselective synthesis of the *cis*-dimethylcyclobutane (*25*), and later on by the differences between the mass spectra of the low boiling and high-boiling isomers (*26*) and the determination of their relative stability (*27*).

Cyclopentene of high purity grade was obtained from Fluka. The purity of each compound was checked by gas chromatography and estimated as higher than 99.9%.

The deuterium (Air Liquid Co.) was purified in the static experiments by diffusion through a palladium thimble and in the flow reactor experiments by being passed over a 10% Pt–Al_2O_3 catalyst at 300°C and through a liquid nitrogen trap. Its isotopic content was 99.4%.

Catalysts

Metal films were obtained in a conventional high vacuum system by evaporation of Specpure palladium (Johnson Matthey). Palladium on pumice was prepared by slowly evaporating a palladous chloride solution over an inactive pumice and reducing the powder with hydrogen (or deuterium) for 3 hr at 300°; this catalyst is referred to as catalyst B in the text. Another type of catalyst, referred to as A, was obtained by regenerating in air at 250° for 2 hr a catalyst which had been used previously and by reducing it again with deuterium for 3 hr at 300°C. Catalysts A and B did not have the same properties, e.g., the ratios of the rates of hydrogenation and of isomerization were very different. Any batch of catalyst A or B gave fairly reproducible results, but only within certain limits.

Even after treatment with HCl the

pumice carrier was inactive at 25°C for the double-bond shift of the olefins and the *cis-trans* isomerization or exchange of the saturated products. Neither *cis-trans* isomerization nor exchange of the dimethylcyclopentanes occurred on palladium-pumice in the experimental conditions envisaged.

Apparatus and Procedure

Static system. A mixture of 50 Torr of deuterium and 5 Torr of olefin was introduced on the freshly prepared film at the desired temperature. The reaction vessel was connected to an AEI MS 2-mass spectrometer. The very fast reaction between deuterium and olefin could not be followed in this way, but one could make sure that no further exchange of the saturated hydrocarbons took place after the deuteration was completed.

Flow system. The apparatus has already been described (*28*). The flow conditions were arranged so as to obtain a very low conversion in deuteration and exchange (less than 10%). A reaction mixture containing 2 or 5% of cycloolefin was prepared by slowly bubbling purified deuterium through the hydrocarbon at the required temperature. This mixture was then passed over 50 to 150 mg of palladium-pumice at a flow rate of 10 cm^3/min.

Separation and Analysis of the Reaction Products

Gas chromatography. In all experiments, the various products obtained after reaction were separated by gas chromatography and analyzed for their deuterium content. Thus mixtures of 1,2-dimethylcyclopentene (I), 2,3-dimethylcyclopentene (II), 1-methyl-2-methylenecyclopentane (III), *cis* and *trans*-1,2-dimethylcyclopentanes (VI, VII) were separated on a 5 m dimethylsulfolane column at 40°C; the mixture of cyclopentene (X) and cyclopentane (XI) was separated on the same column at 25°C. When the reaction was complete, a silicone oil column permitted the separation of the *cis* and *trans* disubstituted cyclopentanes and cyclobutanes.

Mass spectrometry. Electrons of 25 eV were used to ionize the various molecules. The distribution of the deuteromolecules was determined for each compound by using the parent peaks, obtained after simple corrections for natural isotopes and C–H fragmentation. In the case of the cyclopentenes and cyclopentanes three fragments at mass p–1, p–2, and p–3 had to be taken into account; for the other molecules only the fragment at mass p–1 was significant. The calculations were made on a statistical basis.

The mean number of deuterium atoms per molecule was defined as $M = \Sigma i d_i/100$, d_i being the percentage of molecules containing i deuterium atoms. For the reacting olefin, in which d_0 represents both unreacted and reacted molecules, M was replaced by $M' = \Sigma i d_i/100 - d_0$.

In the experiments where the reactions were not completed, three conversions were defined

$$\text{the percentage of deuteration, } \tau_D = \frac{\text{saturated products}}{\text{total products}};$$

$$\text{the percentage of isomerization, } \tau_I = \frac{\text{isomeric olefins}}{\text{total products}};$$

$$\text{the percentage of exchange, } \tau_E = \frac{\text{exchanged olefins}}{\text{nonisomerized olefins}}.$$

RESULTS AND INTERPRETATION

Deuteration over Palladium Films

The deuteration of 1,2-dimethylcyclopentene (I), 2,3-dimethylcyclopentene (II), 1-methyl-2-methylene-cyclopentane (III), 1,2-dimethylcyclobutene (IV) and 1-methyl-2-methylene-cyclobutane (V) was effected over a palladium film at 0° or —20°C. At the temperatures chosen, the reaction was completed in 5 min, and no further exchange of the saturated hydrocarbons was then observed.

The *cis-trans* distribution of the satu-

TABLE 1

DEUTERATION OF DISUBSTITUTED CYCLOOLEFINS WITH FIVE MEMBERED RINGS OVER PALLADIUM

Reacting olefin (T°C)	1-methyl-2-methylene cyclopentane (0°C)		2,3-dimethyl cyclopentene (0°C)		1,2-dimethyl cyclopentene[a] (0°C)	
Distribution of isomer	Dimethylcyclopentanes		Dimethylcyclopentanes		Dimethylcyclopentanes	
	cis 21%	*trans* 79%	*cis* 11%	*trans* 89%	*cis* 22%	*trans* 78%
d_0	1.4	1.3	1.4	1.9	2.2	1.6
d_1	2.1	2.3	2.2	2.8	4.4	4.0
d_2	2.9	3.2	2.9	3.4	7.0	6.4
d_3	3.7	4.2	3.6	3.9	8.6	7.9
d_4	4.6	5.1	3.9	4.5	9.5	8.8
d_5	5.2	5.7	4.6	5.2	9.7	9.15
d_6	5.9	6.2	5.4	6.0	9.3	9.1
d_7	6.4	6.7	6.7	6.9	8.8	8.6
d_8	7.4	7.4	7.9	7.9	7.9	8.0
d_9	8.7	8.5	9.3	9.2	7.0	7.4
d_{10}	10.3	9.9	10.8	10.7	6.2	6.8
d_{11}	12.5	11.9	11.6	12.0	5.9	6.5
d_{12}	12.8	12.7	12.8	12.1	5.6	6.4
d_{13}	11.3	10.5	11.0	9.4	5.2	6.0
d_{14}	4.2	4.3	4.7	3.7	2.8	3.3
M	8.81	8.58	8.83	8.45	6.77	7.67

[a] Ref. (12).

rated hydrocarbons obtained by deuteration and the deuterium distribution of each molecule *cis* or *trans* are given in Tables 1 and 2. Striking differences are apparent between the results in the cyclopentane and cyclobutane series.

1. While the *trans* saturated hydrocarbon is mainly formed from the disubstituted cyclopentenes, the *cis*-dimethylcyclobutane is the predominant reaction product (more than 90%) in the deuteration of the cycloolefins with a four-membered ring.

2. In the cyclopentane series the maximum in the deuterium distribution lies in d_5 or d_6 and the M value is high (between 7 and 9). On the other hand, the dimethylcyclobutanes are poorly exchanged—the distribution has a maximum around d_2 or d_3 and the M values are rather small (3.5–4.5).

In both cases the M value is independent of the configuration *cis* or *trans* of the molecule and roughly independent of the structure of the initial olefin. The M values observed for the *cis*-dimethylcyclobutane formed at 0° are slightly higher than for the *trans*, but the possibility of a slight exchange of this compound at the beginning of the reaction is not excluded at this temperature (*19*).

Reactions of Cycloolefins over Palladium-Pumice Catalyst

Deuteration was so fast over palladium films that it was not possible to determine the extent of the double-bond shift and olefin exchange which are known to accompany this reaction. Several experiments were then carried out over a palladium-pumice catalyst of much lower activity, and the reaction was stopped at partial conversion.

Exchange. Isomerization and Deuteration of Disubstituted Cycloolefins

The reactions of 1,2-dimethylcyclopentene (I) and 1-methylene-2-methylcyclopentane (III) with deuterium have been studied at 25°C for various conversions and over two different types of catalyst,

TABLE 2
Deuteration of Disubstituted Cycloolefins with Four Membered Rings over Palladium Films

Reacting olefin (T°C)	1-methyl-2-methylene cyclobutane				1,2-dimethyl cyclobutene			
	(−20°C) Dimethylcyclobutanes		(0°C) Dimethylcyclobutanes		(−20°C) Dimethylcyclobutanes		(0°C) Dimethylcyclobutanes	
Distribution of isomer	*cis* 94%	*trans* 6%	*cis* 91.5%	*trans* 8.5%	*cis* 94%	*trans* 6%	*cis* 93%	*trans* 7%
d_0	10.8	14.3	6.4	10.0	11.5	14.3	8.2	14.0
d_1	13.4	14.9	9.7	12.6	16.1	16.0	11.3	17.2
d_2	13.8	13.3	12.1	13.3	16.9	17.0	12.3	16.0
d_3	13.1	11.6	25.6	29.0	14.5	13.5	11.1	12.6
d_4	11.7	9.6	10.4	9.8	11.8	10.0	9.9	9.1
d_5	10.1	7.8	8.1	5.1	9.0	7.3	8.6	6.9
d_6	8.3	6.5	6.5	5.2	6.2	5.7	7.5	4.7
d_7	6.6	6.0	5.5	5.0	4.1	5.7	7.3	5.0
d_8	5.0	5.0	5.0	3.3	3.3	4.7	7.9	5.1
d_9	3.6	4.6	4.4	2.2	3.0	2.2	8.0	3.1
d_{10}	2.2	3.5	3.9	2.2	2.6	2.2	5.5	2.5
d_{11}	0.9	2.3	1.3	1.4	0.7	0.8	1.8	2.3
d_{12}	0.3	0.7	1.0	1.0	0.3	0.7	0.7	1.5
M	3.80	3.85	4.15	3.53	3.42	3.38	4.66	3.58

A and B. Catalyst B is used just after the reduction of the palladous chloride. Catalyst A is obtained by oxidizing and reducing a catalyst which has been used previously. The percentages of exchange (τ_E) deuteration (τ_D) and isomerization (τ_I), the ratios $r = \tau_D/\tau_I$, $r' = \tau_E/\tau_D$, $r'' = \tau_E/\tau_I$, and the percentage of *trans* in the saturated products are reported in Table 3. Both types of catalyst A and B may easily be distinguished: The ratio r between the deuteration and the isomerization rates is higher than unity over catalyst B and smaller than unity over the regenerated catalyst A.

It is noticeable that for the same cycloolefin the percentage of *trans* is almost constant, while the ratio r may vary by a factor of 200. This observation suggests that stereoselectivity in deuteration is independent of the isomerization process. The ratios $r' = \tau_E/\tau_D$ and $r'' = \tau_E/\tau_I$ between the rate of exchange and the rate of deuteration or isomerization also vary within large limits (by a factor of 20), showing that the exchange of the olefin is

TABLE 3
Contact Reactions of Disubstituted Cycloolefins over Pd-Pumice

Hydrocarbon	Catalyst weight	τ_D %	τ_I %	τ_E %	$r = \tau_D/\tau_I$	$r' = \tau_E/\tau_D$	$r'' = \tau_E/\tau_I$	*trans* %
1,2-dimethylcyclopentene	250 mg A pois.	0.7	4.2	—	0.16	—	—	72.0
	180 mg A	2.5	4.0	—	0.62	—	—	64.0
	180 mg A pois.	11.0	4.0	48.0	2.75	4.35	12.0	78.0
	30 mg B	0.27	0.05	—	5.4	—	—	71.0
	40 mg B	1.8	0.06	1.32	30.0	0.73	22.0	75.0
1-methyl-2-methylene-cyclopentane	160 mg A pois.	1.4	27.0	27.2	0.05	19.5	1.02	36.0
	130 mg A	1.0	5.0	9.6	0.2	9.6	1.92	40.0

not simply connected with either of the other two processes.

The percentage of *trans*-dimethylcyclopentane, while nearly independent of the relative rate of isomerization, depends upon the structure of the cycloolefin; 38 ± 2% of *trans* is obtained from the 1-methylene-2-methylcyclopentane (III), 70% from the 1,2-dimethylcyclopentene (I). Thus palladium-pumice does not behave exactly like palladium films.

Only 2,3-dimethylcyclopentene is formed by isomerization of 1,2-dimethylcyclopentene; methylene-methylcyclopentane could not be detected in the reaction products. Isomerization of methylene-methylcyclopentane yields both 1,2-dimethyl and 2,3-dimethylcyclopentenes in approximately equal amounts, which is very far from the equilibrium.*

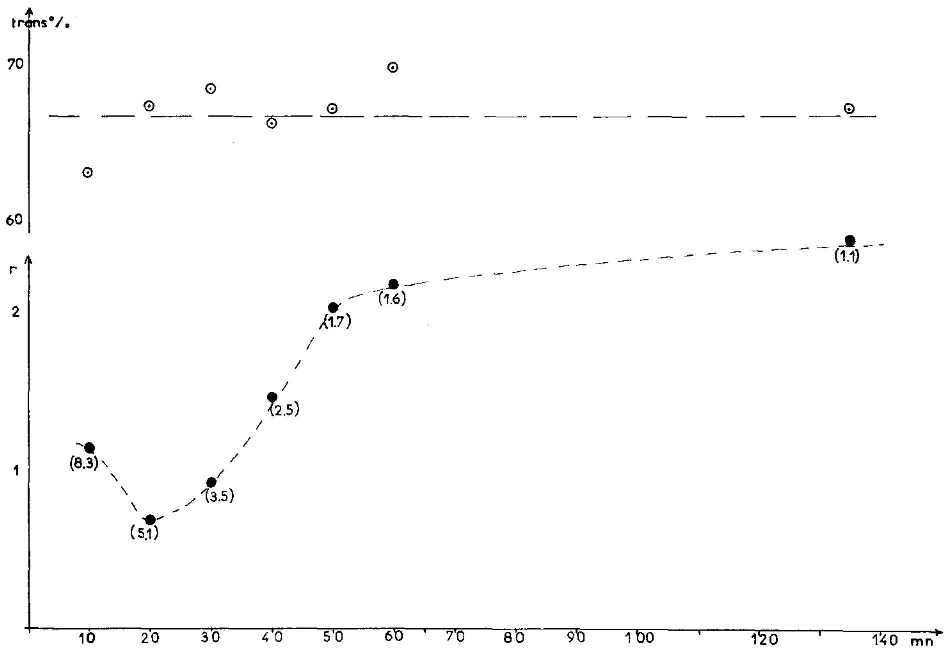


FIG. 1. Deuteration and isomerization of 1,2-dimethylcyclopentene: fast reaction ● r = τ_D/τ_I as a function of time; (total conversions in parentheses) ⊙ percentage of *trans* in the saturated products.

Modification of the Catalyst during the Reactions

The very large difference in selectivity between both catalysts A and B, and a certain irreproducibility of the values of *r* when the same catalyst was used (see Table 3), led us to check whether the properties of a given batch of catalysts were constant with time. Experiments were then done with the same catalyst, and the reaction products were analyzed every 10 min.

The ratio *r* between the rates of hydrogenation and isomerization and the percentage of *trans* in the saturated products are reported vs time in Fig. 1. The plots do not represent the analysis of the reaction mixture at a time *t* but the analysis of the total products obtained between times *t* — 10 and *t*. One can see from the figure that after a slight decrease, *r* increases continuously from 0.7 until it reaches a constant value of 2.5. Meanwhile, the percentage of *trans* is remarkably constant,

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* A quasiequilibrium distribution at 100°C (85% I; 15% II) was obtained by dehydration of the 1,2-dimethylcyclopentanol-1 and isomerization during 1 hr of the resulting olefins in an acidic medium.

TABLE 4
VARIATION WITH TIME OF CATALYST SELECTIVITY OF THE DEUTERATION AND ISOMERIZATION OF 1,2-DIMETHYLCYCLOPENTENE AT 25°C

Time (min)	10	20	30	40	50	60	90	120	135	180
			Fast reaction: 60 mg catalyst type B							
Deuteration %	4.40	2.10	1.69	1.51	1.13	1.23			0.76	
Isomerization %	3.91	3.00	1.82	1.01	0.56	0.46			0.30	
Trans %	63.30	67.70	68.70	66.50	67.60	70.10			67.50	
			Slow reaction: 250 mg catalyst type B							
Deuteration %			1.95			0.69	0.48	0.72		0.58
Isomerization %			4.34			4.22	1.73	1.48		0.70
Trans %			73.30			72.30	74.70	72.40		73.20

68 ± 2%. The corresponding percentages of deuteration and isomerization are reported in Table 4. Obviously the modification of selectivity is due to a decrease in activity larger for the isomerization (by a factor of 13) than for the hydrogenation (factor of 5.8). This experiment suggests again that different sites are involved in isomerization and hydrogenation, and that the ease of poisoning of each type of site is very different.

An experiment much slower than the preceding one is represented in Fig. 2 and Table 4. The same shape of the $r = f\ (t)$ curve was observed but the initial decrease of r was observed during at least the first 30 min of reaction. This rules out one possible explanation for this effect: the nonachievement of steady-state flow conditions during the first minutes of reaction, resulting in a chromatographic effect on the carrier.

Deuterium Distribution of the Reaction Products

Initial distributions. The various products, olefinic and saturated, obtained at a very low conversion from 1,2-dimethyl-

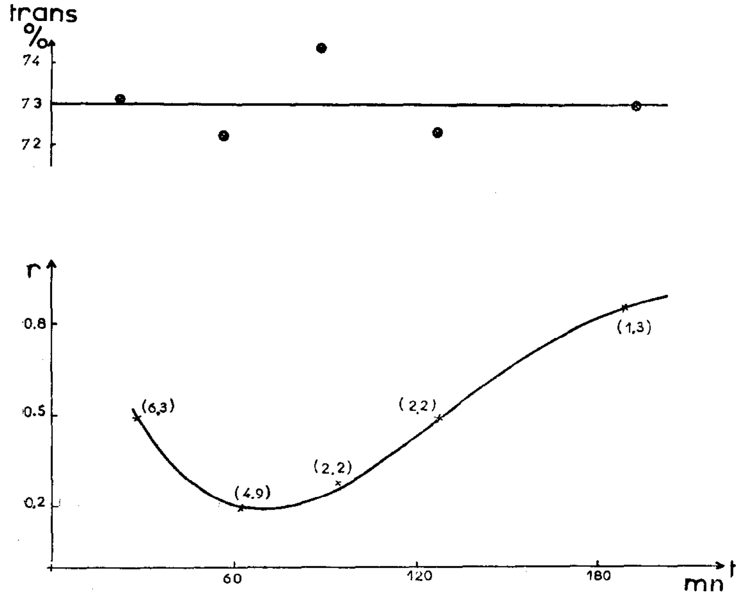


FIG. 2. Deuteration and isomerization of 1,2-dimethylcyclopentene: slow reaction $\times$ $r = r_D/r_I$ as a function of time; (total conversions in parentheses) ⊗ percentage of *trans* in the saturated product.

cyclopentene and methylene-methylcyclopentane were analyzed for their isotopic content. The results of three such experiments are reported in Table 5. One sees that the distribution patterns are very different for the cycloolefins and the dimethylcyclopentanes. d_0 and d_1 always represent more than 60% of the dimethylcyclopentenes (I and II) obtained by isomerization of methylene-methylcyclopentane (III) and more than 80% of the 2,3-dimethylcyclopentene obtained from 1,2-dimethylcyclopentene (I). Similarly the exchanged fraction of the reacting olefin contains mainly d_1 in Expts. 2 and 3 and d_1 and d_2 in Expt. 1.

On the other hand, the *cis* and *trans* dimethylcyclopentanes are extensively exchanged. Only one maximum in d_{14} appears in the distributions of the two deuteration products of 1,2-dimethylcyclopentene, which are very similar. Fifty-three percent of the dimethylcyclopentanes contain more than ten deuterium atoms per molecule. In the deuteration of methylene-methylcyclopentane, the deuterium distributions of the *cis* and *trans* saturated products are close, but not exactly similar. Two maxima appear in d_{14} and d_2 and the mean number of deuterium atoms M is lower than in the preceding case (5–6 instead of 9).

Experiments at high conversions. The deuteration of 1,2-dimethylcyclopentene (I) has been studied at higher conversions. The distributions are reported in Table 6. The small amount of light olefin left (30–50%) suggests that the readsorption process has been very important. This would explain the extensive exchange of reactant and isomerized olefins. Perdeutero-molecules are observed in appreciable amounts. Due to this exchange, significant isotopic dilution of the deuterium takes place on the surface and shifts the maximum from d_{14} to d_5 or d_6 in the deuterium distributions of the saturated products. These results show how misleading distributions which have not been obtained at a very low conversion may be.

Deuteration and exchange of cyclopentene. In order to compare the distributions of the olefinic and saturated products, the deuteration of a more simple model compound, cyclopentene, has been effected. The results of three experiments are reported in Table 7; two of them correspond to a very low τ_D conversion and a very high deuterium to hydrocarbon ratio. Especially in the first experiment, the corresponding distributions may be considered as quasi initial distributions. The deuterium distribution patterns of cyclopentenes and of cyclopentanes are very different. While the initial exchange of olefins does not proceed much beyond the d_1 and d_2 molecules, the cyclopentanes are extensively exchanged. Besides a maximum in cyclopentane d_1, a second maximum appears in cyclopentane d_{10}, and at least 25% of the saturated molecules contain more than five deuterium atoms. On the other hand, the main deuterocyclopentene initially formed is the d_1 species, though the exchange cannot be considered as a simple exchange process.

In the third experiment presented in Table 7, due to the higher extent of deuteration and exchange, the isotopic dilution of the reacting deuterium is rather noticeable; both maxima in the cyclopentane distributions have shifted one mass below.

DISCUSSION

The striking differences observed between their deuterium distributions strongly suggest that the olefins and saturated hydrocarbons are formed by different processes. The fact that the ratio of the rate of isomerization or of exchange to the rate of deuteration varies widely, while the stereoselectivity of this latter reaction does not change, indicates that these various processes are independent. Two authors in the past arrived at a similar conclusion.

T. I. Taylor *et al.* studied carefully the reactions of butenes and deuterium over a nickel wire (*29*, *30*). They obtained equal rates for olefin exchange and isomerization but found different activation energies for these reactions and for the deuteration (*31*). Moreover, they noticed that the butanes were more exchanged than the butenes (*30*); however, the difference between

TABLE 5

DEUTERATION, ISOMERIZATION AND EXCHANGE OF DISUBSTITUTED CYCLOOLEFINS OVER PALLADIUM-PUMICE

Reacting olefin	1,2-dimethylcyclopentene				1-methyl-2-methylene-cyclopentane									
Experiment	1				2					3				
Catalyst	40 mg B				130 mg A					160 mg A				
% Hydrogenation	1.8				1					1.4				
% Isomerization	0.06				5 (1,2 = 60) (2,3 = 40)					27 (1,2 = 52) (2,3 = 48)				
% *trans*	75				40					36				
Distribution of products	Dimethylcyclopentenes		Dimethylcyclopentanes		Methylene methylcyclopentane	Dimethylcyclopentenes		Dimethylcyclopentanes		Methylene methylcyclopentane	Dimethylcyclopentenes		Dimethylcyclopentanes	
	1,2	2,3	*cis*	*trans*		1,2	2,3	*cis*	*trans*		1,2	2,3	*cis*	*trans*
d_0	98.68	41.7	2.8	1.5	90.4	36.9	27.3	8.5	7.8	72.80	30.9	26.9	7.5	8.1
d_1	0.41	41.0	1.9	0.9	7.2	33.0	42.6	10.9	2.6	24.50	32.7	37.2	4.6	11.0
d_2	0.56	5.0	2.0	1.5	2.1	14.1	15.8	18.2	25.6	2.00	17.7	18.7	24.6	28.9
d_3	0.15	4.1	2.7	3.4	0.2	9.4	11.3	5.9	3.0	0.80	12.0	13.8	6.6	9.7
d_4	0.07	1.3	4.0	4.1	0.03	2.2	1.5	5.9	3.4	0.10	2.6	2.0	5.8	6.1
d_5	0.06	1.0	6.6	5.8		1.2	0.7	5.3	4.0	0.04	1.2	1.0	5.2	3.1
d_6	0.05	0.6	5.6	6.8		0.9	0.4	5.6	4.1		0.8	0.5	4.4	2.1
d_7		0.7	6.6	7.7		0.7	0.3	5.0	5.6		0.5	0.2	5.5	3.8
d_8		0.6	7.8	8.1		0.6	0.2	4.4	6.1		0.4	0.1	5.0	4.0
d_9		0.8	7.4	7.4		0.4		4.1	5.0		0.3		4.9	3.2
d_{10}		0.8	7.8	7.8		0.3		3.2	4.5		0.3		3.8	3.0
d_{11}		1.3	7.9	8.3		0.2		3.2	4.3		0.3		2.8	2.8
d_{12}		1.0	8.8	8.6		0.1		4.4	3.5		0.3		3.2	2.4
d_{13}		—	11.6	11.6	—	—	—	10.3	6.2	—	—	—	4.1	4.8
d_{14}			16.7	16.6				5.3	14.4				12.0	6.9
M	2.19	1.29	9.33	9.41	1.27	1.29	1.24	5.84	5.86	1.15	1.45	1.52	6.04	4.87
x_{max}			0.05	0.05				0.12	0.03				0.02	0.05

TABLE 6

DEUTERATION OF 1,2-DIMETHYLCYCLOPENTENE OVER PALLADIUM-PUMICE AT HIGH CONVERSION

Catalyst	250 mg B				180 mg A				80 mg B			
% Hydrogenation	27%				11%				21%			
% Isomerization	7%				4%				6%			
% *trans*	73%				78%				78%			
Distribution of products	Dimethylcyclopentenes		Dimethylcyclopentanes		Dimethylcyclopentenes		Dimethylcyclopentanes		Dimethylcyclopentenes		Dimethylcyclopentanes	
	1,2	2,3	*cis*	*trans*	1,2	2,3	*cis*	*trans*	1,2	2,3	*cis*	*trans*
d_0	28.8	9.3	0.7	0.4	52.0	1.6	2.0	1.0	53.5	9.3	1.1	0.5
d_1	13.2	19.3	1.0	0.4	8.0	32.1	2.2	1.3	8.6	32.1	1.2	1.0
d_2	9.8	12.5	2.5	3.4	6.5	14.1	3.8	3.9	6.8	14.2	3.7	4.3
d_3	10.5	14.8	6.8	10.1	7.5	16.5	8.6	11.0	6.9	13.8	8.7	10.5
d_4	9.1	11.3	11.8	12.3	7.0	10.9	14.0	12.7	6.1	9.6	13.8	12.7
d_5	8.2	9.6	18.0	15.4	5.9	8.6	20.8	15.4	5.4	7.3	18.0	15.4
d_6	7.1	8.3	13.5	15.5	5.0	6.5	13.3	14.8	4.3	5.3	13.5	15.2
d_7	4.8	5.3	12.9	13.7	3.2	3.9	10.6	12.7	2.9	3.1	11.6	13.1
d_8	3.4	3.7	10.0	9.9	2.1	2.4	8.2	7.8	2.0	2.0	9.1	9.1
d_9	2.3	2.6	7.4	5.9	1.3	1.6	4.8	4.4	1.4	1.4	5.7	5.0
d_{10}	1.4	1.5	5.0	4.2	0.7	0.8	3.0	2.8	0.9	0.8	4.1	4.0
d_{11}	1.0	1.1	3.9	3.1	0.5	0.6	2.0	1.7	0.7	0.6	3.5	2.7
d_{12}	0.6	0.7	1.9	1.8	0.3	0.4	1.4	1.2	0.4	0.4	1.8	2.0
d_{13}	—	—	2.4	1.8	—	—	1.6	1.8	—	—	2.6	1.9
d_{14}			2.3	2.4			3.5	7.4			1.7	2.6
M	2.98	3.57	6.60	6.40	4.12	3.21	5.97	6.38	4.10	2.82	6.24	6.24

TABLE 7

Deuteration of Cyclopentene over Palladium-Pumice at 25°C

Exp. No.	1		2		3	
Catalyst weight	50 mg		90 mg		150 mg	
$\frac{P_{HC}}{P_{D_2}}$	$\frac{1}{55}$		$\frac{1}{55}$		$\frac{1}{21}$	
Conversion	0.6%		3%		17%	
Distribution of products	Olefin	Saturated	Olefin	Saturated	Olefin	Saturated
d_0	88.1	12.9	46.1	18.1	39.1	23.6
d_1	8.7	18.1	28.7	20.8	33.6	19.8
d_2	1.6	15.7	12.6	15.3	15.4	12.3
d_3	0.8	9.6	6.1	9.7	7.7	8.4
d_4	0.3	9.4	2.9	7.5	2.7	5.3
d_5	0.2	5.5	1.8	4.6	1.0	4.6
d_6	0.2	5.2	1.1	3.7	0.2	4.4
d_7	0.1	4.7	0.5	2.8	0.2	4.9
d_8	0.1	5.2	0.3	2.5	0.2	5.0
d_9	—	6.4	—	4.1	—	6.0
d_{10}	—	7.3	—	10.9	—	5.8
M or M'	1.59	3.80	1.95	3.61	1.72	3.26
$q + s$	0.45		0.15		−0.2	
qs	0.61		0.25		0.25	
$x_{\max}$	0.08		0.04		0.10	

both distributions was not very striking, and one could account for it by statistical calculations. Taylor *et al.* concluded from their studies that the deuteration and the double-bond migration were two independent processes, and they proposed an explanation of the isomerization and the olefin exchange in terms of a hydrogen switch mechanism very similar to the one suggested by Turkevitch in the case of acidic catalysts (*32*).

Smith and Burwell, studying the reactions of deuterium and hexenes or octalins over platinum in the liquid phase, obtained saturated products showing multiple exchange, an almost simple exchange of the olefin and no significant double-bond migration (*33*). Since the double-bond shift is excluded, the olefin exchange cannot proceed by a classical mechanism, and to explain this reaction, the authors proposed as an intermediary an olefin dissociatively adsorbed in an allylic position.

However, since in most of the recent studies, double-bond shift and olefin exchange have always been discussed in terms of the Horiuti–Polanyi mechanism, we felt it necessary to check this mechanism by comparing quantitatively the various olefinic and saturated products obtained in the deuteration of cyclopentene. A simple correlation may be drawn in this case between the deuterium distributions of the cyclopentenes ($\delta_0, \delta_1, \delta_2, \ldots, \delta_8$) and the cyclopentanes ($d_0, d_1, \ldots, d_{10}$) expressed by the following equations (*34*):

$$\begin{aligned}
d_0 &= K\delta_0,\\
d_1 &= K[\delta_0(q+s)+\delta_1],\\
d_2 &= K[\delta_0 qs+\delta_1(q+s)+\delta_2],\\
d_p &= K[\delta_{p-2}qs+\delta_{p-1}(q+s)+\delta_p],\\
d_9 &= K[\delta_7 qs+\delta_8(q+s)],\\
d_{10} &= K\delta_8 qs,\\
K &= p(1+p)/(1+q)(1+r)(1+s),
\end{aligned} \tag{1}$$

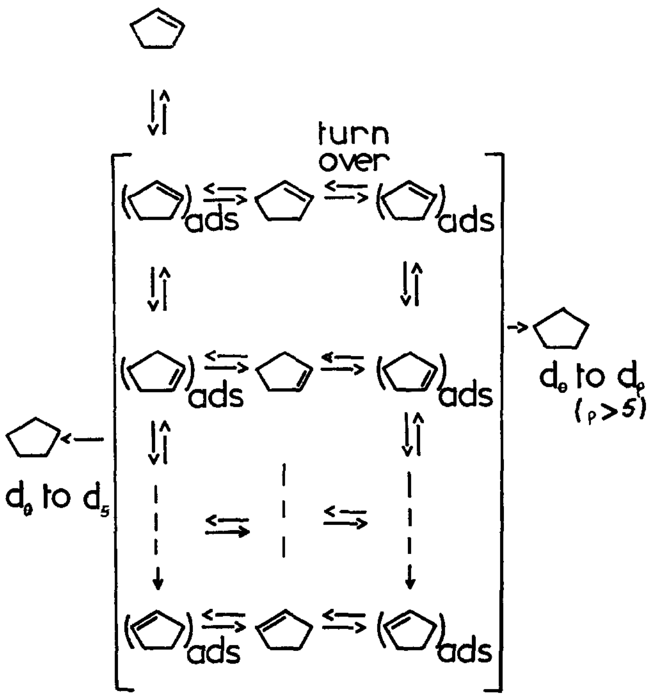
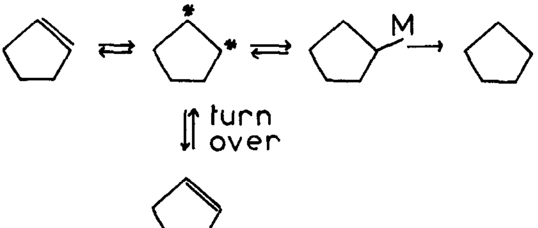


FIG. 3. Double bond migration by dissociative adsorption.

where p, q, r, s are four parameters introduced by Kemball in his study of the deuteration of ethylene (*35*); p represents the ratio of the chances of an adsorbed olefin giving an adsorbed alkyl radical or leaving the surface as an olefin molecule; r is the ratio of the chances of an alkyl radical giving an adsorbed olefin or being desorbed as a cyclopentane molecule; q is the ratio of the chances of an adsorbed olefin adding a deuterium or an hydrogen atom to give an alkyl radical; s represents the ratio of the chances of an alkyl radical adding a deuterium atom or an hydrogen atom to give a cyclopentane molecule.

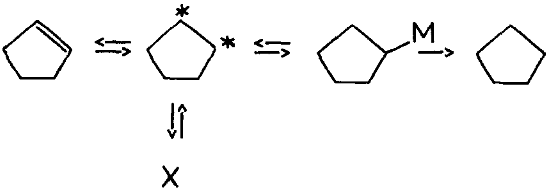
To derive Eqs. (1) it was supposed that the only operating mechanism was the interconversion between mono and diadsorbed species and that the highly deuterated molecules were obtained, as suggested by Siegel, by successive olefin desorption, turnover and readsorption (Scheme 1). However, the calculations are also valid for any formally similar mechanism, where an additional Species X, formed by a side reaction, introduces a deuterium atom on the side of the adsorbed molecule away from the surface (Scheme 2).



Schema 1

Species X may be the symmetrical species proposed by Hussey *et al.* It could also be the π-allylic species, which adds the deuterium atoms on both sides of the ring.

Equations (1) were tested for the values δ_i, d_i of the various deuteromolecules re-



Schema 2

ported in Table 7. Intuitively, it would appear impossible for the observed distributions to fit the equations. Quantitatively it can be shown in two different ways.

Since δ_0 is unknown, the percentage of cyclopentenes reported in the table represents not δ_i, but proportional numbers. Therefore, one can consider the first equations yielding d_0, d_1, d_2, d_3 as four equations with four unknowns δ_0, K, $q + s$ and qs. Elimination of K, δ_0 and qs yields a third degree equation in $(q + s)$; the coefficients in this equation are simple expressions of δ_2/δ_1, δ_3/δ_1, d_i/d_0 and may be deduced from the observed distributions. The values of $q + s$ and qs may then be easily calculated for each experiment and are reported in Table 7. They obviously do not match the necessary conditions $q + s > 0$ and $(q + s)^2 > 4\ qs$. Therefore, the distributions of cyclopentenes do not verify Eqs. (1), as far as less deuterated molecules are concerned.

The disagreement for the end of the distributions, i.e., for the perdeutero-molecules, is even more striking. By dividing the last two equations of set 1, one obtains:

$$\frac{d_9}{d_{10}} = \frac{\delta_7}{\delta_8} + \frac{q + s}{qs}.$$

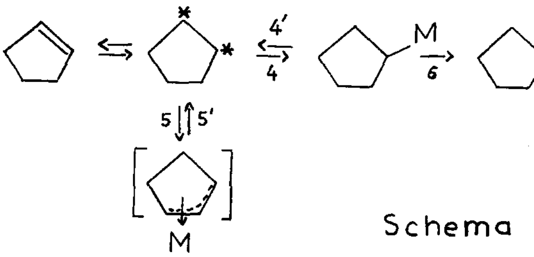
Accordingly $d_9/d_{10} > \delta_7/\delta_8$ ought to be verified, but the reverse is observed. The higher the number of deuterium atoms in the molecule, the smaller is the percentage of deuteroolefin and the bigger the percentage of deuterocyclopentanes.

In the case of the dimethylcyclopentene and of the methylene-methylcyclopentane a correlation such as the one described by Eq. (1) is difficult to derive. However, it is obvious that the distribution of the more deuterated saturated species cannot be related to the distribution of the olefins, which are poorly exchanged. In the case of the 1,2-dimethylcyclopentene no saturated hydrocarbons are formed with a low content in deuterium, and there cannot be any connection at all between the cycloparaffins and the cycloolefins. In the case of the methylene-2-methylcyclopentane, the only possible relation is between the cycloolefins and the less deuterated cyclopentanes. In neither case may the multiple exchange to perdeutero-molecules and the *trans* selectivity related to it, be explained by the desorption and readsorption of the olefins, as suggested by Siegel (*14*).

From all this evidence, it seems clear that the deuteration of the cycloolefins does not involve the same mechanism as their isomerization and exchange. Therefore, we shall discuss in turn each of the three reactions: hydrogenation, exchange, and double-bond migration.

Deuteration

Striking differences have been observed on palladium films between the deuteration of the cycloolefins with four-membered and five-membered rings. Dimethylcyclopentenes yield mainly *trans*-dimethylcyclopentane, extensively exchanged; *cis*-dimethylcyclobutanes with a low content of deuterium are obtained from cycloolefins with a cyclobutane skeleton. These results are entirely in favor of the participation of π-allylic species, and the deuteration may thus be represented by the following scheme:



Schema 3

In the case of the cyclopentenes, the large number of interconversions between the π-allylic intermediates and the diadsorbed species determines the *trans* stereoselectivity and the high deuterium content of the saturated products. In the case of the cyclobutenes, the mono and diadsorbed species are largely predominant; this means a *cis* addition of the hydrogen to the double bond and a low deuterium content of the cyclobutanes.

The results over supported palladium are also in agreement with this mechanism;

the strong parallelism between the *cis-trans* ratio and the extent of exchange in the saturated molecules has always been considered a test for the participation of π-allylic species (*16*, *17*, *19*). Here 1,2-dimethylcyclopentene (I) and methylenemethylcyclopentane (III) behave differently. The former (I) gives 70% of *trans* saturated hydrocarbons which are *highly* exchanged; the latter (III) gives approximately equal amounts of *cis* and *trans* cycloparaffin with a deuterium content of the saturated molecules much smaller than in the preceding case.

As such, however, the preceding scheme is too simple to explain all the results. When the analysis of the saturated products is given for a very low conversion, in the deuteration of disubstituted cycloolefins and of cyclopentenes, it is possible to distinguish between two parts of the distribution. One covers the less deuterated molecules between d_0 and d_4 with a maximum in d_1 or d_2. The second part of the distribution is ascending; it includes the highly exchanged molecules with a maximum at the perdeuterocyclopentane. We believe that these two partial distributions correspond to two different Reactions I and II with different reaction mechanisms.

Reaction I. The presence of d_0 and d_1 in the distribution suggests that a substantial isotopic dilution of the deuterium takes place in the first reaction. This isotopic dilution was determined in the case of cyclopentene by assuming that five hydrogens on one side of the ring only were exchanged by a classical Horiuti–Polanyi mechanism.

The calculations were made in the following way: let us call P the ratio between the rates of step 4′ and 6, x and $(1-x)$ the probability of adding a hydrogen or a deuterium atom during steps 4 or 6. Using the recurrent relation of Anderson and Kemball (*36*), (d_0–d_5) were calculated as functions of x and P (see Appendix). The values of x and P for which there is the best agreement between the calculated and observed values were then determined using a computer. Since part of the deutero species is due (1) to a process exchanging all the hydrogens of the cyclopentane (such as step 5 in the scheme) and (2) to the second reaction which yields the perdeutero-isomers, only the d_0, d_1, d_2, d_3 cyclopentanes were used for this calculation.

Very similar values were found for Expts. 1 and 2 in Table 7; in both cases the isotopic dilution is rather high, and so is the P value: ($P = 17$, $x = 0.64$) and ($P = 18$, $x = 0.67$), but the agreement between the observed and calculated distributions was not very good (Table 8). This suggests that Reaction 1 may be composite. This is not surprising since the supported palladium catalysts seem very complicated. For example, Burwell and Schrage found that the observed distributions in the exchange of cyclopentane with deuterium resulted from the combination of at least five different mechanisms (*37*).

Reaction II. Unlike Reaction I, Reaction

TABLE 8

DEUTERATION OF CYCLOPENTENE: OBSERVED AND CALCULATED DISTRIBUTIONS[a,b]

	d'_0	d'	d'_2	$'_3$	Δ
	Experiment No. 1 in Table 7				
Obsd	22.9	32.1	27.8	17.0	
Calcd with P = 17, $x = 0.64$	18.3	37.0	30.9	13.8	0.144
	Experiment No. 2 in Table 7				
Obsd	28.3	32.6	23.9	15.2	0.265
Calcd with P = 18, $x = 0.67$	21.1	38.3	28.9	11.6	

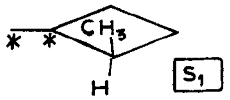
[a] d'_0, d'_1, d'_2, d'_3 are proportional to d_0, d_1, d_2, d_3 in Table 7 with $\Sigma d'_i = 100$.

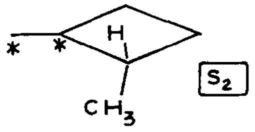
[b] $\Delta = \sum_i \left(\frac{(d'_i)_{\text{calcd}} - (d'_i)_{\text{obsd}}}{(d'_i)_{\text{calcd}}} \right)^2$

II corresponds to a negligible isotopic dilution. An upper limit $x_{\max}$ of the probability x of adding a hydrogen atom may be found by assuming that all the d_9 cyclopentane in Table 7, and all the d_{13} dimethylcyclopentane in Table 5 is due to the presence of light hydrogen on the surface: $d_9/d_{10} = 10\ (x/1 - x)$; $d_{13}/d_{14} = 14\ (x/1 - x)$. The $x_{\max}$ values are reported in Tables 5 and 7; they never exceed 0.10 and are probably much smaller.

Therefore at least two deuteration reactions occur on the surface, presumably on different sites. For one reaction the reacting "deuterium" is largely contaminated by the light hydrogen. This means that on the corresponding sites the surface reaction is much faster than the desorption of adsorbed hydrogen. On the other hand for the second reaction, the deuterium is practically uncontaminated. The surface reaction on the corresponding sites may be considered slower than the desorption of hydrogen.

We believe that the differences between Reactions I and II lie in the rate of step 4 leading to the half hydrogenated state. In Reaction I, steps 4 (and 4′) are fast; therefore, step 5 may be neglected, which explains the low content in deuterium of the saturated product. Simultaneously the reacting deuterium is largely diluted by the hydrogen since the desorption of surface hydrogen is slow in comparison with the surface Reaction 4, 4′.





In Reaction II, step 4 is slow, and its rate is probably much lower than the rate of step 5. The role of π-allylic species then becomes predominant; this explains the high extent of exchange (by steps 5, 5′) before desorption as saturated products. The rate of desorption of surface hydrogen in this case is faster than the rates of steps 5 (5′) and 4 (4′) and there is no noticeable isotopic dilution.

The difference of behavior between 1,2-dimethylcyclopentene (I) where Reaction I is negligible, and cyclopentene or methylene-methylcyclopentane (III) favors the above explanation. It has been shown that the formation of the monoadsorbed species on palladium was very sensitive to the steric hindrance from the surface (*19*). This steric hindrance is expected to be much more pronounced for (I) than for (III) or for cyclopentene. This could explain why Reaction I occurs in the deuteration of cyclopentene and of the exocyclic olefin and not in the deuteration of 1,2-dimethylcyclopentene. The higher percentage of *cis* saturated product from III than from I is explained in the same way since the predominance of *cis* is also related to Reaction I (step 4 much faster than step 5).

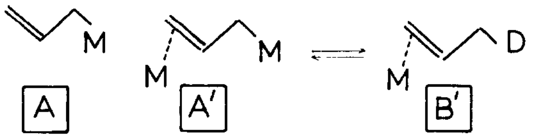
Another example of the steric hindrance by the surface, this time in a diadsorbed species, is provided by the results of the hydrogenation of the methylene-methylcyclobutane. Ninety-two percent of *cis*-dimethylcyclobutane is formed from this molecule. This shows that, of the two possible diadsorbed species S_1 and S_2, only the one with the methyl group away from the surface is formed (S_1); this can only be explained by a steric hindrance of the surface on the methyl group in an α position to the double bond.

Exchange of the Reacting Olefins

Since the deuterium distribution of the saturated products is not related to the distribution of the olefins, any proposed mechanism common to isomerization or olefin exchange and to deuteration should be ruled out. Moreover, whenever the percentage of exchange or isomerization is small, definite breaks appear in the deuterium distribution of the olefins. For the exchanged olefin such a break appears after d_1 (Expt. 1, Table 7 or Expt. 2, Table 5) or

d_2 (Expt. 1, Table 5); for the isomerized olefin, one observes a very pronounced discontinuity after d_1 (Expt. 1, Table 5). It would be impossible to account for such breaks with a simple Horiuti–Polanyi mechanism or even with a modified model such as the one represented in Schemes 1–3. Therefore, we believe that the reactions of olefin exchange and double-bond shift should be explained with species *other than* the classical mono, α,β,diadsorbed and π-allylic species.

The distributions of the cyclopentene and of the methylene-methylcyclopentane obtained at a very low conversion show that the main exchange reaction of the olefin is a simple process; however, a multiple exchange may introduce an additional deuterium atom into the molecule, which is the case with the dimethyl-1,2-cyclopentene. Like Smith and Burwell (*33*), we suggest that the species responsible for the exchange is an olefin, dissociatively adsorbed in an allylic position. A slight bond between the double bond and the metal could allow the multiple exchange without desorption. We believe that this additional bonding (in Species *A′* and *B′*) could be pictured as one of the π-bond type with a weak overlap between the olefin and the metal orbitals.

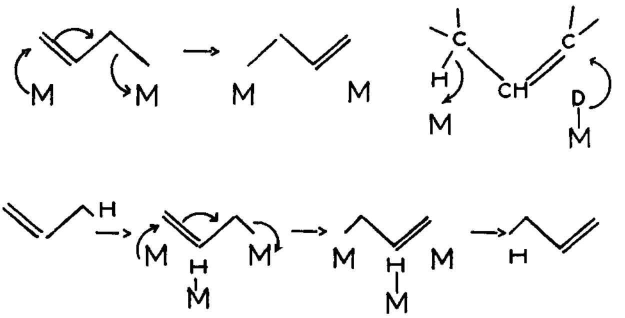


The only way to prove the existence of Species *A* (or *A′*) would be to localize the position of the deuterium in the mono exchanged molecule. This is very difficult indeed in the case of disubstituted cycloolefin, but in the case of propene, by using microwave spectroscopy, Hirota *et al.*, showed that over palladium, and not over other metals, propene-3-d was the major product of exchange with deuterium. Propene-2-d, which is expected mainly with an associative mechanism (as is the case over nickel) represents only 15% of the monodeuteroolefin (*38–40*).

Isomerization

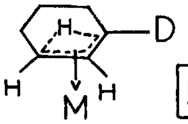
Sixty to 80% of the olefins obtained by isomerization of dimethylcyclopentenes are d_0 and d_1 in approximately equal amounts. d_1 could be easily explained by a mechanism involving a dissociatively adsorbed olefin; two such mechanisms are represented below: a concerted displacement of charge on the σ-allylic species responsible for exchange, and the Taylor and Dibeler mechanism (*31*).

It is much more difficult, however, to account for the formation of d_0. At first glance one could assume that d_0 results from an isotopic dilution of the deuterium on the surface. An explanation of this type was proposed by Smith and Menon for the isomerization of *cis*-cyclododecene into *trans*-d_0-cyclododecene over palladium–carbon in the presence of carbon tetrachloride (*41*). However, if this was the case in our experiments, the probability x of adding a hydrogen atom to Species *A* would be about 0.5. That would mean that on the particular type of sites responsible for exchange and isomerization of the olefins, the rate of surface reaction would be very fast

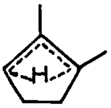


in comparison with the desorption of hydrogen. As a possible explanation, one could suppose that the allylic hydrogen atom removed from the molecule to form Species *A* does not migrate very far from the allylic species and reacts immediately after the double-bond shift has occurred. If that is the case, a rather large part of the apparently unreacted olefin will have been dissociated and will have reacted with light hydrogen.

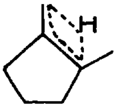
Another possible mechanism would be an intramolecular shift without any break of C–H bond. Smith and Swoap proposed a mechanism of this type to explain the results of the exchange of cyclohexene and deuterium (*42*). By using NMR analysis, they found approximately equal numbers of deuterium atoms in allylic and vinylic positions; they deduced that the products of exchange and of isomerization, i.e., cyclohexene-3-d and cyclohexene-1-d, resulted from a common intermediary *B* with a bridged hydrogen between carbons 1 and 3.



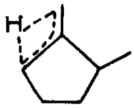
B



B_1



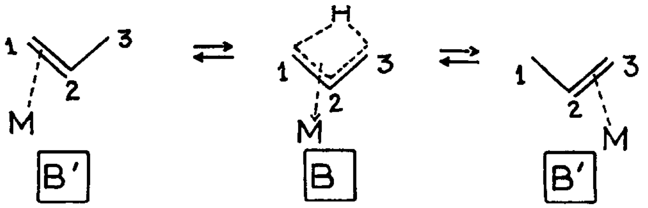
B_2



B_3

From our results, it is not obvious that the olefin exchange and the double-bond migration are necessarily related; for similar catalysts, the ratio τ_E/τ_I between the rates of these two reactions varies widely, by a factor of five, and greatly exceeds unity. This could be explained in the case of a common intermediate by the fact that Species *B* is no longer symmetrical. That the ratio of olefin exchange and isomerization is very high in the case of 1,2-dimethylcyclopentene would imply that the formation of a primary or secondary C–H bond in species B_1 and B_2 is much easier than the formation of a tertiary C–H bond. But if that was the case, the isomerization should be much faster than the exchange where methylene–methylcyclopentane (III) is concerned (Species B_2 and B_3); the reverse, however, is observed: the exchange of (III) is faster than its isomerization. Therefore, we believe, that while Species *B* may be responsible for isomerization, which would account for the formation of d_0 isomeric olefins, it is not sufficient to explain the exchange process.

On the other hand, in the mechanism proposed for cyclohexene exchange (*42*), intermediate *B* was formed from classical diadsorbed or π-allylic species, so that exchange and deuteration ought to have been interconnected, which was not the case. In our opinion, a species like *B* and its precursors should be distinguished from the π-allylic species and the diadsorbed species responsible for deuteration. In Species *B* the orbitals of C_1 and C_3, which are coupled with the orbital of the hydrogen, keep a definite *s* character and are only loosely overlapping with the metal orbitals. Species



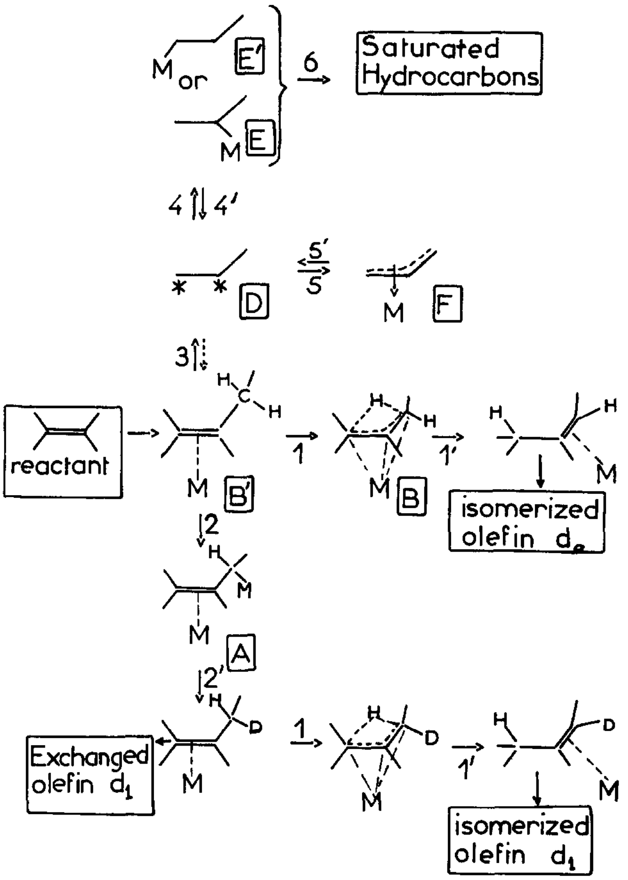


FIG. 4. Exchange, isomerization and deuteration—possible reaction paths.

B' is also only loosely bound to the metal; it is responsible for the multiple exchange, as already suggested, and also for the highly deuterated isomerized olefins. In the case of methylene-methylcyclopentane, several conversions between *B* and *B'*, combined with exchange and free rotation of the methyl group, explain the formation of an appreciable amount of d_2 and d_3 dimethylcyclopentenes. Such a process is not possible in the isomerization of 1,2-dimethylcyclopentene to 2,3-dimethylcyclopentene, and a strong break in the distribution is observed after d_1.

CONCLUSION

An attempt to picture the three reactions, exchange, isomerization and deuteration over palladium, is represented in Fig. 4. The three main olefinic reaction products, *viz.* non-isomerized olefin d_1, and isomerized olefins d_0 and d_1, are produced via Species *B*, *B'* and *A* by steps 1 and 2 (or 1' and 2'). Repetition of these steps may lead to more highly exchanged olefins in small amounts.

Strong adsorption of the olefin (step 3) leads to Species *D* which might be a true π-olefinic complex (*18*, *43*, *44*), or a di-σ adsorbed radical (*37*, *45*), or have some intermediate structure. Interconversion between species *D* and monoadsorbed Species *E* (steps 4, 4') or between *D* and π-allylic species (steps 5 and 5') determined the deuterium content and the stereochemistry of the saturated hydrocarbon desorbed in step 6. Step 3 is almost irreversible which explains the differences between the distributions of olefins and saturated hydrocarbons.

In this reaction scheme, the interchange reactions between alkyl radicals and adsorbed olefins were not considered (*46*); they should lead to statistical distributions of the saturated products, which were never observed in our experiments.

This mechanism as such can hardly be extended to other metals, since some additional processes may occur, such as dissociative adsorption of a vinylic carbon atom (*39*, *40*). However, it can be taken as a basic scheme, although some simplification may be introduced. For example, it has been shown that over some deactivated nickel catalysts, the addition of hydrogen was exclusively *cis* (*12*); in this case step 5 is not operating. Over nickel, rhodium and platinum, double-bond migration being of minor importance, step 1 has then to be discarded.

APPENDIX

Let us assume that the deuteration of cyclopentene takes place according to the Horiuti–Polanyi mechanism; suppose that the five hydrogens of the molecule away from the surface are not exchangeable; call P the ratio of the chances of an alkyl radical reverting to an adsorbed molecule or desorbing as cyclopentane.

The distribution N_2, N_3, N_4, N_5 of the deuterocyclopentanes which would be obtained if only deuterium atoms were present on the catalyst surface may easily be calculated by using the recurrent relation of Anderson and Kemball (*36*).

$$N_2 = \frac{2}{P+2}$$

$$N_3 = \frac{4P}{(P+4)(P+2)}$$

$$N_4 = \frac{2P^2(3P+4)}{(P+2)(P+4)(P^2+8P+8)}$$

$$N_5 = \frac{P^3}{(P+4)(P^2+8P+8)}$$

Now if hydrogen and deuterium atoms are both present on the surface, call x and $(1-x)$ the probability of an adsorbed olefin or an alkyl radical adding a hydrogen atom and a deuterium atom respectively. N_i molecules of cyclopentane d_i will be replaced by $N_i x^i$ molecules of cyclopentane d_0, $N_i x^{i-1}$ $(1-x)$ C_i^1 of cyclopentane d_1, . . . , $N_i x^{i-j}$ $(1-x)^j$ C_i^j of cyclopentane d_j.

Therefore the observed distribution d_0, $d_1 \ldots d_5$ will be:

$$d_p = \sum_{i=2}^{i=5} N_i C_i^p x^{i-p}(1-x)^p \text{ when } p \leqslant 2$$

$$d_p = \sum_{i=p}^{i=5} N_i C_i^p x^{i-p}(1-x)^p \text{ when } p > 2$$

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