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Hydrogenation of 2-Methylcyclopentanone on Metal Catalysts

D. CORNET AND F. G. GAULT

From the Department of Chemistry, Faculté des Sciences de Caen,
Caen, France

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The gas-phase hydrogenation and deuteration of 2-methylcyclopentanone and 2-methylcyclohexanone into the corresponding *cis-* and *trans-*2-methylcyclanols, are investigated on various metal catalysts, using a microreactor pulse technique.

In the range of temperatures considered (80° to 160°C), a fast *cis-trans* isomerization of the cyclanols is found to occur, and this isomerization does not proceed via a dehydrogenation into ketone.

The amounts of *cis* and *trans* alcohols formed initially by hydrogenation of the ketone are nearly independent of the catalyst and the temperature. A high *cis* selectivity appears only on a poisoned catalyst, or when the reacting ketone has not been drastically purified.

The deuterium distributions of both the *cis* and the *trans* alcohol obtained by deuteration are very similar.

The results here obtained cannot be accounted for by a *cis* addition of hydrogen on diadsorbed ketonic species. Other mechanistic possibilities are discussed, the most likely involving addition or removal of hydrogen from both sides of the adsorbed molecules.

INTRODUCTION

The mechanism of the catalytic hydrogenation of ketones was studied in two different ways.

1. *Stereoselectivity in Hydrogenation*

Skita and Vavon first studied the stereoselectivity of the catalytic hydrogenation of α-substituted cyclic ketones in the liquid phase, on various catalysts (*1–4*).

The stereoselectivity of this reaction, i.e., the relative amounts of the *cis* and the *trans* alcohols formed in the hydrogenation, widely varied according to the catalyst, the medium, and the size of the substituent. Skita suggested that platinum and an acidic medium favored the *cis* alcohol, while nickel and a neutral or basic solvent induced the formation of the *trans* isomer.

Vavon explained the formation of the *cis* alcohol by supposing that the ketone was lying flat on the surface, and that both hydrogens were added from the side of the ring opposed to the substituent, i.e., from the metal surface (*3*).

Very similar mechanisms were presented by Siegel and Hückel in the case of cyclohexanones, using the concepts of conformational analysis (*5, 6*).

However, a number of more recent investigations by Hückel and Cornubert and their co-workers (*7, 8, 9*) showed that the selectivity varied widely and irreproducibly, even when apparently the experimental conditions were unchanged. Even the Skita rule appeared to be not very strict, since, in some experiments, *cis*-2-methylcyclohexanol was formed predominantly on Raney nickel from 2-methylcyclohexanone, while the *trans* isomer was obtained on platinum in an acetic medium (*9*).

To explain these discrepancies in the results, we thought it would be of interest to study the hydrogenation of the 2-methylcyclopentanone and 2-methylcyclohexanone in the gas phase; the possible influence of the solvent would thus be avoided and on the other hand, the extent of the reaction could be better controlled than in the liquid phase, thus making possible the simultaneous study of the kinetics and of the selectivity. Such a study appeared to be necessary to determine the exact role of the *cis–trans* isomerization of the alcohols. This reaction, first observed on nickel (*10*) was always considered as proceeding via a ketone intermediate. But a direct isomerization is quite possible and has even been strongly suggested by the work of Burwell (*11*), who proved the direct racemization of *d*-butanol on copper.

2. Deuteration

On the other hand the replacement of hydrogen by deuterium in the hydrogenation of ketones has allowed more information to be obtained about the reaction mechanisms.

Farkas and Farkas (*12*) showed that the deuteration of acetone on platinum foil at 80°C implied not only the addition of two deuterium atoms on the carbonyl group, but also the replacement by the deuterium of the hydrogens of the methyl groups.

Studying the deuteration of acetone on metal films, Kemball and Stoddart (*13*) were able to deduce the distributions of the deutero alcohols at any time from the distributions of the deutero ketones, by supposing that "the deuteration was the simple act of adding two deuterium atoms to the adsorbed ketones." However, the correlation between the two distributions, established on experiments on nickel films at 0°C, no longer held at higher temperatures.

In this paper, the deuterium contents of the ketone, the *cis*, and the *trans* alcohol obtained during the deuteration of the 2-methylcyclopentanone will be compared under various conditions. It was thought that such a comparison could afford an explanation for the mechanism of hydrogenation of ketones.

EXPERIMENTAL

1. Apparatus and Procedures

Gas-phase hydrogenation. A microreactor technique was used for the experiments in the gas phase on supported catalysts. The reactor was inserted in the flow line of a gas chromatograph using hydrogen as carrier gas; it consisted of five Pyrex tubes in parallel filled with various amounts of catalysts. The hydrogen flow could be directed into any of the tubes, and it was thus possible to change easily the contact time. In any run, 3 mg of liquid was injected in the reactor through a vaccine cap and a preheater. Hydrogen pressure was atmospheric in the reactor and at the entrance of the chromatography column, below atmospheric pressure at the exit of the column; a needle valve made it possible to alter the flow rate, and this added possibility of changing the contact time was used to determine the equilibrium mixtures of ketone and alcohols.

The amounts of platinum-pumice and nickel-pumice in each reactor tube varied from 0.15 to 1.5 g. In the experiments on Adams platinum or Raney nickel, capillary reactors and very small amounts of catalysts (0.010 to 0.150 g) were used.

The microreactor technique was not suitable for the very slow hydrogenation on palladium; the reaction and the chromatographic analysis were thus done separately. A slow hydrogen stream (0.5 to 2 cc(NTP)/min) bubbled into the ketone, was brought to a constant temperature (60°C), and then passed into a reactor containing 10 g of palladium catalyst. The reaction products were collected at the exit of the reactor for about 1 hr and analyzed. The ketone flow rate could be controlled by changing the hydrogen flow rate.

The experiments on evaporated films were done in a conventional high-vacuum system; at the end of a run, the reaction products were condensed in liquid nitrogen, removed, and analyzed by gas chromatography.

Liquid-phase hydrogenation. A static system was used for the hydrogenation at room temperature. One gram of ketone was hydrogenated in a 25-ml vessel mechanically shaken. At higher temperatures (50–100°C), the hydrogen was circulating through the mixture of ketone and catalyst. The ratio of the weights of ketone and catalyst was 10 and 2 for platinum and nickel, respectively.

Deuterations. The deuteration of the 2-methylcyclopentanone on a supported catalyst was performed in a flow system. The ketone (30 μl) brought to a temperature of 85°C in a saturator was carried by a stream of deuterium at atmospheric pressure through a batch of catalyst and the reaction products trapped in liquid nitrogen. The temperature of the saturator and the gas flow rate were adjusted so that the ratio of the partial pressures of deuterium and ketone was 10 to 1. Different conversions were obtained by varying the amount of catalyst in the reactor.

The static reactor used for the deuteration of 2-methylcyclopentanone on metal films is the same as the one described by Kemball (*14*). The reaction is mass spectrometrically followed and thus can be stopped at approximately the desired conversion, by trapping the products in liquid nitrogen.

2. Catalysts

The 10% platinum-on-pumice catalyst was prepared according to Pines, Olberg, and Ipatieff (*15*). After each run, the catalyst was regenerated by oxygen at 300°C for 1 hr, and reduced by hydrogen at 300°C overnight. A 20% nickel-on-pumice catalyst was prepared according to Adkins and co-workers (*16*); a single experiment was done with any batch of catalyst. Hydrogen was replaced by deuterium for the preparations of the catalysts used in the experiments of deuteration. It was checked that the pumice used as a carrier was inactive for the *cis–trans* isomerization of the alcohols, up to 250°C. Adams platinum was obtained from "Baker catalysts"; when used in the gas phase, it was reduced in the microreactor.

Raney nickel W6 was prepared in the usual way (*17*), just before use. In the gas-phase experiments, a mud of catalyst was deposited in the capillary microreactor and dried in a flow of hydrogen.

The preparation of the metal films has previously been described (*14*); wires of various Spec-pure metals were obtained from Johnson-Matthey.

3. Materials

2-Methylcyclopentanone was prepared by oxidation of 1-methylcyclopent-1-ene by performic acid according to Plate and Melnikov (*18*). After distillation, no impurity could be detected by chromatography on different columns; in any experiment the distilled ketone was used after purification by gas chromatography.

Pure grade 2-methylcyclohexanone was obtained from Prolabo.

Pure *cis-* and *trans*-2-methylcyclopentanols were prepared by gas-liquid chromatography of mixtures of both stereo isomers on a diglycerol–polyethylene glycol column (*19*). A mixture of 72% of *trans* and 28% of *cis* was obtained by reduction of 2-methylcyclopentanone by lithium aluminum hydride. The hydrogenation on Raney nickel at 100°C under 150 atm of hydrogen gave a mixture containing 80% of the *cis* isomer.

Cylinder hydrogen was used for the reactions after purification on platinum-alumina at 320°C (supported catalysts) or after diffusion through a palladium thimble (metal films). Deuterium with an isotopic purity higher than 99% was obtained from General Dynamics Co. In the experiments on metal films, it was purified by diffusion through a palladium thimble.

4. Gas Chromatography

In the hydrogenation experiments, the columns used for analytical and preparative purposes were made of a mixture of diglycerol and polyethylene glycol (*19*). Ucon columns, although less efficient, were preferred for the deuteration experiments, on account of the higher stability of the stationary phase.

5. Mass Spectrometric Analysis

The 2-methylcyclopentanone, the *cis* and the *trans* alcohols, separated by chromatography, were analyzed by mass spectrometry to determine the distributions of the deutero isomers. In some experiments, the *cis* alcohol and the mixture of *cis* and *trans* alcohol were separately analyzed.

The ketones ($m/e = 98$ to 108) and the alcohols ($m/e = 101$ to 111) were analyzed using the parent peaks after the usual corrections for the fragmentation and the natural isotopes. In the analysis of the alcohols, the replacement of the deuterium of the hydroxyl group by a hydrogen in the mass spectrometer was taken into account (*13*).

RESULTS AND INTERPRETATION

1. *Cis–Trans Isomerization of 2-Methylcyclopentanols*

The reactions of *cis*- or *trans*-2-methylcyclopentanols in the presence of hydrogen were studied in a flow system at 118–158°C on platinum or nickel supported on pumice. Three reactions took place under these conditions: (1) hydrogenolysis to hydrocarbons; (2) *cis–trans* isomerization; (3) dehydrogenation to ketone. The hydrogenolysis was always small: less than 5% of hydrocarbons were obtained in the reaction products.

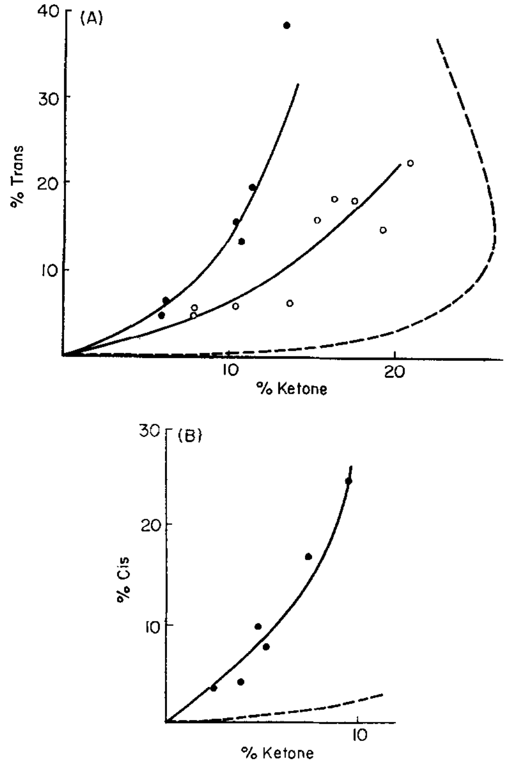


FIG. 1. Isomerization and dehydrogenation of 2-methylcyclopentanols at 118°C.

(*a*) Isomerization of *cis*: ●, on nickel-pumice; o, on platinum-pumice.

(*b*) Isomerization of *trans* on nickel-pumice.

Every plot corresponds to an experiment with (ordinate), the amount of the isomerized alcohol, and (abscissa), the amount of ketone, expressed as percent of the total oxygenated compounds. The dashed line is the corresponding curve if isomerization and dehydrogenation were consecutive reactions.

In order to find out whether the dehydrogenation and the formation of the *trans* or *cis* isomer were consecutive or parallel reactions, the product distributions were determined at various contact times. In Figs. 1(a) and 1(b) are represented the experiments at 118°C on platinum or nickel supported on pumice. Every experiment is represented by a plot: the amount of ketone, z, in the abscissa and the amount of the *cis* or *trans* stereoisomer, x or y, in the ordinate are expressed as percents of the total oxygenated compounds. It can be seen that both the *trans* isomer and the ketone are initially formed from the *cis* alcohol [Fig. 1(a)]; similarly the amount of the *cis* alcohol obtained from the *trans* isomer was never negligible when compared to the amount of ketone [Fig. 1(b)]. The initial ratio of *trans* alcohol and ketone $(y/z)_0$ obtained from the *cis* isomer and the initial ratio of *cis* alcohol and ketone $(x/z)_0$ obtained from the *trans* isomer were 0.95 and 0.80, respectively, on nickel-pumice at 118°C. On platinum-pumice, $(y/z)_0$ was found equal to 0.40 at 118°C and 0.55 at 158°C. On the same catalyst, $(x/z)_0$ was determined only at 158°C and equalled 0.55.

The equilibrium concentrations of alcohols and ketone under 1 atm of hydrogen were determined at various temperatures, by approaching the equilibrium from each direction. The results are listed in Table 1. A heat of isomerization of 1.5 kcal could thus be calculated. From these equilibrium concentrations and from the initial *cis–trans* ratio in hydrogenation (determined later on) it was possible to calculate the amount of

TABLE 1

EQUILIBRIUM DISTRIBUTIONS OF *cis* AND *trans* 2-METHYLCYCLOPENTANOLS AND 2-METHYLCYCLOPENTANONE

Temperature	Ketone (%)	*cis* Alcohol (%)	*trans* Alcohol (%)	$\frac{cis}{cis + trans} \times 100$
100°	9	—	—	—
118°	17	25	58	30
132°	22.5	—	—	—
147°	31.5	23	45.5	33.5
158°	39	21	40	34.5
177°	—	—	—	36.5

isomerization which could have been obtained if dehydrogenation and isomerization were consecutive:

$$cis\text{-alcohol} \leftrightarrows \text{ketone} \leftrightarrows trans\text{-alcohol} \quad (1)$$

The kinetic model used in this calculation assumes simple first order kinetics. The corresponding curves are represented by dashed lines on Figs. 1(a) and 1(b).

2. *Hydrogenation*

Hydrogenation of 2-Methylcyclopentanone

The gas-phase hydrogenation of 2-methylcyclopentanone was studied at 60–160°C on platinum-pumice. The amounts of hydrocarbons formed were always very small and have been neglected.

The variation of the *cis–trans* distribution with the extent of hydrogenation was envisaged at any temperature. The percent of *cis* alcohol in the mixture of *cis* and *trans* isomers, referred to further as the *selectivity factor* $s = x/(x + y)$, was thus plotted as a function of the *conversion* ρ, defined as the relative amounts of *cis* and *trans* alcohols in the oxygenated compounds $\rho = (x + y)/(x + y + z)$. Typical $s = f(\rho)$ plots are represented in Figs. 2 and 3. The selectivity factor decreased as the conversion increased; this variation was larger at high conversions when the reaction mixture was close to equilibrium. The values obtained for s at a given conversion were reproducible within ±1.5%, provided that the catalyst has been previously regenerated.

In Fig. 2 is represented as a dashed line the $s = f(\rho)$ curve obtained if it is assumed that *cis–trans* isomerization occurs only by rehydrogenation of an intermediate ketone [reaction (1)]. Although the calculation shows that the selectivity factor should decrease with increasing conversion, even in the earlier stages of the reaction, the decrease was found much faster than one would expect from such a mechanism. The direct *cis–trans* isomerization occurs simultaneously with the hydrogenation and this isomerization reaction can be appreciated by the initial slope $(-p)$ of the $s = f(\rho)$ plots.

The effect of the temperature on the shape of the $s = f(\rho)$ plots is shown in Fig. 3. The lower the temperature, the smaller is the decrease of the selectivity factor with the conversion. The initial slope $(-p)$ of the curve was determined at various temperatures and an activation energy of 7.5 kcal could be associated with its variation. The initial selectivity s_0 was obtained by extrapolation of the $s = f(\rho)$ plots; its value, 60% ± 2% did not vary in the large range of temperature considered (60–160°).

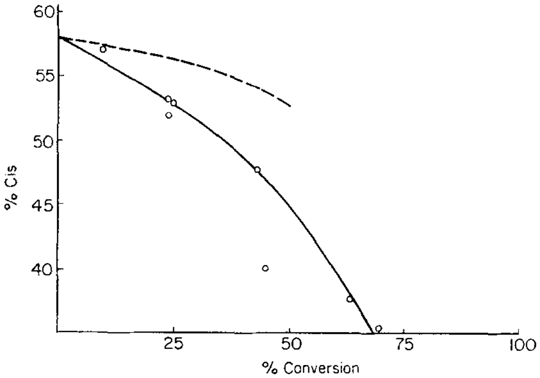


FIG. 2. Hydrogenation of 2-methylcyclopentanone on platinum-pumice at 158°C; $s = f(\rho)$ curve. The percent of *cis* (s) (ordinate) represents the percent of *cis* in the mixture of *cis* and *trans* isomers. The conversion ρ (abscissa) is expressed as the percents of *cis* + *trans* alcohols among the oxygenated compounds. The dashed line is the corresponding curve if isomerization and dehydrogenation were consecutive reactions.

Similar results were obtained in the gas-phase hydrogenation of 2-methylcyclopentanone on nickel-pumice. The reproducibility was not so good in the experiments on nickel-pumice as on platinum, though a new batch of catalyst was used for every experiment; variations up to ±3% of the percent of *cis* were observed from the mean value, for a given conversion. Sixty percent of the *cis* was initially obtained, as on platinum, at any temperature. The initial slope $(-p)$ of the $s = f(\rho)$ plots was higher at 90° on nickel than on platinum, but its variation with temperature was smaller: the associated activation energy was only 4.5 kcal.

The hydrogenation was much slower on palladium-pumice than on platinum or nickel; at 120°C the reaction was initially nonselective ($s_0 = 50\%$); the decrease of

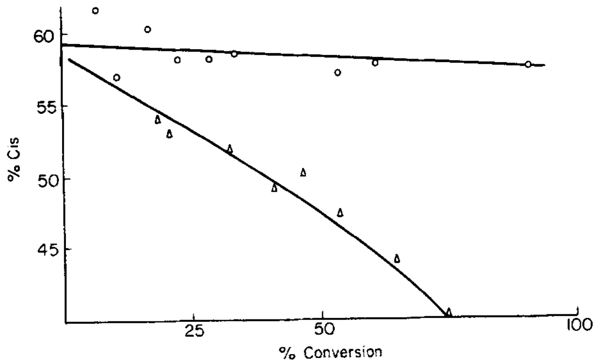


FIG. 3. Hydrogenation of 2-methylcyclopentanone on platinum-pumice: ○, at 80°C; △, at 138°C. The percent of *cis* (ordinate) and the conversion (abscissa) are defined as in Fig. 2.

the selectivity factor with the conversion on palladium was approximately the same as on nickel.

Since Adams platinum and Raney nickel were frequently used in previous work, the gas-phase hydrogenation on these catalysts was also studied. The initial selectivity for both catalysts was very small: 50% *cis* on Adams platinum, and 53% on Raney nickel were initially formed at 60°C. The variations of s with the conversions were slightly larger than on the corresponding supported catalysts.

In one experiment on a platinum film at 0°C, 43% *cis* was obtained for a conversion of 70%. An experiment on a nickel film at 80°C gave the same selectivity as the corresponding experiment on supported nickel.

Hydrogenation of 2-Methylcyclohexanone

The gas-phase hydrogenation of 2-methylcyclohexanone was studied on platinum-pumice at 80–160°C and on nickel-pumice at 120–170°C. No initial selectivity was found in any experiment: s_0 was always equal to 50% ± 2%. But the increase with temperature of the initial slope ($-p$) of the $s = f(\rho)$ plots was smaller than in the hydrogenation of the 2-methylcyclopentanone.

3. Stereoselectivity and Poisoning of the Catalyst

The preceding results of hydrogenation were entirely modified when the ketone had not been purified by gas chromatography, or when the same catalyst was used several times without regeneration. In these cases, the *cis* alcohol was always the major hydrogenation product, even at high conversions.

Stereoselectivity in Gas Phase

When several doses of unpurified 2-methylcyclohexanone were successively passed on the same amount of nickel-pumice (50 mg) at 120°C, a progressive decrease of the conversion was observed. Simultaneously, the amounts of the *cis* alcohol in the reaction products increased, much more than expected according to the decrease of the conversion.

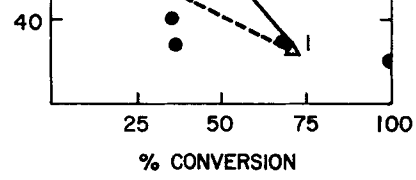


FIG. 4. Hydrogenation of 2-methylcyclopentanone on nickel-pumice at 120°C: ●, renewed catalyst; △, successive injections on the same batch of catalyst.

In Fig. 4 the plots labeled 1–5 represent the successive hydrogenation experiments. The other plots and the dotted line belong to a "normal" $s = f(\rho)$ curve obtained with a gas-chromatographed ketone and with renewed amounts of catalysts. The increase of the selectivity factor by a progressive poisoning is quite apparent in this figure.

Similar experiments were done with an unpurified sample of 2-methylcyclopentanone. Up to 75% and 80% of the *cis* alcohol were, respectively, obtained on platinum and nickel on pumice, after several doses of ketone had been successively passed on the same amount of catalyst.

Stereoselectivity in the Liquid Phase

The appearance of the *cis* selectivity was studied in the liquid-phase hydrogenation of 2-methylcyclopentanone on Raney nickel. Several samples of the ketone with various purities were hydrogenated and the results are represented in Fig. 5. Plots I correspond to a ketone, gas-chromatographed just before use (sample I). The absence of initial selectivity and the fast *cis–trans* isomerization are apparent in the figure. Plots VI correspond to a ketone which has only been distilled and not purified by gas chromatography (sample VI). The *cis* alcohol was predominantly formed and there was no decrease of the selectivity at high conversions and therefore no isomerization. Plots II, III, IV, and V were obtained with mixtures of samples VI and I. The higher the percentage of the unpurified ketone in the mixture, the higher is the selectivity.

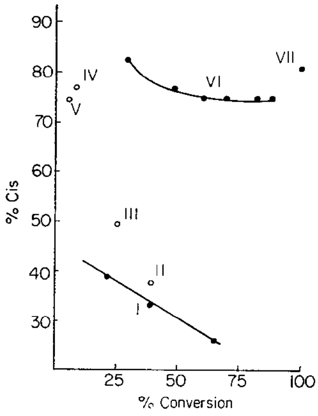


FIG. 5. Liquid-phase hydrogenation of 2-methylcyclopentanone on Raney nickel at 60°C: I, chromatographed ketone; VI, nonchromatographed ketone; II to V, mixtues of chromatographed and nonchromatographed ketones—II and III, 10% of I; IV, 17% of I; V, 21% of I—VII, experiment in autoclave.

4. Deuteration

Tables 2 and 3 summarize the results obtained on three different metals under various conditions. In the alcohol analysis, no alcohol containing less than two deuterium atoms is reported since the absence of the parent peak ($m/e = 100$), corresponding to $C_5H_{10}OD$, showed that the isotopic dilution of the deuterium was negligible. Therefore the alcohol $C_5H_{10}CDOH$ was assumed to be absent and the parent peak at $m/e = 101$ was attributed to the deutero alcohol $C_5H_{10}CDOD$ only.

Deuteration on Adams platinum and nickel films are presented as examples of nonselective deuteration; *cis* and *trans* alcohols were formed in approximately equal amounts on these catalysts. Platinum, nickel, or rhodium supported on pumice were the best catalysts to induce the selective deuteration, i.e., the selective formation of the *cis* isomer.

The distributions of the deutero ketones are given in the tables, together with the number φ, of deuterium atoms by molecule, and the mean number of deuterium atoms by exchanged molecules, expressed as $100\varphi/(100 - d_0) = M$. M characterizes the exchange of the ketone during the deuteration. Apparently the correlation between M and the selectivity depends upon the catalyst. On platinum, the exchange of the ketone increased with the selectivity. M equalled 1.49 and 2.31 on Adams platinum and platinum-pumice, where the selectivities, expressed as percent of the *cis* isomer, were, respectively, 41.5% and 81.6%. On the contrary, on nickel films and nickel-pumice M decreased when the selectivity was increased.

In the last lines of the tables the distributions of the deutero alcohols, *cis* and *trans* are reported. The most apparent feature in these results is that *there is no significant difference* between the distributions of the *cis* and the *trans* isomers in any experiment considered, whatever the stereoselectivity may be.

TABLE 2
GAS-PHASE DEUTERATION OF 2-METHYLCYCLOPENTANONE ON PLATINUM AND RHODIUM CATALYSTS

Catalyst:	Adams Pt, 30 mg		Pt-pumice, 118 mg		Rh-pumice, 235 mg			
Experimental procedure:	Flow system		Flow system		Flow system		Flow system	
T(°C):	60		120		120		120	
Alcohols(%):	29.5		23		7		39.5	
Cis(%):	41.5		81.6		61		67	
Ketone								
d_0	81.3		7.9		—		—	
d_1	11.7		21.4		—		—	
d_2	4.9		35.9		—		—	
d_3	2.1		25.9		0.1		0.1	
d_4	—		4.8		0.5		0.4	
d_5	—		2.2		2.8		1.4	
d_6	—		1.1		9.4		5.6	
d_7	—		0.5		24.6		15.8	
d_8	—		0.2		37.3		29.9	
d_9	—		—		18.7		33.3	
d_{10}	—		—		6.8		13.6	
φ	0.28		2.13		7.8		8.3	
M	1.49		2.31		7.8		8.3	
Alcohols	*cis*	*cis* + *trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
d_2	61.5	59.2	20.7	18.1	—	—	—	—
d_3	20.4	24.1	24.6	22.3	—	—	—	—
d_4	12.2	11.2	27.7	25.5	0.3	0.4	—	0.3
d_5	5.9	5.5	18.1	19.4	0.5	0.8	—	1.0
d_6	—	—	4.2	5.3	1.0	1.4	0.3	2.2
d_7	—	—	2.3	3.5	2.5	3.3	0.7	3.8
d_8	—	—	1.1	2.1	8.9	9.7	3.8	7.8
d_9	—	—	0.6	1.7	20.1	20.8	18.5	16.4
d_{10}	—	—	0.3	1.	29.0	29.7	30.1	28.2
d_{11}	—	—	0.1	0.3	26.5	25.5	31.8	28.9
d_{12}	—	—	—	—	11.2	8.3	14.9	11.5
$N = \Sigma_2^{12}(i-2)d_i$	0.57	0.63	1.76	1.96	7.95	7.8	8.33	7.94

The comparison between the distributions of the ketone and the alcohols are also of interest. In the selective experiments, the amount of the d_2 alcohol was always higher than the amounts of the d_0 ketone. On the contrary, in the nonselective experiments the amount of the d_2 alcohol was always much smaller than the amount of the d_0 ketone.

In the experiment reported in the third column of Table 3 (Nickel film at 80°C), the variations of the ketone distributions were followed mass spectrometrically; the theoretical distribution of the alcohols calculated with the simple assumption of the addition of two deuterium atoms to the adsorbed ketone could thus be derived and differed widely from the observed distribution.

DISCUSSION

1. *Cis–Trans Isomerization of the Cyclanols*

The results clearly show that the *cis–trans* isomerization of 2-methylcyclopentanols proceeds directly and not via a ketone intermediate.

One of the two carbon atoms C_1 and C_2 of the alcohols, or both, should then be inverted during the reaction process.

Both inversions of the function atom C_1 and of the carbon atom α to the hydroxyl group C_2 have been shown to occur on metals. Badin and Pacsu showed that the

TABLE 3
Gas-Phase Deuteration of 2-Methylcyclopentanone on Nickel Catalysts

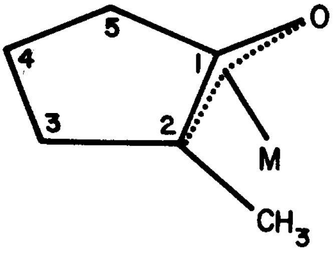
Catalyst:	Ni-pumice, 25 mg		Ni-pumice,107 mg		Ni film, 15 mg				Ni film, 6.1 mg	
Experimental procedure:	Flow system		Flow system		Static system				Static system	
T(°C):	120		120		80				118	
Alcohols(%):	46		68		15				3	
Cis(%):	64		85		44				72	
Ketone										
d_0	6.9		18.7		25.8				81.8	
d_1	14.2		33.3		26				15.3	
d_2	29.1		30.2		26.2				2.4	
d_3	36.6		15.4		17.				0.4	
d_4	10.1		1.6		3.6				—	
d_5	2.3		0.4		1.1				—	
d_6	0.8		0.2		0.4				—	
d_7	0.1		—		—				—	
d_8	—		—		—				—	
d_9	—		—		—				—	
d_{10}	—		—		—				—	
φ	2.4		1.5		1.52				0.213	
M	2.58		1.84		2.05				1.17	
Alcohols	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis* + *trans*	Calc.	*cis*	*trans*
d_2	9.7	14.3	48.8	52.3	18.4	22.3	20.5	66.1	84.2	80.1
d_3	16.4	18.1	28.3	23.8	25.5	26.5	26.1	18.6	12.7	15.6
d_4	27.2	26.1	15.3	13	30.3	28.1	29.1	10.7	2.1	2.9
d_5	32.5	29.7	6.3	8.8	21.6	19.2	20.3	3.9	0.9	1.4
d_6	10.4	9.0	0.8	1	4.3	3.8	4	0.6	—	—
d_7	2.6	2.1	0.4	0.6	—	—	—	—	—	—
d_8	0.9	0.6	0.2	0.4	—	—	—	—	—	—
d_9	0.1	0.1	—	—	—	—	—	—	—	—
d_{10}	—	—	—	—	—	—	—	—	—	—
d_{11}	—	—	—	—	—	—	—	—	—	—
d_{12}	—	—	—	—	—	—	—	—	—	—
$N = \Sigma_2^{12}(i-2)d_i$	2.3	2.1	0.84	0.86	1.68	1.55	—	—	0.20	0.25

racemization accompanied the hydrogenation of optically active methyl-2-butanal (*20*). Burwell observed the racemization of *d*-butanol under the conditions of its dehydrogenation (*11*). It is thus likely that the *cis–trans* isomerization of 2-methylcyclopentanol results from the combination of two inversion processes.

Now the simplest way to explain the inversion of a carbon atom is to assume that this inversion occurs during the reaction of an adsorbed species with hydrogen. The *cis–trans* isomerization of disubstituted cycloalkanes was thus explained by assuming that a π-allylic triadsorbed species was formed and could react with atomic hydrogen from the bottom of the ring and with molecular hydrogen from the top (*21*). In this case we shall assume that *both* the function carbon atom and the carbon atom α to the hydroxyl group may react with hydrogen in two different ways.

The double reactivity of the C_2 carbon atom (α to the hydroxyl group) is strongly supported by the exchange and deuteration experiments.

Kemball and Stoddart have shown that the four hydrogen atoms in the α positions were initially exchanged in cyclopentanone and cyclohexanone (*22*). That shows that the triadsorbed species A responsible for the multiple exchange can also be responsible for a carbon inversion and *cis–trans* isomerization.



Triadsorbed species A
(OC_1C_2)

Species A could thus be compared to the hydrocarbon π-allylic species and are also probably π-bonded to the surface.

2. *Selectivity in Hydrogenation*

The double reactivity of the function carbon atom C_1 cannot be directly proven by exchange experiments, but it will be seen later on that most of the results are consistent with such a mechanism.

If it is assumed that only the α carbon atoms are able to react in the adsorbed state with both atomic and molecular hydrogen, it is not possible to explain in a simple way the observed relationship between the *cis* selectivity in hydrogenation and the absence of *cis–trans* isomerization. The increased selectivity would result from an increased steric hindrance by the methyl groups, as stated by previous workers. On the other hand, the suppression of the *cis–trans* isomerization would be related to the predominance of one mode of attack by hydrogen of the triadsorbed species. Thus a strict correlation between the two phenomena is not to be expected.

On the contrary, let us assume that the operative mechanism under normal conditions, i.e., purified reactants and clean catalyst, is one in which the functional carbon atom C_1 as well as the carbon atoms in the α position react with hydrogen in two different ways: the selectivity of hydrogenation would be quite small and *cis–trans* isomerization would occur. The suppression of one mode of attack would prevent *simultaneously* the formation of *trans* alcohol in hydrogenation and the *cis–trans* isomerization.

The selectivity of hydrogenation can be determined more precisely by choosing a simplified model for the reaction: let us suppose that both triadsorbed species OC_1C_2 and OC_1C_5 can be formed in equal quantities, the methyl group in species OC_1C_5 always being away from the surface. Let us call u and $1 - u$ the probability for either of the α carbon atoms C_2 and C_5 to react with atomic hydrogen and with molecular hydrogen, respectively (from the bottom and from the top of the molecule). Call v and $1 - v$ the corresponding probabilities of attack on the function carbon atom C_1. The probability s of forming the *cis* alcohol is then

$$s = \tfrac{1}{2}[uv + (1 - u)(1 - v)] + \tfrac{1}{2}v$$
$$= uv - \tfrac{1}{2}u + \tfrac{1}{2}$$

Provided that u and v do not differ much, it can easily be seen that s may remain approximately constant within a large range of values of u and v; for instance, if $u = v$, $s = 0.5 \pm 0.06$ for $0 \leq u \leq 0.6$. The selectivity becomes large only when u is close to unity. The fact that the selectivity of hydrogenation does not depend upon temperature is difficult to explain with any other mechanism. With this mechanism, the selectivity may remain constant. Slight modifications of the initial assumptions should of course be done to adjust the constant value of s to the appropriate value.

There is, however, one important objection to the elaboration of such a mechanism: the possibility for the functional carbon atom to react with hydrogen in two different ways implies that adsorbed ketone and adsorbed olefin are quite different in nature. Indeed, only a *cis* addition of hydrogen is possible on the latter molecule (*23*). A participation of the p electrons of the oxygen atom in the bonding could make the properties of an adsorbed ketone very different from an adsorbed olefin. If we tentatively picture the diadsorbed species as being π-bonded to a metal atom. then the electrons of the oxygen could form an additional donor bond with a neighbor site of the surface.

3. *Deuteration Experiments*

The results of the experiments with deuterium confirm the proposed mechanism.

In fact the double attack of the carbon atom of the carbonyl group by hydrogen is the *only* satisfactory explanation for the identity of distributions in the two stereoisomers *cis* and *trans*. If the *cis–trans* ratio was determined only by the mode of reaction of the C_2 carbon atom, one would expect different distributions for the *cis* and *trans* alcohols, at least on platinum and nickel.

On rhodium a complete exchange of all the hydrogens of the molecule is observed, and it is no more possible to recognize the exchange of the hydrogens in the α position.

The exchange of the various hydrogens in polysubstituted cyclopentanones was studied on palladium (*24*). It was shown that the hydrogens in the β position could be exchanged below 120°C only when they were not separated from the CO group by a quaternary carbon atom. Therefore the species responsible for the exchange of the β hydrogen in this case are probably similar to that intervening in the exchange of hydrocarbons, but initiated by C–C–O triadsorbed species A. The pattern of the deutero alcohols obtained on rhodium could be explained in the same way, since rhodium is known to be one of the best catalysts for the multiple exchange of hydrocarbons. On rhodium the facility to form mono- and diadsorbed species of the hydrocarbon type would thus be similar to the ease of forming the triadsorbed species A (C–C–O).

The correspondence between the distributions of the deutero ketones and the deutero alcohols on nickel and platinum shows that the alcohols are not merely the result of an addition of two deuterium atoms to the adsorbed ketone. If such was the mechanism, the relative amount of d_2 among the deutero alcohols should be larger than the amount of d_0 among the ketones, which is not true in many experiments. Moreover the distributions (d_2, d_3 . . . d_{n+2}) of the alcohols and (d_0, d_1, d_2 . . . d_n) of the ketones are very close in some experiments of nonselective hydrogenation on nickel (experiments indicated in columns 1 and 3 of Table 3). That seems to indicate that a large number of interconversions occurs between the adsorbed ketones and the species responsible for exchange (A or others) before the molecules, ketone or alcohol, are desorbed.

A redistribution process* could be another possible explanation for the discrepancy between the observed distributions of alcohols and those calculated according to a simple addition mechanism. However such a process could not explain the similarity of the distributions of ketones and alcohols, when it happens.

4. Interchange Reaction

The distributions of ketones and alcohols allow one also to discard an alternative mechanism which would take into account the interchange reaction between alcohol and ketone (*25*).

Since in this process the configuration of the carbon atom C_1 in the reacting adsorbed alcohol is not retained, it is no longer necessary to assume two different kinds of reaction of hydrogen with the diadsorbed ketone. Thus one could suppose that hydrogenation is merely a *cis* addition of two hydrogen atoms; but as a result of the interchange, the alcohol desorbed from the surface would consist of *cis* and *trans* in equal amounts. This mechanism would explain nicely the relationship between nonselectivity and *cis–trans* isomerization. Poisoning the catalyst would result in reducing the interchange reaction and therefore the *cis–trans* isomerization and the nonselective hydrogenation. But in this case the *trans* alcohol is mostly formed by a reaction between the ketone and the *cis* alcohol. The deutero distributions of the *cis* and *trans* alcohols could thus be similar only if the transfer of two deuterium atoms from an alcohol A to the ketone would give a new molecule C′ or T′ with the same number of deuterium atoms, i.e., if the distribution (d_2, d_3 . . . d_{n+2}) of the *cis* alcohol is the same as the distribution (d_0, d_1 . . . d_n) of the ketone: that was shown to happen in some *nonselective* hydrogenation (as seen before), but never in *selective* hydrogenations.

In conclusion, the mechanism involving a double mode of reactivity of the diadsorbed

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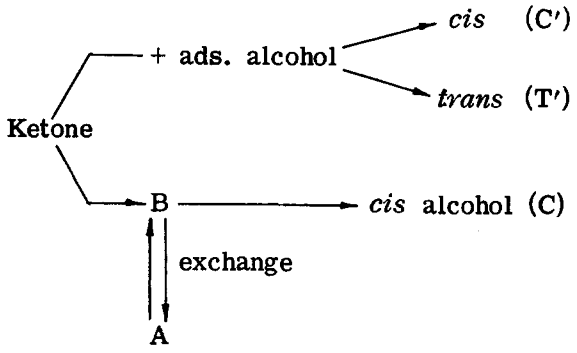
* The eventuality of such a mechanism was suggested to us by one of the referees.



A: Triadsorbed species
B: Diadsorbed species

ketone seems the most likely, though it is difficult at the present stage to discard completely any other mechanism.

On the other hand, the simplicity of some of the observed results, as far as the selectivity is concerned, might be due to the simplicity of the molecules chosen as models, and it thus seems desirable in the future to study the hydrogenation of other substituted ketones with a larger substituent.

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