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THE MECHANISM OF THE HETEROGENEOUS CATALYSIS OF α AND γ-CYCLIC SIX-MEMBERED AMINOKETONES

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Abstract - On the basis of catalytic deuteration of cyclic α and γ-aminoketones in 1-2N DCl/D_2 or H_2, in the presence of PtO_2, it is assumed that the mechanism of heterogenous catalysis for both classes of compounds is ionic in character, and that the reaction takes place in the electrical double layer at the interface of solid and liquid. As a consequence of the reduction, two deuteriums (or hydrogens if HCl is used) from the reduction medium are introduced into the molecule, the catalyst only facilitating and not participating in the reaction itself.

It is generally accepted that the mechanism of heterogenous catalysis related to the hydrogenation of olefins is the best recognized one, and can be explained by the Horiuti-Polanyi mechanism[1a] expounded by other authors.[1b] The mechanism of hydrogenation of polarized double bands such as carbonyl groups has been carefully investigated by Brewster[2] and Augustine.[3] Both these authors, in their mechanistic considerations on hydrogenation of the ketone group in substituted cyclohexanones took into account the influence of the reaction medium on the direction of catalytic reaction.[2,3] The explanation they provide for the formation of axial alcohols in acidic media[2,3] and equatorial alcohols in neutral[2] and basic media[3] is that ketones might be able to accept a proton from the solvent, and the equivalent of a hydride ion from the catalyst, in distinct steps.[2,3]

Investigations on the stereochemistry of catalytic reduction of the ketone group in cyclic six-membered γ-aminoketones have shown that in neutral medium, in the presence of platinum oxide, the reaction of catalytic hydrogenation proceeds easily and unidirectionally only to the alcohols.[4-7]

In water, in the presence of protonic acids the ketone group of these compounds undergoes easy hydrogenolysis in the presence of PtO_2.[4-8] It is postulated that the intermediate products of hydrogenolysis are not alcohols but unstable carbinol ammonium cations.[4-7] In the course of further studies it has been established that proton transfer via the hydrogen bond system of a geminal diol (product of the ketone group hydration in aqueous solutions of strong acids)[6] is the driving force of the hydrogenolysis reaction.[7] In such a situation, the inhibition of proton transfer by changing the reaction medium from water to methanol results in a lack of hydrogenolysis.[7]

Although this mechanistic hypothesis is strongly supported by chemical[5-8] and physical methods (IR, ^{13}C-NMR)[6] and (UV,CD)[9] it still requires further verification.

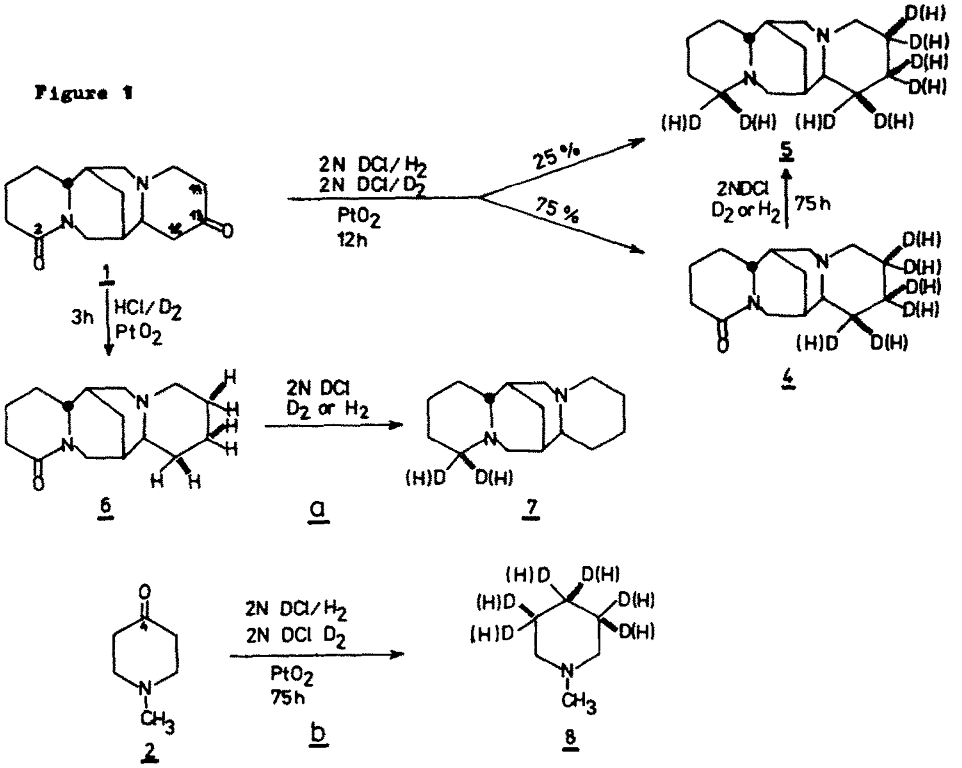
This paper presents the results of experiments in which the reaction of hydrogenolysis has been carried out in three different types of conditions: by deuterium in 2N DCl, hydrogen in 2N DCl and deuterium in 2N HCl.

RESULTS

The main subject of those studies was 2,13-dioxo 6β,11α sparteine (1), suggested by the short time needed for the hydrogenolysis of the ketone group of this compound (1.5 h), as well as by the presence of the lactam group. For comparison, investigations were carried also for 1-methylpiperidone-4 (2) and cyclohexanone (3).

A 12 h catalytic reduction of 2,13-dioxo-6β,11α sparteine (1) by deuterium in 2N DCl, in the presence of PtO_2, yielded a mixture of deuterated products, namely: 2-oxo-6β,11α sparteine (4) and 6β,11α sparteine (5) in ratio of 1:3 (figure 1a).

Figure 1



The replacement of deuterium by hydrogen led to the same mixture of deuterated compounds 4 and 5. When gaseous deuterium and aqueous hydrochloric acid were used, the deuteration did not take place. To gain better insight into the reaction, reduction was also conducted in the following manner: the catalyst was suspended in hydrochloric acid (1 or 2N), saturated with deuterium, and shaken for seven days. Next, aminoketone was introduced. After 12 h of reduction a mixture of undeuterated compounds 4 and 5 was obtained. The above results indicate that the deuteriums which enter into the molecule have their source in the reaction medium, i.e. DCl, and not in the gaseous deuterium. Reduction by gaseous deuterium and aqueous undeuterated hydrochloric acid leads to undeuterated preparations. The mixture of compounds 4 and 5 afforded by the reduction was separated by way of distillation with steam. The resulting pure substances 4 and 5 were analyzed with the help of mass spectroscopy and IR. The complicated image of the molecular ion which in 4 was made up of masses: 250,251,252,253,254, and in 5 of: 237,238,239,240,241,242, indicated that apart from the deuteriums introduced by way of reduction into compounds 4 and 5, the number being 2 and 4 respectively, four hydrogens on α carbons in respect to the carbonyl group were replaced by a deuterium (figure 1a). The IR spectra of compounds 4 and 5 showed the absorption band ascribed to the stretching vibrations of νC-D bonds, in the region of 2000-2200 cm^{-1}. The subtle structure characteristic for this band allowed to distinguish the maxima of absorption, which for compound 4 were: 2200,2185,2165, 2155,2110 cm^{-1}(figure 2a) and for compound 5: 2005,2022,2095,2155,2165 and 2185 cm^{-1} (figure 2b).

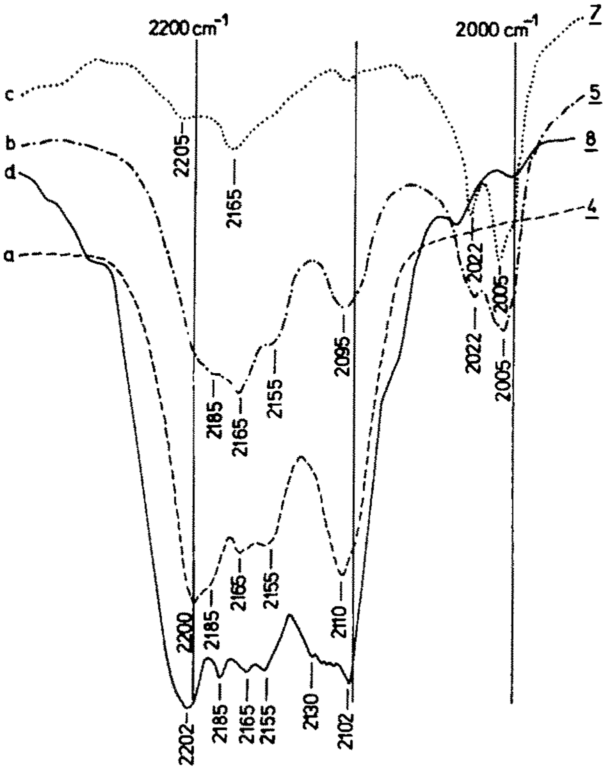


Figure 2

The absorption bands ascribed to the stretching vibrations of νC-D bands of compounds 4,5,7 and 8 performed on a Perkin-Elmer 580 apparatus in 2M $CHCl_3$ solution, in a NaCl cuvette 0.1mm thick, using quintuple enlargement and enforcement.

Compound 4 was further reduced in 2N DCl/H_2, which in 75 h led to compound 5, whereas compound 6 reduced in identical conditions yielded 2^2-dideutero 6β,11α sparteine (7).

Mass spectra exhibited an increase in mass by 2 units as compared with 6β,11α sparteine. From the above it follows that lactam carbonyl had been replaced by two deuteriums. IR spectrum showed two bifurcate absorption bands in the region of the νC-D stretching vibrations; the first band at 2005 and 2022 cm^{-1}, and the second one at 2165 and 2205 cm^{-1} (figure 2c). Deuterated 1-methylpiperidine (8) was the product of reduction in 2N DCl/D_2 or H_2 (in the presence of PtO_2) of 1-methylpiperidone-4 (2) (figure 1b). IR spectrum of 8 (figure 2d) showed in the region of 2100-2300 cm^{-1} the following νC-D bands: 2102,2130,2155,2165,2185 and 2202 cm^{-1}. Mass spectra were furthermore characterized by a complicated structure of the molecular ion. The following masses, pointing to the presence of d_2-d_6-1-methylpiperidine (8) mixture could be distinguished: 101,102,103,104,105 and 106.

Catalytic deuteration of compounds 1,2 and 6 led to deuterated compounds 4, 5 and 7. In order to gain better insight into this mechanism, the replacement of hydrogens by a deuterium in compounds 1,2,3 and 6 in basic (NaOD) and acidic (2N DCl) media, without the use of a platinum catalyst, was traced. The course of the $H \rightleftarrows D$ replacement reaction was followed with the aid of ~10 eV mass spectra, the electron energy just sufficient for the formation of the molecular ion. Scheme 3 shows the molecular peak region in mass spectra of samples taken at different time intervals during 24 h, while the $H \rightleftarrows D$ replacement in 2,13-dioxo $6\beta,11\alpha$ sparteine (1) was under way.

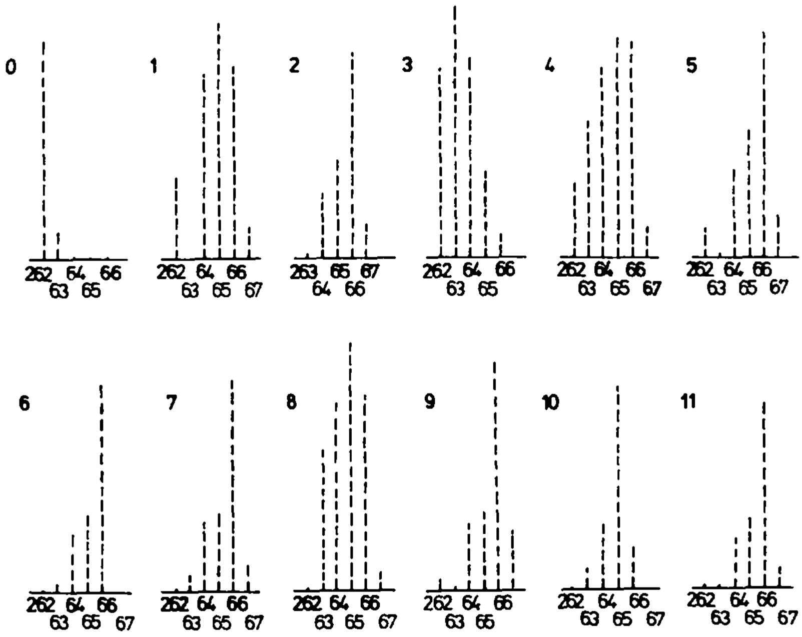


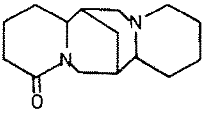
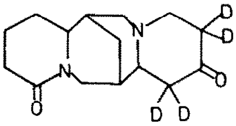
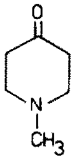
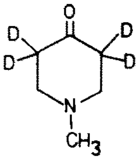
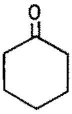
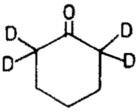
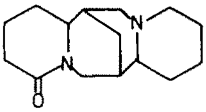
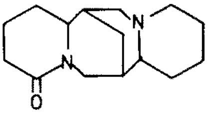
Figure 3

The molecular peak region in mass spectra of samples taken at different time intervals during 24 h, while the $H \rightleftarrows D$ replacement was under way:
1) 15 min, 2) 30 min, 3) 45 min, 4) 60 min, 5) 90 min, 6) 120 min, 7) 150 min, 8) 180 min, 9) 240 min, 10) 270 min, 11) 24 h.

In these spectra the composition of the molecular ion was labile, which testifies that the replacement was very dynamic. Maximum $H \rightleftarrows D$ replacement was observed in samples 2,5,6,7,9, and 11, the corresponding times of replacement being: 30,90,120,150,270 min and 24 h. In all the above mentioned samples a mixture of $12^2,14^2$ d_2-d_4 2,13-dioxo $6\beta,11\alpha$ sparteine in ratio of 0,6:1:2 was present. A similar image of replacement was obtained for compounds 2 and 3, when samples were shaken with 2N DCl. Table 1 gives mass spectroscopy and IR data of the investigated compounds.

The deuterated compounds were mixtures of four, three and two deuteriums. In further investigations it was assumed that the sufficient time of $H \rightleftarrows D$ replacement is 30 min for compounds 1 and 2, and 45 min for compound 3.

Table 1

(1) Compound	Composition of molecular ion (M^+)	Time of replacement (min)	Product	νC–D bands (cm^{-1})
 1	263,264 265,266	30	mixture of d_2-d_4 1 	2220,2130,2120 figure 4a
 2	114,115 116,117	30	mixture of d_2-d_4 2 	2225,2148,2109 figure 4b
 3	99,100 101,102	45	mixture of d_2-d_4 3 	2228,2132 figure 4c
 4	248	24		

In alkaline medium the optimal $H \rightleftharpoons D$ replacement took place after 5 min of shaking γ-aminoketone with NaOD. On the basis of mass spectra as well as the intensity and symmetry of νC–D bands in IR spectra, one can conclude that in the acidic and alkaline mediums the number of deuteriums introduced is identical, and equals four. The products of deuteration constituted a mixture of four, three or two deuterated compounds.

In the case of deuterated 2,13-dioxo 6β,11α sparteine (12^2,14^2 d_2-d_4 1) this composition was confirmed by precise measurements of molecular ion mass, using the high resolution method. Results are collected in Table 2.

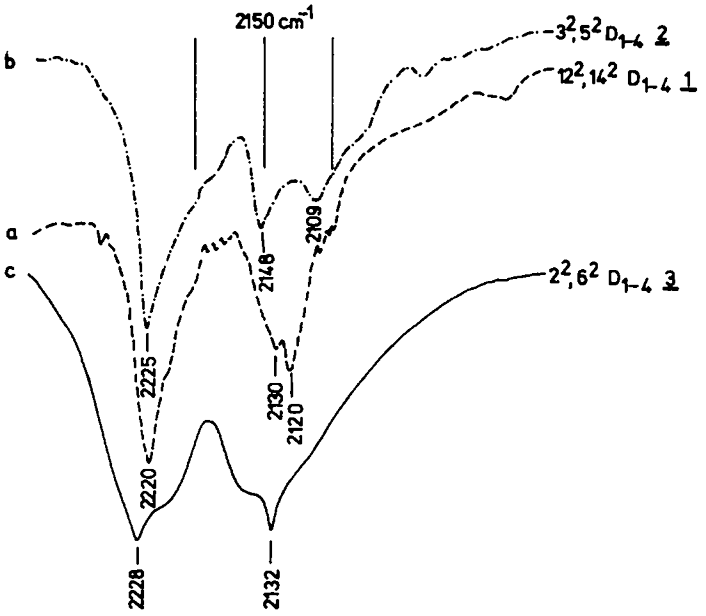


Figure 4

The absorption bands ascribed to the stretching vibrations of ν C–D bands of compounds $12^2,14^2$ d_1–d_4 1, $3^2,5^2$ d_1–d_4 2 and $2^2,6^2$ d_1–d_4 3 performed on a Perkin-Elmer 580 apparatus in 2M $CHCl_3$ solution, in a NaCl cuvette 0.1mm thick using quintuple enlargament and enforcement.

Table 2

Molecular formula	Mass of molecular ion	Mass		Mean intensity
		measured	calculated	
$C_{15}H_{22}N_2O_2$	262	262.16676	262.16800	0.0001
$C_{15}H_{21}N_2O_2D$	263	263.17141	263.17182	0.01
$C_{15}H_{20}N_2O_2D_2$	264	264.17733	264.17762	0.6
$C_{15}H_{19}N_2O_2D_3$	265	265.18528	265.18444	1
$C_{15}H_{18}N_2O_2D_4$	266	266.19171	266,19226	2

Compound $12^2,14^2$ d_2–d_4 1, which has been given a precise spectral characteristic, was subjected to catalytic reduction with hydrogen in 2N HCl, in the presence of PtO_2.
IR and MS spectra testify that after 1.5 h of shaking the ketone group underwent reduction in 100%. However, deuteriums remained unaffected. The molecular ion was made up of masses ranging from 249 to 252 respectively, from which it follows that the compound is a mixture of $12^2,14^2$ d_2–d_4-2-oxo-6β,11α sparteine.

In turn, from the determined weight of the molecular ion it appears that the number and intensity of deuteriums in the compound after reduction are the same as before it Table 3 .

Table 3

Molecular formula	Mass of molecular ion	Mass		Mean intensity
		measured	calculated	
$C_{15}H_{24}N_2O_2$	248	248.1855	248.18873	0.000
$C_{15}H_{23}N_2O_2D$	249	249.19121	249.19155	0.01
$C_{15}H_{22}N_2O_2D_2$	250	250.19815	250.20037	0.6
$C_{15}H_{21}N_2O_2D_3$	251	251.2044	251.20219	1
$C_{15}H_{20}N_2O_2D_4$	252	252.21055	252.21001	2

In the 2250–2000 cm^{-1} region the IR spectrum exhibits a broad band attributed to the νC–D stretching vibrations, with distinct maxima at 2190, 2150, and 2105 cm^{-1} (figure 5b).

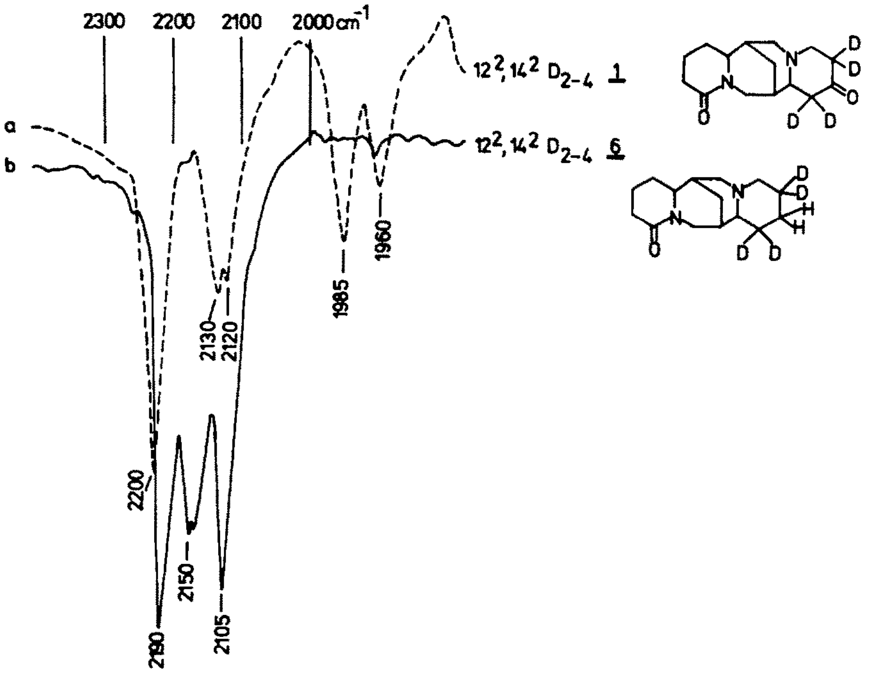


Figure 5

The absorption bands ascribed to the stretching vibration of νC–D bands of compounds $12^2,14^2$ d_2–d_4 1 and $12^2,14^2$ d_2–d_4 6 performed on a Perkin-Elmer 580 apparatus in 2M $CHCl_3$ solution, in a NaCl cuvette 0.1mm thick, using quintuple enforcement.

As appears from the above data D ⇄ H replacement proceeds much more slowly than hydrogenolysis of the ketone group and the H ⇄ D replacement, the latter taking place already after 30 min. To gain more precise information about the time of D ⇄ H replacement, compound $12^2,14^2$ d_2–d_4 1 was dissolved in 2N HCl and shaken for 24 h. Samples were taken every 30 min., and analysed on a mass spectrometer at ~10 eV. (figure 6). From the structure of molecular ions it could be seen that in the first 2.5 h no noticable replacement of the D ⇄ H type occurred. After 3.5 h of shaking with 2N HCl the molecular ion of the analysed sample consisted of the following masses: 262,263,264,265. This leads to the statement that the preparation with the highest degree of deuteration possesses only three deuterium atoms. After additional 1.5 h of shaking with acid, the $D \rightleftarrows H$ replacement was practically completed. In the molecular ion only masses 262 and 263 could be observed (figure 6).

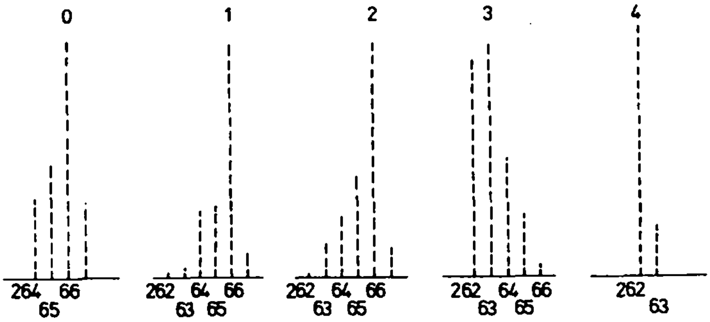


Figure 6

The molecular peak region in mass spectra of samples taken at different time intervals during 5 h, while the $D \rightleftarrows H$ replacement in $12^2,14^2$ d_2-d_4 1 was under way:
1) 1 h, 2) 2.5 h, 3) 3.5 h, 4) 5 h.

DISCUSSION OF RESULTS

In investigations on the mechanism of hydrogenolysis of the ketone group in cyclic six-membered γ-aminoketones, it has been assumed that in the intermediate product, i.e. the carbinol ammonium cation while it is being formed, the N-C and C-O bonds undergo hydrogenetic break-up on contact with the catalyst. In heterogenous catalysis of organic compounds two types of reactions have to be taken into consideration:

a reactions on the surface of the catalyst
b reactions in the gas or liquid phase.

However, ionic processes may involve also a third type of reaction, namely - in the double electrical layer formed at the interface of the catalyst and the solution.[10]

In the case of reaction which proceeds on platinum catalyst in aqueous solution of hydrochloric acid one can presume that the hydrogen adsorbed on the surface of the catalyst behaves like a reversable electrode. The platinum electrode itself does not participate in the reaction, but only facilitates the exchange of electric charges according to the equation:

$$\frac{1}{2}\,H \rightleftarrows H^{+} + \bar{e}$$

Protons may undergo transfer to solution or the catalytic process of discharge in accordance with the equation:

$$H^{+} + \bar{e} \rightleftarrows H\cdot$$

This situation is similar to electrochemical reduction on low overvoltage metal (metals of periodic group 8 and the subgroup 1). In the instance of heterogenous catalysis the way in which the produced electron reaches the molecule has to be taken under consideration.

Due to the negative charge on the surface of the catalyst, and the presence of protons in the surrounding layer, i.e. in the solvent, a double electrical layer is formed at the interface of the solution and the solid.[10] Therefore, one can imagine that the surface of the catalyst possesses a negative potential sufficient, with regard to the solution, to cause transition of a few electrons to the acceptor molecule. Theoretical studies have shown, that transfer of electron to the acceptor molecule may take place via solvent layer with the assistance of the tunnelling effect.[11] On the basis of this picture, the mechanism for catalytic hydrogenolysis of N-C and C-O bonds in a carbinol ammonium cation can be proposed.

In this cation, protonation of the hydroxyl group results in the formation of a double cation, which approaches the negatively charged catalyst. Four electrons are transferred successively from the catalyst surface to the acceptor molecule. In consequence, the water molecule is eliminated, the N-C bond is broken and the solvated double charged anion is formed. The addition of two protons successively from the reaction medium by the negatively charged molecule leads to the formation of an amine.

According to this mechanistic hypothesis based on experimental data, two and only two hydrogens, originating from the reaction medium, are introduced into the reduced molecule on hydrogenolysis of the ketone group in the investigated γ-aminoketones.

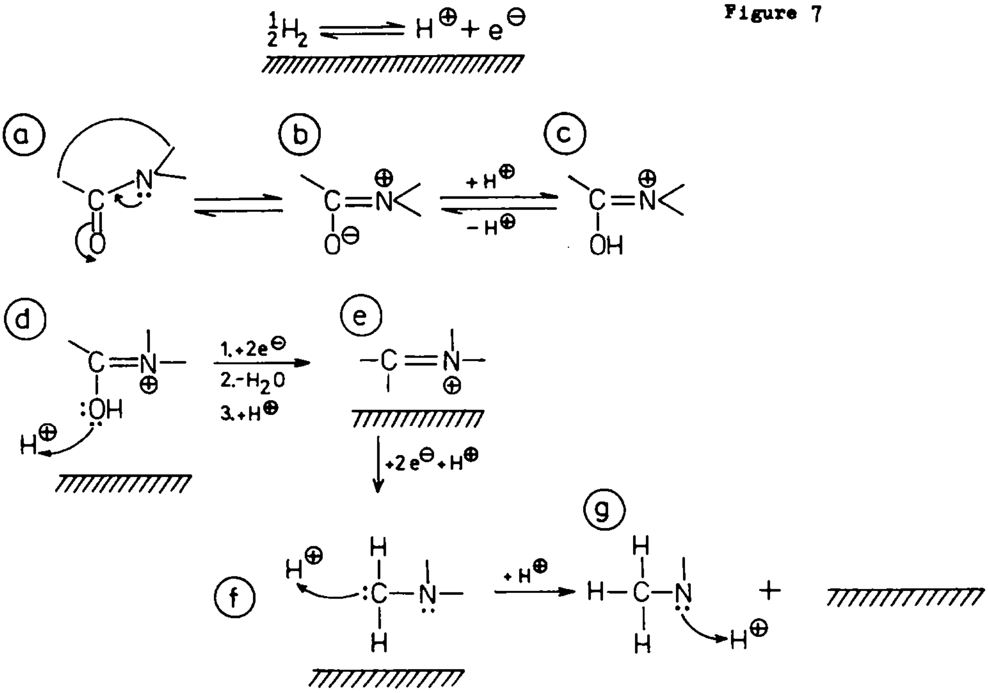
Hydrogenolysis of the lactame group in cyclic α-aminoketones is a much slower process than the hydrogenolysis of the ketone group in γ-aminoketones. Depending on the conditions, the reduction proceeds as follows:

Table 4

Compound reduced	Reaction medium	Time of reduction (h)	Product
4	2N HCl/H_2	75	6β,11α sparteine
	2N DCl/D_2	300	5
	2N DCl/H_2	143	5
9	2N HCl/H_2	80	N-methylpiperidine
	2N DCl/D_2	240	2^2-dideuteropiperidine
	2N DCl/H_2	160	2^2-dideuteropiperidine

The reaction medium is the source of the deuterium both in 2-oxo 6β,11α sparteine (6), and N-methylpiperidine-2 (9). Therefore, one can suppose that the mechanism of heterogenous catalysis of cyclic α-aminoketones is ionic in character and proceeds in a manner similar to the mechanism of hydrogenolysis of the ketone group in γ-aminoketones. For α-aminoketones it has to be accepted that in the aqueous medium in the presence of strong acids, it is the hydroxy immonium cation and not the free lactame group which undergoes reduction (figure $7a \rightleftarrows b \rightleftarrows c$).

Figure 7



As a result of protonation of the hydroxyl group in a hydroxy immonium cation, a hydronium immonium dication is formed (figure 7d), which will be strongly attracted to the negatively charged surface of the catalyst. Within several Å from the surface of the acceptor molecule two electrons will be supplied successively. This in turn will lead to the elimination of the water molecule and an intantenous stabilization of the newly formed zwitterion by the addition of one proton from the reaction medium (figure 7e). When two further electrons from the surface of the catalyst are supplied, the bond is broken, and a pair of electrons is transferred to the nitrogen atom. Consequently, a solvated double ion is established (figure 7f). This anion will be strongly repelled from the negatively charged catalyst surface towards the mass of the solvent. The addition of another proton from the reaction medium affords an amine (figure 7g).

To have a better understanding of the cyclic lactams reduction process also $\Delta^{1,6}$ dehydrosparteine was subjected to reduction in 2N DCl in the presence of hydrogen. The yield was 2^2 d_1-d_2 dideutero 6β,11α sparteine. The reduction of this compound takes 140 h, which is comparable with the reduction time of 2-oxo-6β,11α sparteine (6) in 2N DCl/H_2. It follows from the above that the elimination of the water molecule from 2-oxo 6β,11α sparteine (6) proceeds rapidly (3 h), and that the reduction of the immonium cation is the rate determinning step.

EXPERIMENTAL

2,13-dioxo $6\beta,11\alpha$ sparteine (1) was obtained via oxidation of 2-oxo-13-hydroxy $6\beta,11\alpha$ sparteine according to the method previously described.[12]

1-methylpiperidone-2 (9): commercial product of Aldrich.

1-methylpiperidone-4 (2): commercial product of Aldrich, purified by way of vacuum distillation (70-72°/17mm Hg).

Cyclohexanone: commercial product from Gliwice, analytically pure, purified via distillation.

PtO_2: commercial product of Anachemia, Montreal, Canada.

$\Delta^{1,6}$ dehydrosparteine was obtained according to the method previously described.[13]

Mass spectra were performed on a Jeol MS100 spectrophotometer at 10 or 70 eV. Mass of molecular ions in compounds $12^2,14^2$ d_2-d_4 1 and $12^2,14^2$ d_2-d_4 4 were determined at high resolution, R=7500. IR spectra in the region of the γC-D band were performed on a Perkin-Elmer 580 apparatus in 2M chloroform solutions, in a NaCl cuvette 0.1 mm thick using quintuple enlargement and enforcement. Gas deuterium was obtained from D_2O with the aid of lithium, in the following manner. 5 g of lithium were fractionated with a hammer into thin sheets, which in turn were cut with scissors into small pieces and washed with gasoline to remove remnants of paraffin oil. The lithium was then placed in a 250 ml flask containing 100 ml of dioxane. On stirring the contents of the flask with a magnetic stirrer, 10 ml of D_2O were instilled at the rate of 0.2 ml/min. The deuterium was collected through a system of two conjoint glass balloons (the gas deuterium forced the water from one glass balloon into the other). The total product afforded by 10 ml of D_2O was 6 l of deuterium.

Thin layer chromatography (TLC) was performed on plates covered with silica gel (Merck). Spots were made visible by the Dragendorff reagent. For spot development the following phases were used:

1 chloroform - ethanol 3:2 V/V, (system A)
2 acetone - methanol - NH_4OH 10:10:1 V/V, (system B)

Reduction was carried out in a simple glass apparatus under hydrogen or deuterium pressure with a possibility of measuring the quantity of deuterium or hydrogen used up.

Drying of glass. Glass was dried for 25 h at 250°, then flushed with D_2O and dried under vacuum (0.2 mm Hg) heated up to 250°.

Catalytic reduction of 2,13-dioxo-$6\beta,11\alpha$ sparteine (1) leading to the deuterium mixture of d_6-2-oxo-$6\beta,11\alpha$ sparteine 4 and d_8-$6\beta,11\alpha$ sparteine (5).

10 ml of 2N DCl were dissolved in 2N DCl/D_2 PtO_2 : 0.5 g 1 and placed in a flask containing a magnetic stirrer and 0.05 g of platinum black suspended in 5 ml of 2N DCl (obtained from the reduction of PtO_2). After 12 h of reduction with deuterium (when traces of 1 disappeared on the plates) the platinum was filtered off, and 6 ml of dioxane and a piece of NaOH were added to the solution. The whole was shaken and the organic layer was separated from the aqueous. The dioxane solution was dried with NaOH and evaporated dry under vacuum. The product 0.495 g was a mixture of 5 and 4 in ratio of 1:3 (5:4).

b in 2N DCl/H_2 PtO_2

0.5 g of 1 was reduced under hydrogen pressure in conditions as in point a . 0.491 g of a mixture of compounds 5 and 4 in ratio of 1:3 was obtained.

Separation of a mixture of compounds 5 and 4 via distillation with steam. 0.45 g of a mixture of 5 and 4 was dissolved in 5 ml of distilled water, and subjected to distillation with steam. The water solution was made alkaline, extracted with Et_2O and dried with NaOH. After ether had been evaporated, 0.095 g of pure compound 5 (d_8-$6\beta,11\alpha$-sparteine) was obtained. M^+ 234-242. The residue in the flask, which did not distillate with steam was made alkaline, extracted with petroleum. After drying NaOH and distilling off the petroleum, 0.292 g of substance 4 (d_6-2-oxo-$6\beta,11\alpha$ -sparteine) was obtained. M^+ 248-252.

Reduction of 2-oxo-$12^2,13^2,14^2$ d_2-d_6 $6\beta,11\alpha$ sparteine(4) leading to $2^2,12^2,13^2,14^2$ d_2-d_8 $6\beta,11\alpha$ sparteine (5).

in 2N DCl/H_2: 0.5 g of 4 was dissolved in 10 ml of 2N DCl and added to a 25 ml flask containing 0.05 g of PtO_2. After 143 h of reduction the product was isolated as in point 1a. As a result 0.495 g of 5 was obtained.

The base-catalyzed and acid-catalyzed exchange hydrogens on α carbons to the ketone group in compounds 1,2 and 5.

a via acidic catalysis: 0.1 g of ketone was stirred with 5 ml of 2N DCl for 30-45 min, then was made alkaline with solid NaOH and extracted with dry CH_2Cl_2. After separation the layer of CH_2Cl_2 was dried with dry Na_2SO_4 and distilled off in vacuum. The substance was analyzed with the help of mass and IR spectra.

b via basic catalysis: 0.1 g of the substance was dissolved in 5 ml of CH_2Cl_2 and shaken for 10 min with 5 ml of D_2O containing 1 scale of NaOH. After separation from the aqueous layer the layer of CH_2Cl_2 was shaken with D_2O. When the aqueous layer was separated from the organic one, the solution of CH_2Cl_2 was dried in Na_2SO_4 and evaporated off. The obtained product was analyzed with the help of mass and IR spectra.

Catalytic reduction of 2,13-dioxo-$12^2,14^2$ d_2-d_4 $6\beta,11\alpha$ sparteine leading to 2-oxo-$12^2,14^2$ d_2-d_4 $6\beta,11\alpha$ sparteine.
0.5 g of substance $12^2,14^2$ d_2-d_4 1 was dissolved in 10 ml of 2N HCl and added to a 25 ml flask containing 0.05 g of reduced PtO_2 suspended in 5 ml 2N HCl. The whole was reduced with hydrogen. After 2 h of reduction (no traces of $12^2,14^2$ d_2-d_4 1 on plates with SiO_2) the catalyst was filtered off. The acidic solution was then made alkaline with NaOH and extracted with petroleum. The obtained 0.49 g of substance was characterized with the aid of mass and IR spectra as a mixture of 12^2, 14^2 d_2-d_4 2-oxo,$6\beta,11\alpha$ sparteine.

Catalytic reduction of 2-oxo,$6\beta,11\alpha$ sparteine.
a in 2N DCl/D_2
0.248 g of lupanine (6) was dissolved in 20 ml of 2N DCl to which 25 mg of PtO_2 were added. The whole was exhaustively reduced. After 300 h total disappearance of 6 on thin-layer plates was observed. Platinum was filtered off, the filter was made alkaline with solid NaOH and extracted with CH_2Cl_2. The solution of CH_2Cl_2 was dried and condensed until dry. The obtained 0.225 g of oily product was characterized on the basis of IR and mass spectra as d_1-d_2 $6\beta,11\alpha$ sparteine.
b in 2N HCl/D_2
0.248 g of 6 was dissolved in 20 ml of 2N HCl, 25 mg of PtO_2 were added, and the whole was exhaustively reduced. After 200 h, the disappearance of 6 on the plates was observed. When the product of reaction was processed as in point a, 0.220 g of an oily substance, characterized as $6\beta,11\alpha$ sparteine was obtained.
c in 2N DCl/H_2
0.248 g of 6 was dissolved in 20 ml of 2N DCl, 25 mg of PtO_2 were added, and the whole was reduced with hydrogen. After 193 h a complete disappearance of 6 on thin-layer plates was observed. When the product was processed as in point a, 0.221 g of oil, characterized as d_1-d_2 $6\beta,11\alpha$ sparteine was obtained.

Catalytic reduction of $\Delta^{1,6}$ dehydrosparteine in 2N DCl/H_2.
0.150 g of $\Delta^{1,6}$ dehydrosparteine was dissolved in 10 ml of 2N HCl, 15 mg of PtO_2 were added and the whole was reduced with hydrogen. After 140 h of reduction a complete disappearance of the initial product was observed. The product of reduction was processed as in point 6a. As a result d_1-d_2 $6\beta,11\alpha$ sparteine was obtained.

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