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SOLID STATE KETO-ENOLIC TAUTOMERIZATION

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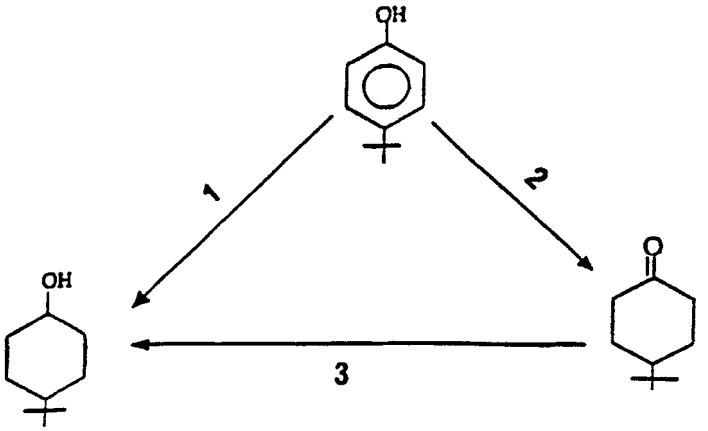
Abstract Deuteration of solid 4-tert-butylcyclohexanone is studied to clarify solid state hydrogenation mechanisms of phenolic compounds. The deuterium incorporation in the carbonyl linkage and in the alicyclic ring, followed by a statistical method, allows one to consider in the solid state the existence of two types of carbonyl intermediates. Ketonic and or enolic forms are involved in the solid state hydrogenation and deuteration.

Keywords: keto-enol tautomerization, solid state reaction, deuterium labeling, solid state hydrogenation

INTRODUCTION

In previous work dealing with comparative study on the isomeric distribution obtained during catalytic hydrogenation of both solid 4-tert-butylphenol and 4-tert-butylcyclohexanone, we have reported that the solid state hydrogenation process of a phenol occured in two distinguished steps, depending on the nature of the solid catalyst[1]. When rhodium catalysts are used the *cis* and *trans* 4-tert-butylcyclohexanol are directly obtained , the *cis* isomer is mainly formed. When platinum catalysts are used, a ketonic intermediate is observed and the *trans* alcohol is mainly formed.



SCHEME 1 : Solid state hydrogenation process

In an attempt to gain some insight into the mechanism of solid state hydrogenation of phenolic compounds we have studied the deuteration of solid 4-tert-butylcyclohexanone in presence of rhodium and platinum catalysts. Deuteration of the ketonic intermediate, followed by a statistical method affords information about the deuterium incorporation on the carbonyl linkage and into the alicyclic ring. The localization of the deuterium atoms allows us to understand how the solid state hydrogenation occurs, and it clarifies the role of the ketonic intermediate on the imomeric distribution of the reaction products.

EXPERIMENTAL

The reaction is carried out with 4-tert-butylcyclohexanone powder (m.p. 47 °C). Rh/Al_2O_3, Rh/C and Pt/C are used as catalysts and mixed with 4-tert-butylcyclohexanone powder in the proportion of 10 % by weight. The reaction temperature is 20 °C deuterium pressure is kept at 1 bar during reaction. Analysis of the products is performed with mass spectrography coupled with gas chromatography.

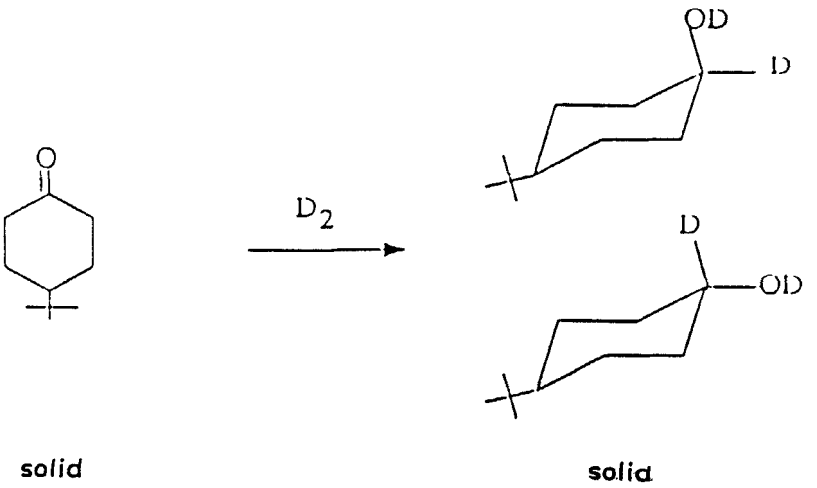


FIGURE 1 : Solid state deuteration of 4-tert-butylcyclohexanone

The distribution of deuterium atoms is evaluated by using a statistical method suggested by HIROTA[2] and applied by AUGUSTINE[3] and TAKAGI[4]. The distribution is calculated from the mass spectrum fragmentation of the two alcohols. The isotopic distribution is given by dn :

$$dn = \frac{n!}{(N - n)\,!\,n!}(x)^n (1 - x)^{N - n}$$

N : Number of hydrogen atoms in the cycle
n : Number of deuterium atoms in the fragment
x : Mean atomic fraction of deuterium atoms in the fragment.

RESULTS AND DISCUSSION

Deuteration of the 4-tert-butylcyclohexanone leads to a solid mixture of the *cis* and *trans* isomers with a good yield. As shown in table 1 the cis/trans ratio depends on the nature of the catalyst. As with hydrogenation, the deuteration in presence of rhodium catalysts leads to the *cis* isomer mainly, and in presence of platinum catalysts the *trans* isomer is mainly formed. The mechanism of both solid reactions, seems to be similar[5].
Molecular fragmentations of the alcohols obtained from mass spectrometry analysis are listed in table 2 and 3. The percentage of the incorporated deuterium atoms is calculated for each fragment.

TABLE 1 - Deuteration of 4-tert-butylcyclohexanone

Catalysts	Conversion %	*cis/trans*
Rh/Al_2O_3	78	1,6
Rh/C activited	98	6,5
Pt/C	99	0,5

TABLE 2 : Fragmentation of the *cis* deuterated alcohol

Pt/C			Rh/C		
m/e	%	Fragmentation	m/e	%	Fragmentation
29	14,46	C_2H_5	29	25,44	C_2H_5
41	82,83	C_3H_5	41	92,81	C_3H_5
57	100,00	C_4H_9 (t.Bu)	57	100,00	C_4H_9 (t.Bu)
68	30,87	C_5H_6D	68	30,73	C_5H_6D
82	28,26	C_6H_8D	82	26,8	C_6H_8D
99	6,36	$C_7H_{11}D_2$	99	4,16	$C_7H_{11}D_2$
124	3,47	$C_9H_{12}D_2$	124	2,17	$C_9H_{12}D_2$
142	2,11	$C_{10}H_{18}D_2$	142	2,84	$C_{10}H_{18}D_2$
157	0,91	$C_{10}H_{17}D_2$ (M-1)	57	1,11	$C_{10}H_{17}D_2$ (M-1)

Rh/Al_2O_3

m/e	%	Fragmentation
29	62,47	C_2H_5
41	100,00	C_3H_5
57	81,83	C_4H_9 (t.Bu)
68	22,81	C_5H_6D
82	17,87	C_6H_8D
99	14,20	$C_7H_{11}D_2$
124	5,64	$C_9H_{12}D_2$
142	2,01	$C_{10}H_{18}D_2$
157	0,41	$C_{10}H_{17}D_2$ (M-1)

TABLE 3 : Fragmentation of the *trans* deuterated alcohol

Rh/C

m/e	%	Fragmentation
29	27,14	C_2H_5
41	100,00	C_3H_5
57	95,25	C_4H_9 (t.BU)
68	22,13	C_5H_6D
82	33,13	C_6H_8D
99	4,84	$C_7H_{11}D_2$
124	10,62	$C_9H_{12}D_2$
139	6,75	$C_{10}H_{16}D_2$ (M-19)

Pt/C

m/e	%	Fragmentation
29	29,10	C_2H_5
41	80,14	C_3H_5
57	100,00	C_4H_9 (t.Bu)
68	22,83	C_5H_6D
82	31,36	C_6H_8D
99	6,18	$C_7H_{11}D_2$
124	13,25	$C_9H_{12}D_2$
139	9,18	$C_{10}H_{16}D_2$ (M-19)

Rh/Al_2O_3

m/e	%	Fragmentation
29	55,97	C_2H_5
41	100,00	C_3H_5
57	95,79	C_4H_9
68	16,08	C_5H_6D
82	18,10	C_6H_8D
99	7,54	$C_7H_{11}D_2$
124	6,12	$C_9H_{12}D_2$
139	4,45	$C_{10}H_{16}D_2$ (M-19)

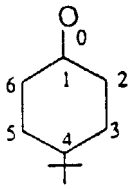
For both alcohols, the isotopic abundance is predominant for the m/e = 68 and 82 peaks. These peaks, according to the literature correspond to the molecular

fragment containing the carbons 1 and 2 of the ketonic ring. The (M-1) peak is present in the *cis* isomer mass spectrum, and not detectable in the *trans* isomer spectrum. The fragments (M-1) for the *cis* alcohol and (M-19) for the *trans* alcohol are considered as bearing the carbonyl group. In table 4, we give the statistical distribution of the deuterium atoms in each obtained fragment. d_0, d_1, $d_{2,6}$, $d_{3,5}$ represent the deuterium distribution for atoms of the ketonic cycle.
These results are in agreement with those found by TAGAKI[4] for the same compounds in the liquid state.

TABLE 4 : Statistical distribution of deuterium for *cis* and *trans* alcohols.

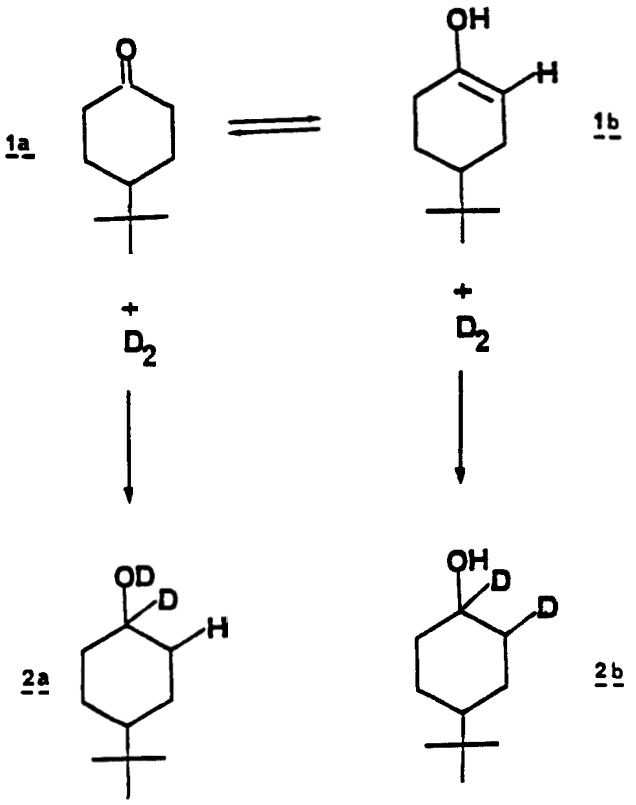
Catalysts	*cis/trans*	isomers	d_0	d_1	$d_{2,6}$	$d_{3,5} + d_4$
Rh/Al_2O_3	1,6	*cis*	30,1	37,1	26,4	6,4
		trans	27,6	37,1	26,4	8,9
Rh/C activated	6,5	*cis*	30,1	37,1	26,4	6,4
		trans	26,3	37,1	26,4	11,2
Pt/C	0,5	*cis*	30,1	37,1	26,4	6,4
		trans	26,3	37,1	26,4	11,2

The carbon atoms are numbered as follows



The interpretation of these results permit us to consider that the deuterium addition to the carbonyl linkage is more or less accompanied by deuterium incorporation into the ketonic cycle, especially into the positions 2 and 6 (scheme 3).
So we could consider that in the solid state ketone and alcohol compete to give a

keto-enolic tautomerization and that the addition reaction occurs as well on a ketonic (**1a**) as on a enolic (**1b**) form.

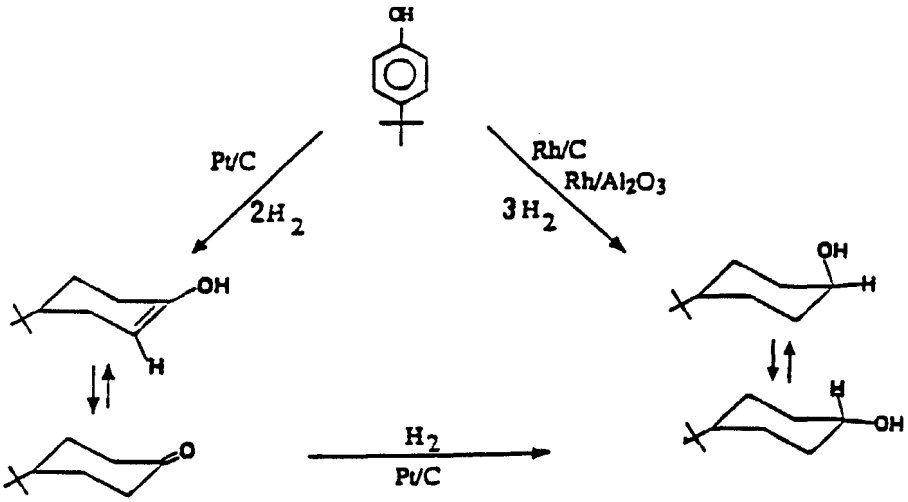


SCHEME 3 : Keto-enolisation mechanism

CONCLUSIONS

Deuterium reacts in mild conditions with the carbonyl linkage of the solid 4-tert-butylcyclohexanone. The incorporation of deuterium atoms on the alicyclic ring, especially in the position 2 or 6 shows the possibility of a keto-enolic tautomerization in the solid state.

The stereoisomeric distribution (*cis/trans*) of solid state hydrogenation of phenol will be dependent on the ketonic intermediate and of its tautomerization. The solid state hydrogenation of solid 4-tert-butylphenol can be represented by the following steps (scheme 4).



SCHEME 4 : Solid state hydrogenation mechanism

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