

## Alumina: Catalyst and Support. XL (1) Ring Expansion During the Dehydration of Alcohols Over Alumina Catalysts (2)

HERMAN PINES AND STANLEY M. BROWN

*The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry,  
Northwestern University, Evanston, Illinois 60201*

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An investigation of ring expansion during the alumina-catalyzed dehydration of alcohols was made by the micro-pulse technique. The dehydration at 380°C over fresh alumina of cyclobutane-, cyclopentane-, cyclohexane-, and cycloheptane-methanol yielded 99, 55, 7, and 6% of ring-expanded product, respectively, whereas over alumina which has been deactivated by passing large quantities of alcohol over it, 100, 74, 19, and 18% of the ring-expanded products were found. The stereochemical aspects of this catalytic reaction were investigated by the dehydration of *cis*- and *trans*-4-*t*-butylcyclohexanemethanol. More ring expansion and a higher conversion to olefins occurred in the dehydration of the *cis* alcohol than of the *trans* alcohol. In the dehydration of 1-methyl-1-cyclohexanemethanol at 310°C, 60% of product formation involved methyl migration whereas 40% involved ring expansion. The percentage of ring expansion increased to 55 when deactivated catalyst was used. More skeletal rearrangement was found in dehydrations over alumina which had been deactivated by passing either an unsaturated or a saturated hydrocarbon over it than when fresh catalyst was used. Although the presence of sodium ions or pyridine on the catalyst lowered the amount of double bond isomerization which occurred, it did not affect the amount of skeletal rearrangement or the deactivation of the catalyst. The dehydration of 2-methylpropanol over alumina catalyst was reinvestigated and it was found that the extent of skeletal isomerization to produce *n*-butenes increases with the deactivation of the aluminas.

### INTRODUCTION

Early in this century, the dehydration of cyclobutanemethanol by oxalic acid at 170°C was reported to yield cyclopentene in addition to methylenecyclobutane (3). Similarly, the dehydration of cyclohexanemethanol yielded cycloheptene and methylenecyclohexane (4). In the 1920's, the dehydration of cyclobutanemethanol and cycloheptanemethanol over alumina was found to yield cyclopentene (5, 6) and cyclooctene (7), respectively.

The alumina catalyzed dehydration of tetrahydrofurfuryl alcohol (8) and tetrahydropyran-2-methanol (9) gave the ring

expanded products dihydropyran and 2,3,4,5-tetrahydrooxepine, respectively. For comparison with this work, Misono *et al.* dehydrated cyclohexanemethanol over various aluminas at 280-410°C. They found methylenecyclohexane and 1-methylcyclohexene but no cycloheptene.

Kotani *et al.* found ring expansion in studies of the pyrolysis (10, 11), oxalic acid dehydration (11), and Demjanov rearrangement (12, 13) of cyclohexanemethyl and 1-methylcyclohexanemethyl systems. Mori (14) studied the solvolysis of *cis*- and *trans*-4-*t*-butylcyclohexanemethyltosylate in acetic acid and ethanol.

This study of the alumina-catalyzed dehydration of cyclobutane-, cyclopentane-, cyclohexane-, and cycloheptanemethanol was made to investigate the effect of aluminas and the effect of ring strain on the product distribution. To better understand the stereochemical requirements of this catalytic reaction, *cis*- and *trans*-4-*t*-butylcyclohexanemethanol were dehydrated. A comparison of the migratory aptitude of methyl and ring methylene groups was made from the dehydration of 1-methyl-1-cyclohexanemethanol.

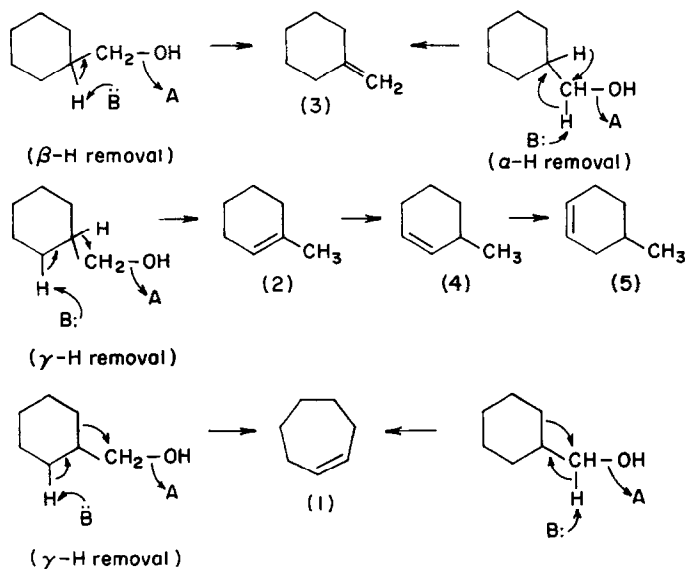
### PROCEDURE

Dehydrations over 2-35 mg of alumina of various mesh sizes were studied using

### RESULTS AND DISCUSSION

#### I. Dehydration of Cyclohexanemethanol Over Fresh Alumina—Effect of Diffusion and of Intrinsic Acidic Sites

Extrapolation to zero conversion of plots of the product composition from the dehydration of this alcohol over pure alumina, which has been in contact with less than 100  $\mu$ l of alcohol solution at 310°C, 360°C (Fig. 1) and 410°C, indicates that approximately 3% of cycloheptene (1), at least 48% of 1-methylcyclohexene (2), less than 48% of methylenecyclohexane (3), and a few percent of 3- (4) and 4-methylcyclohexene (5) was formed. Formation of the products can be pictured as follows:



a microreactor directly attached to a gas chromatograph (15), according to the procedure described previously (1, 16). Injections of 10 to 25  $\mu$ l of solutions of alcohol, internal standard, and in some cases solvent were made by syringe into the reactor through which helium or hydrogen flowed at a rate of 80 ml/min. Olefinic products could be hydrogenated by placing palladium on charcoal catalyst between the reactor and chromatograph.

The B: and A designate the intrinsic basic and acidic sites of the aluminas (16, 17).

Gil-Av and Shabtai (18) reported the equilibrium mixture at 250°C consisting of 62.9 (2), 16.5 (4), 18.8 (5), and 1.8% (3). Isomerization of methylenecyclohexane (3) would be fast since protonation leads to a tertiary carbonium ion. Therefore, due to the ease of ion formation and the equilibrium being so much in favor

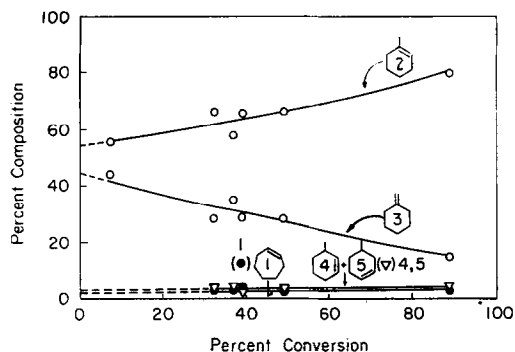


FIG. 1. Dehydration of cyclohexanemethanol over alumina at 360°C.

of the *endo*-cyclic olefins, a large amount of isomerization is possible.

Less of product (3) was found at the higher temperatures where isomerization is more likely to occur. When pure methylcyclohexane or mixtures of the olefin with *t*-butyl alcohol were injected over the catalyst, isomerization to 1-methylcyclohexene was found. Whereas no isomerization of (2) or (3) to (1) was found, some isomerization of (1) to (2) and (3) was detected. Therefore, the percentage of (1) formed as primary product may actually have been slightly larger than indicated by the observed product distribution.

The dehydration of cyclohexanemethanol in the presence of pyridine over alumina which had been treated with pyridine (Table 1), yielded a larger *exo*-cyclic : *endo*-cyclic olefin ratio than that found from the extrapolated values of product distribution from plots such as Fig. 1. Pyridine therefore seems to inhibit the double bond migration.

A possible diffusion effect was investigated by comparing the results of dehydration over alumina of 80/100 and 20/40 mesh size (Table 1). At each temperature, dehydrations over 2.2 mg of 80/100 mesh alumina gave a higher *exo*-cyclic : *endo*-cyclic olefin ratio, although not as high as with pyridine treated 20/40 mesh catalyst. A diffusion effect, therefore, was shown to exist.

Dehydrations in the presence of pyridine over pyridine-treated 80/100 mesh alumina produced higher *exo*-cyclic : *endo*-cyclic olefin ratios than over untreated 80/100

TABLE 1  
DEHYDRATION OF CYCLOHEXANEMETHANOL  
OVER VARIOUS ALUMINAS

Catalyst <sup>a</sup>	% Conversion	% Composition of the dehydrated product	
		(2 + 4 + 5)	(3)
310°C			
A	0	50.0	50.0
B	8.1	28.0	72.0
C	4.1	38.4	61.6
D	21.5	39.6	60.4
E	1.7	27.8	72.2
360°C			
A	0	54.5	45.5
B	17.9	34.7	65.3
C	12.8	46.3	53.7
D	43.4	64.2	35.8
E	8.0	37.5	62.5
410°C			
A	0	66.7	33.3
B	28.0	56.5	43.5
C	34.7	56.1	43.9
D	62.0	72.2	27.8
E	7.9	37.2	62.8
F	1.0	25.7	74.3
G	4.6	29.5	70.5

<sup>a</sup> A, 20/40 mesh; results extrapolated to 0% conversion. B, 6 mg pyridine-treated and with pyridine in solution, 20/40 mesh. C, 2.2 mg, 80/100 mesh. D, 6 mg, 80/100 mesh. E, 2.2 mg pyridine-treated and with pyridine in solution, 80/100 mesh. F, 6 mg alumina containing 0.4% Na<sup>+</sup>. G, 35 mg alumina, same as in F.

mesh catalyst. At 310 and 360°C pyridine treatment eliminated the diffusion effect. In all of these experiments, the lower *exo*-/*endo*-cyclic olefin ratio which was found as the temperature was raised was probably due to increasing amounts of isomerization.

The highest *exo*-cyclic : *endo*-cyclic olefin ratio was obtained when cyclohexanemethanol was dehydrated at 410°C over an alumina impregnated with 0.4 wt % sodium ions.

It can thus be concluded from Table 1 that the dehydration yields at least 74% of (3) as primary product, which quickly undergoes double bond isomerization to (2).

This dehydration study indicates that conclusions as to the true initial product

distribution cannot be made solely on the basis of extrapolation to zero conversion in product composition *vs* conversion plots. It is possible that much isomerization occurs in the region of 0–2% conversion.

Furthermore, injection of an olefin in the presence of an alcohol does not reproduce the actual dehydration conditions since the alcohol, being more basic than the olefin, is preferentially adsorbed on the acidic sites responsible for isomerization. However, during the dehydration reaction, the olefins are formed within the pores and isomerization due to readsorption before leaving the pore, is more likely to occur.

## II. Dehydration of Cyclohexanemethanol and *cis*- and *trans*-4-*t*-Butylcyclohexanemethanol—Effect of Life of Catalyst Upon the Product Distribution

The mechanism discussed above can also be applied for the dehydration of *cis*-(6) and *trans*-4-*t*-butylcyclohexanemethanol (7). To simplify the analysis, the products were hydrogenated over Pd/C to *cis*- and *trans*-1-*t*-butyl-4-methylcyclohexane (8) and *t*-butylcycloheptane (9).

Initially, the amount of compound (8) produced decreased whereas that of (9) either remained constant or increased slightly as the conversion dropped due to deactivation of the catalyst (Table 2). At

TABLE 2  
DEHYDRATION OF *cis*-(6) AND *trans*-4-*t*-BUTYLCYCLOHEXANEMETHANOL (7) AT 410°C<sup>a</sup>  
Relation between activity of the catalyst and the composition of the product.

Alcohol sample	% Conversion	Hydrogenated product composition, %		
		(8) <i>trans</i>	(8) <i>cis</i>	(9)
(7)	48.3	69.5	26.9	3.6
(6)	49.9	65.7	25.8	8.5
(5 × 20 μl (7)) <sup>b</sup>				
(7)	44.5	66.0	26.0	8.0
(6)	40.7	62.2	23.6	14.1
(5 × 20 μl (7))				
(7)	33.0	64.0	26.2	9.8
(6)	36.5	59.9	24.6	15.5
(5 × 20 μl (7))				
(7)	30.7	65.8	24.4	9.8
(6)	31.3	60.1	24.0	15.9
(3 × 20 μl (6) + 2 × 20 μl (7))				
(7)	22.3	63.8	25.7	10.5
(6)	25.8	57.9	25.2	16.9
(10 × 40 μl (7))				
(7)	23.5	63.4	25.4	11.2
(6)	26.7	58.7	24.6	16.7
60: 40 nitrogen-oxygen mixture passed over catalyst at 460°C for 4 hr; then helium passed over for 0.2 hr and hydrogen for 4 hr at 410°C.				
(7)	20.1	61.9	27.3	10.8
(6)	21.1	58.2	26.8	15.1
(10 × 20 μl (7))				
(6)	14.7	56.3	24.5	19.2

<sup>a</sup> Catalyst was 1.9 mg 40/50 mesh alumina from aluminum isopropoxide; hydrogen flow rate, 80 ml/min; sample, 20 μl of a solution consisting of 32% alcohol, 4% internal standard and 64% solvent.

<sup>b</sup> Quantity of alcohol (7) passed over the catalyst between experiments.

a later stage in the deactivation, the decrease in (8) and (9) was almost equal.

Two unidentified peaks, which were not present when the catalyst was fresh, appeared in the dehydrations over deactivated catalyst. At 410°C the percentage of each of these peaks was about 5, whereas at 310°C the percentage was less than 2.

The alumina did not undergo regeneration when a 60:40 nitrogen-oxygen mixture was passed over it at 460°C for four hours; the dehydration activity of the catalyst and the product distribution remained the same.

A similar change of selectivity with the deactivation of the catalyst was observed with cyclohexanemethanol (Table 3). As with alcohols (6) and (7), the percentage of ring expanded product increased as the conversion decreased. The percentage of (3) dropped whereas that of (4) and (5) increased. Similar distribution changes were found at 310°C.

The experiments made at 360°C in the presence of pyridine and over pyridine-treated alumina show that the increase in cycloheptene (1) was not due to increased isomerization, whereas formation of (4) and (5) was a secondary reaction. Only 14.0% of (3) formed on the pyridine-treated catalyst as compared to 27.9% on 5.8 mg fresh catalyst at 360°C, and 65.3% on 5.8 mg pyridine-treated fresh catalyst.

The percentage of (2) found was 70.1 on the pyridine-treated aged catalyst, 66.5 on the fresh catalyst, but only 34.7 on the pyridine-treated fresh catalyst.

Therefore, a higher percentage of (2) and a lower percentage of (3) were formed as primary products over the deactivated catalyst. It was proposed that in the formation of cycloheptene (1) either an  $\alpha$ - or a  $\gamma$ -hydrogen is removed, in the formation of methylenecyclohexane (3) either an  $\alpha$ - or a  $\beta$ -hydrogen is removed, and in the formation of 1-methylcyclohexene (2) a  $\gamma$ -hydrogen is removed. The deactivated catalyst caused more removal of a  $\gamma$ -hydrogen yielding increased percentages of (2) and (1) and less removal of a  $\beta$ -hydrogen yielding a lower percentage of (3). These data do not suggest whether removal of an  $\alpha$ -hydrogen was affected by deactivation of the catalyst.

The amount of ring expansion and conversion to olefins in the dehydration of alcohols (6), (7) and (10) at various temperatures over deactivated alumina is compared in Table 4. Separate injections of equimolar quantities of each alcohol were made by syringe. Below 360°C, the conversion to olefin of alcohol (6) was approximately 1.5 times greater than that of alcohol (7) which was about 1.8 times greater than that of alcohol (10). Conversion of alcohols (6) and (7) were equal at

TABLE 3  
DEHYDRATION OF CYCLOHEXANEMETHANOL (10)<sup>a</sup>

Relation between the activity of alumina and composition of products.

Injected sample	Temp °C	% Conversion	Product composition, %			
			(2)	(3)	(4) + (5)	(1)
(10)	410	48.4	68.0	22.3	5.3	4.4
(500 $\mu$ l (10)) <sup>b</sup>	410					
(10)	410	34.1	71.9	8.4	9.7	10.0
(1000 $\mu$ l (10))	410					
(10)	410	24.6	69.8	8.0	10.3	11.9
(1000 $\mu$ l (10))	410					
(10)	410	18.0	67.7	6.0	10.6	15.7
(10)	360	14.0	72.7	5.9	7.3	14.1
(2000 $\mu$ l pyridine)	360					
((10) + 15 $\mu$ l pyridine)	360	4.6	70.1	14.0	trace	15.9

<sup>a</sup> Catalyst, 5.5 mg alumina from isopropoxide, 40/50 mesh size; hydrogen flow rate, 80 ml/min.; sample, 18  $\mu$ l of a solution of (10) and standard.

<sup>b</sup> Amount of material injected between experiments.

TABLE 4  
DEHYDRATION OF CYCLOHEXANEMETHANOL AND  
*cis*- AND *trans*-4-*t*-BUTYLCYCLOHEXANEMETHANOL  
OVER DEACTIVATED ALUMINA AT  
VARIOUS TEMPERATURES<sup>a</sup>

Alcohol	Temp °C	% Conversion	% Ring enlargement
(6)	440	24.2	14.3
(7)	440	24.7	9.6
(10)	440	23.9	18.0
(6)	410	24.5	13.8
(7)	410	23.8	9.4
(10)	410	21.6	17.6
(6)	360	24.8	12.6
(7)	360	24.8	8.8
(10)	360	14.7	13.9
(6)	310	18.4	12.0
(7)	310	12.2	6.0
(10)	310	8.1	12.3
(6)	260	6.8	10.1
(7)	260	4.0	6.0
(10)	260	1.5	trace
(6)	210	1.5	7.7
(7)	210	1.1	trace
(10)	210	0.8	—

<sup>a</sup> Catalyst, 5.4-mg alumina from isopropoxide, 40/50 mesh size, deactivated with 7-ml cyclohexanemethanol; hydrogen flow rate, 80 ml/min.

360°C and the conversions did not increase as the temperature increased above this temperature. Alcohol (10) reached the conversion level of the other alcohols above 410°C. This indicates that at the higher temperatures, a transport step may have been rate determining whereas at temperatures below 360°C, the surface reaction step may have been rate determining.

Allinger *et al.* (19) have calculated the energy difference between the axial and equatorial conformations of *t*-butylcyclohexane to be 5.41 kcal/mole. The *t*-butyl group tends, therefore, to remain in an equatorial conformation. In gas phase and solution studies, the *t*-butyl group has

often been used to fix the reacting group in either an axial or equatorial position, without exerting any other steric or polar effect on the reaction (20, 21).

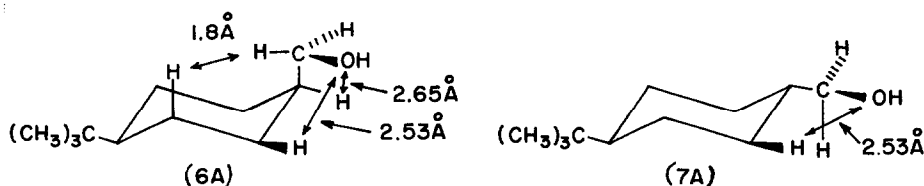
In the solvolysis of *cis*-4-*t*-butylcyclohexyl tosylate (21), acetolysis of 4-*t*-butylcyclohexylcarbonyl- $\beta$ -tosylate (14b) and in the dehydration of *cis*-4-*t*-butylcyclohexanol (22) in which the departing group is axial, a steric acceleration due to the relief of crowding between this group and the axial hydrogens has been found and the *cis* isomer reacted from 4.2 to 6.5 times faster than the *trans*.

Because of the relief of the crowding between the axial hydroxy methyl group of the *cis*-alcohol (6A) and the axial ring hydrogens, (6) might be expected to dehydrate more easily than (7) in which there is much less strain.

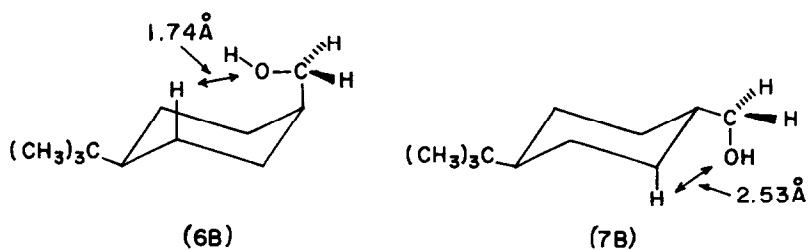
Since *trans* elimination has been shown to be favored in dehydrations over alumina, the *trans*-alcohol in which the  $\beta$ -hydrogen and the hydroxyl group can more easily assume a *trans* conformation (7B) might be expected to dehydrate more easily than the *cis* isomer.

Since below 360°C over both fresh and deactivated catalyst, the *cis*-alcohol (6) had a higher conversion to olefins, the relief of strain is probably the more important factor.

More ring expansion was expected for the *cis*-alcohol in which it is more difficult to have the  $\beta$ -hydrogen and hydroxyl group in a *trans* conformation (6B) and therefore, anchimeric assistance by the ring would be more important than in the case of the *trans* alcohol (7B). Dehydration of the *cis*-alcohol over fresh and aged catalysts at all temperatures studied was found to undergo more ring expansion than the *trans* isomer, but the difference was only a factor of about 1.6.



Most stable chair conformations



$\beta$ -Hydrogen and hydroxyl group in *trans* conformation

Below 410°C the cyclohexanemethanol (10) conversion to olefins was lower than that of alcohols (6) and (7). The *t*-butyl group, by keeping as far as possible from the surface, may favorably orient these alcohol molecules for dehydration. The transport step, therefore, may become the

rate determining step at a lower temperature in the dehydration of (6) and (7) than in the reaction of (10).

Dehydration of (10) yielded more ring expanded product than the dehydration of alcohol (6). Although the equatorial conformation of cyclohexanemethanol is

TABLE 5  
DEHYDRATION OF CYCLOALKYLMETHANOLS OVER ALUMINA

Sample	Cat. <sup>a</sup>	Temp °C	% Conversion	Hydrogenated product composition, % <sup>b</sup>	
 (11)	A	310	8.0	-CH <sub>3</sub>	
	B	380	61.6	4.7	95.3
	C	310	10.0	1.1	98.9
	C	380	21.3	trace	100.0
 (12)	A	310	6.0	-CH <sub>3</sub>	
	B	380	54.0	55.7	44.3
	C	310	5.2	45.2	54.8
	C	380	14.7	23.1	6.9
 (10)	A	310	8.4	-CH <sub>3</sub>	
	B	380	42.0	100.0	0.0
	C	310	4.4	93.1	6.9
	C	380	14.3	84.3	15.7
 (13)	A	310	11.2	-CH <sub>3</sub>	
	B	380	46.6	96.1	3.9
	C	310	8.0	94.0	6.0
	C	380	16.3	81.8	18.2

<sup>a</sup> A, 3.0 mg of 80/100 mesh fresh alumina; B, 5.7 mg of 80/100 mesh fresh alumina; C, 5.7 mg of 80/100 mesh alumina which has been deactivated by mechanically pumping 32 g of a solution composed of cyclohexanemethanol, 31 wt %, and cyclohexane, 69 wt %, and manually injecting by syringe 4.2 ml of cyclohexanemethanol, over the catalyst.

<sup>b</sup> Olefinic products hydrogenated over Pd/C.

thermodynamically more stable than the axial, the alcohol may react in the axial conformation, which in the case of 4-*t*-butylcyclohexanemethanol gave a higher dehydration conversion, since the energy barrier (less than 2 kcal/mole) is considerably less than the activation energy of the dehydration reaction (2*S*). This would explain the amount of ring expansion in the dehydration of (10) being equal to but not greater than that of alcohol (6).

### III. Dehydration of Cyclobutane-, Cyclopentane-, Cyclohexane-, and Cycloheptanemethanol

Results of the dehydrations of these alcohols over fresh and deactivated alumina at 310 and 380°C are given in Table 5. An equimolar amount of each alcohol was injected separately and the olefins produced were hydrogenated.

To check for possible skeletal isomerization of the olefins during the dehydration reaction, pure olefins were injected over the alumina at 380°C. No olefins were found to rearrange to a ring expanded compound. However, injection of 2  $\mu$ l of cyclohexene over alumina and hydrogenation of the products yielded 0.9% methylcyclopentane. Similarly 3  $\mu$ l of cycloheptene yielded 5.0% methylcyclohexane and 3  $\mu$ l of cyclooctene yielded 2.6% methylcycloheptane. Therefore, ring expanded products are primary products and possibly have formed in a slightly higher yield than reported.

Ring expansion during the dehydration of cyclobutane- (11) and cyclopentane-methanol (12) would form more stable products whereas in the dehydration of cyclohexane- (10) or cycloheptanemethanol (13), products of less stability would be formed.

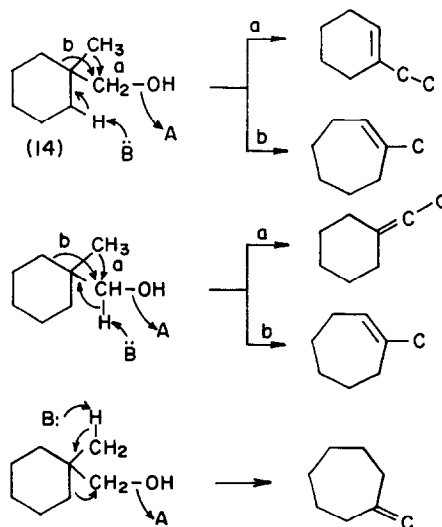
Highly strained alcohol (11) yielded almost entirely cyclopentane and slightly strained alcohol (12) yielded a large amount of cyclohexane. Expansion of a six to a seven membered ring is less favorable than expansion of a seven to an eight membered ring. Since both occurred and in

nearly equal amounts, it appears that ring strain did not influence the dehydration of (10) and (13) as it did the dehydration of (11) and (12). Ring expansion can be viewed as the migration of either of two  $\gamma$ -methylene groups to the  $\alpha$ -carbon atom of the alcohol.

As found in the dehydrations of the alcohols discussed previously, more ring expanded product was formed in the reaction of each of these alcohols using the deactivated catalyst than the fresh catalyst. Dehydration of cyclopentanemethanol over pyridine-treated fresh and deactivated alumina showed, as had the dehydration of cyclohexanemethanol, a decrease in the amount of *exo*-cyclic olefin formed.

### IV. Dehydration of 1-Methylcyclohexanemethanol and 2-Methylpropanol

The dehydration of 1-methylcyclohexanemethanol (14) was studied to directly compare the migration of a  $\gamma$ -methyl group to ring expansion which can be viewed as the migration of either of two  $\gamma$ -methylene groups.



The hydrogenated product composition from the dehydration of (14) over fresh alumina and alumina deactivated by injection of a large quantity of cyclohexanemethanol is shown in Table 6. The amount of ring expansion in the dehydration of

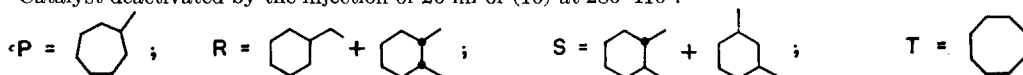


TABLE 6  
 DEHYDRATION OF 1-METHYLCYCLOHEXANEMETHANOL (14)

Alcohol	Catalyst <sup>a</sup>	Temp °C	% Conversion	Hydrogenated product composition % <sup>c</sup>				Migratory aptitude $\frac{\text{CH}_3}{-\text{CH}_2-}$
				P	R	S	T	
(14)	A	310	7.6	38.6	60.5	0.9	—	3.1
(14)	A	380	34.4	44.5	53.8	1.7	—	2.3
(13)	A	380	48.0	93.7	—	—	6.3	
(10) <sup>b</sup>	A							
(13)	B	380	17.3	82.7	—	—	17.3	
(14)	B	310	4.5	54.6	45.4	—	—	1.6
(14)	B	380	13.8	53.5	43.8	2.6	—	1.6
(14)	C	350	26.3	43.1	55.7	1.2	—	2.5
(14)	D	350	4.0	60.3	39.7	trace	—	1.3

<sup>a</sup> A, 4.9 mg of 80/100 mesh alumina from aluminum isopropoxide; B, deactivated A; C, 11.6 mg of 80/100 mesh alumina treated with 100  $\mu$ l pyridine at 210°C; D, alumina aged with (7) at 380°C and then treated with 500  $\mu$ l pyridine.

<sup>b</sup> Catalyst deactivated by the injection of 20 ml of (10) at 280–410°.



cycloheptanemethanol was used to indicate the degree of deactivation of the catalyst by comparison with previous studies.

Column R, Table 6 gives the percentage of ethylcyclohexane, the methyl-migration product, and any *cis*-1,2-dimethylcyclohexane produced: these products were not separable on the gas chromatographic columns tried. Column S, (Table 6) contains the percentage of *trans*-1,2-dimethylcyclohexane and/or 1,3-dimethylcyclohexane produced.

The amount of ring expanded product, methylcycloheptene, increased whereas the amount of methyl-migration product decreased as the catalyst was aged. The migratory aptitude ratio of methyl group: ring  $\gamma$ -methylene group (corrected for the fact that there are two ring  $\gamma$ -methylene groups) decreased as the catalyst was aged. Similar results were found when (14) was dehydrated over pyridine-treated alumina at 350°C.

Formation of both ethylcyclohexane and methylcycloheptane, after hydrogenation, can occur by removal of either an  $\alpha$ - or a  $\gamma$ -hydrogen. However, there are both ring methylene and methyl  $\gamma$ -hydrogens which can be removed. Possibly the ratio of

methyl  $\gamma$ -hydrogen removal to methylene  $\gamma$ -hydrogen removal is higher on the aged catalyst than on the fresh catalyst. Since removal of a methyl  $\gamma$ -hydrogen produces only ring expanded product, more expansion would then occur on the aged catalyst.

#### V. Dehydration of 2-Methylpropanol

The results discussed above show that dehydrations over deactivated alumina are accompanied by more ring expansion than those over fresh alumina. The dehydration of 2-methylpropanol over pure alumina, pyridine-treated alumina, and Harshaw alumina containing 0.35% sodium at 350°C has been reported to yield 12, 14, and 23% of skeletal rearrangement, respectively (24). However, deactivation of the catalyst and its influence on the amount of skeletal rearrangement was not considered in that study.

Table 7 contains the results of the dehydration of 2-methylpropanol. The presence of either sodium ions or pyridine on the catalyst did not affect the amount of skeletal rearrangement as did the deactivation of the catalyst. Differences in the amount of rearrangement over the deacti-

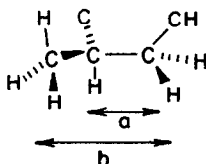
TABLE 7  
DEHYDRATION OF 2-METHYLPROPANOL OVER ALUMINA

Catalyst <sup>a</sup>	Temp °C	% Conversion	Hydrogenated product composition %	
			$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C} \end{array}$	$\text{C}-\text{C}-\text{C}-\text{C}$
A	310	5.5	93.4	6.6
A	380	19.5	89.3	10.7
B	310	0.5	70.6	29.4
B	380	2.3	67.3	32.7
C	350	14.1	91.4	8.6
D	350	1.2	77.4	22.6
E	380	4.4	88.6	11.4
E	430	5.1	86.7	13.3
F	380	0.3	60.0	40.0
F	430	0.9	57.1	42.9

<sup>a</sup> A, 15.5 mg of 40/50 mesh alumina prepared from aluminum isopropoxide; B, A which was deactivated by contact with cyclohexanemethanol and *trans-t*-butylcyclohexanemethanol (7); C, 11.6 mg of 80/100 mesh alumina treated with 100  $\mu$ l pyridine; D, C deactivated with (7) and then treated with 500  $\mu$ l pyridine; E, 4.9 mg of 50/80 mesh alumina purchased from Harshaw Chemical Company and containing 0.35% sodium; F, E which was deactivated with 2-methylpropanol and (7).

vated catalysts are most likely due to differences in the degree of deactivation.

The observed increase in the percentage of skeletal rearrangement during the dehydration reactions is believed to be due to the much greater decrease in the rate of removal of  $\beta$ -hydrogens as compared to removal of  $\gamma$ -hydrogens. If the deactivation of the alumina is caused by the *random* deposition of organic material on both acidic and basic sites of the catalyst, the average distance between an acidic and a basic site would increase as fewer uncovered sites remain on the catalyst. Removal of  $\gamma$ -hydrogen requires a greater distance (b) between the acidic and basic sites taking part in the elimination reaction than when a  $\beta$ -hydrogen is removed (distance a).



Therefore, if deactivation does increase the average distance between acidic and basic sites, a lower percentage of  $\beta$ -hydrogen removal would be expected.

In an attempt to learn which type of compounds might have deactivated the alumina during the dehydration reactions, the following compounds were passed in a stream of hydrogen over the catalyst prior to dehydration: 1,3-cyclooctadiene, 1-methylcycloheptene, trimethylacetaldehyde and cyclohexane. From the dehydration of cyclohexanemethanol at 380°C it was found that all these compounds deactivated the alumina and caused more ring expansion to occur. Increased skeletal rearrangement in the dehydration of 2-methylpropanol over the deactivated catalysts was also found.

Gravimetric and spectroscopic studies of the deactivation process would possibly indicate the quantity and identity of the organic compounds adsorbed on the alumina. The deactivated catalyst could not be regenerated and was black. The presence of pyridine or sodium on the catalyst did not affect the deactivation process.

## EXPERIMENTAL SECTION

### A. Apparatus

The apparatus was the same as described in the preceding paper (1).

### B. Analytical Procedures

**1. Hydrogenation of dehydration products.** Initially a study was made of the conditions necessary to achieve complete hydrogenation and to avoid any reactions other than hydrogenation of the olefinic double bond.

Complete hydrogenation of olefin products occurred when 47.0 mg of 10% Pd/C (#SC13902, E. H. Sargent and Co., Chicago, Illinois) mixed with an approximately equal amount of 80/100 mesh Gas Pack W at 140°C and a hydrogen flow of about 80 ml/min was used. Whereas the chromatographic peaks of low molecular weight (C<sub>4</sub>-C<sub>8</sub>) compounds which had been hydrogenated were of acceptable shape, tailing of the peaks of C<sub>11</sub>H<sub>22</sub> hydrocarbons required trapping the products before chromatographic analysis. The first 30 cm of the chromatographic column was wound into a small coil having a diameter of about 30 mm which could be immersed in a Dewar flask filled with liquid nitrogen. Six minutes after injection, the Dewar flask was removed and the column was heated to the temperature required for analysis.

Injection of pure methylenecyclobutane, methylenecyclopentane, and 1-methylcyclopentene showed that when hydrogenation was complete, no ring expansion occurred.

Injection of 20 μl of 4-*t*-butylcyclohexanemethanol over the Pd/C at 140°C

yielded 1.9% of *t*-butylcyclohexane. At 185°C, 5.0% of hydrogenolysis occurred. Since alumina was found not to cause such hydrogenolysis, the *t*-butylcyclohexane formed was not included in the product distribution data presented previously.

**2. Gas chromatographic columns.** Listed in Table 8 are the columns used for the dehydration product analyses and preparative gas chromatographic separations.

**3. Identification of the reaction products.** The products, olefins or hydrogenated olefins, of all reactions except the dehydration of 4-*t*-butylcyclohexanemethanol were identified by comparison of their relative retention times to those of known samples. Two columns, G and H, were used to calculate the cyclopentanemethanol dehydration product percentages due to the overlapping of two peaks on every column tried.

*t*-Butylcycloheptane, *cis*-, and *trans*-1-*t*-butyl-4-methylcyclohexane, products from the dehydration of *cis*- and *trans*-4-*t*-butylcyclohexanemethanol, were collected separately by preparative chromatography on column F. Identifications of *cis*- and *trans*-1-*t*-butyl-4-methylcyclohexane was made by comparison of their gas chromatographic retention times and nmr spectra with those of pure samples prepared by the hydrogenation of *p*-*t*-butyltoluene. *cis*-isomer: nmr (CCl<sub>4</sub>) δ 0.82 [s, 9, (CH<sub>3</sub>)<sub>3</sub>C], 0.92 (d, 3, CH<sub>3</sub>), 1.45 ppm (m, 10, CH<sub>2</sub>-CH); *trans*-isomer: nmr (CCl<sub>4</sub>) δ 0.82 [s,

TABLE 8  
GAS CHROMATOGRAPHIC COLUMNS

Columns	Substrate	Solid support <sup>a</sup> (mesh)	Length <i>m</i>	o.d. <sup>b</sup> (in.)
F	18% Carbowax <sup>c</sup> 20M	Gas Pack W (80/100)	2.7	0.375
G	33% 2, 4-Dimethylsulfolane	Gas Pack P (80/100)	2.2	0.25
H	10% AgNO <sub>3</sub> -Diethylene Glycol	Firebrick (100/200)	0.6	0.25
I	15% Ucon <sup>d</sup> 75H 90,000	Chromosorb W	10	0.25
J	18% Carbowax 20M	Gas Pack W (60/80)	2.5	0.25
K	33% 2, 4-Dimethylsulfolane	Firebrick (80/100)	6	0.25
L	15% Carbowax 20M	Gas Pack P (40/60)	2	0.375

<sup>a</sup> Gas Pack, Chromosorb, and Firebrick are diatomaceous earth.

<sup>b</sup> Column H was of Pyrex glass; other columns were of copper.

<sup>c</sup> Carbowax is a polyethylene glycol.

<sup>d</sup> Ucon is a polypropylene glycol.

$\text{CH}_3)_3\text{C}]$ , 0.92 (d,  $\text{CH}_3$ ), 1.72 ppm (m,  $\text{CH}_2 = \text{CH}$ ).

*t*-Butylcycloheptane was identified by its nmr spectra which unlike those of *cis*- and *trans*-1-*t*-butyl-4-methylcyclohexane showed only one type of methyl-proton peak: nmr ( $\text{CCl}_4$ )  $\delta$  0.82 [s, 9,  $(\text{CH}_3)_3\text{C}$ ], 1.52 ppm (m, 13,  $\text{CH}_2\text{-CH}$ ).

The following are the relative retention times of the products from the dehydration of the various alcohols, before and/or after hydrogenation.

*Cyclohexanemethanol* (10). Column G, 45°C, He-80 ml min<sup>-1</sup>. Cyclohexane, 1.00 (internal standard); (4), 2.65; (5), 2.85; (3), 2.88; (2), 3.21; (1), 4.15.

Column H, room temp., He-80 ml min<sup>-1</sup>. Cyclohexane, 1.00; (2), 5.14; (4), 11.6; (5), 11.6; (3), 20.3; (1), 70.0.

Column G, 45°C, H<sub>2</sub>-80 ml min<sup>-1</sup>. 2-Methylhexane (internal standard), 1.00; methylcyclohexane, 2.10; cycloheptane, 4.17.

*Cyclopentanemethanol*. Column G (as above). Methylcyclopentane, 0.47; cyclohexane, 0.64; methylcyclohexane (internal standard), 1.00.

Column G, 40°C, He-77 ml min<sup>-1</sup>. 3-Methylcyclopentene, 0.53; 1-methylcyclopentene, 0.89; methylenecyclopentane, 0.89; methylcyclohexane (internal standard), 1.00; cyclohexane, 1.14.

Column H, room temp., He-80 ml min<sup>-1</sup>. 1-Methylcyclopentene, 1.00; methylenecyclopentane, 2.17; 3-methylcyclopentene, 3.00; cyclohexane, 3.08.

*Cyclobutanemethanol*. Column K, room temp., H<sub>2</sub>-80 ml min<sup>-1</sup>. Methylcyclobutane, 0.36; cyclopentane, 0.63; methylcyclopentane (internal standard), 1.00.

*1-Methylcyclohexanemethanol*. Column J, temp. 65°C, H<sub>2</sub>-80 ml min<sup>-1</sup>. Cyclohexane, 1.00; 1,3-dimethylcyclohexane, 2.31; *trans*-1,2-dimethylcyclohexane, 2.31; ethylcyclohexane, 3.21; *cis*-1,2-dimethylcyclohexane, 3.21; methylcycloheptane, 4.26.

*Cycloheptanemethanol*. Column J, 65°C, H<sub>2</sub>-80 ml min<sup>-1</sup>. Hexane (internal standard), 1.00; methylcycloheptane, 4.65; cyclooctane, 1.58.

*4-t-Butylcyclohexanemethanol*. Column I, 140°C, H<sub>2</sub>-80 ml min<sup>-1</sup>. Isopropylcyclohexane, 1.00; unknown, 1.55; *trans*-1-*t*-butyl-4-methylcyclohexane, 1.65; *cis*-1-*t*-butyl-4-methylcyclohexane, 1.85; unknown, 2.35; *t*-butylcycloheptane, 2.57.

### C. Preparation of Alcohol

**1. *cis*- and *trans*-4-*t*-Butylcyclohexanemethanol.** The *cis*-alcohol in the absence of any *trans*-alcohol was obtained from *p*-*t*-butylbenzoic acid by the method of Mori (25). The acid was hydrogenated under pressure at 150°C in the presence of platinum oxide to *cis*-4-*t*-butylcyclohexanecarboxylic acid. The *cis*-isomer was separated by crystallization from water-ethanol mixture, converted to ethyl ester, and reduced by lithium aluminum hydride to the *cis*-alcohol, mp 57.5–58.0°C (lit. (25) 56–57°C) bp 94–95°C (5 mm); ir (neat) 3220 cm<sup>-1</sup>(O-H).

The *trans*-alcohol was also prepared by the method of Mori (25) by hydrogenating *p*-*t*-butylbenzoic acid in 6% sodium hydroxide solution with Raney nickel. The *trans*-4-*t*-butylcyclohexanecarboxylic acid was converted to its ethyl ester, and reduced with lithium aluminum hydride to *trans*-4-*t*-butylcyclohexanemethanol, bp 105–106.5°C (7 mm.)  $n_D^{20}$  1.4695 (lit. (25)  $n_D^{20}$  1.4683); ir (neat) 3300 cm<sup>-1</sup>(O-H).

**2. Cyclopentane-, cyclohexane-, and cycloheptanemethanol.** These alcohols were obtained commercially (cyclopentane- and cycloheptanemethanol from Aldrich Chemical Co., Inc., Milwaukee, Wis. and cyclohexanemethanol from Eastman Chemicals, Rochester, N. Y.) and were purified by preparative gas chromatography on column F.

**3. Cyclobutanemethanol.** Cyclobutanecarboxylic acid (10 g, 0.10 mol) was reduced with lithium aluminum hydride (7.3 g, 0.18 mol) yielding after distillation pure cyclobutanemethanol: bp 82–83°C (70 mm);  $n_D^{20}$  1.4471 (lit. (26) bp 142–143.5°C,  $n_D^{20}$  1.4450); ir (neat) 1055 and 3250 cm<sup>-1</sup>(O-H).

**4. 1-Methylcyclohexanemethanol.** 1-

Methylcyclohexanecarboxylic acid (10 g, 0.07 mol) was reduced with lithium aluminum hydride (5.3 g, 0.14 mol) yielding after distillation 1-methylcyclohexanemethanol: bp 57–57.5°C (5 mm);  $n_D^{20}$  1.4691 [lit. (27) bp 85°C (14 mm),  $n_D^{20}$  1.4674°C]; ir (neat) 1052 and 3340  $\text{cm}^{-1}$  (O–H).

#### D. Preparation of Saturated Hydrocarbons.

**cis- and trans-1-t-Butyl-4-methylcyclohexane.** *p-t*-Butyltoluene (15 g, 0.095 mol) was hydrogenated in one hour at room temperature and at 34 psi initial hydrogen pressure in a Parr hydrogenation apparatus using platinum oxide catalyst. The resulting 60:40 mixture of 1-*t*-butyl-4-methylcyclohexane isomers was separated by preparative gas chromatography on column F. It was assumed that the isomer formed in the larger percentage was the *cis* one as was found in the similar hydrogenation of *p-t*-butylbenzoic acid (28). *cis*-isomer: nmr ( $\text{CCl}_4$ )  $\delta$  0.82 [s, 9,  $(\text{CH}_3)_3\text{C}$ ], 0.92 (d, 3,  $\text{CH}_3$ ), and 1.45 ppm (m, 10,  $\text{CH}_2\text{-CH}$ ); *trans*-isomer: nmr ( $\text{CCl}_4$ )  $\delta$  0.82 [s,  $(\text{CH}_3)_3\text{C}$ ], 0.92 (d,  $\text{CH}_3$ ), and 1.72 ppm (m,  $\text{CH}_2\text{-CH}$ ).

**Methylcyclobutane.** Methylenecyclobutane was hydrogenated with 10% Pd/C in a micro-hydrogenation apparatus at atmospheric pressure to give methylcyclobutane.

#### E. Preparation of the Catalysts

Pure alumina was prepared by the hydrolysis of 125 g of distilled aluminum isopropoxide with 1 liter of distilled water (16). The resulting aluminum hydroxide was filtered, redispersed in 500-ml of water, filtered, and then dried at 120°C for 24 hours. This material was then calcined at 650°C for four hours in a stream of nitrogen, crushed, and sized to various mesh sizes.

Alumina containing alkali metal ions was prepared in a similar manner except that prior to the drying step, the aluminum hydroxide was dispersed in 500 ml of a 0.019 M sodium carbonate solution, and

stirred for five hours. The mixture was filtered and by titration of the filtrate, the amount of sodium carbonate in the filter cake was calculated. This material was then dried and calcined as described above for the alkali-free alumina. The resulting catalyst contained 0.4 wt % of sodium ions.

A commercial alumina was obtained from the Harshaw Chemical Co., Cleveland, Ohio (lot number AL-0104T  $\frac{1}{8}$  in., 580 005-45). It contained 0.37 wt % of sodium (29).

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