

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

## Alumina: Catalyst and Support. X.<sup>1a</sup> Modification of Alumina by Bases. Mechanism of Dehydration of Menthol and Neomenthol<sup>1b</sup>

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The dehydration of menthol and neomenthol over different alumina catalysts was studied. In agreement with the previous reports in the literature, it was found that alumina catalysts prepared from sodium aluminate are only weakly acidic and do not cause extensive isomerization of olefins during dehydration. On the other hand, alumina prepared from aluminum isopropoxide was strongly acidic and dehydration of alcohols on this catalyst was accompanied by extensive isomerization. This isomerization can be suppressed by exposing the catalyst to bases like ammonia, trimethylamine and piperidine. The stronger the base, the more effective it was in suppressing isomerization. The major primary product of dehydration of menthol was 2-menthene and that of neomenthol, 3-menthene. The rate of dehydration of neomenthol was about 3 times as fast as that of menthol. These lead to the conclusion that elimination of water takes place preferentially from adjacent *trans* (diaxial) hydrogen and hydroxyl. On the catalysts having high intrinsic acidity, dehydration is usually followed by extensive double bond and skeletal isomerization of olefins. Possible mechanisms of these reactions are discussed.

### Introduction

In earlier papers in this series, the differences in catalytic activity of alumina catalyst prepared by various methods were discussed.<sup>1,3</sup> An attempt was made to understand the confused picture in the literature regarding the dehydration of alcohols over alumina and the accompanying isomerization of olefins. It appeared that by using catalysts of low acidity secondary isomerizations can be avoided and dehydration reactions better understood. Hence a systematic study of the dehydration of alcohols over alumina catalysts, especially those that contained only weak acid sites, was undertaken. In the present paper, the dehydration of menthol and neomenthol are discussed.

The mechanism of the dehydration of alcohols over alumina is quite unclear both with respect to the active centers on the alumina and with respect to the nature of the adsorbed species or active intermediates involved.<sup>4</sup> Some aspects of this problem have been clarified in a previous paper.<sup>1a</sup> The main objectives of the present study are to understand the stereochemistry of dehydration and to study the possibility of modifying alumina to obtain catalysts of low acidity.<sup>5</sup>

Acid-catalyzed dehydrations in solutions have been shown to proceed with a preference for *trans* orientation of leaving groups.<sup>6</sup> However, this has never been established unequivocally for dehydrations over alumina, though such preferred *trans* orientation of leaving groups has been assumed<sup>7</sup> by analogy with reactions in aqueous systems.

Indirect evidence against a concerted *cis* elimination has been obtained from the study of the dehydration of 2-butanol.<sup>1</sup> However, it was desirable to obtain more direct evidence in this matter also.

Menthol and neomenthol are ideally suited for the study of the stereochemistry of elimination. Ester pyrolysis, decomposition of quaternary ammonium hydroxides, etc., in menthyl and neomenthyl systems lead to olefins, following the expected steric course.<sup>8,9</sup> These alcohols are also suitable to study the isomerizing activity of the different types of aluminas because of the ease with which the menthenes can be isomerized in the presence of acidic catalysts.

### Experimental Part

**Materials.**—*l*-Menthol was obtained commercially. *d*-Neomenthol,  $\alpha_D^{20} + 17.5^\circ$ , was prepared by the reduction of *l*-menthone.<sup>10</sup> The final separation of *d*-neomenthol from *l*-menthol was accomplished by fractional distillation on a spinning-band column rather than by partial esterification.<sup>11</sup> The yield was 30% on the basis of *l*-menthol used.

**Catalysts.**—The alumina catalysts were prepared by the methods described by Pines and Haag.<sup>3</sup> The catalysts of the A series were prepared by hydrolyzing aluminum isopropoxide with water. The precipitate was compressed to 120,000 p.s.i., broken up into 8–10 mesh particles and calcined at 600° for 20 hours in air. The catalysts of the B series were precipitated from sodium aluminate solution by carbon dioxide and washed by decantation a specified number of times. Thus, catalyst B2 was washed twice and B8, eight times. These catalysts were compressed and broken up into 10–14 mesh particles and heated at 300° in a stream of nitrogen for 24 hours. The commercial catalysts used were Harshaw alumina, Lot No. AL-0104T 1/8", 580-005-45 (The Harshaw Chemical Co., Cleveland, Ohio) and Alcoa alumina, Grade F10 (Aluminum Co. of America, Pittsburgh, Penna.). Some of these catalysts were also studied after they were modified by exposing them to ammonia, trimethylamine or piperidine at the temperature of the reaction, before or during the reaction.

The intrinsic acid strength of all the catalysts was checked by studying their ability to isomerize 3,3-dimethyl-1-butene to isomeric hexenes.<sup>3</sup> The alumina prepared from aluminum isopropoxide (A series) and Alcoa alumina were shown to contain strong acid sites on the basis of this test. Aluminas from sodium aluminate (B series), Harshaw alu-

(1) (a) For part IX of this series, see H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **83**, 2847 (1961); (b) paper III of the series, Dehydration of Alcohols; for paper II see ref. 1a.

(2) Taken in part from the Ph.D. Thesis of C. N. Pillai, Northwestern University, Aug., 1960. Grateful acknowledgment is made to the donors of the Petroleum Research Fund for the support of this research.

(3) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

(4) For a review of dehydration mechanisms, see M. E. Winfield in "Catalysis," Vol. 7, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1960, pp. 93–182.

(5) A preliminary report was published; H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2401 (1960).

(6) (a) G. Vavon and M. Barbier, *Bull. soc. chim.*, [4] **49**, 567 (1931). (b) C. C. Price and J. V. Karabinos, *J. Am. Chem. Soc.*, **62**, 1159 (1940). (c) H. J. Schaeffer and C. J. Collins, *ibid.*, **78**, 124 (1956).

(7) J. V. Karabinos and A. T. Ballum, *ibid.*, **76**, 1380 (1954).

(8) W. Hüchel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

(9) A. C. Cope and E. M. Acton, *J. Am. Chem. Soc.*, **80**, 355 (1958).

(10) (a) L. T. Sandborn, "Organic Syntheses," Coll. Vol. I, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 340. (b) L. M. Jackman, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.* 2461 (1949).

(11) W. J. Grubb and J. Read, *J. Soc. Chem. Ind.*, **53**, 52T (1934).

mina and the aluminas exposed to bases were all of the weakly acidic type, causing little or no isomerization of 3,3-dimethyl-1-butene.

**The Catalytic Reactions.**—The catalytic reactions were carried out in the apparatus previously described.<sup>1,3</sup> The liquid reactant, menthol or neomenthol as 66% solution in cyclohexane, was passed over the catalyst in a Pyrex tube which was kept heated in a vertical furnace. The feed was introduced from a stainless steel syringe-type pump. The products were collected in a water-cooled liquid receiver.

**Gas Chromatographic Identification of Components.**—Dehydration products of menthol were analyzed using a 20-foot column of di-*n*-propyl tetrachloro-*o*-phthalate (7% by weight deposited on 30–60 mesh Chromosorb) at 120°. Helium at the rate of about 80 ml. per minute was used as a carrier gas. The relative retention times, calculated as the ratio of the distance from the air peak to the component to the distance from the air peak to the peak due to *p*-cymene, are given in Table I.

TABLE I<sup>a</sup>  
RELATIVE RETENTION TIMES OF THE DEHYDRATION PRODUCTS OF MENTHOL

Component	Rel. retention time	Component	Rel. retention time
Toluene <sup>b</sup>	0.243	8(9)-Menthene	0.648
Alkylcyclopentene I <sup>c</sup>	.369	1(7)-Menthene	.697
Alkylcyclopentene II <sup>c</sup>	.389	4(8)-Menthene	.770
Alkylcyclopentene III <sup>c</sup>	.492	1-Menthene	.817
3-Menthene	.547	<i>p</i> -Cymene <sup>b</sup>	1.000
2-Menthene	.613		

<sup>a</sup> Column of di-*n*-propyl tetrachloro-*o*-phthalate (7% on 30–60 Celite), 20 ft. long, 120°, helium 80 ml./hr. <sup>b</sup> Toluene and *p*-cymene are included for reference. <sup>c</sup> These components were not identified independently.

Unreacted alcohol in the total dehydration product was estimated on a 6-ft. column of silicon 550, deposited on 30–60 mesh firebrick (40% by wt.) at 200°.

**Treatment with Amines.**—The catalyst was exposed to amines either during the dehydration of the alcohol or before. In the latter case, the catalyst tube was maintained at the required reaction temperature and ammonia was slowly passed over the catalyst for about 15 minutes. In the case of the other bases, 10 ml. of piperidine or 10 ml. of a solution of trimethylamine in methanol was dropped on the catalyst in the course of 20 minutes. The tube was then flushed out with nitrogen for about 10 minutes before carrying out the reaction. For better reproducibility of results, the second method, where 1–10% by weight of piperidine is mixed with the alcohol feed, is recommended (see Discussion).

## Discussion

**Dehydration of Menthol.**—The results of the various dehydration experiments with menthol are listed in Table II. Examination of the data shows that on the less acidic aluminas, namely, B series, base-modified catalysts and Harshaw alumina, 2-menthene is the major product of dehydration of menthol. The general picture also shows that 3-menthene is also formed in all the experiments even when the extent of dehydration is very small. Also revealing is the fact that traces of 1-menthene are formed at all times even though 1-menthene is not to be expected from a simple 1,2-elimination of the elements of water. On the more acidic catalysts, the percentage of 2-menthene decreases considerably and other isomeric menthenes are formed. Skeletal isomerization to form cyclopentene derivatives also takes place.

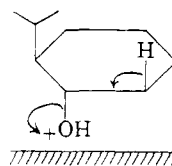
The results on the weakly acidic catalysts at low temperatures and low contact times (*e.g.*, expt. 10) represent true primary dehydration

products. The free olefins are not isomerized under the conditions of the reaction.

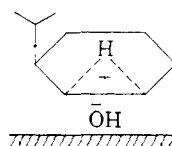
### Preferred Stereochemistry of Dehydration.

It can be seen that the major product of the reaction is 2-menthene. If there was no selectivity and the dehydration took the statistical course, 2- and 3-menthene would have formed in a 2:1 ratio. On the other hand, if a *trans* orientation of the eliminated groups was rigorously required, 2-menthene would have been the only product. The results show that *trans* elimination is indeed the preferred reaction.

It is difficult to explain *trans* elimination on a solid surface. The reason for *trans* elimination in general is that the pair of electrons that form the double bond comes in preferentially from the back side to the leaving group.<sup>12</sup> If the alcohol is attached to the surface of the alumina through the hydroxy group, *trans* elimination may be represented as



The obscure point in this picture is the fate of the proton that is eliminated. It has been demonstrated that in many elimination and solvolysis reactions, the initial ionization is facilitated by the participation of a neighboring hydrogen resulting in a protonium ion.<sup>13</sup> As was pointed out,<sup>1a</sup> such participation may be quite important for ionization over solid catalyst. Such participation in menthol will result in a protonium ion such as



The bridged ion can now release the proton to the surface if it turns over on the surface so that the proton comes into proximity with the surface. However, it is also possible that the dehydration actually takes place within cavities in the alumina so that as the OH group is lost to a surface below the plane of the molecule, the hydrogen is lost to a surface above.<sup>14</sup> It seems best to leave the actual mechanism of the removal of the proton unanswered at this stage.

The 3- and 1-menthene, which are also apparently primary reaction products, cannot arise from a simple *trans* elimination. The simplest explanation for the formation of these products is that part of the reaction proceeds by a classical

(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 467.

(13) (a) S. Winstein and S. Takahashi, *Tetrahedron*, **2**, 396 (1958); (b) W. B. Smith, R. E. Bowman and T. F. Kmet, *J. Am. Chem. Soc.*, **81**, 997 (1959); (c) D. J. Cram and J. Tadanier, *ibid.*, **81**, 2737 (1959).

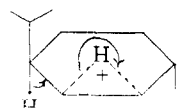
(14) "Crevice sites" on silica-alumina catalyst have been proposed on the basis of racemizations and exchange reactions of hydrocarbons; R. L. Burwell, H. A. Porte and W. M. Hamilton, *ibid.*, **81**, 1828 (1959).

TABLE II  
 DEHYDRATION OF MENTHOL OVER ALUMINA CATALYSTS

Expt.	Cut, <sup>a</sup> cc.	Catalyst <sup>b</sup>	Base <sup>c</sup>	Temp., °C.	HLSV <sup>h</sup>	3-Menthene	2-Men- thene	1-Menthene	Others	Dehydra- tion, %
1	1(0)	A(0)	None	290	1	31.0	27.4	35.8	5.9	100
1	2(3)	A(0)	None	290	1	29.7	28.0	35.7	6.7	100
1	3(6)	A(0)	None	290	1	29.8	30.5	35.1	4.7	100
2	...	A(0)	None	290	3.5	25.2	51.4	21.0	2.5	100
3	...	A(0)	None	290	8	22.5	61.4	13.7	2.2	100
4	1(0)	A(0)	Pip.	290	3.5	17.6	79.6	2.7	0	59
4	3(7)	A(0)	Pip.	290	3.5	16.6	80.1	3.2	0	94
4	5(19)	A(0)	Pip.	290	3.5	19.2	77.5	3.3	0	100
5	1(0)	A(0)	Pip. <sup>d</sup>	290	3.5	20.5	74.3	5.2	0	79
5	3(9)	A(0)	Pip. <sup>d</sup>	290	3.5	17.3	79.9	2.7	0	78
5	5(16)	A(0)	Pip. <sup>d</sup>	290	3.5	16.6	80.8	2.5	0	70
6	1(0)	A(0)	Pip. <sup>e</sup>	290	3.5	16.5	81.0	2.3	0	49
6	3(8)	A(0)	Pip. <sup>e</sup>	290	3.5	17.0	80.6	2.4	0	43
6	5(16)	A(0)	Pip. <sup>e</sup>	290	3.5	16.2	81.1	2.7	0	32
7	1(0)	A(0)	Pip. <sup>f</sup>	290	3.5	15.9	82.0	2.0	0	20
7	3(11)	A(0)	Pip. <sup>f</sup>	290	3.5	16.4	80.6	3.0	0	26
7	5(19)	A(0)	Pip. <sup>f</sup>	290	3.5	16.9	80.5	2.6	0	23
8	...	A(0)	Pip. <sup>f</sup>	290	8	15.3	82.8	1.9	0	11
9 <sup>g</sup>	...	A(3)	None	280	8	37.4	15.2	10.4	37.0	100
10	...	A(0)	NH <sub>3</sub>	243	8	9.5	90.5	Trace	0	1
11	...	A(0)	NH <sub>3</sub>	280	8	13.2	84.6	2.2	0	59
12	...	A(3)	NH <sub>3</sub>	280	8	29.0	65.1	4.4	1.1	87
13	...	A(4)	TMA	280	8	17.9	78.0	4.1	0	100
14	...	A(5)	Pip.	280	8	15.6	82.7	1.6	0	44
15	...	A(7)	NH <sub>3</sub>	280	8	41.0	21.0	7.0	31.0	100
16	...	B2(0)	None	330	1	28.5	69.2	2.3	0	83
17	...	B2(0)	None	330	3.5	23.5	74.1	2.4	0	33
18	...	B2(0)	None	330	8	21.6	76.2	2.2	0	23
19	...	B2(1)	None	330	8	35.8	48.0	6.7	9.5	31
10	...	B2(2)	None	330	8	35.8	29.2	8.0	26.9	50
21	...	B8(0)	None	330	8	19.3	75.2	3.5	2.0	100
22	...	B8(0)	None	280	8	16.9	81.1	2.0	0	17
23	...	B8(0)	NH <sub>3</sub>	280	8	16.5	83.5	Traces	0	2
24	...	Alcoa	None	330	8	48.9	11.7	30.9	8.5	100
25	...	Alcoa	None	280	8	35.0	62.0	3.0	0	39
26	...	Alcoa	Pip.	280	8	41.3	58.8	Traces	0	3
27	...	Harshaw	None	330	8	42.1	56.9	1.0	0	9
28	...	Harshaw	Pip.	330	8	39.6	59.4	0.9	0	4

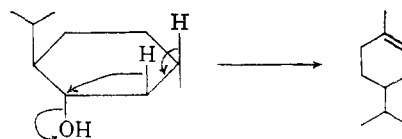
<sup>a</sup> The number of ml. of feed passed over the catalyst before the particular cut was taken is given in parentheses. <sup>b</sup> A refers to alumina prepared from the isopropoxide; B2 and B8 are catalysts prepared from sodium aluminate and washed 2 and 8 times, respectively. The numbers in parentheses refer to the number of times the catalyst was regenerated in air at 500°. <sup>c</sup> The bases used are represented by Pip., TMA and NH<sub>3</sub> for piperidine, trimethylamine and ammonia, respectively. <sup>d</sup> Feed mixed with 1% by weight of piperidine. <sup>e</sup> Feed mixed with 5% by weight of piperidine. <sup>f</sup> Feed mixed with 10% by weight of piperidine. <sup>g</sup> In addition to the menthenes listed, the following also were identified: 8(9)-menthene, 4.3%; 4(8)-menthene, 5.2%; 7(1)-menthene, 1.7%; alkylicyclopentenes, 25.6%. <sup>h</sup> HLSV = hourly liquid space velocity = volume of menthol charged per volume of catalyst per hour.

carbonium ion mechanism without any stereo-specificity. It is not impossible that the 3-menthene is formed by a concerted *cis* elimination. 3-Menthene also can be formed from the hydrogen bridged carbonium ion



The *trans* nature of the hydrogen at the 4-position can help this process. The formation of 1-menthene by the following mechanism (not necessarily concerted) also cannot be ruled out.

**Dehydration of Neomenthol.**—That *trans* elimination is the preferred reaction is further supported by the results obtained on dehydration of neomen-



thol (Table III). Neomenthol, in its most stable conformation, has an axial hydroxy group with one axial (*trans*) hydrogen on each adjacent carbon. It should be recalled that in menthol, the hydroxy group and the *trans*-β-H are in a diequatorial conformation in the most stable form and for strict *trans* elimination, it has to flip over to the less stable diaxial form.

In neomenthol, since the leaving groups are in the right conformation, dehydration by *trans* elimination should be easier than in menthol.

TABLE III  
COMPARISON OF THE PRODUCTS OF DEHYDRATION OF MENTHOL (M) AND NEOMENTHOL (N)

Expt.	Catalyst	Base	Temp., °C.	HLSV	Alcohol	3-Menthene	2-Menthene	1-Menthene	Dehydration, %
1	A(0)	Pip.	280	1	M	22.4	73.5	4.1	91
2	A(0)	Pip.	280	1	N	95.4	3.5	1.1	100
3	A(0)	Pip.	280	3.5	M	20.0	77.2	3.0	54
4	A(0)	Pip.	280	3.5	N	91.9	7.6	0.6	100
5	A(0)	Pip.	280	8	M	19.8	77.1	3.1	32
6	A(0)	Pip.	280	8	N	88.1	11.5	0.5	88
7	B2(0)	None	330	8	M	30.1	66.0	3.9	16
8	B2(0)	None	330	8	N	74.9	24.5	0.7	54

Comparing the extent of dehydration under similar conditions (expt. 5 with 6 and 7 with 8), it is seen that the dehydration of neomenthol is about 3 times as fast as that of menthol.

In menthol, *trans* elimination leads to only one product, 2-menthene. However, in neomenthol, both 2- and 3-menthene can be formed by *trans* elimination. It is seen that the preferred product is the more stable olefin, 3-menthene.

The concentration of 2-menthene from neomenthol increases with the increase in hourly liquid space velocity (expt. 2, 4, 6, Table III). At the lower space velocity the 2-menthene, which is the primary product of dehydration, is re-adsorbed on the catalyst and isomerized to the thermodynamically more stable 3- and 1-menthene.

It has been reported that neomenthyl trimethylammonium hydroxide on Hofmann elimination also yields predominantly 3-menthene.<sup>9,15-17</sup>

**Comparison of the Dehydration of Menthol over the Different Aluminas.**—Alumina of the A series and Alcoa alumina cause extensive isomerization of olefins during dehydrations (see, for example, expt. 9 and 24). In addition to the menthenes, alkylcyclopentenes are also formed on acidic catalysts (see footnote g, Table II). Formation of carbonaceous materials on the catalyst is not appreciable at the low temperatures studied. Hence in the present study, for short runs, the activity of the catalyst was essentially unchanged with time (see Expt. 1, cuts 1-3).

Alumina of the B series and Harshaw alumina cause much less isomerization of olefins (e.g., expt. 21) compared to the A and Alcoa aluminas. Also, as expected,<sup>3</sup> when alumina is prepared from sodium aluminate, the activity increases with the number of times the precipitate was washed (see Expt. 18 and 21).

**The Effect of Bases on Alumina.**<sup>5,18</sup>—It has been shown<sup>3</sup> that exposure of the alumina to ammonia before reaction caused the isomerizing activity of the catalyst to decrease. This was shown to be due to the preferential poisoning of the strong acid

(15) N. L. McNiven and J. Read, *J. Chem. Soc.*, 158 (1952).

(16) E. D. Hughes and J. Wilby, *ibid.*, 4094 (1960).

(17) See ref. 16 for a discussion of the direction of elimination in neomenthyl systems.

(18) In the preliminary communication (ref. 5) it was implied that "selective" dehydration is an exclusive feature of the base-modified catalyst and that dehydration proceeds without selectivity on the unmodified catalyst. This statement, without clarification, may be misleading. The main difference between the two types of catalysts is that on the unmodified catalyst, secondary reactions (olefin isomerization) usually interfere, whereas, on the modified aluminas, such secondary reactions are a minimum. The mechanism(s) of the primary dehydration reaction is probably basically similar on both types of catalysts.

sites of the alumina by the base. It was thought that by following this procedure, the alumina could be modified to obtain a catalyst of low isomerization activity, still retaining good dehydration activity. Examination of the data of Table II shows that the desired objective was attained quite successfully by this procedure. The bases ammonia, trimethylamine and piperidine were used and all three were effective. Experiments 9, 12, 13 and 14 were designed to compare the effect of the three bases. It is seen that piperidine (expt. 14) is the most effective of the three in suppressing isomerization, with trimethylamine (expt. 13) and ammonia (expt. 12) following in that order. These results are to be compared with the results with the unmodified catalyst in experiment 9. In weakening the catalyst, piperidine also decreases the dehydration activity to a larger extent than trimethylamine or ammonia. The effect of the bases is in the same order as the base strength of the amines.

It was mentioned earlier that the bases preferentially poison the strong acid sites of the catalyst and that this is the reason why selectivity is improved on base-modification. In agreement with this it is seen that alumina from sodium aluminate, which does not contain strong acid sites and hence normally show good selectivity, is not improved appreciably on exposure to base (expt. 22 and 23). Dehydration activity, however, is decreased considerably, showing that the weak acid sites are also neutralized to some extent by the base.

When the catalyst is first exposed to piperidine and then dehydration carried out for a prolonged time without the addition of piperidine, the catalyst slowly regains activity as seen from expt. 4, cuts 1-5, in Table II. This regaining of activity is evident from the increase in dehydration activity. The selectivity remains essentially constant. When the base is mixed with the alcohol feed (expt. 5, 6 and 7) both dehydration activity and selectivity remain essentially unchanged with time. Percentage of base added to the alcohol feed (1%, 5% and 10% of piperidine in expt. 5, 6 and 7, respectively) affect the extent of dehydration. However, selectivity is not increased very much by increasing the piperidine content from 1% to 10%.

Contact time has little effect on the product distribution in the case of the B catalysts and modified catalysts (expt. 16, 17 and 18 of Table II and 1, 3 and 5 of Table III). This shows that on these catalysts, the olefins, once they are formed, are not isomerized to any appreciable extent.

As expected, the isomerization increases with contact time on the acidic alumina (expt. 1, 2 and 3 of Table II).

#### The Effect of Regeneration of Catalysts.—

It was observed that all catalyst preparations increased in acidity on regeneration in air at 500°. This effect on the B2 alumina can be seen by comparing experiments 18, 19 and 20 (Table II) which were conducted after 0, 1 and 2 regenerations in air at 500° for 16 hr. This increase in acidity can be so great that after several regenerations, exposure to ammonia has little effect in suppressing isomerization (see Expt. 11, 12 and 15 which were

conducted after 0, 3 and 7 regenerations, respectively). Evidently during regeneration new strong acid sites are being formed. Ammonia is not strong enough to neutralize these acid sites. The stronger bases, trimethylamine and piperidine, are more effective (see Expt. 12, 13 and 14).

The increase in acidity during regeneration can be somewhat corrected by carrying out the process at as low a temperature as possible by diluting the air with nitrogen. However, for synthetic purposes, where secondary reactions are to be avoided, it is best to use non-regenerated alumina.

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## Alumina: Catalyst and Support. XI.<sup>1</sup> Mechanism of Dehydration of Aliphatic Alcohols and the Formation of Cyclopropanes during Dehydration<sup>2</sup>

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The dehydration of several aliphatic alcohols over weakly acidic alumina catalysts were studied. It was found that the dehydration of neopentyl-type alcohols is usually accompanied by rearrangement and that during rearrangement the double bond is formed in preference between the 2- and 3-carbon atoms with respect to the original position of the hydroxyl group. The direction of elimination shifted from Saytzeff to Hofmann as the alcohol became highly branched. Primary and secondary neopentyl-type alcohols gave small amounts of cyclopropanes on dehydration. Possible mechanisms of these reactions are discussed.

In earlier papers of these series,<sup>1,4</sup> the dehydration of certain aliphatic and cyclic alcohols over various aluminas was reported. It was shown that secondary isomerizations accompanying dehydration could be avoided by using aluminas containing only relatively weak acid sites. Modification of alumina by the use of organic bases was found to be the most practical method for obtaining such catalysts.

The products of dehydration corresponded to *trans* elimination of the elements of water.<sup>1</sup> Simple alcohols like 2-butanol and 2-pentanol dehydrated to form more of the internal olefins than of the terminal olefins (Saytzeff elimination).<sup>4</sup> When the internal olefins were formed, the thermodynamically less stable *cis*-olefin was formed in preference to the *trans*.

In the present paper, the dehydration of several aliphatic alcohols, including neopentyl-type alcohols, is discussed.

### Experimental Part

The catalysts were prepared as described before.<sup>1</sup> The reactions were carried out in the apparatus previously described. Where piperidine was used to modify the alumina, it was mixed with the alcohol feed, usually 10% by weight of the alcohol.

Pinacolyl alcohol was prepared by the reduction of pinacolone over a nickel catalyst at 100° and an initial hydrogen pressure of 100 atmospheres; b.p. 120–122°,  $n_D^{20}$  1.4160.

(1) For part X of these series, see H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **83**, 3270 (1961).

(2) Paper IV of the series: Dehydration of Alcohols; for paper III, see ref. 1.

(3) Taken in part from the Ph.D. thesis of C. N. Pillai, Northwestern University, 1960. Grateful acknowledgment is made to the donors of the Petroleum Research Fund for the support of this research.

(4) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **83**, 2847 (1961).

Neopentyl alcohol was prepared by the reduction of trimethylacetic acid<sup>5</sup> by lithium aluminum hydride<sup>6</sup>; b.p. 112–114°.

2,3-Dimethyl-2-butanol was prepared by Grignard reaction from 3-methyl-2-butanone and methyl iodide; b.p. 120–121°,  $n_D^{20}$  1.4176.

3,3-Dimethyl-2-pentanol was prepared by Grignard synthesis from *t*-amyl chloride and acetaldehyde. By distillation of the crude product on a semi-micro spinning band column, pure 3,3-dimethyl-2-pentanol, b.p. 146.8–147.2° at 750 mm.,  $n_D^{20}$  1.4301, was obtained in 15% yield; reported<sup>7</sup> b.p. 147–148°.

2,3-Dimethyl-2-pentanol was similarly prepared from *sec*-butyl bromide and acetone. After distillation, 2,3-dimethyl-2-pentanol, b.p. 139.9–140° at 750 mm.,  $n_D^{20}$  1.4268, was obtained in 22% yield; reported<sup>7</sup> b.p. 129–130.5°.

2,3,3-Trimethyl-2-butanol was prepared by the reaction of acetone with *t*-butylmagnesium chloride and the crude hydrate was purified by sublimation to obtain crystals melting at 82°, reported<sup>7</sup> m.p. 80°.

1,1,2-Trimethylcyclopropane.—A mixture of 21 g. of zinc-copper couple,<sup>8</sup> 54 g. (0.2 mole) of methylene iodide, 21 g. (0.3 mole) of 2-methyl-2-butene, a crystal of iodine and 80 ml. of anhydrous ether was stirred and refluxed under anhydrous conditions for 30 hours. At the end of this time, gas chromatographic analysis of the reaction product showed that 1,1,2-trimethylcyclopropane had formed in 41% yield based on methylene iodide. The mixture was filtered free of solids, washed with 5% HCl, 5% sodium bicarbonate and water and dried over MgSO<sub>4</sub>. By distillation on a semi-micro spinning band column, 3.1 g. of pure 1,1,2-trimethylcyclopropane, b.p. 50.8–51.1° at 738 mm.,  $n_D^{20}$  1.3831, was obtained; reported<sup>9</sup> b.p. 52.6°,  $n_D^{20}$  1.3834.

(5) S. V. Puntambeker and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524.

(6) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

(7) G. Edgar, G. Calingaert and R. E. Marker, *ibid.*, **51**, 1483 (1929).

(8) H. B. Simmons and R. D. Smith, *ibid.*, **81**, 1256 (1959).