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Dehydration of Alcohols over Oxide Catalysts

γ-Eliminations—Stereospecificity and Selectivity

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The effect of alkali impregnation on alumina catalysts has been investigated by a physicochemical study of pure and modified alumina catalyst samples. The stereospecificity and selectivity of dehyration reactions, as well as the incidence of γ-elimination, have been studied by passing suitable substrates over catalyst samples. There was a change in the acidity–basicity balance in the sodium-impregnated alumina samples vis à vis pure alumina, while the surface area virtually remained constant. A higher propensity for γ-elimination was noticed with increases in basicity of the catalyst. 1-Olefin formation was found to be larger in more basic alumina- and thoria-catalyzed dehydration reactions. Thoria was strikingly unique in its capacity to dehydrate only alcohols, which have at least one β-hydrogen atom. Neopentyl alcohol could not be dehydrated even under drastic conditions. The modes of elimination in the case of alumina and thoria have been shown to be *anti* and *syn*, respectively, from the results of the dehydration studies with *threo*-3-methyl-2-pentanol. Studies of alcohols with proper β-substituents revealed that the *cis* preference is not universal in all catalytic eliminations but, in fact, depends on the mode of elimination. While *cis*-preference was noticed in alumina-catalyzed *anti* eliminations, *trans*-olefin was formed to a major amount in thoria-catalyzed *syn*-elimination processes.

INTRODUCTION

The elimination of elements of water from alcohols to furnish olefins, brought about by oxide catalysts, is a well-known reaction. These dehydration reactions have been studied, in detail, with alumina catalysts (*1–4*). Taking into account the role of acidic and basic sites, a concerted mechanism analogous to the one in E2 reactions has been proposed (*5*). This involves a synchronous weakening of the C–O bond by an acidic site and extraction of β-hydrogen atom by a basic site. It has been discerned by ir studies that the β-hydrogen atom of the substrate-alcohol is strongly bonded to the catalyst surface (*6*).

The mode of elimination in dehydration reactions over alumina catalyst has been shown to be *anti* from antiperiplanar conformation (*1, 7*). There had been reports that, when there is a possibility for formation of different geometrical isomers, the *cis* isomer is predominantly formed (*1–4, 8*). These observations also appear to be common for all heterogeneously catalyzed elimination reactions in dehydrohalogenations over salt catalysts (*9, 10*).

The explanation for *anti*-elimination and *cis* preference is still a matter of controversy. Pines and co-workers assumed that the reaction took place in the crevices or pores in the solid, with the aid of favorably located acidic and basic sites (*1, 11*). However, the alternate model proposed by

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Notari (*4*) eventually led to a *syn* elimination. Based on the experimental studies of product distribution and Arrhenius parameters, a new transition state model was proposed by Knözinger (*12*), which satisfactorily explains the *cis* predominance as well as the *anti* mode of elimination. This model has been successfully used in explaining the observations made by Noller and co-workers (*13*) during the dehydration of diastereomeric 2-butanol-3-d over alumina.

The *anti* mode of elimination need not always be due to a reaction between surfaces in a pore or a crevice, as suggested by Hall *et al.* (*14*). On the surface of alumina, partial dehydration of the surface leads to a situation where large O^{2-} ions (of a size as large as the methyl group) and Lewis acid sites are covering adjacent lattice positions. Thus, when the alcohol is adsorbed through the alcoholic oxygen atom at a Lewis acid site, the basic center, an O^{2-} ion, effects the dehydration. The anti β-hydrogen atoms are more easily discharged and hence the observed stereospecificity and selectivity.

The dehydration studies conducted with diastereomeric 2-butanol-3-d alcohols over hydroxyapatite and alumina conducted by Hall *et al.* showed that the dehydration over alumina is by an *anti* mode with a high *cis–trans* ratio. The hydroxyapatite eliminated hydrogen via the *syn* mode, but the *cis–trans* ratio was higher than unity. The *cis–trans* ratio with hydroxyapatite was lower than with alumina-catalyzed dehydration.

The variation of product distribution with increase in alkali content, over alumina catalyst samples, has not been convincingly explained by the available data. The theory of variable E2 transition states, proposed by Steffa and Thornton (*15*), has been employed to explain the variation. The reaction, though concerted, might pass through one ot the existing ranges of transition states between an E1CB extreme and an E1 extreme. Depending on the nature of the leaving group and the temperature and strength of the base employed, there could be a shift in E2 transition states in elimination reactions. The elimination reaction can be made to proceed by an E1-like or E1CB-like transition state, by suitably changing the parameters.

A recent paper (*16*) deals with the effect of base strength upon the structure of transition states in elimination reactions. The authors report a significant decrease in the C_α–leaving group bond and an increase in E1CB character with an increase in base strength.

Along with the normal β-elimination reaction, concerted γ-eliminations, accompanied by migration of a group or atom, do take place during dehydration of alcohols (*1, 8, 17*). The impregnation of an alumina catalyst with sodium ions is known to cause changes in acidity–basicity balances (*18*).

Chuang and Dalla Lana (*19*) investigated the effect of sodium impregnation on the selectivity for dehydration and dehydrogenation processes. A decrease in BET surface area was noticed with an increase in the amount of the dopant. The high-surface-area catalysts were reported to be more selective for dehydration, whereas low-area catalysts were selective for dehydrogenation.

A *syn* mode of elimination has been proposed for dehydration reactions over thoria catalysts. A six-atom cyclic transition state model, similar to the one in gas-phase pyrolysis, has been suggested by Lundeen and Van Hoozer (*20, 21*) to explain the high selectivity for 1-olefin formation (Hofmann selectivity). Brey *et al.* (*22, 23*) have reported that the mode of preparation and pretreatment of the thoria catalyst affected activity as well as selectivity in these reactions. It was shown that the high-surface-area thoria catalyst was selectively dehydrating, while the low-surface-area thoria catalyst was selectively dehydrogenating. In the case of thoria-

TABLE 1

Protonic Acidity of Pure and Sodium-Impregnated Alumina Catalyst Samples

Sample No.	Percentage Na content (w/w)	Protonic acidity (mmol/g)
1	0	0.043
2	0.19	0.037
3	0.29	0.031
4	0.68	0.029
5	0.95	0.021
6	1.50	0.008
7	1.71	0.006
8	2.20	Not measurable

catalyzed dehydration reactions, no γ-elimination has been reported.

MATERIALS AND PROCEDURES

The γ-alumina catalyst, used in the present study, was obtained from aluminum isopropoxide by weathering (aerial hydrolysis) and by calcining the aluminum hydroxide samples thus obtained at 600°C for 6 hr. This pure alumina sample was used for sodium impregnation. The sodium-impregnated alumina catalyst samples were made by keeping a known weight of alumina sample immersed in sodium carbonate solutions of different strengths. The amount of sodium ions (w/w) impregnated was indirectly determined by titrating the excess base left behind in the supernatant solution with standard acid. By this procedure, a range of sodium-impregnated alumina catalyst samples containing varying percentages of sodium was prepared.

The thoria catalyst samples were prepared by *two* methods:

(a) Precipitation of thorium hydroxide from thorium nitrate solution and calcination of thorium hydroxide at 500°C for 6 hr, yielding Thoria-I.

(b) Direct calcination of thorium nitrate crystals at 600°C for 5 hr, yielding Thoria-II.

Most of the substrate alcohols were prepared by Grignard reaction. Benzyl methyl ketone was prepared from phenylacetic acid and acetic acid (1:3) by a decarboxylative ketonization reaction over thoria catalyst at 400°C. The ketone was reduced by sodium borohydride to give the benzylmethylcarbinol.

Threo-3-Methyl-2-Pentanol was prepared by a hydroboration reaction from 3-methyl-*trans*-2-pentene (Fluka Busch) using boron trifluoride dietherate in diglyme. The product contained a small amount of diglyme, which did not interfere with either the reaction or the analysis. The purity of the alcohol samples was ascertained via gas chromatography.

The dehydration studies were conducted in a continuous flow-type integral reactor. The reactants were discharged into the reactor by an automatic liquid dispenser (Sage Model 249-3). The reaction was done with a coarse sample and was repeated with a pulverized sample. No change in activity was observed. Under these conditions, employing catalysts with small particle sizes, diffusion should be negligible. The reactions were done at three different flow rates (6, 12, 18 ml/hr), and the results indicated that secondary isomerization reactions were minimal under the conditions employed for the reaction. Piperidine-poisoning studies were carried out by mixing the feed with piperidine (10%, v/v). The catalyst was rendered ineffective for secondary processes, as the strong acidic sites were selectively poisoned by the base.

The product olefins were analyzed in a Varian Aerograph 1800 dual-column machine with a thermal detector. *n*-Hexane was used as an internal standard, and calibrations were made for calculation of responses of individual components for quantitation. The stationary phases used were dimethylsulfolane, Carbowax-1500, Ucon-500, and silicone-SE-30, coated on Chromosorb-W (80–100 mesh).

One gram of finely powdered catalyst

sample was used in these studies, and reactions were carried out at 300°C over alumina catalyst samples and at 350°C over thoria catalyst samples. The Brønsted acidity of alumina and sodium-impregnated alumina samples was determined by an aqueous ion-exchange method (*24*). The basicity measurements were made by a phenol and trichloracetic acid adsorption method (*25*).

Surface areas of the samples were computed by the BET method at liquid nitrogen temperature. Pore volume measurements were made by the mercury intrusion method, using a mercury porosimeter, Carlo Erba 70.

RESULTS AND DISCUSSION

Effect of Sodium Impregnation on Alumina

A study of the parameters that are affected by the impregnation of alumina catalysts with sodium ions was made. There was a marked decrease in Brønsted sites with an increase in the amounts of dopant (Table 1). But the reduction in the number of Brønsted sites was not commensurate with the amount of sodium ions incorporated into the catalyst. An alumina sample containing 0.29% (w/w) sodium has 0.1275 mmol/g of sodium ions. Considering the acidity of a pure alumina sample, this number of sodium ions is sufficient enough to replace all the acidic hydrogens from the surface of the catalyst. It is significant to note that, on the contrary, the presence of even a high amount of dopant, viz., 1.71% sodium, still leaves the catalyst definitely acidic. This seems to indicate that even if an excess of alkali ions is present, they do not exchange with all the replaceable Brønsted acid centers on the catalyst surface. This corroborates the conclusion put forth by Schwab and Kral (*18*) that the doping agents do not act as such, but being bases by themselves, they neutralize and eliminate acidic sites. They are, probably, not completely incorporated into the lattice but, in part, are free on the surface.

TABLE 2

Basicity of Pure and Sodium-Impregnated Alumina Catalyst Samples

Sample No.	Percentage Na content (w/w)	Basicity (mmol/g)	
		Phenol adsorption	TCA[a] adsorption
1	0	0.15	0.98
2	0.29	0.22	1.20
3	0.68	0.28	1.35
4	1.50	0.29	1.76
5	1.71	0.31	1.83

[a] TCA—Trichloracetic acid.

Pines and Haag (*26*) suggested that alumina exhibits both strong and weak types of Brønsted acid character. The total number of hydroxyl-type acidic sites on alumina can be measured by dehydrating 1-butanol and a fraction of these sites, which are strong, can be determined by cyclohexene isomerization. It could be that the sodium ions interact with only a particular set of hydroxyl acidic sites of certain acidic strength, leaving the other hydroxyl groups intact on the surface. Chuang and Dalla Lava (*19*) indicated that while both pure and sodium-doped alumina samples are active toward dehydration, the latter was ineffective in causing isomerization of cyclohexane. Studies conducted in this laboratory also indicated that sodium poisoning renders the alumina catalyst less effective in causing skeletal isomerization of olefins, like 3,3-dimethyl-1-butene.

The basicity measurements were made by both the phenol and trichloracetic acid adsorption techniques to get the amount of strong and total basic sites, respectively, present on the surface of pure and sodium-impregnated alumina samples (Table 2). There was a marginal increase in the number of strong basic sites, while the total number of basic sites registered a substantial increase. This suggests that there

TABLE 3

BET Surface Area of Samples

Sample No.	Catalyst description	Surface area (m^2/g)
1	γ-Al_2O_3	150
2	0.12% Na^+-Al_2O_3	137
3	0.19% Na^+-Al_2O_3	160
4	0.68% Na^+-Al_2O_3	156
5	0.95% Na^+-Al_2O_3	154
6	1.71% Na^+-Al_2O_3	148
7	2.2% Na^+-Al_2O_3	160
8	Thoria-I	50
9	Thoria-II	42

is an increase in the number of weak basic sites, which are formed due to the incorporation of alkali ions into the alumina surface.

Surface area measurements of these catalysts did not show any appreciable variation (Table 3). The pore volume measurements made by mercury intrusion (Table 4) indicated that the micropore volume (up to 50 Å) remained almost constant, whereas the macropore volume increased considerably with increases in sodium content.

With surface area and micropore volume remaining constant, the variation in product distribution between pure and sodium-impregnated alumina samples could be attributed to the variation in acidity–basicity balance. The changes in the relative amounts of acidic and basic sites seems to be the main reason for the observed differences in selectivity during dehydration of alcohols.

γ-Elimination Accompanying Dehydration

A study of dehydration of neopentyl alcohol was made with pure and sodium-doped alumina catalyst samples. This substrate is a primary alcohol without β-hydrogen atoms. The normal 1,2-elimination being impossible due to the lack of β-hydrogen atoms, the only mode of dehydration could be by an extraction of γ-hydrogen atoms, and this furnishes the skeletally rearranged product (Fig. 1).

It could be seen that such an elimination process would lead to 2-methyl-1-butene as the main product (Table 5). Under nonisomerizing conditions, by piperidine poisoning, over alumina, the terminal olefin is formed to a larger extent. The other olefin, 2-methyl-2-butene, is also formed to a significant extent, suggesting the operation of an E1-like (carbonium ion) pathway, giving rise to more internal olefin. Even though concerted γ-elimination is the main pathway leading to more 2-methyl-1-butene, the E1 pathway cannot be ruled out and hence the observed product distribution. To explain the formation of 2-methyl-2-butene, a nonclassical carbonium ion intermediate was proposed by Frazer and Hofmann (*27*), but this postulation, made without proper experimental evi-

TABLE 4

Pore Volume Data of Catalyst Samples

Sample No.	Catalyst description	Micropore volume (ml) (<50 Å)	Macropore volume (ml) (>50 Å)	Total pore volume (ml)
1	γ-Al_2O_3	0.09	0.53	0.62
2	0.12% Na^+-Al_2O_3	0.08	0.67	0.75
3	0.9% Na^+-Al_2O_3	0.07	4.67	4.74
4	1.7% Na^+-Al_2O_3	0.08	6.72	6.80
5	Thoria-I	0.012	0.128	0.14
6	Thoria-II	0.01	0.128	0.138

dence, was subjected to criticism by many workers.

The formation of 2-methyl-2-butene could also be due to an isomerization of the primarily formed 1-olefin. Although skeletal isomerization is not feasible over sodium-doped alumina, double bond isomerization is a facile reaction.

The dehydration of neopentyl alcohol over sodium-doped alumina samples provided more of the terminal olefin. As the sodium ions make the catalyst less acidic and more basic, the transition state shifts from a more polar (in the case of pure alumina with maximum acidity) to a more concerted pathway and hence the increase in the amount of 2-methyl-1-butene with increases in sodium content. Although piperidine poisoning and sodium poisoning at higher levels gave a similar product distribution, in pure alumina we observe a thoroughly different trend. It must be noted, however, that dehydration studies with neopentyl alcohol were done by Pines and Pillai only with piperidine poisoning (10%, w/w) (*28*). In the present case, the piperidine poisoning studies have given similar product distributions.

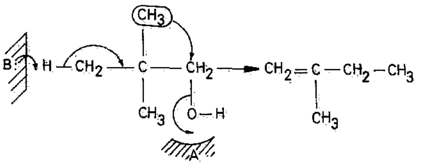


FIG. 1. Dehydration of neopentyl alcohol γ-elimination.

Dehydration studies with pinacolyl alcohol using these catalyst samples showed an enhanced propensity for γ-elimination with an increase in sodium content. Pure alumina mainly afforded the unrearranged olefin, i.e., 3,3-dimethyl-1-butene, during the dehydration of pinacolyl alcohol (Table 6). The rearranged olefins are also formed in these reactions. The piperidine-poisoning studies indicate that 3,3-dimethyl-1-butene and 2,3-dimethyl-1-butene are the primary products of the reaction.

The activity for dehydration reactions dropped rapidly with increases in sodium

TABLE 5

Dehydration of Neopentyl Alcohol over Alumina and Thoria Catalyst Samples

Sample No.	Catalyst	Flow rate (ml/hr)	Percentage conversion	Percentage product distribution		
				2-M-1-B[a]	2-M-2-B[b]	Rest*
1	γ-Al_2O_3	18	67	32.0	66.0	2.0
2	γ-Al_2O_3 + piperidine (10% V)	18	18	67.0	31.0	2.0
3	0.12% Na^+-Al_2O_3	18	48	32.0	66.5	1.5
	0.12% Na^+-Al_2O_3	12	72	31.5	67.0	1.5
4	0.19% Na^+-Al_2O_3	18	36	45.0	53.5	1.5
	0.19% Na^+-Al_2O_3	12	65	44.0	54.5	1.5
5	0.41% Na^+-Al_2O_3	18	23	45.0	53.5	1.5
	0.41% Na^+-Al_2O_3	12	54	43.0	55.0	2.0
6	0.68% Na^+-Al_2O_3	18	15	48.0	50.0	2.0
	0.68% Na^+-Al_2O_3	12	40	47.0	51.0	2.0
7	1.11% Na^+-Al_2O_3	18	10	58.0	40.0	2.0
	1.11% Na^+-Al_2O_3	12	24	57.0	41.0	2.0
8 9	Thoria-I Thoria-II	No reaction even at 450°C			—	—

* 1,1-Dimethylcyclopropane.

[a] 2-M-1-B: 2-Methyl-1-butene.

[b] 2-M-2-B: 2-Methyl-2-butene.

TABLE 6

Dehydration of Pinacolyl Alcohol over Alumina and Thoria Catalyst Samples

Sample No.	Catalyst	Flow rate (ml/hr)	Percentage conversion	Percentage product distribution		
				3,3-DMB-1[a]	2,3-DMB-1[b]	2,3-DMB-2[c]
1	γ-Al_2O_3	18	66	69.0	27.0	4.0
2	γ-Al_2O_3 + piperidine (10% V)	18	66	71.0	27.0	2.0
3	0.12% Na^+-Al_2O_3	18	47	60.0	33.0	7.0
	0.12% Na^+-Al_2O_3	12	71	59.0	33.0	8.0
4	0.19% Na^+-Al_2O_3	18	40	54.0	39.0	7.0
	0.19% Na^+-Al_2O_3	12	63	53.0	39.0	8.0
5	0.41% Na^+-Al_2O_3	18	26	51.0	39.5	9.5
6	1.11% Na^+-Al_2O_3	18	16	47.0	44.0	10
	1.11% Na^+-Al_2O_3	12	27	47.0	44.0	10
7	Thoria-I	12	8.0	98.0	2.0	—
8	Thoria-II	12	5.0	98.0	2.0	—

[a] 3,3-DMB-1: 3,3-Dimethyl-1-butene.
[b] 2,3-DMB-1: 2,3-Dimethyl-1-butene.
[c] 2,3-DMB-2: 2,3-Dimethyl-2-butene.

content in the catalyst sample. This is a common observation during dehydration with sodium-doped alumina samples.

If the formation of rearranged olefins were due to a secondary process, then more skeletal isomerization must have resulted at higher contact times. This is not our observation. The product distribution does not vary at different contact times. Furthermore, the sodium-impregnated alumina samples are less acidic than pure alumina and eventually should lead to less skeletal rearrangement. The isomerization studies conducted with the 3,3-dimethyl-1-butene

TABLE 7

Isomerization of 3,3-Dimethyl-1-butene

Sample No.	Catalyst	Flow rate (ml/hr)	Percentage conversion	Percentage product distribution	
				2,3-DMB-1[a]	2,3-DMB-2[b]
1	γ-Al_2O_3	6	34	44	56
	γ-Al_2O_3	12	30	31	69
	γ-Al_2O_3	18	27	32	68
2	0.12% Na^+-Al_2O_3	6	7.0	47	53
	0.12% Na^+-Al_2O_3	12	2.5	44	56
	0.12% Na^+-Al_2O_3	18	1.8	44	56
3	0.41% Na^+-Al_2O_3	No isomerization			
4	0.68% Na^+-Al_2O_3				
5	Thoria-I				
6	Thoria-II				

[a] 2,3-DMB-1: 2,3-Dimethyl-1-butene.
[b] 2,3-DMB-2: 2,3-Dimethyl-2-butene.

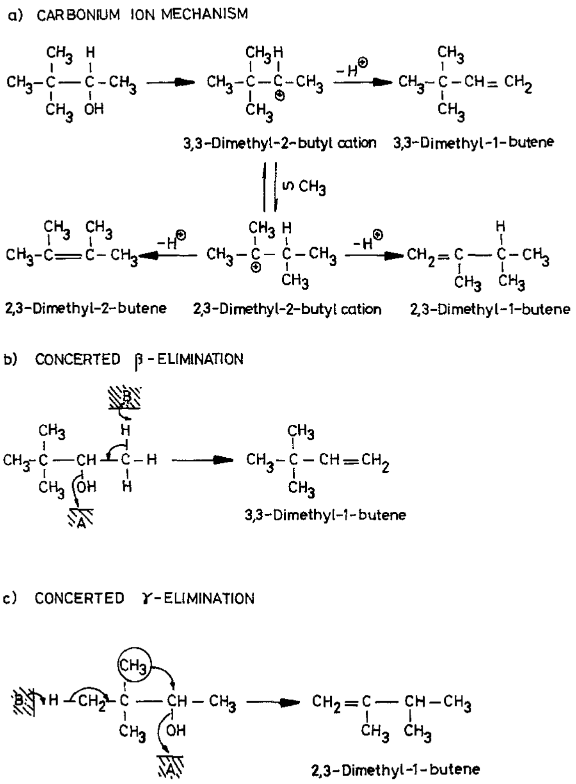


FIG. 2. Dehydration of pinacolyl alcohol.

over sodium-doped alumina samples revealed that sodium-doped catalysts are less effective in causing isomerization (Table 7). Hence, the product distribution can be taken as representative of the true situation. This points out that the γ-elimination takes place *during* and not *after* the reaction.

A carbonium ion mechanism has been proposed for reactions of this type, generally known as Wagner–Meerwein rearrangements (Fig. 2). This indicates an enhanced rearrangement with higher acidic strength. Our results, on the contrary, indicate an increased incidence of rearrangement with less acidic and more basic sodium-impregnated alumina samples. Pinacolyl systems, proceeding through the E1 pathway, had always exhibited extensive rearrangement during elimination. The acid-catalyzed dehydration of pinacolyl alcohol gave typical product distributions for the E1 reaction. Whitmore and Rothrock (*29*) observed a high degree of skeletal rearrangement during the dehydration of pinacolyl alcohol with anhydrous oxalic acid. The ratio of 2,3-dimethyl-2-butene to 2,3-dimethyl-1-butene was 2.5, strikingly more than unity. Hence, it is clear that the present sodium-doped alumina-catalyzed dehydration could not be due to an E1 pathway.

This is true even for pure alumina as the dehydration provides more of the unrearranged olefins and the 2,3-dimethyl-2-butene/2,3-dimethyl-1-butene ratio is very low. The percentage of 2,3-dimethyl-2-butene has also increased but the ratio of internal to terminal olefin still remains less than one. It is possible that a carbonium ion pathway is operative but the incidence of such a pathway is by far less than the concerted one, leading to more terminal

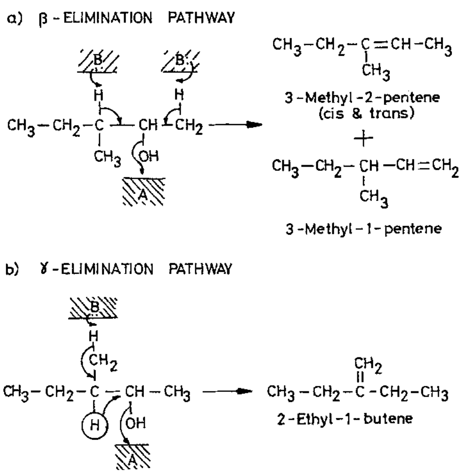


FIG. 3. Dehydration of 3-methyl-2-pentanol β- and γ-elimination pathways.

olefin. A concerted pathway is what is operative over alumina as well as sodium-impregnated alumina samples. The variation in product distribution in the case of sodium-doped alumina catalyst samples can be rationalized by an extension of the theory of variable E2 transition states.

The two transition states leading to unrearranged and rearranged olefins are represented in Figs. 2b and c, respectively. With pure alumina, the most acidic of all the catalyst samples dealt with here, an E1-like transition state is highly probable. The elimination proceeds by a concerted process with a slight E1-like character. As the base strength is not high, the competition between 2b and 2c would have little to do with the extraction of β-hydrogen atoms. Structure 2b may be preferred on the principle of least structural change and hence more normal 1,2-elimination providing unrearranged olefin in major amounts is observed (Table 8).

On the less acidic and more basic sodium-impregnated alumina samples, the E2 transition state shifts to an E1CB-like extreme, and the contribution of structure 2c becomes important, due to a larger number of γ-hydrogen atoms available in the molecule. This leads to γ-elimination with skeletal rearrangement furnishing 2,3-dimethylbutenes with a higher percentage of the terminal olefin. The concept of shift in the transition state, in pinacolyl systems, has been verified in homogeneous systems as well (*30*).

Dehydration studies were conducted with a 50:50 mixture of *erythro* and *threo* diastereomeric 3-methyl-2-pentanols. This study also indicated that the propensity for γ-elimination (in this case not a skeletal rearrangement as the migrating function happens to be a hydrogen atom) steadily increased in the case of sodium-impregnated alumina catalyst samples, suggesting the operation of a shift in transition state from E1 to E1CB under increased basic conditions. Here, the product resulting from γ-elimination is not high, due mainly to a lesser number of γ-hydrogen atoms in this substrate vis à vis an overwhelming number in pinacolyl alcohol (Fig. 3).

Moreover, in 3-methyl-2-pentanol, there is only one migrating atom (hydrogen) and migration of the methyl group is not observed, as the migratory aptitude is of the order H > CH_3.

The absence of 2-methyl-2-pentene, which would have been the product arising out of migration of the methyl group, indicates that methyl group migration is not taking place, in preference to hydrogen migration.

In the pinacolyl alcohol system, apart from the large number of γ-hydrogen atoms, there are two migration functions (methyl groups) and hence a proper orientation for migration could be attained easily with pinacolyl alcohol, resulting in extensive rearrangement.

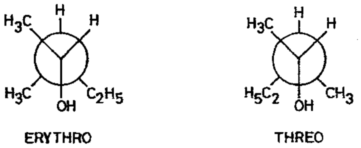


FIG. 4. *Erythro* and *threo* diastereomers of 3-methyl-2-pentanol.

TABLE 8

Dehydration of 3-Methyl-1-pentanol over Alumina and Thoria Samples

Sample No.	Catalyst	Flow rate (ml/hr)	Percentage conversion	Percentage product distribution			
				3-M-1-P[a]	2-E-1-B[b]	3-M-2-P[c]	
						cis	*trans*
1	γ-Al_2O_3	18	65	19.5	3.5	40.0	37.0
		12	83	18.5	3.5	40.0	38.0
2	γ-Al_2O_3 + piperidine (10% V)	18	31	21.0	3.0	39.0	37.0
3	0.12% Na^+–Al_2O_3	18	54	20.0	3.5	38.5	36.0
	0.12% Na^+–Al_2O_3	12	69	19.0	4.0	38.5	36.5
4	0.19% Na^+–Al_2O_3	18	47	21.5	4.0	38.0	36.5
	0.19% Na^+–Al_2O_3	12	58	21.0	4.0	38.0	37.0
5	0.41% Na^+–Al_2O_3	18	35	25.0	4.5	39.0	31.5
	0.41% Na^+–Al_2O_3	12	47	24.5	4.5	40.0	31.0
6	0.68% Na^+–Al_2O_3	18	28	30.0	5.0	34.5	30.5
	0.68% Na^+–Al_2O_3	12	40	29.5	5.0	35.0	30.5
7	1.11% Na^+–Al_2O_3	18	15	30.0	6.0	33.5	30.5
	1.11% Na^+–Al_2O_3	12	30	30.0	6.0	34.0	30.0
8	Thoria-I	18	8	92.0	—	4.0	4.0
		12	12	92.0	—	4.0	4.0
9	Thoria-II	18	6.0	93.0	—	3.5	3.5
		12	11.0	93.0	—	3.5	3.5

[a] 3-M-1-P: 3-Methyl-1-pentene.
[b] 2-E-1-B: 2-Ethyl-1-butene.
[c] 3-M-2-P: 3-Methyl-2-pentene.

Gas chromatographic analysis of the product-alcohol mixture showed that there was no change in the relative reactivities of these two diastereomers (Fig. 4).

There are *two* factors which can decide the reactivity of these alcohols. (i) The first is the inclination of the molecule on the surface; i.e., molecule should react to yield a product through a transition state, where bulky groups are kept off the surface of the catalyst. If such a steric crowding in the transition state is important, then the *threo* diastereomer should react faster than the *erythro*, as the *threo* can incline on the surface with the methyl and ethyl groups away from the surface. (The erythro would keep only two methyl groups away from the surface.) (ii) The steric crowding in the molecule decides the reactivity i.e., the conformer, where there is very little steric crowding, is the one reacting faster. If this were the case, then the *erythro* form, which is sterically less crowded, must be the faster reacting of the two diasteromers.

The present observation is that they react at almost equal rates. It is presumed that both these factors are operative, and the net effect is zero as the one factor nullifies the effect of the other. It is also evident that there is no isomerization of one diastereomer into another taking place under the set of conditions employed for the present reaction.

γ-*Elimination and Thoria Catalysts*

By extension of the theory of variable-transition E2 transition states to a distinctly basic catalyst like thoria, we would predict an increase in γ-elimination. The dehydration studies done with neopentyl, pinacolyl, and 3-methyl-2-pentanol alcohols over thoria did not show any palpable formations of γ-elimination products. What appears puzzling is why basic thoria could not effect γ-elimination, when a more basic sodium-impregnated γ-alumina sample (compared to a less basic pure alumina) enhances γ-elimination. It is thought that this difference might be due to the differences in the modes of elimination with these *two* catalyst samples.

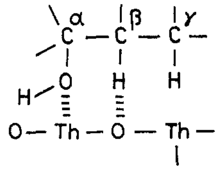


FIG. 5. Model for thoria-catalyzed reaction lack of γ-elimination.

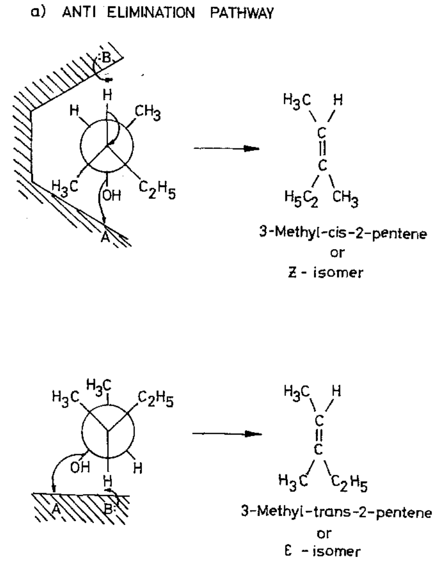


FIG. 6. Dehydration of *threo*-3-methyl-2-pentanol: *syn* and *anti* modes of elimination.

When one considers the model for dehydration over alumina, as suggested by Knözinger, it is clear that adsorbed alcohol still has one degree of freedom—translational. It moves along the surface of the catalyst and whenever a favorably located basic site is approached by a β-hydrogen atom, elimination takes place by a flipping or inclination on the surface. It is also possible that in these circumstances, a γ-hydrogen could also be extracted (if a suitable basic center is available), which would lead to γ-elimination.

It must be remembered that while alumina dehydrates by an *anti* mode, it also gives γ-elimination products during dehydration, whereas in the *syn* elimination involving acetates, xanthates, and amine oxides, very little γ-elimination or skeletal rearrangement has been observed (*31*).

Tomatsu *et al.* (*32*) suggested that the dehydration occurs mainly on the basic sites of the catalyst surface. The alcohols, which exhibited a high reactivity over thoria catalysts were, without exception, the ones in which the carbon bearing the hydroxyl group was attached to a methyl group. From the stereo-model of ethanol, the mean distance between OH and H of the methyl group was estimated to be 2.42 Å. On the thoria surface, when an oxygen atom acts as a basic site and a thorium atom as an acidic site, the mean distance between these two atoms would be only slightly larger than 2.42 Å (the sum of the ionic radii of the two atoms).

TABLE 9

Dehydration of *threo*-3-Methyl-2-pentanol

Sample No.	Catalyst	Flow rate (ml/hr)	Percentage conversion	Percentage product distribution			
				3-M-1-P[a]	2-E-1-B[b]	3-M-2-P[c]	
						cis	*trans*
1	γ-Al_2O_3	18	64	17.0	3.5	61.5	19.0
	γ-Al_2O_3	12	83	15.5	3.5	61.0	20.0
	1.11% Na^+-Al_2O_3	18	24	16.5	3.5	62.0	18.0
2	γ-Al_2O_3 + piperidine (10% V)	18	31	19.0	3.5	62.0	15.5
3	Thoria-I	18	8.0	88.0	—	2.0	10.0
4	Thoria-II	18	7.0	91.0	—	1.0	8.0

[a] 3-M-1-P: 3-Methyl-1-pentene.

[b] 2-E-1-B: 2-Ethyl-1-butene.

[c] 3-M-2-P: 3-Methyl-2-pentene.

Hence, the dehydration of secondary alcohols proceeded favorably over thoria by a concerted *syn* mode of elimination.

When a substrate-like neopentyl alcohol was used, dehydration was not observed even under drastic conditions, indicating that the thoria-catalyzed dehydration would take place only when there is a minimum of β-hydrogen atoms in the substrate. When the alcohol is adsorbed through oxygen on the thorium atom of the surface, there would not, in all probability, be a favorably located site (oxygen) on the surface to extract a γ-hydrogen atom (Fig. 5). Hence γ-elimination is not observed to a significant extent during thoria-catalyzed dehydration reactions.

Stereospecificity and Selectivity in Dehydration Reactions

Apart from the operation of factors such as acidity and basicity, the mode of elimination is a factor which has control over the product distribution and selectivity for the formation of any single product. The two catalysts, alumina and thoria, are shown to dehydrate alcohols by *anti* and *syn* modes, respectively (Table 8).

Dehydration studies conducted with *threo*-3-methyl-2-pentanol over alumina and thoria samples proved, unambiguously, the operation of different stereospecific modes of elimination (Table 9). The substrate provided more of the 3-methyl-*cis*-2-pentene, over alumina, confirming the stereospecific *anti* mode of elimination (Fig. 6). It must also be noted that sodium impregnation had not caused any change in the product distribution during dehydration of *threo* diastereomer, showing that the mode of elimination is still *anti*. The operation of the *syn* mode of elimination over thoria was confirmed by the formation of more 3-methyl-*trans*-2-pentene.

The earlier studies of *threo*-alcohol done by one of us (*33*) gave totally different product distributions for thoria-catalyzed dehydration reactions. We believe that the method of preparation of the catalysts was responsible for such a change. In the present study, a 0.3 *M* solution of thorium nitrate was used with rapid addition of ammonia, as suggested by Brey (*22*), to get a reproducible catalyst (drying of the hydroxide at 120°C for 24 hr and calcination at 600°C for 5 hr). In the earlier study, the catalyst was prepared at 400°C and calcined for

TABLE 10

Dehydration of Menthol and Neomenthol over Alumina and Thoria Samples

Sample No.	Catalyst	Flow rate (ml/hr)	Substrate	Percentage conversion	Percentage product distribution	
					2-Menthene	3-Menthene
1	γ-Al_2O_3	18	Menthol	67	84.0	16.0
	γ-Al_2O_3	12	Menthol	86	83.0	17.0
2	γ-Al_2O_3 + piperidine (10% V)	18	Menthol	30	94.5	5.5
3	Thoria-I	18	Menthol	8.0	98.0	2.0
4	Thoria-II	18	Menthol	7.0	98.0	2.0
5	γ-Al_2O_3	18	Neomenthol	47.0	12.0	88.0
	γ-Al_2O_3	12	Neomenthol	63.0	12.0	88.0
6	γ-Al_2O_3 + piperidine (10% V)	18	Neomenthol	24.0	13.0	87.0
7	Thoria-I	18	Neomenthol	12.5	91.5	8.5
8	Thoria-II	18	Neomenthol	10.0	90.5	9.5

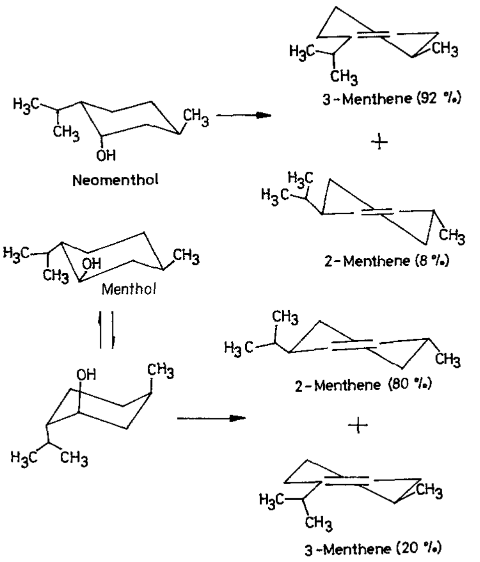


FIG. 7. Dehydration of neomenthol and menthol over alumina.

4 hr; therefore the properties of the catalyst were different since the crystalline size is smaller at lower temperatures and the surface area is very large. The surface would be much less dehydrated, thereby facilitating *anti* elimination from a juxtaposed O^{2-} obtained by partial dehydration.

The selectivity for these reactions is not only decided by the properties of the catalyst alone but also by the mode of elimination.

Dehydration reactions conducted with menthol and neomenthol indicated that the mode of elimination plays an important role, along with other electronic and steric factors, in deciding the product distribution (Table 10). It can be seen that the major product of dehydration of menthol over alumina is the 2-menthene. The menthol molecule has to flip (Fig. 7) in order for a concerted elimination to take place. The elimination would proceed as well from a twist conformation without much steric inhibition. In menthol, only one β-hydrogen atom, *anti* to the hydroxyl group, is available. This *anti* hydrogen atom is preferentially removed to provide 2-menthene. It is evident that the 3-menthene formed over alumina is formed mainly by a secondary isomerization process.

When neomenthol was dehydrated over alumina, the highly substituted 3-menthene was formed to a great extent. In neomenthol, the carbon bearing the hydroxyl group is flanked on either side by carbon atoms having *anti*-disposed β-hydrogen atoms. The transition state, in which the incipient bond is stabilized by electronic factors (hyperconjugation) is preferred, and hence more 3-menthene results from neomenthol.

Both menthol and neomenthol, when passed over thoria, yielded 2-menthene as the major product, which is less substituted when compared to 3-menthene. It is likely that when an acidic catalyst like alumina is employed, the importance of acidity of the β-hydrogen atom is not felt, whereas, with a basic catalyst like thoria, the acidity of the β-hydrogen atom assumes importance and the highly acidic β-hydrogen atom seems to be preferred for elimination.

A few interesting observations were made during dehydration of *cis*- and *trans*-2-methylcyclohexanols over alumina (*34*, *35*) and hydroxyapatite catalysts (*14*).

trans-2-Methylcyclohexanol (structurally similar to menthol) yielded, over alumina, the olefin arising from extraction of the only β-hydrogen atom, *anti*-disposed, available in the molecule (i.e., 3-methylcyclohexene was the major product from this alcohol). This is in agreement with observations in the case of menthol over alumina in the present study. 2-Menthene is the major product from menthol, by abstraction of *only one anti*-disposed β-hydrogen atom available in the molecule.

The *cis*-2-methylcyclohexanol, when passed over alumina, yielded more 1-methylcyclohexene, by extraction of a β-hydrogen atom (*anti*) from a more substituted center. This suggests that in the transition state the electronic factors are playing a vital role, and also, since the catalyst is acidic, the transition state could

TABLE 11

Dehydration of 2-Methyl-3-pentanol over Alumina and Thoria Samples

Sample No.	Catalyst	Flow rate (ml/hr)	Percentage conversion	Percentage product distribution				
				4-M-1-P[a]	4-M-2-P[b]		2-M-1-P[c]	2-M-2-P[d]
					cis	*trans*		
1	γ-Al_2O_3	18	50.0	2.0	40.0	8.0	11.0	39.0
	γ-Al_2O_3	12	72.0	1.5	40.0	8.0	10.5	40.0
2	Thoria-I	18	9.0	—	20.0	73.0	—	7.0
3	Thoria-II	18	7.0	—	20.0	73.0	—	7.0

[a] 4-M-1-P: 4-Methyl-1-pentene.
[b] 4-M-2-P: 4-Methyl-2-pentene.
[c] 2-M-1-P: 2-Methyl-1-pentene.
[d] 2-M-2-P: 2-Methyl-2-pentene.

have a slight E1-like character and hence decide the product distribution. Similarly, neomenthol has also provided more 3-menthene, over alumina, by extraction of a hydrogen atom from a more substituted center.

When there is a choice of β-hydrogen atoms available for elimination, over the surface of alumina, the hydrogen from a highly substituted center is preferred, as evidenced by formation of 1-methylcyclohexene and 3-menthene from *cis*-2-methylcyclohexanol and neomenthol, respectively.

Dehydration of *trans*-2-methylcyclohexanol over hydroxyapatite has led to more 1-methylcyclohexene. Hydroxyapatite has been shown to eliminate by a *syn* mode, and the preference for the hydrogen extraction from a more substituted center (tertiary hydrogen) shows that the catalyst is fairly acidic and that the hyperconjugative effect had played a part in providing more substituted olefin. When the catalyst used is acidic, irrespective of *syn* or *anti* mode, the acidity of the hydrogen atom is not important in deciding the orientation of the double bond, whereas when a typically basic catalyst like thoria is used, it yields a product arising out of extraction of a highly acidic β-*syn*-hydrogen atom. This derives from the fact that both neomenthol and menthol had given, over thoria, the same olefin, viz., 2-menthene, as the major product which is obtained by removal of a secondary hydrogen atom in preference to a tertiary one. In these cases, no dehydrogenation has been noticed, presumably due to the high surface area of the thoria catalyst. Usually, high-surface-area thoria catalyst samples are selectively dehydrating, while low-surface-area thoria catalyst samples are dehydrogenating.

Even though the *cis*- and *trans*-2-methylcyclohexanols had yielded different 1-olefin/3-olefin ratios during dehydration over hydroxyapatite and hence could not be due to a carbonium ion intermediate, the deviation from synchroneity toward the E1 extreme (to different extents for different substrates) could cause such variations in product distribution.

Thoria and hydroxyapatite differ in their acid–base properties, though both of them dehydrate by *syn* mode. Neither the mode of elimination nor the acidic–basic characteristics alone can decide the orientation or regiospecificity, and only a combination of these two factors (to varying extents with various substrate–catalyst systems) seems to be responsible for the observed selectivity differences.

Dehydration studies were made with a series of alcohols, where the mobility (acidity) of β-hydrogen atoms was either

TABLE 12

Dehydration of Benzylmethylcarbinol over Alumina and Thoria Samples

Sample No.	Catalyst	Flow rate (ml/hr)	Percentage conversion	Percentage product distribution		
				Benzene	Propenyl benzene	
					cis	*trans*
1	γ-Al_2O_3	18	59.0	26.0	47.0	27.0
	γ-Al_2O_3	12	84.0	27.0	44.0	29.0
2	γ-Al_2O_3 + piperidine (10% V)	18	17.0	32.0	53.0	15.0
3	Thoria-I	18	10.0	8.5	19.5	72.0
	Thoria-I	12	14.0	7.0	19.0	74.0
4	Thoria-II	18	7.0	6.5	22.5	71.0
	Thoria-II	12	12.0	6.0	21.0	73.0

enhanced or decreased by proper substitution to discern the relative importance of various factors.

2-Methyl-3-pentanol is an acyclic alcohol, having an environment for the hydroxyl function similar to that in menthol (i.e., the carbon-bearing hydroxyl group being flanked by methylene and methine carbon atoms). Due to the acid-weakening effect of alkyl groups, the secondary hydrogen is more acidic than the tertiary one. This alcohol or dehydration over alumina provided typical product distribution with a high *cis–trans* ratio and little γ-elimination (Table 11).

The dehydration over thoria provided 4-methyl-2-pentene (by extraction of a secondary hydrogen) as the major product, and no γ-elimination was observed. The formation of lesser amounts of 2-methyl-2-pentene, the product arising out of extraction of a tertiary hydrogen atom, shows clearly that the acidity of a β-hydrogen atom is the deciding factor in thoria-catalyzed dehydration.

Apart from the obtainment of a product, involving extraction of a highly acidic hydrogen atom, a very low *cis–trans* ratio was observed in this reaction.

Benzylmethylcarbinol is a typical substrate in which the acidity of a primary hydrogen (of the methyl group) is less than that of a secondary hydrogen (of the methylene group), due to phenyl substitution. It was thought that dehydration studies, if done with this alcohol, would unequivocally clarify the nature of factors deciding the orientation. This alcohol yielded, on dehydration over alumina, mainly propenylbenzene (Table 12). The *cis–trans* ratio was ~2.0. On the dehydration over thoria, benzylmethylcarbinol yielded propenylbenzene predominantly, indicating that the acidity factor is important in thoria-catalyzed dehydration reactions.

If the steric crowding in the transition state alone is important, as suggested by Lundeen and Van Hoozer (*20, 21*), then the terminal olefin, viz., allylbenzene, will be the major product. On the other hand, if the acidity of β-hydrogen is important, then more internal olefin will result. The formation of more propenylbenzene indicates that the acidity factor is very important, and it can and did offset the steric factor. Hence it is positively confirmed that a highly acidic hydrogen is preferentially extracted over a thoria catalyst.

It must be borne in mind that with 2-methyl-3-pentanol, menthol, and neomenthol, the steric factor reinforces the acidity factor since the transition state leading to less-substituted olefin (less-crowded) would involve hydrogen from a less-substituted and hence more acidic center. This is the reason why these substrates display Hofmann selectivity.

Here too, the *cis–trans* ratio was low (0.3), indicating the importance of the steric factor in deciding between the geometrical isomers of the internal olefin.

The three transition-state structures leading to the terminal, the *cis*, and the *trans* olefin are represented in Fig. 8.

From these transition-state structures leading to various olefins, by a *syn* elimination from *syn*-periplanar conformation, it is clear that structure I is least hindered sterically and hence most preferred, in the absence of complicating electronic factors. This situation would lead to more terminal olefin. Between structures II and III, steric crowding between substituents is least in II (when compared to III) and hence a higher percentage of *trans* olefin results.

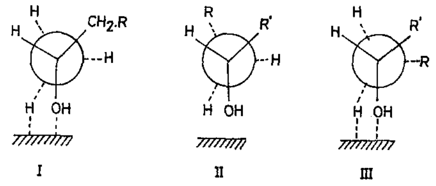


FIG. 8. Transition state structures.

In the alumina-catalyzed dehydration, steric crowding between substituents is not important as the reaction proceeds from *anti*-periplanar conformation. The steric crowding between substituents and the surface is important and, due to inclination of the molecule on the surface, the substituents are kept away from the surface, and hence a high preference for *cis* results.

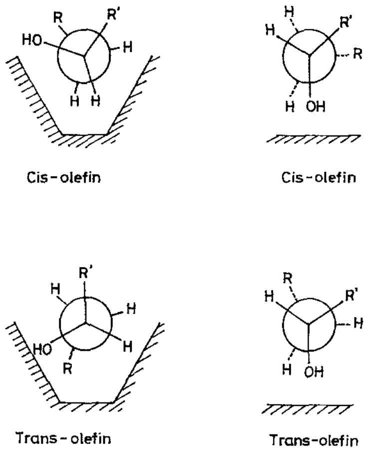
To confirm the operation of such steric factors, a variety of substrates with different β-substituents were subjected to dehydration over the two catalysts (Table 13). Over thoria, it can be seen that as the bulk of the β-substituent increases, the contribution due to structure II becomes more pronounced vis-à-vis structure III,

TABLE 13

Dehydration of Alcohols over Alumina and Thoria—Effect of β-substituents

$$R{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}R'$$

Catalyst	Flow rate (ml/hr)	Substrate	Substituents		1-olefin	*cis*-olefin
			R	R′	2-olefin	*trans*-olefin
γ-Al_2O_3	18	2-Butanol	CH_3	CH_3	0.3	4.2
	18	2-Pentanol	CH_3	C_2H_5	0.3	3.3
	18	2-Octanol	CH_3	C_6H_{11}	0.6	3.0
	18	4-Methyl-2-pentanol	CH_3	$(CH_3)_2CH-$	0.55	3.0
	18	Benzylmethyl carbinol	CH_3	C_6H_5	0.5	3.2
	18	Phenylethylcarbinol	C_6H_5	H	—	3.5
	18	1,2-Diphenylethanol	C_6H_5	C_6H_5	—	2.8
Thoria	18	2-Butanol	CH_3	CH_3	12.0	1.0
	18	2-Pentanol	CH_3	C_2H_5	12.0	1.0
	18	2-Octanol	CH_3	C_6H_{11}	9.0	0.7
	18	4-Methyl-2-pentanol	CH_3	$(CH_3)_2CH-$	9.0	0.4
	18	Benzylmethyl carbinol	CH_3	C_6H_5	0.1	0.3
	18	Phenylethylcarbinol	C_6H_5	H	—	0.3
	18	1,2-Diphenylethanol	C_6H_5	C_6H_5	—	0.06



Cis-olefin Cis-olefin

Trans-olefin Trans-olefin

FIG. 9. Elimination by *syn* and *anti* modes.

resulting in formation of more of the *trans* isomer. With 2-butanol, where both R functions are methyl, the highest *cis–trans* ratio was obtained (~1.0), whereas the ratio reached a phenomenal low of 0.06 with 1,2-diphenylethanol, where both R functions are phenyl.

Considering the effect of steric factors in alumina-catalyzed dehydration, it is evident that the effect is felt less and is almost insignificant. Even 1,2-diphenylethanol gave a *cis–trans* ratio of 2.8, though the ratio for 2-butanol was 4.2.

This suggests that the steric crowding between substituents is not important in the *anti* mode of elimination over alumina, and the transition state in which the two substituents are kept away from the surface is preferred, the requirement being minimum substituent–surface interaction (Fig. 9).

Where a *syn* mode of elimination is operative, the groups are already kept away from the surface, and steric interaction between substituents becomes restricted, leading to more *trans* isomer. This indicates that the *cis* preference is not universal for all heterogeneously catalyzed reactions but is decided by the mode of elimination and the importance of steric and electronic factors.

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