

New Transition-State Models and Kinetics of Elimination Reactions of Tertiary Alcohols over Aluminum Oxide

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A new transition-state model was developed in order to justify the anti intramolecular E2 elimination with cis (*Z*)-preference over pure alumina and intermolecular E2 elimination with trans (*E*)-preference over doped alumina. The reactions of model compounds 1,2,3-triphenyl-2-propanol (**1**), 1,2-diphenyl-2-propanol (**2**), and 3,3,3-trideuterio-1,2-diphenyl-2-propanol (**3**) with aluminum oxides with a pH range of 4.5–9.5 and thorium oxide in the temperature range of 200–350 °C in 2-hexanol have been investigated. Over acidic alumina (pH = 4.5 ± 0.5), the ratio of *E*-isomer to *Z*-isomer ($E/Z \cong 2$) for **2** was found to remain unchanged in this temperature range. At 300 °C, however, Saytzeff elimination favored Hofmann. Over pure alumina the *E/Z* ratio was equal to 0.650 (2-alkene/1-alkene = 0.750). At equilibrium, the *E/Z* ratio for **2** was equal to 4.5 with the formation of trace amounts of Hofmann adducts. The ratio of Saytzeff to Hofmann elimination was found to be pH independent. Any decrease in pH caused a slight increase in the *E/Z* ratio. The average primary kinetic isotope effect (k_H/k_D) for elimination at 230 °C was equal to 3.775 ± 0.227. The ratio of *E/Z* over thorium oxide at 300 and 350 °C was similar to that of aluminum oxide at 300 °C, but the Saytzeff elimination was surprisingly favored over Hofmann! The energy of activation (E_a), entropy of activation (ΔS^\ddagger), selectivity, isotope effect (k_H/k_D), and semiempirical calculation (AM1) all agreed with concerted E2 elimination.

Introduction

Recent interest in stereoselective synthesis of olefins^{1–3} via the reaction of triphenylphosphine in tetrachloromethane promoted a study of the reaction of model compounds 1,2,3-triphenyl-2-propanol (**1**), 1,2-diphenyl-2-propanol (**2**), and 3,3,3-trideuterio-1,2-diphenyl-2-propanol (**3**) with aluminum oxide and thorium oxide.

Metal oxides are excellent and widely used catalysts for the dehydration of alcohols.^{4–16,18–23} It has been shown that many discrepancies can result from different catalytic properties of the aluminum oxide and thorium

oxide catalysts used in different laboratories and/or from different reaction conditions. These catalysts can vary widely in their activity for skeletal isomerization and for double-bond shift of olefinic hydrocarbons.

The nature of the acidity of various catalysts and catalyst supports on the mode of elimination has been a matter of controversy for many years. A variety of techniques have been used to measure acidity, including titration, measurement of quantity of chemisorbed ammonia at various temperatures, use of dealkylation rate of alkyl aromatics, the use of isomerization and dehydration rate, and determination of IR spectra of chemisorbed ammonia or pyridine.¹¹ The application of these techniques has given conflicting and widely differing results from the same materials. A decrease in surface area has been noted with an increase in the amounts of the dopant (sodium). The high surface area catalysts have been reported to be more selective for dehydration, whereas low-surface catalysts were selected for dehydrogenation.²² The effect of temperature on stereoselectivity and/or regeoselectivity has been reported: an increase in the percentage of Hofmann adducts is observed at higher temperatures.¹⁶

The mode of elimination in the dehydration reaction over alumina catalyst has been shown to be anti from antiperiplanar conformation with the preference of the cis (*Z*)-isomer, where there is a possibility of formation of geometric isomers. The explanations for anti elimination and cis preference have been a matter of controversy. A syn mode of elimination similar to pyrolysis of esters has been reported for the dehydration of alcohols over metal oxides.^{10,13,16}

Stereochemistry of elimination (anti or syn) in concerted homogeneous reactions depends on the properties of the system and mainly upon those of the substrate and

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Table 1. Reaction of **2** in 2-Hexanol with Strongly Acidic Aluminum Oxide (pH = 4.5)^{a,b}

$1/T \times 10^3$ (K ⁻¹)	4/5	4 + 5/6	% 4	% 5	% 6
1.7450	2.0	2.450	48 (1.80)	23 (1.40)	29 (1.50)
1.8760	2.25	0.630	27 (1.40)	12 (1.10)	61.5 (1.80)
1.9880	2.30	0.550	25 (1.40)	11 (1.0)	64 (1.80)
2.1140	2.20	0.470	22 (1.30)	10 (1.0)	68 (1.80)

^a Values in (log % alkenes). ^b The relative percent was calculated by ¹H NMR.

the steric interactions of the intermediates and/or the transition states.¹ Anti elimination occurs from gauche conformations of the molecule and syn elimination from eclipsed conformations.^{12,14,15,20–23}

The stereochemistry of elimination reactions of secondary and tertiary alcohols are meaningful with respect to both regioselectivity (Hofmann vs Saytzeff) and/or stereoselectivity (anti vs syn) only when it is obtained under the conditions where primary products are produced with minimum secondary isomerization.

We believe we have found just the right system, which can shed more light on the mechanism for the dehydration reactions over aluminum oxide; the system can also help gain more insight into the reaction mechanism and selectivity for alcohol dehydration over metal oxides. We have undertaken a study of isotope effect, kinetics, and semiempirical calculation (AM1)²⁵ of molecular geometry of the monolayer and the bilayer of a small intermediate and the mechanism of the reactions of model compounds 1,2,3-triphenyl-2-propanol (**1**), 1,2-diphenyl-2-propanol (**2**), and 3,3,3-trideuterio-1,2-diphenyl-2-propanol (**3**). Kinetics of the dehydration reaction were investigated in the temperature range of 200–300 °C. The effect of temperature and pH (surface area, mesh size, flow rate, amounts of catalyst, reactor type, and media were kept constant) on the stereoselectivity as well as regioselectivity have been investigated in detail. It is the purpose of the present paper to provide the evidence that serves to establish the fact that the mechanism of the reaction of tertiary alcohols with aluminum oxide is concerted anti E2, the cis preference is not universal, and the Saytzeff rule depends on the steric interactions of the intermediates and/or the transition states. Results are compared with the homogeneous reagent triphenylphosphine in carbon tetrachloride, with cross-linked diphenylphosphine polystyrene in carbon tetrachloride, and with thorium oxide.

Results

Reaction of 1,2-Diphenyl-2-propanol (2). Alcohol (**2**) in 96% 2-hexanol was passed over acidic aluminum oxide (pH = 4.5 ± 0.5) with a flow rate of 30 cm³/h at a temperature range of 200–300 °C. Results are summarized in Table 1 (results with pure γ -Al₂O₃ prepared from aluminum isopropoxide are presented in Table 4) and Figures 1 and 2. The results for 2-hexanol (conversion, dehydration vs dehydrogenation, and 2-hexenes/1-hexenes ratio) for several aluminum oxides and thorium oxide are summarized in Table 2.

Kinetics. The rates of appearance of (*E*)-alkene (**4**), (*Z*)-alkene (**5**), and 1-alkene (**6**) were followed at various temperatures by proton nuclear magnetic resonance

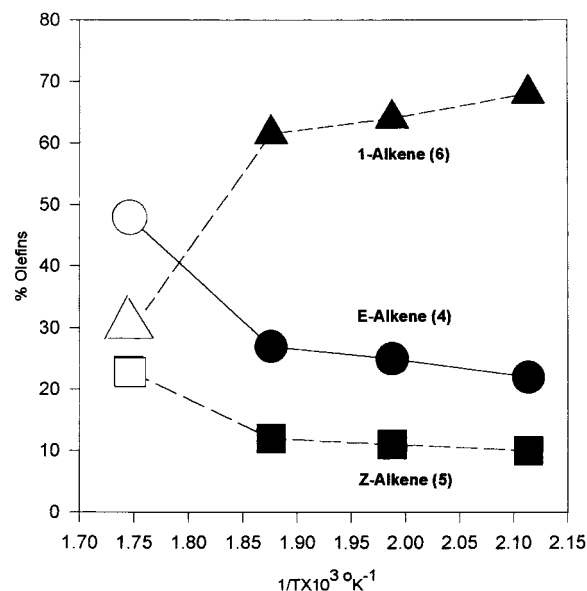


Figure 1. Effect of temperature on alkene distribution for the reactions of **2** over 2 g of strongly acidic alumina (pH = 4.5 ± 0.5), flow rate 30 cm³/h (8 cm³/h, unfilled symbols).

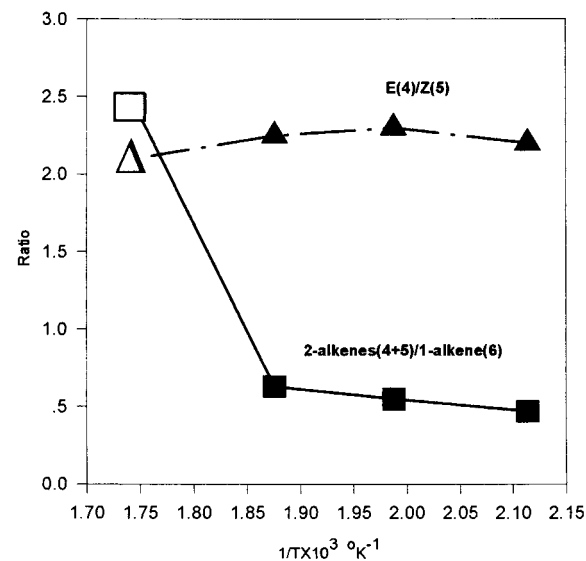


Figure 2. Effect of temperature on anti/syn and Saytzeff–Hofmann elimination for the reactions of **2** over strongly acidic γ -alumina (pH = 4.5 ± 0.5), flow rate 30 cm³/h (8 cm³/h, unfilled symbols).

Spectroscopy (PMR). The rates of disappearance of alcohol (**2**) and the rate of formation of intermediate were fast and nonmeasurable (Scheme 1). We accepted the statements made by several investigators that the alcohols first adsorb on the catalyst surface forming an intermediate.^{8,9,11,19,20,23,24} Of course, for alcohol **2** this intermediate appears to have a very short life (a very weak Al–O–C α bond, 100% conversion for **2** vs 5% conversion for 2-hexanol under similar conditions), converting rapidly to a transition state and then in a rate determination step to alkenes. According to the Hammett postulate then, the transition state must resemble the intermediates **2A–C**. This is substantiated by the optimized structure shown in Scheme 5. The extended bond-making–bond-breaking is equal in the more polar alumina backbone (transition state-like), but bond-breaking–bond-making is not enhanced in the alcohol **2**

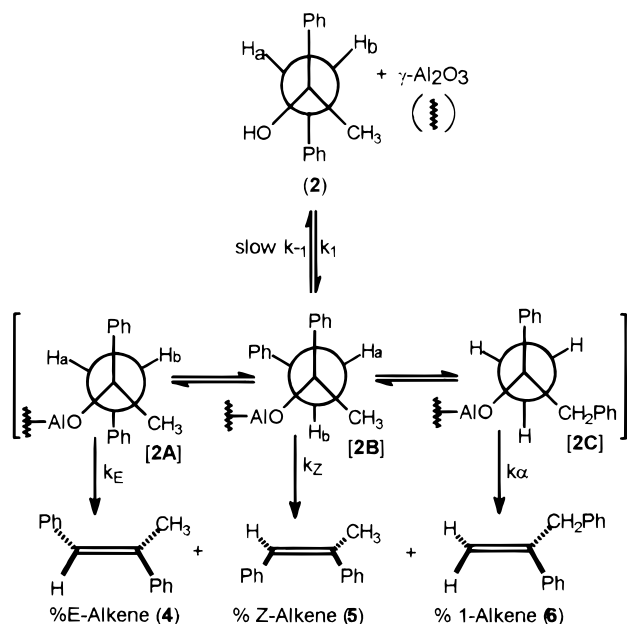
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Table 2. Conversion of 2-Hexanol over Aluminum Oxides and Thorium Oxide^a

catalysts	<i>T</i> (°C)	convn (%)	2-hexenes/ 1-hexene		hexenes/ 2-hexanone
			2-hexenes/ 1-hexene	hexenes/ 2-hexanone	
Al ₂ O ₃ -P ^b	230	4.5	2.70	30	
Al ₂ O ₃ -N ^c	230	5.0	1.30	15	
Al ₂ O ₃ -LA ^d	230	5.0	1.40	13	
Al ₂ O ₃ -H ^e	230	15	1.70	f	
Al ₂ O ₃ -H ^g	230	45	1.80	f	
Al ₂ O ₃ -H	200	4.30	1.50	f	
Al ₂ O ₃ -B ^h	230	17.0	2.0	22	
ThO ₂ ⁱ	350	42.0	0.10	4.0	

^a Flow rate is 30 mL/h unless otherwise stated. ^b Prepared from aluminum isopropoxide. ^c Neutral alumina, pH = 7. ^d Low acidic alumina, pH = 6. ^e Acidic alumina, pH 4.5. ^f Trace amount of 2-hexanone was formed. ^g Flow rate 8 mL/h. ^h Basic alumina, pH = 9.5. ⁱ Flow rate 4 mL/h.

Scheme 1

backbone (intermediate-like). Activation energies for the alkene formation step were calculated by the slope of the plot of log % alkenes versus reciprocal of temperatures (Table 1, Figure 4, a typical plot). The entropies of activation were calculated using the intercept of the Arrhenius plot (log *A*) using the following expressions: $\log = -E_a/RT + \log A$, $A = (\kappa kT/h)e^{\Delta S^\ddagger/R}$. Data points at 300 °C were ignored in the calculation of the energy of activation due to large deviation from linearity. Data points at 200–260 °C produced slopes with good correlation coefficients (*r*) (Table 8, Figure 4).

Isotope Effects in the Elimination Reactions of 1,2-Diphenyl-2-propanol in 2-Hexanol. The kinetic isotope effect was run on a 4% solution of 3,3,3-trideuterio-1,2-diphenyl-2-propanol (**3**) in 2-hexanol on 2 g of fresh strongly acidic γ -Al₂O₃ (pH = 4.4 ± 0.5) at 230 °C. The relative percent of alkenes were then compared with those obtained from alcohol **2** in a separate run but exactly under similar conditions using 2 g of fresh catalyst, Table 3. Under these conditions, for both reactions the conversion of 2-hexanol is 4.7 ± 0.3%. In other words, when the conversion of these mixtures is effected under similar conditions, the relative rate of formation of 1-alkene-*d*₀ (*K*α)_H to 1-alkene-*d*₂ (*K*α)_D can

Table 3. Corrected Primary Isotope Effect for the Conversion (4.7 ± 0.3) of Alcohols 2 (*d*₀) and 3 (*d*₃) with 2 g of Strongly Acidic (pH = 4.5) Aluminum Oxide at 230 °C (30 mL/h)

time (min)	%E (4)		%Z (5)		%1-alkene (6)		<i>k</i> _H / <i>k</i> _D ^a
	<i>d</i> ₀	<i>d</i> ₃	(<i>d</i> ₀)	(<i>d</i> ₃)	(<i>d</i> ₀)	(<i>d</i> ₂)	
2	27	44	10	21	63	35	4.0
7	27	44	10	17	63	39	3.50
14	25	44	11	17	64	39	3.60
22	25	44	11	21	64	35	4.0

^a Corrected values (see eq 1).

be utilized as a basis for obtaining the kinetic isotope effect. The isotope effects are corrected for 15% protium using eq 1.

Calculation of Kinetic Isotope Effect. The corrected kinetic isotope effects for the elimination step were calculated using the relative rate of formation of (α -benzylstyrenes (Table 3) using eq 1, where *K*_E, *K*_Z, and *K*α are the relative rates of formation of (*E*)-isomer (**4**), (*Z*)-isomer (**5**), and 1-alkene (**6**), respectively.

$$[k_H/k_D]_{\text{elim}} = \frac{\left(\frac{K\alpha}{K_E + K_Z}\right)_H}{\left(\frac{K\alpha - 0.15K\alpha}{K_E + 0.15K\alpha(B) + K_Z + 0.15K\alpha(B')}\right)_D} \quad (1)$$

$$B = \left(\frac{K_E}{K_E + K_Z}\right) \quad B' = \left(\frac{K_Z}{K_E + K_Z}\right)$$

Effect of pH. The effect of acidity and/or basicity of catalysts on stereoselectivity (*E*/*Z*) and regioselectivity (Hofmann–Sytzeff) was tested on various aluminum oxides with a wide range of pH values (4.5–9.5). Generally, the pH values refer to aqueous solution (in dehydration of alcohols water molecules are produced at reaction sites!); however, the relative acidity–basicity and the amounts of alkali that alumina contains (when compared with pure alumina) is what we are concerned with but not the absolute pH values. To minimize the deviation in product distribution, the surface area (150 m²/g), the mesh size (150, 58 Å), the flow rate (30 cm³/h), the media (4% **2** in 2-hexanol), the reactor type, and the amounts of catalyst (2.0 g fresh) were kept constant (Figure 3).

Reaction of 2 with Pure γ -Aluminum Oxide. Results of the reaction of **2** via pure γ -aluminum oxide (prepared from aluminum isopropoxide followed by calcination at 600 °C for 6 h) are reported in Table 4. To lower the conversion of alcohols, 0.50 g of pure alumina was diluted with 1.50 g of powdered glass beads. Results of the reaction of 2-hexanol with pure γ -aluminum oxide is presented in Table 2.

Reaction of 2 with Thorium Oxide. Results of the reaction of **2** with thorium oxide (prepared from thorium nitrate through calcination of thorium nitrate at 600 °C for 6 h) are reported in Table 5. Results of the reaction of 2-hexanol with thorium oxide is presented in Table 2.

Reaction of 1,2,3-Triphenyl-2-propanol (1). Alcohol (**1**) in methyl acetate when passed over strongly acidic alumina (pH = 4.5 ± 0.5) at 200 °C under similar conditions as for **2** converted 100% to a mixture of 48% (*E*)-1,2,3-triphenyl-2-propene (**1E**) and 52% (*Z*)-1,2,3-triphenyl-2-propene (**1Z**).

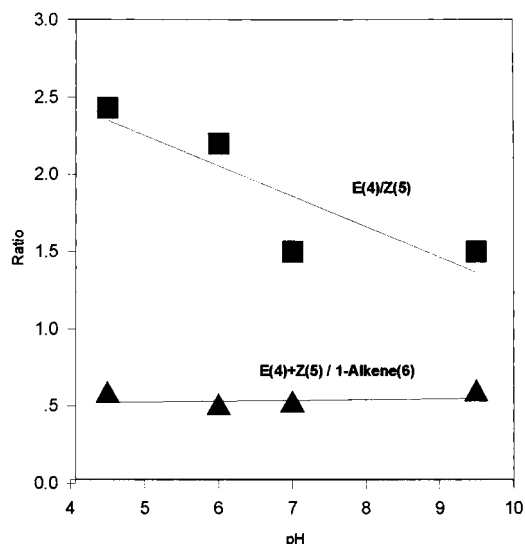


Figure 3. Effect of pH on anti/syn elimination (*E/Z*) and on Saytzeff-Hofmann (2-alkenes/1-alkene) elimination for the reactions of **2** over aluminum oxides at 230 °C.

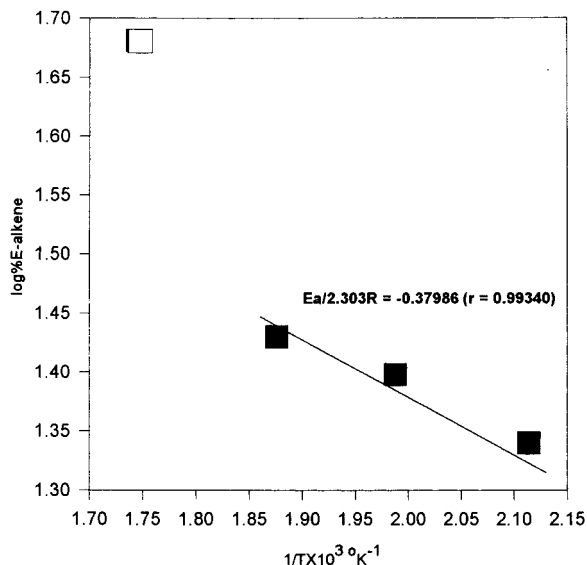


Figure 4. Typical Arrhenius plot for the rate of appearance of **4** with strongly acidic $\gamma\text{-Al}_2\text{O}_3$, flow rate 30 cm^3/h (8 cm^3/h , unfilled symbols).

Discussion

Both homogeneous and heterogeneous dehydration of secondary and tertiary alcohols are among the most studied of all major organic processes.¹⁻²³ There have been a number of attempts to relate the mechanisms of these two systems; many discrepancies, however, have resulted from the different reaction conditions and reagents used (Tables 6 and 7).

Homogeneous Systems. Dabbagh et al.^{1,3} recently reported that triphenylphosphine in carbon tetrachloride converted 100% of **2** to a mixture of 28% 1,2-diphenyl-2-chloropropane, 37% **4**, 35% **6**, and a trace of **5** at 78 °C. They demonstrated that stereoselectivity and regioselectivity of elimination in concerted homogeneous reactions depend on the properties of the system and mainly on the steric interaction of the intermediate and/or transition state. It was also reported³ that, under homogeneous acidic conditions, **2** produced kinetically

Table 4. Conversion of **2** to Olefins via Pure $\gamma\text{-Aluminum Oxide}$ at 230 °C^{a,b}

run no.	time (min)	% 4	% 5	% 6	4/5	4 + 5/6
1	4	20	25	55	0.80	0.80
2	8	15.50	29	55.50	0.50	0.80
3	12	17	26	57	0.60	0.750
c	80	76	24	0	3.20	
d	120	80.5	18.5	1	4.30	99

^a Aluminum oxide was prepared from aluminum isopropoxide (0.5 g Al_2O_3 + 1.5 g of powder glass beads). ^b Average conversion (93%). ^c 2.0 g of catalyst was used. ^d Equilibrium composition.

Table 5. Conversion of **2** to Olefins via Thorium Oxide at 350 °C

run no.	% convn	time (min)	% 4	% 5	% 6	4/5	4 + 5/6
1	80	4	55	26	19	2.10	4.30
2	78	8	49	21	30	2.30	2.30
3	86	12	58	30	14	1.90	6.30
a	0	30					
b	30	25	47	21	32	2.20	2.10

^a Reaction temperature at 230 °C. ^b Reaction temperature at 300 °C.

Table 6. Comparison of the Dehydration Reaction of 2-Butyl System

intermediates	2-B/1-B ^a	cis/trans	ref
$[\text{P-OR}]^+\text{X}^-$ ^b	2.570	4.30	4
$[\text{I-OR}]^+\text{X}^-$ ^c	1.270	3.0	4
$[\text{H}_2\text{O-OR}]^+\text{TSO}^-$ ^d	3.760	1.70	3
$[(\text{CH}_3)_3\text{N-OR}]^+\text{HO}^-$	0.060	1.45	4
$[\text{H}_2\text{O-OR}]^+\text{SO}_4^-$	8.10	0.70	3
$[\text{Ph}_3\text{P-OR}]^+\text{Cl}^-$	5.30	0.50	1
$[(\text{CH}_3)_2\text{SOR}]^+\text{C}_2\text{H}_5\text{O}^-$	0.350	small ^e	4

^a Ratio of 2-butenes/1-butene. ^b P = pure alumin. ^c I = sodium-doped alumina. ^d Thermodynamic equilibrium, TSO = $\text{C}_7\text{H}_7\text{SO}_3$. ^e Mostly trans.

Table 7. Comparison of Product Distribution of Dehydration Reaction of (**2**)

reagent	T (°C)	% 4	% 5	% 6	<i>E/Z</i>	4 + 5/6
$\text{Ph}_2\text{P-(P)}^a$	80	≈100	trace	trace	VL ^b	VL
$\text{Ph}_3\text{P-CCl}_4$ ^c	78	51.5	<1	48.5	large	1.10
$\text{TSOH-C}_6\text{H}_6$ ^d	70	81	19	0	4.20	
$\gamma\text{-Al}_2\text{O}_3\text{-H}^e$	230	25	11	64	2.30	0.560
ThO_2 ^f	350	49	21	30	2.30	2.30
ThO_2 ^g	300	47	21	32	2.20	2.10
$\gamma\text{-Al}_2\text{O}_3\text{-B}^h$	230	19	16	56	1.20	0.630
$\gamma\text{-Al}_2\text{O}_3$ ⁱ	230	17	26	57	0.65	0.750

^a Cross-linked diphenylphosphine polystyrene (see ref 2). ^b VL = very large. ^c See ref 1. ^d Equilibrium composition (see ref 3). ^e Strongly acidic alumina (pH = 4.5). ^f Conversion 78%. ^g Conversion 30%. ^h Basic alumina (pH = 9.5). ⁱ Pure alumina prepared from aluminum isopropoxide.

controlled α -benzylstyrene (**6**) approximately in equal amounts (1:1) with *trans*- α -methyl stilbene (**4**) in 0.4 h, rapidly converting to an equilibrium mixture of olefins in 2 h. They reported that the reaction of **2** with cross-linked diphenylphosphine polystyrene in carbon tetrachloride mainly produced *trans*- α -methylstilbene **4** with trace amounts of **5** and **6** (Table 7).² Steric interaction at the transition state or intermediate is shown to be responsible for the observed selectivity. Dabbagh et al.¹⁷ have reported that elimination is the minor pathway for the reaction of *erythro*-3-deuterio-2-butanol with triphenylphosphine (>98% anti elimination in favor of Saytzeff orientation with a primary deuterium isotope effect of 2) (Table 6); 2-methyl-2-propanol produced almost 90% 2-methylpropene ($k_H/k_D = 2$).

Heterogeneous Systems. Pine and co-workers⁴⁻⁷ studied the dehydration of alcohols over aluminum oxide extensively and provided evidence that initial products arise from concerted trans elimination. Participation of two catalyst surfaces (crevices or pores of the solid) was proposed to achieve the required steric arrangement.⁶ Of course, if the dehydration proceeds only in crevices of molecular size, then the reaction must be diffusion-controlled, a phenomenon that has never been observed.

Pine and Haag⁷ explained the cis preference by assuming an intermediate proton-olefin complex, since the cis π -complex is more stable than the trans π -complex. Noller and co-workers¹² and Notari¹³ explained the cis preference in the E1-like mechanism on the grounds of steric considerations.

Hall et al.⁸ rejected the proposed model that anti elimination must be due to a reaction between surfaces in a pore or a crevice. They suggested that large O^{2-} ions adjacent to the Lewis acid site alcolate are responsible for the abstraction of the β -hydrogen.

Knozinger and co-workers⁹ proposed a new transition-state model that explains the anti mode of elimination with the cis preference. They assumed a localized adsorption of the reacting molecule on the surface and further that the steric restrictions in the transition state are most likely to determine the cis/trans ratio of the respective isomeric olefins.

A possible alternative is suggested by the Peri model of the alumina surface.²⁴ Here the dual acid-base sites are aluminum ions, exposed where the terminal OH groups are missing, and large O^{2-} ions replacing the OH groups and covering adjacent lattice positions. If it is assumed that an alcoholic hydroxyl group covers the aluminum ion with the alcoholic hydrogen pointing away from the surface, then hydrogen atoms on the β carbon atom in the trans position to the hydroxyl group can be discharged on top of the adjacent O^{2-} ions more readily than those in the cis positions.

Thoria-catalyzed dehydration of 2-butanol is shown to be similar to the pyrolysis of *sec*-butyl acetate and of trimethyl-*sec*-butylammonium hydroxide. The mode of elimination is stereospecific syn elimination in favor of Hofmann orientation. The dehydration of tertiary-2-alkanols over thoria is not stereoselective.^{12,13}

The question raised here was whether aluminum oxide with tertiary alcohols could be used in a stereoselective synthesis of hindered olefins. If so, what is then the mechanism of elimination for these reactions? What is the effect of temperature and pH on the stereoselectivity and regioselectivity? How comparable are the dehydrations of **2** in a heterogeneous system with that of homogeneous triphenylphosphine in carbon tetrachloride and with that of semiheterogeneous cross-linked diphenylphosphine polystyrene in carbon tetrachloride?

To answer these questions, we first studied the effect of varying the pH and temperature on reactivity, stereoselectivity (e.g., the ratio of syn/anti elimination), and regioselectivity (e.g., the ratio of Saytzeff/Hofmann elimination). Second, we calculated the kinetics of elimination reaction [e.g. the energy of activation (E_a) and the entropy of activation (ΔS^\ddagger)]. Then, we studied the elimination reaction of 3,3,3-trideutero-1,2-diphenyl-2-propanol (**3**) and obtained a primary kinetic isotope effect. In the next step, we compared the reactivity and selectivity of pure alumina with those of doped alumina (surface areas of 150 m²/g) with 2-hexanol both as a solvent and as

isomerization preventer. Fifth, we ran the dehydration on thorium oxide at several temperatures. Finally, we optimized the geometry of adsorbed **2** and 2-butanol on alumina via the semiempirical calculation (AM1).²⁵

The major factors contributing to the inconsistencies of the dehydration mechanism of alcohols over alumina are variation in surface area, mesh size, temperature, acidity-basicity, flow rate, amounts of catalyst, media, and reactor type. In our investigation, the effects of two major contributors, i.e., temperature or acidity-basicity, on product distribution are sought; other variables are kept constant.

Effect of Temperature. The product distribution (% olefins) shows a small variation at the temperature range of 200–260 °C (a kinetically controlled process) with a sudden change at 300 °C (Figure 1). The ratio of (*E*)-alkene/(*Z*)-alkene (stereoselectivity) shows a small change at higher temperatures; however, the regioselectivity, e.g., the ratio of 2-alkene/1-alkene, increased drastically at 300 °C to a flow rate of 8 cm³/h (approaching the thermodynamically controlled process). Two factors may have contributed to this effect: the weakening of the $C\alpha$ -O bond of the adsorbed alcohol on the surface at higher temperatures or secondary isomerization of 1-alkene to 2-alkenes. To test the latter effect, pure **4** passed over acidic alumina at 230 °C. No isomerization was observed. All attempts to isolate pure **5** or **6** failed. However, no isomerization was observed when a mixture of mostly 1-alkene **6** (68% and 32% of **4** and **5**) was allowed to pass over fresh acidic alumina at 230 or 250 °C under conditions similar to those in each of the previous runs. At 300 °C, **6** (68%) isomerized to near-equilibrium composition (**4** + **5**/**6** = 7.3, with the ratio of **4**/**5** = 2.60). To prevent isomerization of olefins, conversion of 2-hexanol was maintained in the range of 1–15% at the temperature range of 200–300 °C. Alcohol **2**, however, converted 100% at all temperature and pH values (unless stated otherwise).

Effect of pH. The second major factor that has been reported to have pronounced effect on the mechanism of the dehydration of alcohols is the acidity-basicity of the catalyst. The major problem in the investigation on this effect has been the inconsistency in the preparation of the catalyst.

The effect of acid-base strength upon the structure of transition states in elimination reactions has not been convincingly explained in the literature. Aluni et al.²⁰ reported that with an increase in base strength there was a significant decrease in the $C\alpha$ -leaving group bond and the transition state subsequently leaned toward E1cB. A decrease in BET surface area was noticed with an increase in the amount of dopant; high surface-area catalysts were more selective for dehydration, but low surface-area catalysts were selective for dehydrogenation.²¹ Siddhan and Narayanan²² studied the change in the acidity-basicity balance in the sodium-impregnated alumina samples vis-à-vis pure alumina. In our investigation, we purchased several catalysts with the same surface area (150 m²/g) and mesh size (150, 58 Å) with a wide range of pH values (4.5–9.5) from Aldrich Chemical Co. The reactivity and selectivity of these catalysts were compared with that of prepared catalysts. Within our experimental error at 230 °C, the ratio of 2-alkene/1-alkene (regioselectivity) remained unchanged in this pH range. A slight increase for the ratio of (*E*)-alkene/(*Z*)-alkene (stereoselectivity) was observed at lower pH

Table 8. Energetics (cal/mol) for the Rate of Appearance of Alkenes over γ -Alumina at 503 K^a

comp no.	E_a (cal/mol)	r^b	A^c	ΔS^\ddagger (cal/mol)
(<i>E</i>)-alkene (4)	1.720	0.9930	137.0	-53.80
(<i>Z</i>)-alkene (5)	1.530	0.9990	51.0	-55.70
1-alkene (6)	0.760	0.9990	30.0	-56.90

^a pH = 4.5. ^b Correlation coefficient. ^c Arrhenius parameter.

values (Figure 3). Addition of dopant to the alumina surface in order to change the acidity–basicity nature of the catalyst would occupy certain reaction sites but not all. The reactivity is decreased, but enough free acidic sites and basic sites are available for adsorbing the alcohols and abstraction of β -hydrogen(s), respectively. Dopant also make the catalyst more rigid (increases the ionic nature of the catalyst), less flexible, and less selective. Pure alumina is less rigid (less ionic in nature), more flexible and more selective, Table 7.

Kinetics. The mechanism is consistent with the energetics of the reaction, Table 8. The entropy of activation (ΔS^\ddagger) is appreciably low. The two reacting centers, e.g., the basic site on alumina and the β -hydrogens, must attain a specific geometry to permit the bonding intermediates that occur as the transition state is approached. The entropy of activation (ΔS^\ddagger) for the formation step of all three alkenes ((*E*)-alkene, (*Z*)-alkene, and 1-alkene) is similarly small and negative. The Arrhenius parameter is directly proportional to number of collisions. Collisions of reaction sites with specific geometry decreases the entropy of activation (more negative) and subsequently decrease the Arrhenius parameter (Table 8). This substantiates the fact that the reaction of basic center (Base-4, Scheme 5) with β -hydrogen (s) are molecularly unconstrained. The low activation energies for dehydration of **2** are due to weakness of the bond between Al–O–C α . This is substantiated further by a very high conversion (100%) and also in Scheme 5 (extend of bond-breaking bond-making is enhanced). For 2-hexanol the Al–O–C α is much stronger (10–15% conversion at the same conditions), Scheme 6 (extend of bond-breaking bond-making is not enhanced). The less hindered alcohols show much higher activation energy. Therefore, the dehydration reaction of **2** over pure γ -alumina is a kinetically controlled process (leaning toward the thermodynamically controlled for doped alumina) with low activation energy for the intermediate decomposition step (the rate-determining step). The less stable alkenes (1-alkene and (*Z*)-alkene) are formed in favor of the more stable (*E*)-alkene at low temperatures and then equilibrate to the thermodynamic equilibrium composition at higher temperatures.

The position of the transition state along the reaction coordinate can be estimated by the magnitude of kinetic isotope effect. Reactions that have linear symmetrical transition states with hydrogen positioned centrally between the two acceptor centers are shown to have a maximum isotope effect. The observed averaged deuterium isotope effect (Table 3) equal to 3.775 ± 0.227 indicates that the rate-determining step is the proton loss in a concerted E2-like but not synchronous transition state (Scheme 5). The extent of bond-making bond-breaking is not equal in the dehydration reaction of 2-butanol, a fact that is revealed in the low $k_H/k_D \pm 2.0$ and in Scheme 6.

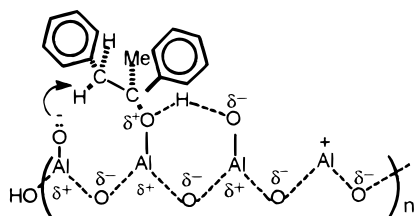
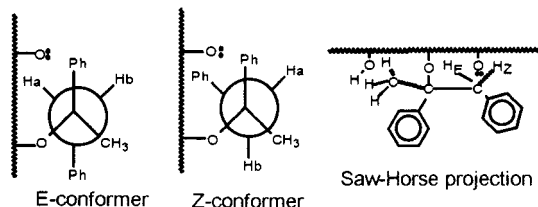
On the basis of our new definition of stereoselectivity¹ (i.e., a reaction should be considered stereoselective if the product distribution is far from that of the thermodynamic equilibrium composition), the reactions of doped aluminum oxides (pH = 4.5–9.5) are less stereoselective than pure alumina. The ratio of **4/5** is equal to 2.2 [approaches that of equilibrium composition (**4/5** = 4.3 at 70 °C)] and 0.60, respectively. A cis preference (**1E/1Z** = 0.920) was observed for the dehydration of **1** over strongly acidic aluminum oxide (pH = 4.5). This ratio was equal to 5.7 for reactions with triphenylphosphine in carbon tetrachloride¹ and very large for cross-linked diphenylphosphine polystyrene in carbon tetrachloride (Table 7).² Reactivity of doped alumina is much lower than that of pure alumina. To obtain the same percentage of 2-hexanol conversion, 0.1 g of pure alumina and 2.0 g of doped alumina were used.

Another interesting observation is that the reaction of 2-butanol over aluminum oxide favored the Saytzeff elimination, but in the case of **2** Hofmann elimination, it showed unusual predominance over the Saytzeff (reaction of **2** with triphenylphosphine produced equal amounts of Saytzeff–Hofmann adducts). This substantiates our earlier prediction¹ that the Hofmann–Saytzeff ratio does not depend on the reagent nor on the product stability, but instead, it depends on the steric interactions in the transition state and/or intermediate. This is demonstrated in Scheme 5. β -Hydrogens producing 1-alkene or (*Z*)-alkene and Base-4 are molecularly constrained as close neighbors and energetically favorable when they are compared to the β -hydrogen producing the most stable (*E*)-alkene.

The next step is to compare the dehydration reactions of 2-butanol (Table 6) and 2-hexanol (Table 2) with that of **2** (Table 7) in both homogeneous and heterogeneous systems. The regeoselectivity (2-alkenes/1-alkene) for 2-hexanol (2.60, this work) and 2-butanol (2.70, ref 4) are similar over pure alumina. Over doped alumina the values of 1.270–2.0 (2.0 for basic alumina, $pK_a = 9.5$) are obtained (this work and ref 4). This value for 2-hexanol is equal to 0.10 over thorium oxide and matches the value of 0.060 for 2-butanol (basic homogeneous Hofmann elimination). The data demonstrate that by increasing the basicity of alumina the regeoselectivity does not approach that of thorium oxide. This is further shown for the elimination reaction of **2** over pure alumina, doped alumina, and thorium oxide. In fact, the regeoselectivity for acidic alumina and for that of basic alumina oxide is similar within the experimental error (Figure 3). The ratio of **4/5** is decreased (lowest for pure alumina) when the amount of dopant (basicity) is increased. This ratio for acidic alumina (**4/5** = 2.3) approaches that of equilibrium composition (**4/5** = 4.20).

Geometry. Geometric conditions for the dehydration of alcohols on γ -alumina and thorium oxide have been studied by Sedlacek²³ with the aid of a computer program. He has concluded that the reaction may proceed on a catalyst surface not only as the syn elimination but also as the energetically more favorable anti elimination.

In the construction of the models used in this work, we used general geometric conditions suggested by Sedlacek.²³ (a) The molecule of alcohol adsorbed via its oxygen atom on a surface by a passive hydrogen bond (Scheme 2) at the electrophilic site on the surface, i.e., the coordinatively unsaturated Al³⁺ ion. Adsorption of alcohol follows quite quickly to the dissociation of the

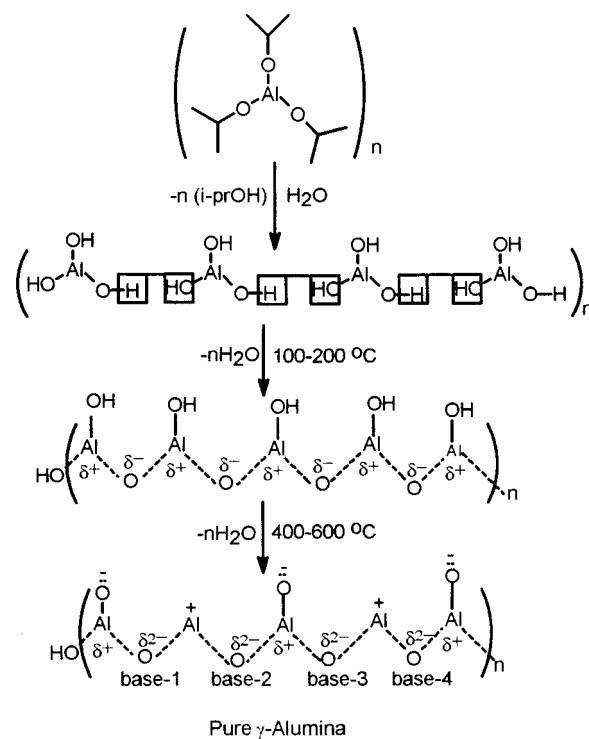
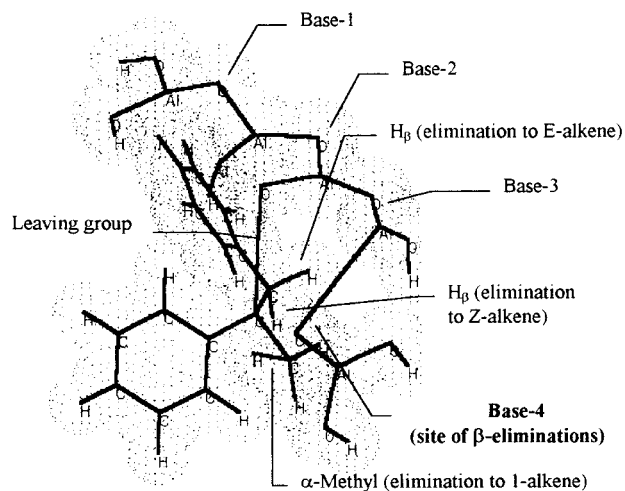
Scheme 2. Six-Membered Ring Hydrogen Bonding of **2 with Neutral Alumina****Scheme 3**

alcohol molecule, yielding the surface alcolate and a hydroxyl group (Scheme 3). According to quantum chemical calculations, the adsorption by passive hydrogen bond increases the ability of the γ -hydrogen to be attacked by nucleophilic species. (b) The alcolate interacts in the adsorption complex through its γ -hydrogen with a surface oxygen ion. (c) The O-C α and C β -H bonds in the transition state are mutually anti and syn periplanar, which determines concerted anti and syn eliminations, respectively. According to quantum chemical calculations, the activation energy is lowest for these conformations.

Generally speaking, the transition-state model has to take into account the properties of the reactant molecule as well as those of the products besides the very specific geometry requirements brought about by the transition state developing on the surface of the solid. The rate of syn elimination is strongly dependent upon the dihedral angle formed between the tetrahedral centered on the carbon atoms α and β . Thus, it would appear that structural considerations within the alcohol molecules control the course of the reaction. The fixed geometry of the surface places constraints on the transition state; however, such constraints are absent in homogeneous media. In the latter, the acid-base can approach the substrate from all directions, and the lower energy pathway leads to complete stereoselectivity. In the heterogeneous reaction, compromises have to be made and complete stereoselectivity cannot be expected. Just as anti elimination is expected to be the rule in homogeneous media (in the absence of special circumstances), geometric constraints are expected to require syn elimination for the surface-catalyzed reaction.

We prepared pure alumina by the method presented in Scheme 4. The structure of pure γ -alumina can be depicted as a polymerization process. The major difference is that bonds in aluminum oxide are ionic in character.

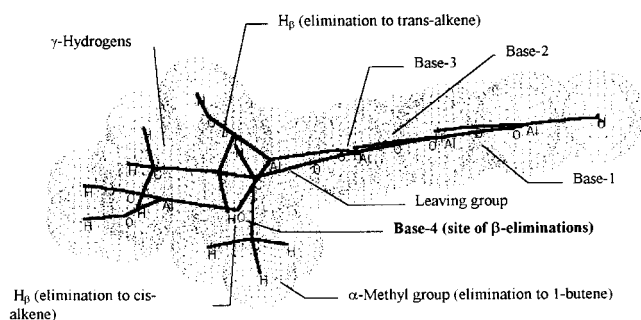
Dabbagh and co-workers recently¹ optimized the geometry of intermediates for the reaction of **2** with triphenylphosphine in carbon tetrachloride by semiempirical calculations (AM1, CNDO, and MNDO)²⁵ and showed that reaction proceeds via intermolecular anti-E2 elimination and substitution (Schemes 4 and 5, ref 1). We applied the same method to the dehydration

Scheme 4**Scheme 5**

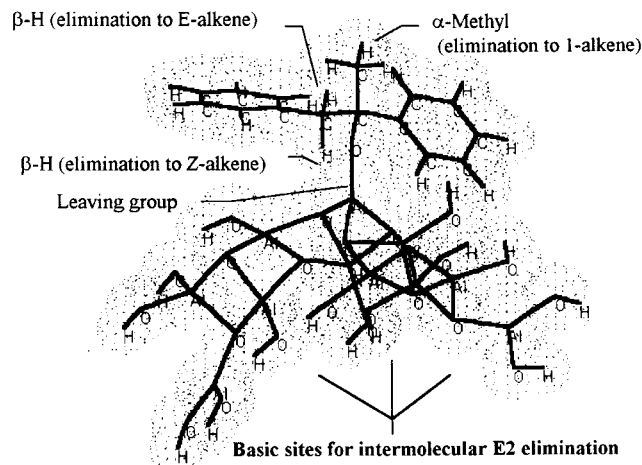
reaction of **2** and 2-butanol over aluminum oxide. The structure of adsorbed alcohol (intermediate) on a small monolayer pure alumina and bilayer doped alumina was optimized by semiempirical calculation (AM1), Schemes 5–7.

These models clearly demonstrate that the partial dehydration on the surface of alumina leads to a situation where, as proposed by Hall and co-workers,⁸ large O²⁻ ions and Lewis acid sites cover adjacent lattice positions. The alcohol **2** or 2-butanol is adsorbed through the alcoholic oxygen atom at Lewis acid site and the basic center, an O²⁻ ion, does the dehydration process. The anti β -hydrogen atoms and the α -methyl hydrogens are more easily discharged, hence the observed stereospecificity, regioselectivity, and intramolecular anti-E2 elimination with cis preference. Thus, two different centers function and the expanded system does not utilize some of the gauche configurations that result in a loss in stereoselectivity. The adsorbed structure **2** with two

Scheme 6



Scheme 7



phenyl groups facing away from the surface (in a *cis* conformation) forces the α -methyl group in a position close to the Base-4 site where elimination leads to the less stable Hofmann olefin. However, there is a strong van der Waals' attraction between the β -phenyl of **2** and the terminal hydroxyl group of alumina, which stabilizes the *cis* configuration (Scheme 5). In the case of 2-butanol, the two methyl groups (there is a strong van der Waals' repulsion between the α -methyl and terminal hydroxyl groups) are forced away from the surface (in a *cis* conformation), pushing the β -hydrogen near the Base-4 site, which leads to the less stable *cis*-2-butene and 1-butene, respectively. The β -hydrogen forming the most stable *t*-2-butene is in unfavorable position with respect to the Base-4 site, Scheme 6.

The new models, however, disagree with the proposal made by Knozinger and co-workers⁹ that the adsorbed structure with *cis* conformation may easily incline backwards toward the surface, whereas a structure with *trans* conformation would bring about a high steric restriction to inclination toward each side. In fact, it is the combination of steric interactions between the surface and the adsorbed species that determine the configuration of the adsorbed alcohol which, in turn, leads to an observed selectivity. An interesting observation is that the structure depicted in Scheme 5 resembles half intermediate (alcohol **2** backbone) and half transition state (aluminum oxide backbone). There are an extended bond breaking for Al–O–C α and the extension of the Al–Base 4 oxygen for abstraction of β -hydrogen (s). No extended bond-making bond-breaking is observed for the alcohol backbone. The more ionic bonds in alumina are more flexible than alcohol **2** covalent bonds. A bilayer model for doped alumina with more ionic character and, therefore, a rigid

surface (strong attraction between cations and anions) has a less flexible surface. In doped alumina, bonds between Al³⁺ and O²⁻ are much stronger, O²⁻ is a weaker base, and therefore, the O¹⁻ of hydroxyl group is the basic site of β -elimination. There is less steric restriction between the adsorbed alcohol and the surface. Therefore, the more stable *anti* configuration with *trans* preference is formed. The *trans*-intermolecular E2 elimination (higher activation energy with lower entropy of activation) with Hofmann preference is favored over *cis*-intramolecular E2 elimination (Scheme 7). This explains the lower observed reactivity of doped alumina over pure alumina. A similar observation is reported for cross-linked polystyryl diphenyl phosphine.^{2,28,29} Strong evidence is presented that the polymer-bound Wilkinson's catalyst can aggregate to form binuclear cluster. The 2% cross-linked are mobile enough to allow the interaction of two active sites. The 20% cross-linked are less mobile (more rigid), and the interaction of the active sites is substantially reduced.

The most intriguing fact is that the new models exactly complement the experimental observations!

Conclusion

Studies of alcohols with proper β -substituents revealed that the *anti* elimination with *cis* preference (justified by optimized geometry calculated through semiempirical AM1 method) is not universal in all catalytic eliminations but that it, in fact, depends on the mode of elimination, temperature, and the catalyst. While *anti* elimination with *syn* preference was noticed in pure alumina, a *trans* olefin was formed to a major amount in doped alumina and thoria at 300 and 350 °C. Kinetic isotope effect and product distribution both indicate that at lower temperatures reaction in pure aluminum oxides proceeds via intermolecular E2 elimination and favors the Hofmann orientation with much lower selectivity than in homogeneous nonacidic dehydrations. At higher temperatures, product distribution is similar to that of equilibrium composition, which indicates an ionic intermediate (e.g., E1). Therefore, we conclude that the dehydration of alcohols over metal oxides depends on not only the steric interaction of the intermediate and/or transition state but is also strongly dependent on the preparation conditions of the catalyst and reaction conditions.

Experimental Section

General. The catalytic reactions were performed in a vertical plug flow reactor made of Pyrex glass and fitted with thermal well extended to the center of the catalyst bed. About 20–30 cm³ of the reactor volume above the catalyst bed contained Pyrex glass beads to serve as preheater. Liquid products were collected at room temperature with increasing time intervals. 2-Hexanols (96%) were used as solvent with 4% **2** to prevent alkene isomerization and to increase the vapor pressure of the alcohol **1–3** and alkenes. It has been shown that 2-octanol is adsorbed strongly enough to essentially eliminate the alkene isomerization reaction at conversion levels of about 50%.^{26,27} Conversion of 2-hexanol was monitored by Shimadzu GC-14A gas chromatography using an SE-

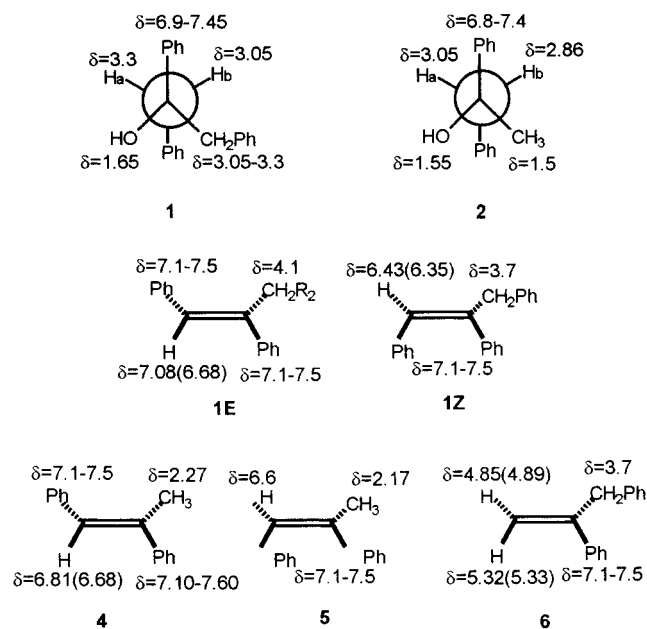
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Scheme 8



30 column, and then the excess 2-hexanol was removed under reduced pressure. Conversion of alcohols **1–3** and the relative product percent were measured by ¹H NMR spectra (Scheme 8), Varian, EM390 (90 MHz).^{1–3} Catalysts (with pH = 4.5–9.5, surface area = 150 m²/g, mesh size = 150, 58 Å) and aluminum isopropoxide were obtained from Aldrich Chemical Co. Pure alumina (BET surface area 150 m²/g)²² was prepared by hydrolysis of aluminum isopropoxide followed by calcination at 600 °C for 6 h. Thorium oxide was prepared through calcination of thorium nitrate at 600 °C for 6 h.²² All runs were performed over 2 g of fresh catalysts (to maintain low conversion 0.50 g of Al₂O₃ prepared from aluminum isopropoxide and 1.5 g of powder glass beads were used) and pretreated in situ in air for 2 h at 400 °C and then with dry nitrogen for 30 min. IR spectra were obtained by Shimadzu ZU-435. Melting points were taken by the Gallenkemp melting point apparatus and are uncorrected. Yields were calculated from ¹H NMR and/or isolated products are not optimized. All starting material or solvents were obtained from Merck or Fluka Chemicals companies and were purified with proper purification techniques.

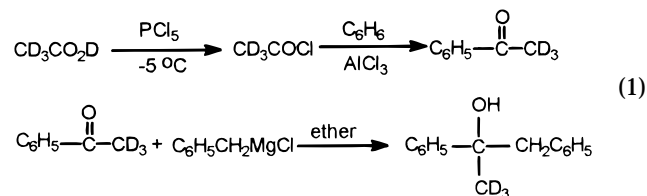
Method of Calculations. All the present semiempirical calculations were carried out with complete geometry optimization unless otherwise stated. The AM1²⁵ calculations were performed with the HyperChem (V.3) program.

1,2,3-Triphenyl-2-propanol (1).³ The reaction of ethyl benzoate (84.94 g, 0.566 mol), benzyl chloride (130 g, 1.24 mol), and magnesium 30.3 g, 1.24 mol) in diethyl ether produced a viscous oil. When crystallized in *n*-hexane, this oil produced 70 g of **2**: mp 83.5–85 °C; ¹H NMR (CDCl₃) δ ppm 1.65 (s, 1H), 3.15 (AB-quartet, 4H *J* = 15 Hz), 6.90–7.45 (m, 15H); IR (KBr) 3300–3400 br.

1,2-Diphenyl-2-propanol (2).³ The reaction of acetophenone (10 g, 0.0833 mol), benzyl chloride (10.5 g, 0.0916 mol), and magnesium (2.23 g, 0.0916 mol) in diethyl ether produced a viscous oil. When crystallized in *n*-hexane, this oil produced 9.0 g of **2**: mp 44–46.5 °C; ¹H NMR (CDCl₃) δ ppm 1.5 (s, 3H), 1.55 (s, 1H), 2.95 (AB-quartet, 2H, *J* = 15 Hz), 6.80–7.40 (m, 10H); IR (KBr) 3300–3400.

α-Trideuterioacetophenone. Tetradeuterioacetic acid (11.10 g, 0.1734 mmol) reacted with phosphorus pentachloride (4.33 g, 0.021 mmol) to give 10.60 g (75% yield) of trideuterioacetyl chloride, bp 44–50 °C. Trideuterioacetyl chloride (8.70 mL, 0.1215 mmol) reacted with 40 mL (0.45 mol) of benzene in the presence of 40 g (0.30 mol) of freshly sublimed aluminum chloride to give 7.70 g (52% yield) of α-trideuterioacetophenone, mp 202 °C.

3,3-Trideuterio-1,2-diphenyl-2-propanol (3). The reaction of α-trideuterioacetophenone (0.4872 g, 0.00406 mol) with 20% excess benzyl chloride in magnesium (1.170 g, 0.04875 mol) in diethyl ether produced a viscous oil. When crystallized in *n*-hexane, this oil produced 6.11.0 g of **3**: mp 47–50 °C; ¹H NMR (CDCl₃) δ ppm 1.50 (s, 3D), 2.0 (s, 1H), 2.95 (AB-quartet, 2H, *J* = 15 Hz), 6.80–7.40 (m, 10H); IR (KBr) 3300–3400. Analysis by ¹H NMR showed 85% deuterium and 15% protium in the methyl group. Correction for kinetic isotope effect for 15% protium were made using eq 1.



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