

Alumina: Catalyst and Support. XXXIX.¹ Benzyl Migration during the Dehydration of 2,2-Dimethyl-3-phenyl-1-propanol over Alumina Catalysts²

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The dehydration of 2,2-dimethyl-3-phenyl-1-propanol at 275–400° over alumina prepared from aluminum isopropoxide was investigated by the micropulse technique. The migratory aptitude ratio of methyl/benzyl was found to be 2.7 and to be constant in the temperature range studied. The suggested mechanism consists of the concerted removal of the hydroxyl group of the alcohol by the intrinsic acidic sites of the catalyst and the abstraction of either an α or a γ proton by the basic sites. γ -Methyl proton abstraction was responsible for 31.5% of the products, whereas 27.2% was from γ -benzyl proton abstraction and 41.3% from α -proton abstraction. Comparisons made with studies of solvolytic reactions of this system support the concept of alumina acting as a "pseudo solvent."

Investigations of the alumina-catalyzed dehydration of alcohols have recently been reviewed by Pines and Manassen³ and by Knözinger.⁴ It was concluded in both reviews that the dehydration of alcohols over alumina occurs by the concerted removal of the hydroxyl group of the alcohol by an acidic site of the catalyst and the abstraction of a proton of the alcohol by a basic site. The similarity between solvolytic elimination reactions and alumina-catalyzed reactions has led to the concept of alumina acting as a "pseudo solvent" which surrounds the alcohol molecule.³

Skeletal rearrangement has been observed during some dehydration reactions. Phenyl migrated about eight times as readily as methyl during the dehydration of 2-phenyl-1-propanol-1-¹⁴C.⁵

In the reactions of ketones with diazomethane which involve migration to an electron-deficient carbon atom,⁶ in the formolysis and acetolysis of 2,2-dimethyl-3-phenyl-1-propyl *p*-toluenesulfonate in which ionization and rearrangement are likely concerted,^{7,8} and in the deamination of 2,2-dimethyl-3-phenyl-1-propylamine,⁷ methyl was found to have a higher migratory aptitude than benzyl.

The present study of the dehydration of 2,2-dimethyl-3-phenyl-1-propanol over alumina offered a comparison of the migratory aptitudes of benzyl and methyl groups as well as a comparison with elimination reactions in solution on this system.

Procedure.—The dehydration was studied by the micro pulse technique which was first used by Emmett and coworkers⁹ and was later modified by Steingaszner and Pines.¹⁰ The detailed experimental procedure was described previously.¹¹ The material consisting of 8 μ l of a mixture of 43.1% alcohol, 4.5% *sec*-butylbenzene, the internal standard used to determine the conversion of alcohol to olefin, and 52.4% cyclohexane, the

solvent, was injected by means of a syringe into the microreactor. Helium flowing at a rate of 81 ml/min carried the sample over the catalyst and directly to a gas chromatograph.

Alumina prepared from aluminum isopropoxide according to the procedure of Schappell and Pines¹¹ and of 20–40 mesh size was used in amounts of 5 to 25 mg. The temperature of the catalyst was varied from 275 to 400°.

Results and Discussion

The dehydration of 2,2-dimethyl-3-phenyl-1-propanol over alumina yielded 2-benzyl-1-butene (1), *cis*-2 and *trans*-2-methyl-1-phenyl-1-butene (3), 2-benzyl-2-butene (4), 3-methyl-1-phenyl-2-butene (5), and 2-methyl-4-phenyl-1-butene (6). Figures 1 and 2 show the product distribution from the dehydration at 300 and 380°, respectively, and at various conversions effected by changes in the amount of catalyst used. Similar results were found at 275, 340, and 400°.

In Figures 1 and 2, extrapolation to zero conversion gives the initial product distribution. The decrease in 1 and 6 and the increase in 3, 4, and 5 as the conversion was increased indicate that some isomerization occurred. At higher temperatures, more isomerization was found.

In an effort to determine further the primary products of the reaction, the catalyst was treated with pyridine. Beranek, *et al.*, showed that, when alumina was treated with pyridine, the isomerizing ability of the catalyst was almost absent, whereas the dehydrating ability was only slightly decreased.¹² Table I shows the effect of this treatment upon the isomerization of 2-benzyl-2-butene (4).

2-Phenyl-1-propanol was injected with compound 4 to study isomerization under conditions similar to those during the dehydration reaction. Less isomerization occurred when alcohol was present than when pure olefin was injected. Pyridine treatment of the catalyst reduced the amount of isomerization but a retreatment had no additional effect. An increase in temperature caused more isomerization to occur.

Results of dehydrations over the pyridine-treated alumina are included in Figures 1 and 2. Figure 2 shows that product distribution changes at high con-

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(2) This research was supported in part by the Atomic Energy Commission Contract AT(11-1) 1096.

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(4) H. Knözinger, *Angew. Chem. Int. Ed. Engl.*, **7**, 791 (1968).

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(12) L. Beranek, M. Kraus, K. Kochloef, and V. Bazant, *Collect. Czech. Chem. Comm.*, **25**, 2513 (1960).

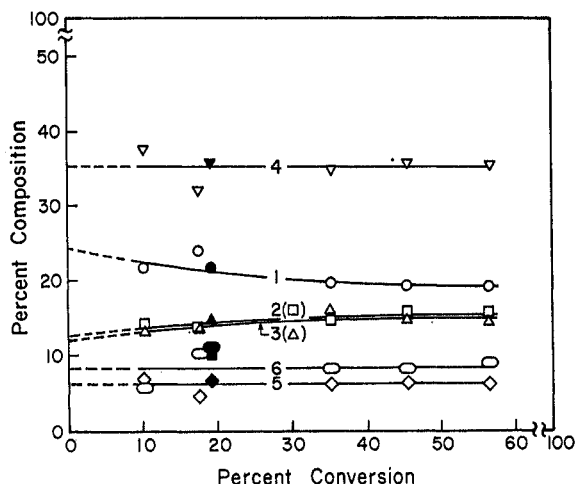


Figure 1.—Composition of olefins from the dehydration of 2,2-dimethyl-3-phenyl-1-propanol at 300° over Al_2O_3 (open symbols) and pyridine-treated Al_2O_3 (filled symbols).

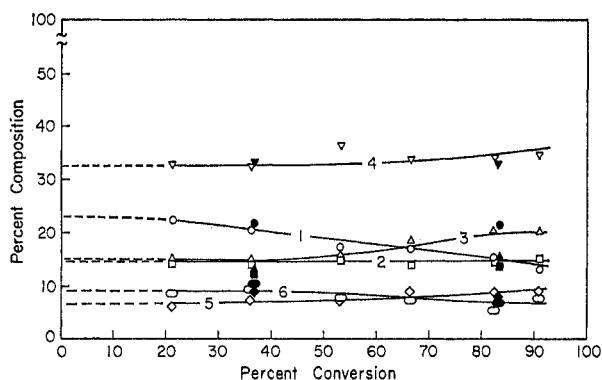


Figure 2.—Composition of olefins from the dehydration of 2,2-dimethyl-3-phenyl-1-propanol at 380° over alumina (open symbols) and pyridine-treated alumina (filled symbols).

TABLE I
EFFECT OF PYRIDINE UPON THE ISOMERIZATION OF
2-BENZYL-2-BUTENE OVER ALUMINA

Expt	Catalyst, mg	Temp, °C	Sample, μl	% unisomerized 2-benzyl-2-butene (4)
1	10	300	4, 1	83.1
2	10 ^a	300	4, 1	96.5
3	10	300	4, 1, and PhCCOH, 4	94.0
4	10 ^a	300	4, 1, 2, and PhCCOH, 5	98.1
5	15	325	4, 3	69.3

^a 15- μl portions of pyridine and three 10- μl portions of a 50:50 cyclohexanol-pyridine mixture were injected at a helium flow of 20 ml/min.

versions are the result of isomerization, since the distribution over pyridine-treated catalyst at high conversions corresponds to that at lower conversions over untreated catalyst.

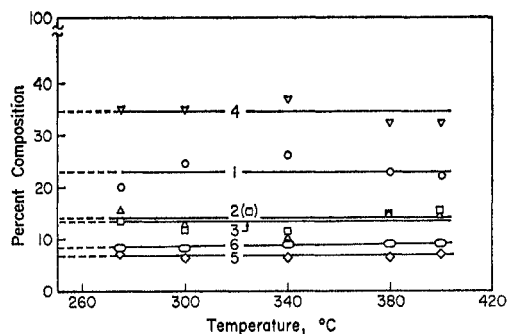
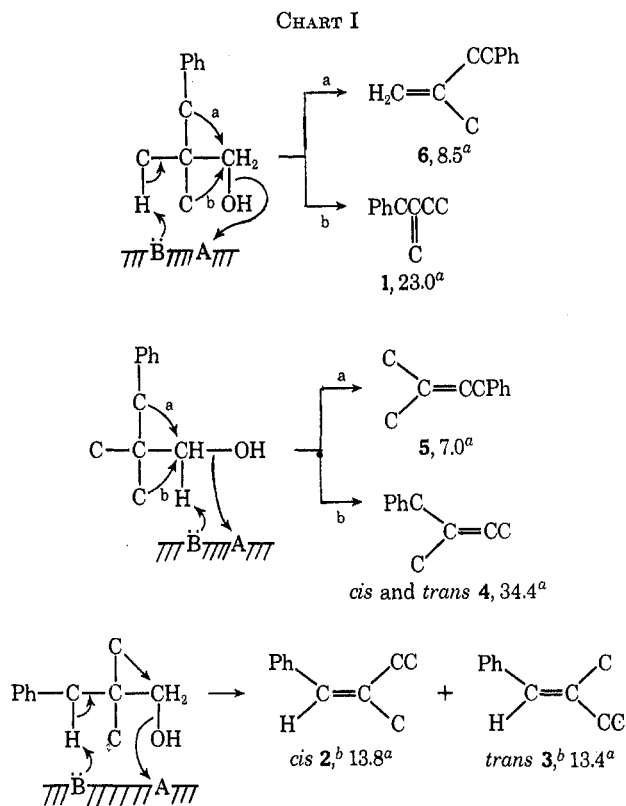


Figure 3.—The effect of temperature upon the product distribution at zero conversion from the dehydration of 2,2-dimethyl-3-phenyl-1-propanol.

Product 1 isomerizes at high conversions and temperatures to 2 and especially to 3 since in these, the double bond is conjugated with the phenyl group. More of olefin 3 than 2 would be expected to be formed since the *trans* isomer is presumably more stable than the *cis*. The small amount of isomerization of product 6 to 5 found is due to the fact that 5, a trisubstituted olefin, is more stable than 6, a disubstituted one. Similarly, the slight increase in 4 can be explained by isomerization of 1 to the more stable 4; the latter is presumably a mixture of *cis* and *trans* isomer, which could not be resolved by vpc.

Extrapolated values for the product distribution at zero conversion are plotted *vs.* temperature in Figure 3 which shows that the initial product distribution, in contrast to the actual distribution, was fairly constant within the temperature range studied.

The formation of the products can be pictured as shown in Chart I.



^a Initial product distribution. ^b The absolute assignment was not made.

TABLE II
 GAS CHROMATOGRAPHIC COLUMNS

Columns	% substrate	Solid support ^a (mesh)	Length, m	Outer diameter, ^b in.
A	15% Reoplex ^c 400	Gas Pack WAB (60-80)	3.6	0.375
B	15% Ucon ^d 75H 90,000	Gas Pack WAB (60-80)	4	0.25
C	8% Apiezon L ^e -8% Bentone 34 ^f	Gas Pack W (80-100)	4	0.25
D	10% GE XF-1150 ^g	Gas Pack W (80-100)	5	0.25

^a Gas Pack W is a diatomaceous earth. ^b Columns were made of copper. ^c Reoplex is polypropylene glycol adipate. ^d Ucon is a polypropylene glycol. ^e Apiezon L is a high molecular weight hydrocarbon grease. ^f Bentone 34 is dimethyldioctadecylammonium bentonite. ^g GE XF-1150 is a silicone fluid.

The relative migratory aptitude of methyl/benzyl in 2,2-dimethyl-3-phenyl-1-propanol, based upon the extrapolated initial product distributions from Figure 3 and corrected for the statistical factor of two methyl groups, is 2.7.

Warrick and Saunders^{7,8} reported finding benzyl migration in the acetolysis of 2,2-dimethyl-3-phenyl-1-propyl *p*-toluenesulfonate and in the deamination of the amine. Although products 1-6 were found in their study, the compounds formed by the removal of a methyl γ hydrogen, 1 and 6, amounted to 2.36 and 1.64%, respectively, compared with 23.0 and 8.5%, respectively, in the present investigation.

The migratory aptitude of methyl/benzyl is 1.85 in the acetolysis reaction and 2.55 in the formolysis reaction,⁸ which is in accordance with the present study.

The fact that the alumina-catalyzed dehydration and these solvolysis reactions yield the same elimination products and similar migratory aptitude ratios supports the concept of alumina acting as a "pseudo solvent".

Experimental Section

Apparatus.—The apparatus used has been described by Steingaszner and Pines¹⁰ and consisted of a microreactor in a furnace, a temperature control panel, and an F & M Model 300 programmed temperature gas chromatograph.

The 150-mm microreactor was constructed of 0.25-in.-o.d. stainless steel tubing. It had stainless steel swagelok fittings on each end and a thermocouple tube welded to the side. A 0.125-in.-o.d. transfer line connected the reactor outlet to the chromatograph inlet.

Analytical Procedures. Gas Chromatographic Columns.—Listed in Table II are the columns used for the dehydration product analyses and preparative gas chromatographic separations.

Identification of the Olefinic Reaction Products.—The reaction products were identified by comparison of their relative retention times with those of known samples. An electronic integrator, Model CRS-11HSB, Infotronics Corp., Houston, Texas, was used to measure chromatographic peak areas.

Since at least two products overlapped on all columns tried, it was necessary to use two separate columns and therefore, to do each run twice under the same experimental conditions. With column C, the 2-methyl-4-phenyl-1-butene (6) and 2-benzyl-2-butene (4) peaks overlapped. Using column D, the percentage of 4 formed was found. By subtracting this percentage from the combined percentage of 4 and 6 as found on column C, the percentage of 6 formed was determined. The percentages of all other olefinic products were determined by using column C.

2,2-Dimethyl-3-phenylpropanol.—This alcohol was prepared in an overall yield of 23% from benzyl chloride and methyl isobutyrate.⁷

2-Methyl-4-phenyl-1-butene (6) and 3-methyl-1-phenyl-2-butene (5) were prepared by Warrick and Saunders,⁷ who kindly supplied us with samples of each.

***cis*- (2) and *trans*-2-Methyl-1-phenyl-1-butene (3), 2-Benzyl-2-butene (4), and 2-Benzyl-1-butene (1).**—A mixture of the four olefins prepared by Warrick and Saunders⁷ was separated into pure olefins by means of preparative gas chromatography on column A. The compounds were identified by comparison of their relative retention times on column B with the reported times on a similar column.⁷ Their relative retention times at 130° were as follows: compound 1, 1.00; 4, 1.19; 2, 1.28; 3, 1.44.

The relative retention times of the products from the dehydration of 2,2-dimethyl-3-phenyl-1-propanol were analyzed on columns C at 130° and D at 110° with a helium flow rate of 81 ml/min, and using *sec*-butylbenzene as an internal standard with a retention time of 1.00. On column C the retention times were as follows: compound 1, 1.86; 4, 2.16; 6, 2.16; 5, 2.59; 2, 2.70; 3, 2.96. On column D the retention times were as follows: 1, 2.00; 4, 2.30; 2, 2.56; 6, 2.56; 5, 2.72; 3, 2.94.

Registry No.—2,2-Dimethyl-3-phenyl-1-propanol, 13351-61-6.