Alumina: Catalyst and Support. XXXIII.[1] Dehydration of 3-Phenylpropanol, 1-Phenyl-2-propanol, and 2-Phenylpropanol over Aluminas and in the Presence of 33% Sulfuric Acid. Dehydration of 2-Phenylpropanol-1-C^{14}[2,3]

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3-Phenyl- and 2-phenylpropanol and 1-phenyl-2-propanol were dehydrated at 250–360° over an "acidic" alumina prepared from aluminum isopropoxide, "nonacidic" alumina containing 1% Na$^+$ and over the "acidic" alumina but in the presence of pyridine. 3-Phenylpropanol formed besides allylbenzene also propenylbenzenes in which the *cis* isomer predominates. The latter compounds were not products of double-bond migration but of γ-hydrogen participation. Phenyl-2-propanol on dehydration yielded allylbenzene and a mixture of *cis*- and *trans*-propenylbenzene with the predominant formation of the thermodynamically least stable *cis* isomer. 2-Phenylpropanol formed besides α-methylstyrene also allylbenzene and propenylbenzenes. The latter were the products of both methyl and phenyl migration as demonstrated by means of radioactive tracer technique. From the dehydration of 2-phenylpropanol-1-C^{14} it was found that the ratio of phenyl/methyl migration was 7.3:9.0, depending on the alumina used. The allylbenzene was demonstrated to be the product of phenyl migration. The mechanisms of dehydration reactions are discussed. Experiments were also made using 33% sulfuric acid as catalyst and the results were compared with those of the alumina-catalyzed reactions.

It was reported previously[5] that the dehydration of 2-butanol over alumina produced *cis*-2-butene in preference to the thermodynamically more stable *trans*-2-butene. The ratio of *cis/trans*-2-butene formed was from three to about six times greater than the calculated equilibrium constant.[6] Similar results were obtained with 2- and 3-pentanol. The dehydration of primary alcohols was also accompanied by γ-hydrogen participation and therefore besides 1-butene both *cis*- and *trans*-2-butene were formed, in which the *cis* isomer predominated. In the case of isobutyl alcohol the dehydration was accompanied by skeletal isomerization and the *cis*-2-butene was produced preferentially over the *trans* isomer.[7] All the isomerization products were initial products of dehydration since the olefins formed in the reaction did not undergo rearrangement.

The present paper describes the extension of this study to include 1-phenyl-2-propanol, 3-phenylpropanol, and 2-phenylpropanol, including 2-phenyl-1-propanol-1-C^{14}. The dehydrations were made in a flow-type system using as catalyst aluminas of various intrinsic acidities. Alumina-A, which is the most acidic, was prepared from aluminum isopropoxide and calcined at 700°.[8] Alumina-B contained 1% by weight of Na$^+$ and was obtained by impregnation of alumina-A with sodium carbonate.[9] Alumina-H was obtained from Harshaw Co. and contained 0.37% Na$^+$.[8] The relative catalytic acidities of the three aluminas, determined by the method described previously, were A > H > B. Dehydrations were also made over alumina-A in the presence of pyridine.

Results

The experimental results are given in Tables I–III. The temperature and the contact time (hourly liquid space velocity) were adjusted to obtain conversions ranging from about 8 to about 50% and preferentially to less than 25%. Thus, the rearrangement of the initial products of dehydration is avoided. This is indicated by the fact that the composition of phenylpropenes obtained from the dehydration of the various phenylpropanols did not change with conversion.

3-Phenylpropanol.—A solution of 75% by volume of the alcohol in *n*-heptane was passed over alumina-A, "nonacidic" alumina H, and over alumina-A in the presence of 10% of pyridine (Table I). The resulting product consisted of allylbenzene, as the major component, and of *cis*- and *trans*-propenylbenzene, in which the ratio of *cis/trans* isomer amounted from about 0.7 to 1.4. The equilibrium ratio of *cis/trans* at 350° is 0.24.[10] The largest ratio of *cis* isomer was obtained when pyridine was added to the alcohol in order to neutralize the relatively strong acidic sites of the alumina.

The formation of allylbenzene can be explained by a *trans*-elimination reaction, in accordance with previous observations made during the dehydration of menthol and neomenthol[11] and of the isomeric 1-decalols.[12] It is not unequivocally proven whether the reaction is of E1 or E2 type, although in the case of menthol and neomenthol strong evidence exists in favor of E2 elimination.

The formation *cis*- and *trans*-β-methylstyrene is a further evidence of γ-hydrogen participation, which seems to be common to many alumina-catalyzed dehydrations.[13] There is a preferential formation of *cis* over the thermodynamically more stable *trans* isomer. The reason for the predominant formation of the *cis* isomer is open to speculation.

Phenyl-2-propanol.—The dehydration was carried out at 280–300° over aluminas-A, -H, and over alumina-A in the presence of pyridine (Table II). The product

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[1] For paper XXXII see J. Herling, N. Sih, and H. Pines, *J. Org. Chem.*, **31**, 4085 (1966).

[2] Paper XII in the series of Dehydration of Alcohols. For previous paper see ref 1.

[3] This research was supported by the Atomic Energy Commission Contract AT(11-1)1096.

[4] On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel, 1961–1964.

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

[6] J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **36**, 559 (1946).

[7] J. Herling and H. Pines, *Chem. Ind.* (London), 984 (1963).

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

[9] J. Manassen and H. Pines, Proceedings of the Third International Congress on Catalysis, North-Holland Publishing Co., Amsterdam, 1964, pp 845–856.

[10] H. Pines and E. Blanc, unpublished results.

[11] H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **83**, 3270 (1961).

[12] F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1735 (1966).

[13] For general review of the literature see H. Pines and J. Manassen, *Advan. Catalysis*, **16**, 49 (1966).

Table I

Dehydration of 3-Phenylpropanol[a]

				Compn of olefins, %				
					PhC=CC			
Catalyst	Temp, °C	HLSV	Dehydration, %	PhCC=C	*cis*	*trans*	*cis/trans*	Allyl/*cis* and *trans*
A	300	47	5.8	80.8	7.9	12.3	0.63	4.0
A	300	29	7.3	83.0	7.8	9.2	0.85	4.9
A	300	15	12.7	83.3	6.7	9.9	0.68	5.0
A	300	8	22.0	82.7	7.5	9.8	0.76	4.8
A-P[b]	320	30	6.2	93.8	3.5	2.7	1.3	15.0
A-P[b]	320	14	9.4	93.4	3.4	3.0	1.4	14.6
A-P[b]	320	8	20.1	93.8	3.4	2.7	1.3	15.4
A-P[b]	320	3	58.8	92.3	4.2	3.5	1.2	12.0
H	360	39	0.7	81.0	8.3	10.7	0.8	4.2
H	360	19	1.5	80.4	8.2	11.4	0.8	4.1
H	360	3	4.0	79.4	8.7	11.9	0.7	3.8

[a] 75% solution of the alcohol in *n*-heptane was used. [b] Pyridine in the amount of 10 volume % of the alcohol solution was used.

Table II

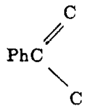
Dehydration of Phenyl-2-propanol[a] over Aluminas

				Compn of olefins, %				
					PhC=CC			
Catalyst	Temp, °C	HLSV	Dehydration, %	PhCC=C	*cis*	*trans*	*cis/trans*	Allyl/*cis* and *trans*
A	280	176	7.9	40.6	37.8	21.6	1.7	0.68
A	280	80	12.0	41.7	40.4	17.8	2.2	0.70
A	280	40	21.9	43.4	42.4	14.1	3.0	0.77
A-P[b]	280	176	8.5	44.7	46.3	9.0	5.1	0.80
A-P[b]	280	80	13.0	43.1	48.6	8.3	5.8	0.75
A-P[b]	280	40	21.0	41.8	49.7	8.5	5.8	0.74
H	300	7.5	8	39.8	31.5	28.7	1.1	0.66
H	300	4.2	14	39.0	33.3	27.7	1.2	0.64
H	300	2.1	25	38.7	30.7	29.6	1.0	0.62
H	300	0.9	52	39.1	32.4	28.5	1.1	0.64

[a,b] See footnotes in Table I.

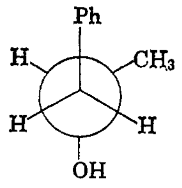
Table III

Dehydration of 2-Phenylpropanol[a] over Aluminas

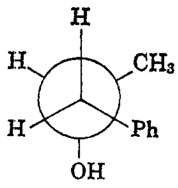
				Compn of olefins, %				
						PhC=CC		
Al_2O_3	Temp, °C	HLSV	Conversion, %	 $PhC(=C)C$	PhCC=C	*cis*	*trans*	*cis/trans*
A	270	2.8	8.2	65.9	12.9	16.3	4.8	3.4
A-P[b]	270	0.5	10.5	52.9	23.8	16.4	6.9	2.4
A-Na[c]	270	0.15	10.0	66.0	17.6	11.3	5.1	2.2
A-H	320	34	20.0	39.0	33.4	18.6	9.0	2.0

[a,b] See footnotes in Table I. [c] Catalyst A impregnated with sodium carbonate to yield 1% by weight of Na^+.

consisted of 41 ± 2% of allylbenzene, the remainder being propenylbenzenes in which the ratio of *cis/trans* isomer ranges from 1.0 to 5.8. The high ratio of *cis* was obtained in the presence of pyridine. It is attractive to think that the preferential formation of the *cis* isomer is due to steric effects in the approach of the alcohol to the active sites of the catalyst. There are three configurations for phenyl-2-propanol. The dehydration cannot proceed *via* conformation a since the removal of the elements of water occurs through a *trans*-elimination reaction as discussed previously.[13] From the examination of the molecular models it appears that there is less hindrance when the hydroxyl group in the molecule having conformation b, rather than c, is approaching the surface of the catalyst. It was suggested by one of us previously that *trans*-elimination takes place within cavities in the alumina.[11] For that reason configuration b having the phenyl and methyl group on one side of the molecule may approach the active sites of the catalyst more easily than configuration c.



a



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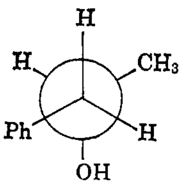


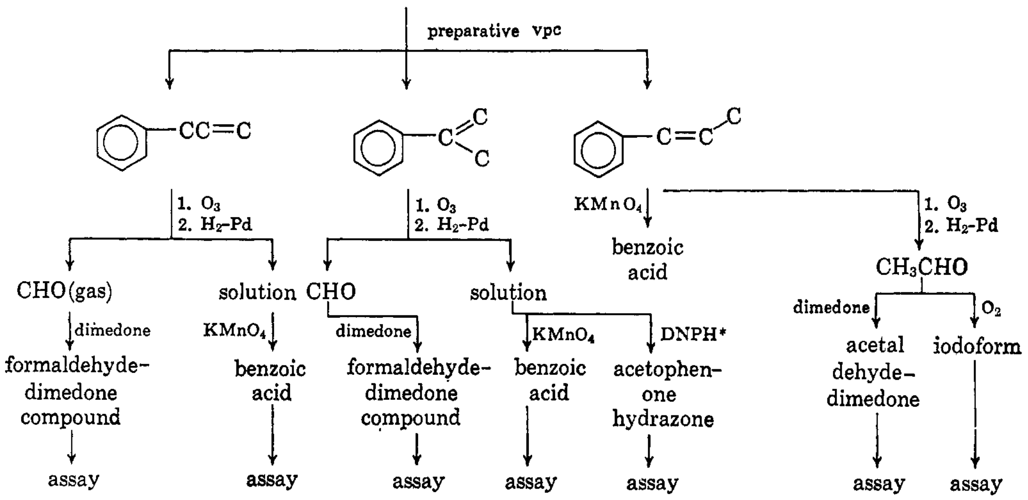
c

The large difference between the results obtained with a catalyst in the absence and presence of pyridine is a subject of further study.

2-Phenylpropanol.—The results of the dehydration of the title alcohol over the various aluminas and at various contact times were reported previously.[7] Table III summarizes the initial olefins produced. The dehydration is accompanied by skeletal isomerization, which is due to both the methyl and phenyl migration as demonstrated with 2-phenylpropanol-1-

SCHEME I

PROCEDURE FOR THE RADIOCARBON DETERMINATION OF THE OLEFIN FROM THE DEHYDRATION OF 2-PHENYLPROPANOL-1-C^{14}



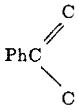
C^{14}. The mechanism of this reaction was discussed previously.[7] As in the case of the other isomeric alcohols, the ratio of *cis/trans* of propenylbenzenes is from 10 to 20 times greater than its equilibrium ratio, which is 0.15 at 250° and 0.24 at 350°.

The formation of allylbenzene can be explained by γ-hydrogen participation, accompanied by phenyl migration, in the elimination step.[11]

Sulfuric Acid Catalyst.—For comparison with aluminas the dehydrations of the three isomeric phenylpropanols were made in the presence of 33% aqueous sulfuric acid at 100° and under efficient stirring (Table IV). Samples were withdrawn for analysis at various intervals in order to differentiate between the initial reactions and products resulting from subsequent isomerization of the olefins.

TABLE IV

DEHYDRATION OF PHENYLPROPANOLS WITH 33% SULFURIC ACID AT 100°

Contact time, min	Conversion, %	Compn of olefins, % 	PhC-C=C	PhC=CC cis	trans	cis/trans
		3-Phenylpropanol				
15	3		66.6	11.5	21.9	0.53
30	14		60.4	12.0	27.6	0.43
60	15		62.6	10.3	27.1	0.38
		2-Phenylpropanol				
15	5	5.9	29.4	21.4	43.3	0.49
30	7	5.6	28.0	22.6	43.8	0.52
60	88	2.9	23.2	18.6	55.2	0.34
		Phenyl-2-propanol				
15	52		23.8	25.2	51.0	0.49
30	88		21.3	23.5	55.2	0.43
60	100		21.0	21.4	57.6	0.37

The ratio of the *cis/trans* of propenylbenzenes is about 0.50 as compared with equilibrium ratio of 0.09 at 150°.[10] Unlike the alumina-catalyzed reactions the dehydration of 2-phenylpropanol gives very little α-methylstyrene, the main products being allylbenzene and *cis*- and *trans*-propenylbenzene.

2-Phenylpropanol-1-C^{14} over Alumina.—The dehydration of 2-phenylpropanol over alumina catalysts is accompanied by skeletal isomerization to *cis*- and *trans*-propenylbenzene and to allylbenzene.[7] The rearrangement which occurs during the dehydration can be attributed to phenyl migration and/or to methyl migration. Methyl migration in the presence of "nonacidic" alumina was encountered in the dehydration of isobutyl alcohol.[7] In order to determine the relative contribution of the phenyl and methyl group 2-phenylpropanol-1-C^{14} was synthesized and dehydrated. In this study were used an "acidic" alumina-A, and a "nonacidic" alumina-B.

The dehydration of the alcohol was made at 270°, and the conversion was kept at 20–37% in order to avoid readsorption of the olefins by the catalyst which could lead to a possible double-bond migration.[5] The experimental data are given in Table V. Allylbenzene, α-methylstyrene, and *trans*-propenylbenzene were separated by preparative gas chromatography. The distribution of the radiocarbons in the olefins were determined by degradation, according to the procedure outlined in Scheme I.

TABLE V

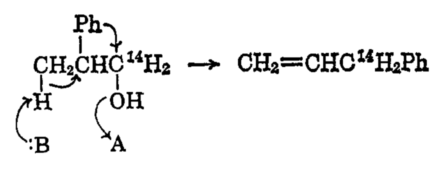
COMPOSITION OF PRODUCT OBTAINED FROM THE DEHYDRATION OF 2-PHENYLPROPANOL-1-C^{14a}

Alumina	Conversion, %	Compn of phenylpropenes, % Allylbenzene	α-Methylstyrene	Propenylbenzene cis	trans
A	37	27	43	19	11
B	20	25	43	20	12

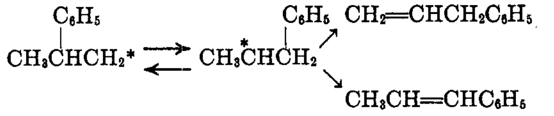
[a] The dehydration was made at 270° and at HLSV; HLSV is cubic centimeters of alcohol/cubic centimeters of catalyst times reciprocal hours.

The radiocarbon distribution in the olefins obtained from the dehydration of the 2-phenylpropanol is given in Table V.

Allylbenzene.—All the radioactivity was located on the terminal vinylic carbon atom, which confirms previous observations of γ participation in the dehydra-



tion reactions over aluminas.[8,14] A common intermediate in phenyl migration leading to the formation of allyl- and propenylbenzene was considered.



This was however abandoned in preference of a concerted mechanism in which the acidic and basic sites are involved in the elimination reaction. The latter mechanism is more in line with E2-type mechanism as applied to menthol and neomenthol[11] and in agreement with the formation of 2,3-octalins from the isomeric 1-decalols.[12]

α-Methylstyrene.—There was almost an equal distribution of radioactivity between C-1 and C-3 atoms and practically none of the C-2 atom. Although a symmetrical intermediate and γ-hydrogen participation reaction cannot be excluded it is more reasonable to assume that facile double-bond migration of α-methylstyrene was responsible for the results.

***trans*-Propenylbenzene.**—This olefin can be produced either by phenyl or by methyl migration. The distribution of radioactivity between the benzylic carbon C_1 and C_2 shows that the relative rate of phenyl *vs.* methyl migration was about 7.3 to 1.0 and 9.0 to 1.0, depending on the type of alumina which was used. The relative ratio of phenyl and methyl migration from the respective treatment of 2-phenylethylamine-1-C^{14} and propylamine-1-C^{14} with nitrous acid was 3.0[14,15] from the dehydration of 2-phenylethanol-1-C^{14},[1] and of propanol-1-C^{14} [16] was 41.

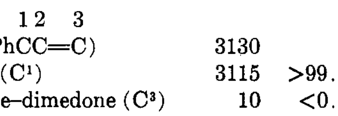
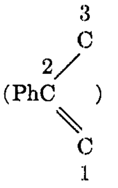


TABLE VI

RADIOCARBON DISTRIBUTION IN PHENYLPROPENES FROM THE DEHYDRATION OF 2-PHENYLPROPANOL-1-C^{14}

Alumina used	A activity[a]	% of total	B activity[a]	% of total
Allylbenzene ($Ph\overset{1}{C}\overset{2}{C}=\overset{3}{C}$)	3130		270	
Benzoic acid (C^1)	3115	>99.5	268	100
Formaldehyde–dimedone (C^3)	10	<0.5	1	0
By difference (C^2)		0		0
α-Methylstyrene ()	1220		1000	
Formaldehyde–dimedone (C^1)	590	49.6	520	53
Acetophenone-2,4-dinitrophenylhydrazone ($C^1 + C^2$)	600		460	
Benzoic acid (C^2)	10	0.8	5	0
By difference (C^3)	590	49.6	455	47
trans-Propenylbenzene ($Ph\overset{1}{C}=\overset{2}{C}\overset{3}{C}$)	1020		950	
Benzoic acid (C^1)	880	88	840	90
Acetaldehyde–dimedone ($C^2 + C^3$)	120		90	
Iodoform (C^3)	5	0	3	0
By difference (C^2)	115	12	87	10

[a] Activity = μcuries/mmole × 10^{-3}.

***cis*-Propenylbenzene.**—This hydrocarbon was not analyzed for its radiocarbon distribution owing to the difficulty encountered of separating it in pure form by preparatory gas chromatography.

Experimental Part

Alcohols. 2-Phenylpropanol.—The alcohol was obtained by the catalytic hydrogenation of 2-phenylpropionaldehyde in ethanol under 100 atm of hydrogen pressure and at 100° in the presence of copper chromite catalyst. The 2-phenylpropanol thus produced was about 99% pure by gas chromatography. It distilled at 135–136° (13 mm), $n^{26}D$ 1.5237.

Phenyl-2-propanol.—This alcohol, which was prepared from phenyl-2-propanone by a procedure similar to the one described above, was over 99% pure and distilled at 126° (41 mm), $n^{26}D$ 1.5193.

3-Phenylpropanol.—The commercially available alcohol was used, after distillation. It was about 99% pure by gas chromatography and distilled at 146–147° (43 mm), $n^{26}D$ 1.5237.

2-Phenylpropanol-1-C^{14}.—α-Phenethylmagnesium chloride which was prepared from 7.0 g (0.05 mole) of α′-phenethyl chloride and 1.33 g (0.055 g-atom) of magnesium in 50 ml of ether, was carbonated with 7.2 g (0.037 mole) of $BaC^{11}O_3$ by the usual technique, using a vacuum line.[17] The 2-phenylpropionic acid–ether solution, to which 15 ml of inactive 2-phenylpropanol was added, was reduced with 12 g of lithium aluminum hydride. The yield of 2-phenylpropanol was 32%, based on $BaC^{14}O_3$ used.

Catalysts. Alumina-A.—It was prepared from aluminum isopropoxide and calcined at 600° for 12 hr.[8] The alumina was broken up to give 20–40 mesh size particles.

Alumina-B.—This catalyst contained 1% by weight Na^+ and was prepared from alumina-A, according to the description given previously.[1]

Alumina-H.—It was obtained from the Harshaw Chemical Co., it contained 0.37% by weight Na^+. The catalytic characteristic of this alumina was reported.[8]

Apparatus and Procedure.—They were the same as described in the preceding paper.[1]

Gas Chromatographic Analysis.—The product of the reaction was analyzed by gas chromatography using an internal standard. The relative retentions of the four phenylpropenes, on a column of 18 ft × $^1/_8$ in. diameter filled with 20% Silicon 550 on 30–60 mesh Celite at 125° and at helium flow of 75 ml/min, were allylbenzene, 0.81; α-methylstyrene, 1.0; *cis*-propenylbenzene, 1.07; and *trans*-propenylbenzene, 1.32.

Analysis of Dehydration Products of 2-Phenylpropanol-1-C^{14}.—The olefinic isomers were separated by means of preparative gas chromatography using 15% SE30 (silicone gum rubber) on Chromosorb P. The purity of three of the isomers was 99%. This was achieved after one pass through the column for allylbenzene and *trans*-propenylbenzene. α-Methylstyrene contained 7% *cis*-propenylbenzene after one pass, after a second pass and dilution its purity was 99%.

Allylbenzene.—One gram of allylbenzene in 15 ml of ethyl acetate was ozonized and reduced with hydrogen using palladium catalyst, according to the description given previously.[1] The formaldehyde was determined as a condensation product with dimedone. The remaining solution was oxidized with potassium permanganate and the benzoic acid was separated, purified by sublimation, and assayed.[1]

α-Methylstyrene.—One gram of the olefin was ozonized and reduced catalytically. The formaldehyde was collected and its activity was measured as the dimedone compound. Five milliliters of the remaining solution was treated, after the removal of the catalyst, with a freshly prepared solution of 2,4-dinitrophenylhydrazone, and a precipitate of the corresponding acetophenone

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[14] J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, **75**, 2070 (1953).

[15] J. D. Roberts and M. Halman, *ibid.*, **75**, 5759 (1953).

[16] N. C. Sih and H. Pines, *J. Org. Chem.*, **31**, 4092 (1966).

[17] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. F. Yankovich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p 180.

hydrazone was obtained. It melted at 248° after recrystallization from aqueous ethanol. The remaining 9 ml of the solution was oxidized to benzoic acid with potassium permanganate.

trans-**Propenylbenzene.**—Two grams of the olefin in 15 ml of butyl acetate was ozonized and reduced at the usual conditions. The acetaldehyde produced was trapped, using the same procedure as for formaldehyde.[1] Special care was taken not to introduce any butyl acetate in the trap and this was achieved by using a long condenser and reducing the flow of nitrogen through the solution. After 3 hr of nitrogen flow, the trap was diluted with 25 ml of dioxane and the solution was treated with 3 ml of 10% aqueous sodium hydroxide. An iodine-potassium iodide solution was then added with shaking, until a slight excess yielded a dark color. The excess of iodine was removed by the addition of a few drops of the aqueous sodium hydroxide. Water was then added and the whole was allowed to stand for several hours. The iodoform thus produced melted at 120°, after recrystallization from dioxane.

The collection of acetaldehyde was afterwards continued for an additional 5 hr. The acetaldehyde was treated with dimedone and the solid thus obtained was recrystallized from methanol-water solution, it melted at 141° (lit.[18] mp 141-142°)

About 0.5 g of the *trans*-propenylbenzene in 60 ml of water was oxidized with 3 g of potassium permanganate to benzoic acid and assayed.

Radioactivity Assay.—The radioactivity of the various compounds was measured by conversion to gaseous of carbon dioxide as described previously.[1]

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[18] E. C. Horning ond M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

Alumina: Catalyst and Support. XXXIV.[1] Dehydration of 1-Propanol-1-C^{14} over Alumina[2,3]

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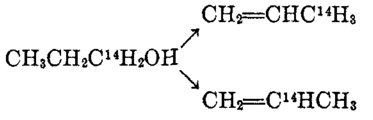
The dehydration of propanol-1-C^{14} at 345° over alumina under nonisomerizing conditions afforded a 46% conversion of which 43.6% was di-*n*-propyl ether and 53.7% gaseous products. The extents of the γ-hydrogen participation and the methyl migration accompanying the dehydration were estimated to be about 2.2 and 0.3%, respectively, from the radioactive carbon distribution in propenes. The propenes amounted to 98.5% of the total gaseous products.

As an extension for the study of the γ-hydrogen participation and methyl migration, both observed previously[4] during the dehydration of alcohols, propanol-1-C^{14} was employed in this investigation. The extent of the γ-hydrogen participation and the methyl migration can be evaluated from the corresponding amounts of prop-1-ene-3-C^{14} and prop-1-ene-2-C^{14} produced from the reaction



$$CH_3CH_2C^{14}H_2OH \nearrow CH_2{=}CHC^{14}H_3 \quad (a)$$
$$CH_3CH_2C^{14}H_2OH \searrow CH_2{=}C^{14}HCH_3 \quad (b)$$

An attempt to prepare propene-1-C^{14} by the dehydration of propanol-1-C^{14} over alumina catalyst was reported earlier by Fries and Calvin.[5] They used Alorco alumina, grade F-1, obtained from the Aluminum Company of America, and an alumina prepared by the hydrolysis of aluminum nitrate. The base used for the precipitation of the aluminum hydroxide was not indicated, although it influences the isomerizing properties of the catalyst.[6] Fries and Calvin found that the propenes produced from the alumina prepared by them consisted of an equilibrium mixture of propene-1-C^{14} and propene-3-C^{14}. The formation of propene-3-C^{14} could be interpreted either by γ-hydrogen participation or by the isomerization of propene-1-C^{14} through readsorption over the alumina. The latter reaction occurs readily when "acidic" alumina is used as a catalyst.[4]

Results

The dehydration reaction was carried out over an alumina (alumina-A) which was prepared by hydrolyzing aluminum isoproxide followed by calcination at 600° for 6 hr.[6] At 345° and at hourly liquid space velocity of 28 in the presence of pyridine, 1-propanol-1-C^{14} yielded a mixture of C_2, C_3, and C_4 gases, propionaldehyde, and di-*n*-propyl ether with a total conversion of 45.8% (Table I). Pyridine was used to neutralize the relatively strong acidic sites which are responsible for the cationic isomerization of olefins.[6] 1-Propanol afforded a complete dehydration under

TABLE I

DEHYDRATION OF 1-PROPANOL-1-C^{14} OVER ALUMINA-A AT 345°[a]

Products	Compn, mole %[b]
Unknown I, II, and III	0.66
Propionaldehyde	1.25
n-Propyl ether	43.6
Gases	53.7
Gases	Compn, mole %[c]
Ethylene	0.16
Propane	0.71
Propene	98.5
Cyclopropane	0.50
1-Butene	0.08
trans-2-Butene	Almost nil
cis-2-Butene	0.05

[a] HLSV of the mixture, 28; total conversion, 45.8%. Propanol: pyridine, 1.00:0.160 (in mole) or 4.00:1.00 (in volume). Carbonaceous material, 2.8 mmoles of carbon dioxide from 5.6 ml of the reactant. The amount of the carbonaceous material is expressed in carbon dioxide equivalent, because part of it might result from pyridine. [b] Molar area responses (area/mole) over an Ucon column in vpc analysis are propanol, 1.00; propionaldehyde, 0.89; and di-*n*-propyl ether, 1.52. [c] Molar area responses (area/mole) for gases over a dimethylsulfonane column in vpc analysis were ethylene, 48; propane, 65; cyclopropane, 65 (assumed); 1-butene, 81; and *cis*-2-butene, 87.

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[1] For paper XXXIII see J. Herling and H. Pines, *J. Org. Chem.*, **31**, 4088 (1966).

[2] Paper XIII in the series of Dehydration of Alcohols.

[3] This research was supported by the Atomic Energy Commission Contract AT(11-1)1096.

[4] For general review of the literature see H. Pines and J. Manassen, *Advan. Catalysis*, **16**, 49 (1966).

[5] B. A. Fries and M. Calvin, *J. Am. Chem. Soc.*, **70**, 2235 (1948).

[6] H. Pines and W. O. Haag, *ibid.*, **82**, 2471 (1960).