g (0.02 mole) of 1,2-dibenzoyl-3,6-diethyl-4,5-diphenylbenzene, 1.52 g (0.04 mole) of sodium borohydride, and 100 ml of diglyme was heated to the boiling point and then cooled. Dilution with water gave a highly viscous gum which was separated by decantation and air dried on a porous plate. The gum was then dissolved in 75 ml of hot acetic anhydride. Cooling gave crystals. To this suspension was added 7 drops of concentrated sulfuric acid and the mixture was briefly boiled. Cooling gave white crystals which were separated by filtration and washed with methanol to yield 2.02 g of crude product. Recrystallization from acetic acid and then *n*-propyl alcohol gave an analytical sample of the phthalan, mp 254–258.5°.

Anal. Calcd for $C_{36}H_{32}O$: C, 90.0; H, 6.7. Found: C, 90.2; H, 6.3.

1,3,4,7-Tetraphenylphthalan.—A mixture of 5 g of 1,2-bis(α-hydroxybenzyl)-3,6-diphenylbenzene, 25 ml of 32% hydrogen bromide in acetic acid, and 25 ml of acetic acid was heated to boiling. Additional acetic acid was added until the mixture was homogeneous at the boiling point. Cooling to room temperature gave crystals which were removed by filtration. Washing with acetic acid and methanol gave 2.5 g of crude phthalan, mp 222.5–227°. Recrystallization from acetic acid gave an analytical sample of the title compound, mp 225.5–229°.

Anal. Calcd for $C_{32}H_{24}O$: C, 90.6; H, 5.7; mol wt, 424. Found: C, 90.2; H, 5.7; mol wt, 424 (mass spectrum).

This same reaction could be carried out by dissolving the glycol in acetic acid and briefly boiling it after adding 48% hydrobromic acid, 85% phosphoric acid, 55% hydriodic acid, concentrated sulfuric acid, or 90% formic acid.

1,4,9-Triphenylanthracene (3). A. From 1,3,4,7-Tetraphenylphthalan.—A mixture of 1.3 g of the phthalan, 10 ml of acetic anhydride, and 1 drop of concentrated sulfuric acid was boiled until it was just homogeneous. Hydrolysis gave a solid which, after recrystallization from acetic acid, afforded 0.68 g of 1,4,9-triphenylanthracene, mp 171.5–174°.

B. From 1,2-Bis(α-hydroxybenzyl)-3,6-diphenylbenzene.—In addition to the general procedure, the title compound was prepared as follows.

A mixture of 8.8 g (0.02 mole) of the glycol, 100 ml of acetic anhydride, and 4 drops of concentrated sulfuric acid was stirred for 5 min. The mixture was heated until it was homogeneous and then poured on ice. The resulting solid was dried, boiled with benzene, and filtered, to yield 0.65 g of unidentified white solid. The filtrate was evaporated and the resulting solid was recrystallized from acetic acid, to yield 5.01 g (62%) of crude 1,4,9-triphenylanthracene. Two recrystallizations from *n*-propyl alcohol gave pure material, mp 170–172.5°.

If this procedure is carried out with larger volumes of concentrated sulfuric acid, subsequent hydrolysis yields a homogeneous solution, presumably as a result of sulfonation of the product.

Alumina: Catalyst and Support. XXXII.[1] Aryl Migration Accompanying the Dehydration of 2-Phenylethanol-1-C^{14} and 2-*p*-Tolylethanol-1-C^{14} over Aluminas[2,3]

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The dehydration of 2-phenyl- and 2-*p*-tolylethanol-1-C^{14} over aluminas was studied at 348° with the purpose of determining the extent of aryl group migration from carbon atom 2 to 1. The catalysts were "acidic' alumina-A, prepared from aluminum isopropoxide, and alumina-B, (containing 1% Na^+), which was made by impregnating alumina-A with aqueous sodium carbonate. Dehydration reactions were also carried out with alumina-A in the presence of pyridine. Phenyl migration occurring during the dehydration of 2-phenylethanol varied from 1.1 to 8.3%, and in the case of 2-*p*-tolylethanol from 8.9 to 18.0%. Maximum isomerization occcurred when pyridine was added to the alcohol.

The neighboring group participation during dehydration of β-substituted propanols over alumina catalysts was previously reported from this laboratory.[5] Under "nonisomerizing" conditions the C_4 olefins obtained from isobutyl alcohol were composed of 11 to 23% of *n*-butylenes. The highest percentage of *n*-butylenes was obtained over alumina having the lowest intrinsic acidity. Similar results were obtained during the dehydration of 2-phenylpropanol. In the presence of the "nonacidic" alumina, 60% of the dehydration was accompanied by skeletal rearrangement leading to the formation of allyl- and propenylbenzene.

As an extension of this study 2-phenylethanol-1-C^{14} and 2-*p*-tolylethanol-1-C^{14} were passed over an alumina of a relatively high intrinsic acidity, (alumina-A) which was prepared from aluminum isopropoxide by the method previously reported[6] and over a doped alumina (alumina-B, containing 1% Na^+) which was made from alumina-A by impregnating it with sodium carbonate solution. Dehydration reactions were also made over alumina-A in the presence of pyridine. The experimental conditions and results are given in Table I (expt 3 and 6).

The two alcohols used in this study were synthesized by carbonation with $C^{14}O_2$ of the Grignard reagents of benzyl chloride and of *p*-methylbenzyl chloride, followed by the reduction of the respective acids with lithium aluminum hydride. The yields were 70% for 2-phenylethanol-1-C^{14} and 67% for 2-*p*-tolylethanol-1-C^{14}, based on the radioactivity of the barium carbonate.

The dehydration experiments were made at 348 ± 2° in a previously described flow system.[6] A 20% solution of 2-phenylethanol and 2-*p*-tolylethanol in *t*-butyl alcohol were used for dehydration. This was done in order to minimize secondary readsorption of the respective styrenes over the catalyst and thus decrease their possible polymerization. The contact time was adjusted by changing the hourly liquid space velocity to obtain about 50 to 70% conversion. (Table I) The side products of dehydration were ethylbenzene and *p*-tolylethane, respectively, amounting to about 4% each based on the styrenes produced. The hydrogenation occurred most probably through a hydrogen transfer reaction between the alcohols and arylalkenes, catalyzed by alumina.

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[2] Paper X in the series of Dehydration of Alcohols. For previous paper see F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1965 (1966).

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

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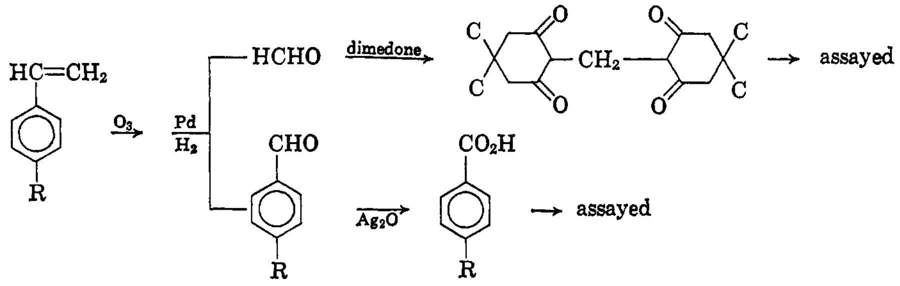
TABLE I

DEHYDRATION OF 2-PHENYLETHANOL-1-C^{14} AND 2-*p*-TOLYLETHANOL-1-C^{14} OVER ALUMINA CATALYSTS

Expt[a]	Alcohol	Alumina	HLSV[b]	Conversion, %	Radioactivity of alcohol μcuries × 10^{-3}/mmole	Radioactivity in ArC²=C¹ C¹	C²	Rearrangement C²/(C¹ + C²), % × 100
1	$PhCH_2C^{14}H_2OH$[c]	A	1.5	68	1330	1320[h]	14[g]	1.1
2	$PhCH_2C^{14}H_2OH$[c]	B	1.9	50	1330	1240[h]	79[g]	6.8
3	$PhCH_2C^{14}H_2OH$[d]	A	29	55[e]	1314	1116[i]	101[g]	8.3
4	*p*-$CH_3C_6H_4CH_2C^{14}H_2OH$[c]	A	1.3	60	1560	1280[h]	260[j]	16.8
5	*p*-$CH_3C_6H_4CH_2C^{14}H_2OH$[c]	B	1.9	68	1560	1420[h]	140[j]	8.9
6	*p*-$CH_3C_6H_4CH_2C^{14}H_2OH$[d]	A	29	72[f]	4380	3580[i]	787[j]	18.0

[a] The dehydration reactions were made at 348 ± 2°. [b] Volume of liquid feed per volume of catalyst per hour. [c] Volume ratio of arylethanol to *t*-butyl alcohol was 1:4. [d] Mole ratio of arylethanol to pyridine was 1.0:0.16. [e] The reaction product consisted of 84.4% styrene, 2.2% phenylacetaldehyde, and 13.5% β,β-diphenylethyl ether. The carbonaceous material deposited on the catalyst amounted to 0.82 mole of carbon dioxide per 2.9 ml of the reactant. Molar area responses (area/mole) over Carbowax column in vpc analysis were: 2-phenylethanol, 1.00; styrene, 1.00; phenylacetaldehyde, 0.96; and β,β-diphenylethyl ether, 2.29. [f] The reaction product was composed of 91.3% *p*-methylstyrene, 1.2% *p*-tolylacetaldehyde, and 7.5% β,β-di-*p*-tolylethyl ether. The carbonaceous material on the catalyst, expressed in carbon dioxide, amounted to 0.91 mmole per 2.9 ml of the reactant. [g] Determined as benzoic acid. [h] Determined as condensation product between formaldehyde and dimedone. [i] Determined as carbon dioxide. [j] Determined as *p*-toluic acid.



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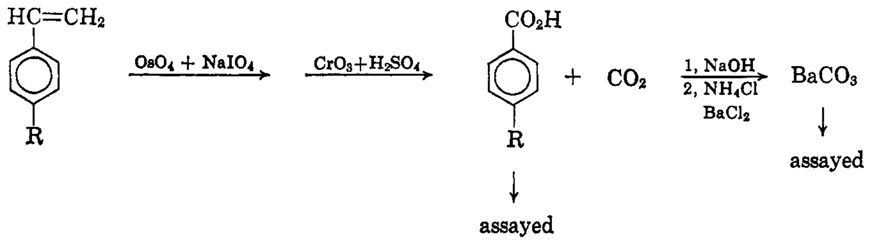


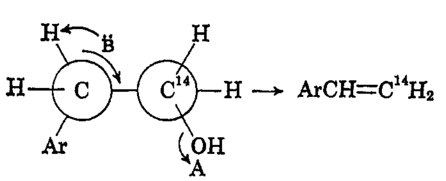
(2)

R = CH_3 or H

Two experiments were made in the presence of pyridine, in order to neutralize the intrinsic acidic sites of the aluminas[6] (Table I, expt 3 and 6). The dehydration product contained besides arylstyrenes 1-2% of the corresponding aldehydes and 7 and 13% of β,β′-di-*p*-tolyl and β,β′-diphenylethyl ether, respectively.

The styrenes obtained from the dehydration of the respective alcohols were separated by preparative gas chromatography and the olefins of 99% purity were degraded by using the following two methods.

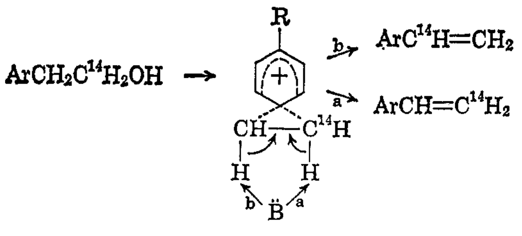
The radiocarbon distribution in the respective arylstyrenes demonstrates the migratory aptitude of the aryl group during dehydration which depends on the acidity of the aluminas and on the aryl group of the alcohol as well (Table I). The dehydration seems to occur through a multiple mechanism, one leading predominantly to the unrearranged and the other to the rearranged arylstyrenes. In accordance with previous observations[1,7,8] *trans*-elimination accounts for the major reaction leading to the formation of the unrearranged styrene and *p*-methylstyrene, and can be presented as follows.



Ar = C_6H_5 or *p*-$CH_3C_6H_4$

(A and B represent the acidic and basic sites on the catalyst)

The aryl group migration during dehydration can best be presented through a phenonium ion.



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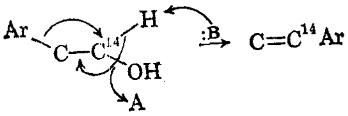
It is however not excluded that the skeletal rearrangement may occur through an aryl participation in a concerted or stepwise manner.



In the presence of "acidic" alumina the skeletal isomerization is smaller than in the case when pyridine is added to the alcohol. Analogy can be drawn between the heterogeneous dehydration of alcohols over aluminas and the solvolysis of β-phenylethyl tosylate. The rearrangement of an aryl group from the α to the β position was reported to be 0.5% in ethanol, 5.5% in acetic acid, and 45% in formic acid.[9]

The results from the dehydration of 2-phenylethanol-1-C^{14} and 2-p-tolylethanol-1-C^{14} exhibit certain differences. On "acid" alumina (alumina-A) the extent of p-tolyl group rearrangement is 15 times greater than that of phenyl group, and this can be attributed to the electron-donating nature of the methyl substituent through hyperconjugation and inductive effect. Under "nonacidic" conditions (alumina-B) the ratio of p-tolyl *vs.* phenyl migration is 1.2 and 2.2, respectively (expt 2 and 3 and 5 and 6), which is in general accord with the migration ratios observed in the acetolysis of 2,2-diarylethyl-1-C^{14} tosylates.[10]

Experimental Part

Alcohols. 1. 2-Phenylethanol-1-C^{14}.—Phenacetic acid-1-C^{14} was prepared by the addition of carbon dioxide obtained from 6.1 g (0.037 M) of $BaC^{14}O_3$, to 7.5 g (0.05 M) of benzylmagnesium chloride according to the procedure described previously.[11] The acid thus produced was diluted with 20 g of inactive phenacetic acid and reduced to the title alcohol with 12 g of lithium aluminum hydride in 500 ml of ether. The yield of the alcohol was 71% based on the radioactivity of the barium carbonate.

2. 2-p-Tolylethanol-1-C^{14}.—p-Methylphenacetic acid-1-C^{14} was made from a reagent prepared from 8.2 g (0.05 M) of p-tolyl chloride and carbon dioxide obtained from 6.1 g (0.03 M) of $BaC^{14}O_3$. The acid was diluted with 25 g of inactive compound and reduced with 12 g of lithium aluminum hydride suspended in 500 ml of ether. The yield of the alcohol was 67%, based on the radioactivity of barium carbonate.

Catalysts. 1. Alumina-A.—This catalyst was prepared from aluminum isopropoxide and calcined at 600° for 12 hr[6] then crushed up to 20–40 mesh size particles.

2. Alumina-B.—This catalyst, containing 1% Na^+ by weight, was obtained by stirring the freshly prepared slurry of alumina-A with a dilute solution of sodium carbonate. The amount of sodium absorbed on the catalyst was calculated by titrating the carbonate solution before and after the impregnation. The catalyst was calcined at 600° for 12 hr.

Apparatus and Procedure.—The dehydrations were performed by passing the reactants over the catalyst placed in a Pyrex tube, according to the procedure described previously.[6] The catalyst (5 ml) was mixed with twice its volume of quartz chips of about the same mesh size.

The styrenes were separated from the small amounts of corresponding arylethanes and other contaminants, by means of preparative gas chromatography. In expt 1, 2, 4, and 5, a 5 m × $^3/_8$ in. 15% SE30 on 40–60 Chromosorb P column was used. In expt 3 and 6, a $^3/_8$ in. × 2 m 15% Carbowax 20M on 40–60 Chromosorb P column was used. The styrene and p-methylstyrene thus separated were over 99% pure.

Analysis of the Styrenes. 1. Ozonolysis.—About 1.5 g of the respective styrenes was dissolved in 15 ml of ethyl acetate and ozonized at −78°. The product was then reduced under a hydrogen atmosphere at room temperature over a palladium-on-charcoal catalyst. The reduced solution was transferred to a two-neck, 100-ml flask which was connected through a small condenser to two U traps cooled at −78°. A slow stream of nitrogen was passed through the system at room temperature and the trapped formaldehyde was allowed to react with 35 ml of 5% aqueous dimedone (5,5-dimethyl-1,3-cyclohexanedione) solution.

The dimedone–formaldehyde condensation product, which precipitated out after a few hours, was recrystallized from a methanol–water mixture and its radioactivity was determined, mp 190° (lit.[12] mp 191°).

After removing the catalyst from the mother liquid and adding 60 ml of water the aldehyde obtained from the ozonolysis of styrene was oxidized with 3 g of potassium permanganate at reflux temperature for 15 hr. The benzoic acid was purified by sublimation and assayed for radioactivity.

The aldehyde obtained from the ozonolysis of p-methylstyrene was oxidized by 2.5 g of silver nitrate in 17 ml of water and 23 ml of ethanol. To this was added dropwise 2.5 g of sodium hydroxide in 65 ml of water and the solution was stirred for 4 hr. The product was then filtered and the filtrate was acidified with dilute hydrochloric acid. The p-toluic acid was recrystallized from hot water, mp 178°.

2. Oxidative Degradation.—The reaction was made in a three-neck flask provided with two dropping funnels and a condenser, and the system was maintained under a slight positive nitrogen pressure. In the reaction flask were placed 0.16 g of styrene, 0.62 g of sodium periodate, 1.5 ml of 0.05 M osmium tetroxide solution, and 10.5 ml of carbon dioxide free water. One dropping funnel contained 1.2 ml of aqueous 2.5 M sodium iodide and the other contained 1.8 g of chromic acid, 3 ml of 96% sulfuric acid, and 6 ml of water.

The contents of the flask was magnetically stirred for 2 hr at room temperature and then the sodium iodide solution was added. A carbon dioxide receiver containing 35 ml of 0.2 N sodium hydroxide was connected to the outlet of the condenser. The chromic acid solution was then added and the flask was brought to a reflux temperature over a period of 0.5 hr. The carbon dioxide was swept into the absorber by a slow stream of nitrogen, and precipitated as barium carbonate by the addition of 15 ml of 0.5 M ammonium chloride and 17 ml of 0.15 M barium chloride. The yield of barium carbonate was 53%. The reaction mixture was cooled to 0° and the benzoic acid was filtered and sublimed, yield 24%.

An identical procedure was used for degradation of p-methylstyrene with a yield of barium carbonate of 24% and of p-methylbenzoic acid of 19%.

Radioactivity Assay.—The radioactivity of the various compounds was measured by their conversion to gaseous carbon dioxide using wet combustion procedure of Van Slyke.[13] The measurements were made in an ionization chamber connected with a vibrating Reed-type electrometer, according to the procedure described previously.[14]

Identification of β,β-Diphenylethyl Ether. The structure of β,β-Diphenylethyl ether was assigned according to the following evidence from infrared spectrum: λ_{max} 6.24 (Ph), 6.69 (Ph), 9.04 (COC), 9.21 (CH_2O), and 13.40 μ ($PhCH_2$); and from nmr $\delta_{TMS}^{CCl_4}$ 7.25 (phenyl-H, singlet), 3.61 (CH_2O, triplet, J = 7.0 cps), and 2.82 ($PhCH_2$, triplet, J = 7.0 cps).

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