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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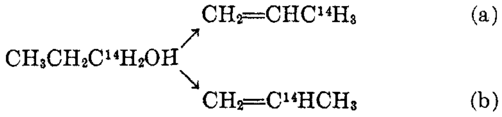
The dehydration of propanol-1-C^{14} at 345° over alumina under nonisomerizing conditions afforded a 46% conversion of which 43.6% was di-*n*-propyl ether and 53.7% gaseous products. The extents of the γ-hydrogen participation and the methyl migration accompanying the dehydration were estimated to be 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).

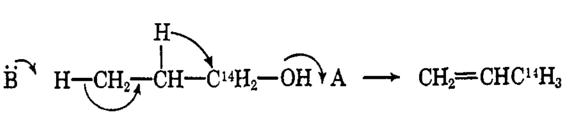
similar reaction conditions in the absence of pyridine. The extent of possible double-bond isomerization over the catalyst was also examined. A mixture of propanol, 1-hexene, and pyridine (3:1:1 by volume) gave a 28% dehydration and 0.4% isomerization (to almost exclusively *cis*-2-hexene). The distribution of the radioactivity in propenes (Table II) indicates that at the most 2.2% of the propene was produced by γ-hydrogen participation (a), while methyl migration amounted to 0.3% (b). It is not excluded that 1,3-hydride shift might also be involved during the dehydration leading to propene-3-C^{14} (c).[7]

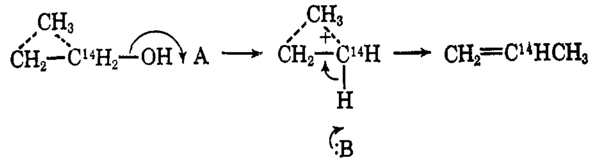
TABLE II

DISTRIBUTION OF RADIOACTIVITY IN PROPENE[a]

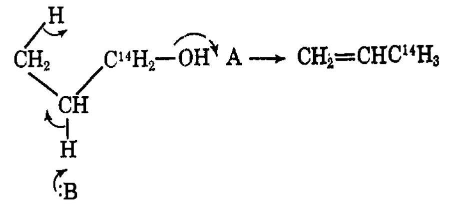
C	Activity in propene, μcuries/mmole	%
C_1 (as barium carbonate)	4.435	97.5
C_2 (as barium carbonate)	0.011	0.3
C_3 (as thiourea)	0.101	2.2

[a] Specific activity of $\overset{3\,2\,1}{CCC^{14}OH}$, 4.51 μcuries/mmole.


(a)


(b)

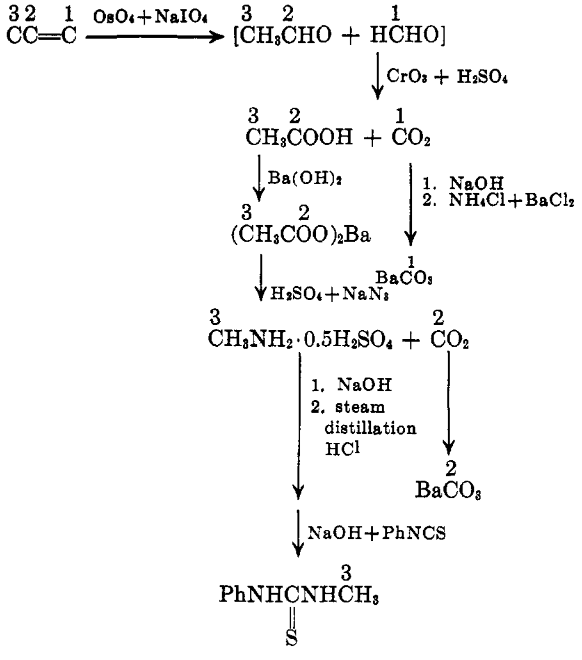
(A and B represent the acidic and basic sites on the catalyst)


(c)

Degradation of Propene.—The product, propene, obtained from the dehydration of 1-propanol-1-C^{14} over alumina-A, was degraded according to a procedure reported by Sixma and co-workers[8] (Scheme I).

SCHEME I

DEGRADATION OF PROPENE



Experimental Part

Preparation of Propanol-1-C^{14}. Propionic Acid-1-C^{14}.—A procedure similar to that of Lemmon[9] was used to synthesize propionic acid-1-C^{14}. To a stirred mixture of 1.8 g (0.074 g-atom) of magnesium and 50 ml of absolute ether was added 10.9 g (0.070 mole) of ethyl iodide in 50 ml of absolute ether. The reaction mixture was refluxed for 0.5 hr, cooled down, and transferred to a Grignard carbonation apparatus which was previously evacuated and filled with nitrogen. The reaction flask was cooled in a liquid nitrogen bath, and the system was again evacuated to 0.001 mm. The Grignard reagent was allowed to react at −20° with carbon dioxide, generated from a mixture of 38 ml of 96% sulfuric acid, 5.3 g (0.050 mole) of inactive sodium carbonate (primary standard grade), and 74 mg of barium carbonate (total activity, 9.6 μcuries) in a period of 1 hr. Five milliliters of water, 10 ml of 10% sulfuric acid, and 14.2 g of silver sulfate powder were added successively to the reaction mixture under constant stirring. The ether layer was decanted out by freezing the aqueous layer out in a Dry Ice–acetone bath. Then the aqueous layer was warmed to room temperature and extracted with four 50-ml of ether after addition of 14.2 g of inactive propionic acid as a carrier. The combined organic layer was dried over anhydrous magnesium sulfate and distilled. Another 2 g of inactive propionic acid was added to the remaining residue when the distillation was almost completed. The propionic acid-1-C^{14}, bp 135–140.5°, weighed 10.8 g.

Propanol-1-C^{14}.—To a mixture of 7.4 g (0.195 mole) of lithium aluminum hydride and 120 ml of absolute ether was added dropwise an ethereal solution (200 ml) of 10.8 g of propionic acid-1-C^{14}. The mixture was allowed to stir overnight; then refluxed for 2 hr, and cooled down prior to the addition of 45 ml of inactive propanol. The decomposition was effected by 120 ml of 6 *N* hydrochloric acid. The ether layer was separated and combined with about four 100-ml ether extracts. An additional 25 ml of inactive propanol was added during extraction. The organic layer was dried and distilled to give 53 g of 1-propanol (specific activity, 4.51 μcuries/mmole), over-all yield, 42%. The fraction, bp 97–98°, purity 99%, was used in the dehydration study.

Dehydration Procedure. A. Catalyst.—Aluminum oxide (16–20 mesh, 2.0 ml, 1.30 g) was prepared from aluminum isopropoxide according to the method described previously.[8]

B. Reaction.—The dehydration of alcohol was carried out in a vertical furnace, and the reactant was charged at a constant rate through a syringe pump.[7] After desired amount of the reactant had passed over the catalyst, a gentle stream of nitrogen was admitted in order to flush out the products. The gases were collected over a brine-filled gas bottle, and the liquid in an ice cooled trap.

Degradation of Propene.—A procedure described by Sixma, *et al.*, was used.[8]

A. Degradation of Propene to Carbon Dioxide and Acetic Acid.—Under nitrogen atmosphere, the oxidation flask was charged with 2.06 g (10 mmoles) of sodium metaperiodate, 35 ml of carbon dioxide free water, and 5 ml of aqueous 0.05 *M* osmium tetraoxide solution (catalytic amount). The solution was cooled down in an ice bath, the system was evacuated, and 202 ml (4.85 mmoles at STP) of propene was introduced from a gas buret. The mixture was stirred intensively for 5 hr at room temperature, cooled down again, and nitrogen was allowed to be sucked into the flask in order to restore the pressure. Then the unreacted propene was flushed out by nitrogen. Four milliliters of 2.5 *M* sodium iodide was added to the mixture, followed

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[7] J. Herling, N. C. Sih, and H. Pines, *J. Org. Chem.*, **31**, 4085 (1966). For pertinent references see G. M. Kramer and T. G. Wallace, *Advan. Petrol. Chem.*, **9**, 241 (1964).

[8] F. L. J. Sixma, E. F. J. Duynstee, and J. L. J. P. Hennekeus, *Rec. Trav. Chim.*, **82**, 901 (1963).

[9] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. F. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1946, pp 178–179.

by a solution containing 10 ml of conecntrated sulfuric acid, 6.00 g (60 mmoles) of chromic oxide, and 20 ml of carbon dioxide free water; meanwhile a carbon dioxide absorber was connected to the system. The mixture was heated up in a oil bath slowly (maximum temperature 112°) under constant stirring for 1 hr. The resultant carbon dioxide carried by nitrogen was absorbed by 50 ml of 0.5 N sodium hydroxide and precipitated as barium carbonate (4.435 μcuries/mmole) after the addition of 55 ml of 0.5 M ammonium chloride and 62.5 ml of 0.15 M barium chloride, followed by washing with carbon dioxide free water, and drying at 110° overnight; yield of barium carbonate was 24% (238 mg).

B. Isolation of Acetic Acid as Barium Acetate.—The above reaction mixture was steam distilled and the distillate (150 ml) was neutralized by 0.1 N barium hydroxide. The water was evaporated off under reduced pressure. The barium acetate was dried overnight at 160°. Over-all yield according to the barium acetate obtained was 18% (220 mg), mainly owing to mechanical loss.

C. Degradation of Barium Acetate to Methylamine and Carbon Dioxide.—Under nitrogen atmosphere 220 mg (0.86 mmole) of barium acetate was dissolved in 2.4 ml of concentrated sulfuric acid, then 3.6 ml of chloroform was introduced, followed by slow addition of 2.6 mg of sodium azide. The carbon dioxide absorber was connected and the stirred reaction mixture was heated to 64° in a period of about 3 hr under a constant flow of nitrogen. Then 18 ml of carbon dioxide free water was added, after the mixture had been cooled down. It was heated up again for 20 min at 70–75°. The activity of barium carbonate (210 mg, 1.06 mmole, 61% yield) was 0.011 μcurie/mmole.

D. Isolation of Methylamine as N-Methyl-N′-phenylthiourea.—The above reaction mixture from the degradation of barium acetate was filtered, made alkaline with 15 ml of 10 N sodium hydroxide, and was steam distilled using 36 ml of 1 N hydrochloric acid as a trapping medium for methylamine. Methylamine hydrogen chloride (63 mg, 0.93 mmole) was obtained after evaporation of water under reduced pressure and dried in a desiccator, yield 54%.

The methylamine hydrochloride was placed in a small vial containing 1 ml of methanol. The solution was made distinctively basic by 3 N sodium hydroxide. Immediately 99 mg (0.73 mmole) of phenyl isothiocyanate was added and the vial was rubber capped. The mixture was shaken for 5 min and warmed in an oil bath for 15 min at about 100°. Then 2 ml of water was added to the vial by a syringe. A flake-like crystal precipitated out instantly. The precipitate was recrystallized from a mixed solvent of cyclohexane and benzene (1.5:1.0 by volume). N-Methyl-N′-phenylthiourea (74 mg, 0.45 mmole, 62% yield) had an activity of 0.101 μcurie/mmole, mp 116–117° (lit.[2] 115.5–116°).

Analysis. A. Vapor Phase Chromatography.—The gases were determined over a 0.25 in. × 2 m 33% dimethylsulfolane on 100–120 mesh firebrick column; the aldehyde, ether, pyridine, alcohol, and hexenes over a 0.25 in. × 4 m 15% Ucon 75H 90,000 on 60–80 WAB column.

B. Radiochemical Assay.—The radiochemical assay of the barium carbonate and thiourea was performed by using a Dynacon model 6000 (Nuclear-Chicago) and rate-of-charge method.[10]

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[10] H. Pines and G. Benoy, *J. Am. Chem. Soc.*, **82**, 2483 (1960).

Alumina: Catalyst and Support. XXXV.[1] 1,2- and 1,4-Phenyl Migrations in 1,1-Diphenylcyclohexane. Dehydroisomerization over "Nonacidic" Chromia–Alumina[2,3]

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The dehydroisomerization of 1,1-diphenylcyclohexane over "nonacidic" chromia–alumina-B was studied using a pulse microreactor. *o*- and *p*-terphenyl were formed by a 1,2- and 1,4-phenyl migration, respectively, in addition to fission products. Free-radical species are proposed as intermediates.

Catalytic dehydrogenation and aromatization have been known and used for many years. Chromia–alumina is one of the catalysts that has been studied quite extensively, and lately it has been realized that the nature of the alumina used as support has an effect upon the behavior of the catalyst.[4]

Alumina has intrinsic acidic properties and its method of preparation has been shown to determine the strength of the acidic sites.[5] For example, alumina obtained by the hydrolysis of aluminum isopropoxide (alumina-A) catalyzed the isomerization of cyclohexene to methylcyclopentenes, which requires a relatively strong acidic catalyst, whereas alumina obtained from potassium aluminate (alumina-B) is less acidic and did not effect this isomerization.

The different natures of the chromia–alumina catalysts prepared from these aluminas were demonstrated by their behavior toward 1,1-dimethylcyclohexane.[6] Dehydrogenation over chromia–alumina-A (catalyst A) gave ethylbenzene and xylenes in addition to toluene and methane, whereas over chromia–alumina-B (catalyst B) only toluene and methane were formed. The more acidic catalyst A was able to promote a cationic-type isomerization of 1,1-dimethylcyclohexane *via* methide migration, but the low acidic character of catalyst B was not. It was suggested recently[2] that radical species are associated with the dehydrogenation reaction over catalyst B and the lack of methyl migration is in accord with this.[7]

Phenyl migrations have been observed in noncatalytic free-radical reactions. Among these are Grignard reactions in the presence of certain metal ions,[8] the thermal decomposition of azo compounds,[9] the oxidation of certain diarylethanes,[10] the pyrolysis of alkylbenzenes,[11] the peroxide-induced decomposition of

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[1] For paper XXXIII, see N. C. Sih and H. Pines, *J. Org. Chem.*, **31**, 4089 (1966).

[2] Paper XIX in the series Aromatization of Hydrocarbons. For paper XVIII see H. Pines and C. T. Goetschel, *J. Am. Chem. Soc.*, **87**, 4207 (1965).

[3] This research was supported by the Atomic Energy Contract AT-(11-1)-1196.

[4] C. T. Chen, W. O. Haag, and H. Pines, *Chem. Ind.* (London), 1379 (1959).

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

[6] H. Pines and C. T. Chen, *ibid.*, **82**, 3562 (1960).

[7] (a) L. H. Slaugh, R. D. Mullineaux, and J. H. Raley, *ibid.*, **85**, 3180 (1963); (b) F. H. Seubold, *ibid.*, **75**, 2532 (1953).

[8] (a) W. H. Urry and H. S. Kharasch, *ibid.*, **66**, 1438 (1944); (b) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

[9] C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958).

[10] H. H. Szmant and J. F. Deffner, *ibid.*, **81**, 958 (1959).

[11] V. N. Ipatieff, B. Kvetinskas, E. E. Meisinger, and H. Pines, *ibid.*, **75**, 3323 (1953).