

Alumina: Catalyst and Support XXXI. Dehydrogenation of 2-Phenylbutane-2-C¹⁴*,†

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2-Phenylbutane-2-C¹⁴ was synthesized and submitted to dehydrogenation in the presence of a "nonacidic" chromia-alumina catalyst in a flow system at 487°. Skeletal rearrangement occurred to yield *n*-butylbenzenes and *n*-butenylbenzenes. After a selective hydrogenation the *n*-butylbenzene fraction consisted of almost equal amounts of 1-phenylbutane-1-C¹⁴ and 1-phenylbutane-2-C¹⁴. The skeletal isomerization is explained by a radical mechanism involving phenyl migration and methyl carbon insertion (1,2-vinyl migration). The *sec*-butylbenzene fraction, especially at the beginning of the experiment, retained the radiocarbon in its original position.

INTRODUCTION

In recent years an extensive study of the mechanism of the dehydrogenation of alkanes to aromatic hydrocarbons was carried out in our laboratory.‡ It was observed that in the presence of "nonacidic" chromia-alumina catalyst noncationic skeletal isomerization and aromatization occur, which involve methyl-carbon insertion reactions, most probably through a 1,2-vinyl migration. A radical mechanism was proposed to explain these reactions.

More positive evidence for the radical participation in the skeletal isomerization accompanying the dehydrogenation reaction was obtained from the study of the behavior of *tert*-butylbenzene over chromia-alumina catalysts (1, 2). It was found that

the main reaction over the "acidic" catalyst yielded benzene and isobutylene, while over the "nonacidic" chromia-alumina the only products were isobutylbenzene and isobutenylbenzenes. Since isobutylbenzene cannot be produced by an acid-catalyzed reaction, while it is readily formed by a free-radical-induced reaction (3), it was concluded that the rearrangements over a nonacidic chromia-alumina catalysts must be of a radical type.

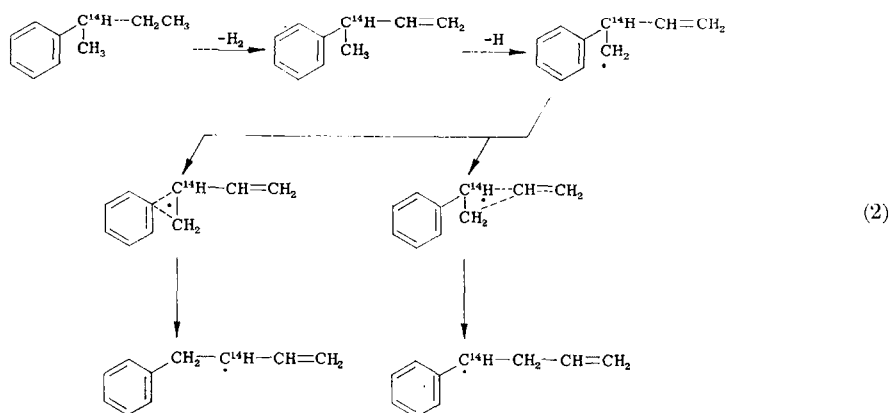
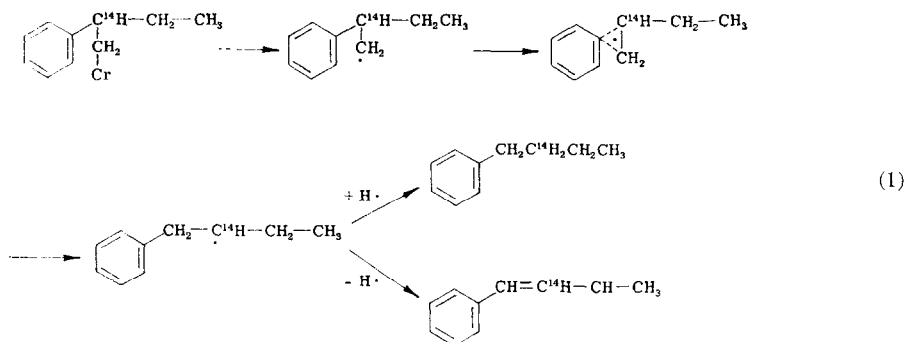
Unlike *tert*-butylbenzene the rearrangement of *sec*-butylbenzene can occur by either phenyl and/or vinyl migration. In order to determine the extent to which each of these groups participates in the rearrangement, 2-phenylbutane-2-C¹⁴ was synthesized and submitted to dehydrogenation over the nonacidic chromia-alumina B catalyst. The rearrangement to *n*-butylbenzene can occur either prior to dehydrogenation, in which case the butylbenzene produced would consist of 1-phenylbutane-2-C¹⁴ and of the corresponding olefins [Eq. (1)] or after dehydrogenation, in which case the rearranged aromatics produced would be composed of 1-phenyl-*x*-butenes-1-C¹⁴ and 1-phenyl-*x*-butenes-2-C¹⁴ [Eq. (2)].

A more detailed picture of the removal

* a. For paper XXX see H. Pines and C. T. Goetschel, preceding paper. b. Paper 3 of the series Dehydrogenation of Aromatics; for 2 see ref. (1a).

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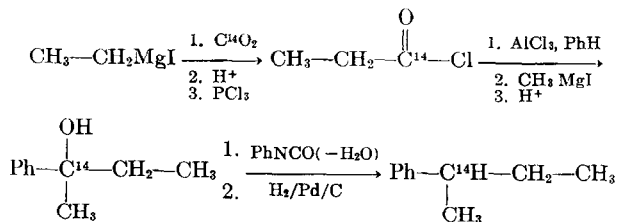
‡ For the "Discussion of the Mechanism of Aromatization of Alkanes in the Presence of Chromia-Alumina Catalysts" and the pertinent literature see Pines and Goetschel, ref. (4).



of hydrogen atoms was described previously (2, 4).

PROCEDURE

The 2-phenylbutane-2- C^{14} was synthesized in over 99% purity by the following sequence of reactions:



The 2-phenyl-2- C^{14} -butane was dehydrogenated at 487° over nonacidic chromia-alumina catalyst by a previously described procedure (5). Table 1 summarizes the reaction conditions and composition of the aromatic fractions produced.

The reaction product was collected in three separate cuts. Each cut was hydrogenated with palladium-on-charcoal catalyst using a microhydrogenation apparatus at atmospheric pressure. The *sec*-butylbenzene and *n*-butylbenzene from each cut were separated and collected in pure form

by preparative gas chromatography. Each was diluted with its respective aromatic compound, and the specific activity of the diluted solution was determined before being oxidized to benzoic acid with hot alkaline potassium permanganate. The specific

TABLE 1
DEHYDROGENATION OF 2-PHENYLBUTANE-2-C¹⁴
OVER NONACIDIC CHROMIA-ALUMINA
CATALYST^a

	1	2	3
Cut Number:			
Length of cuts (in minutes):	8.0	9.0	10.0
Total C ₁₀ H ₁₄ passed (ml):	1.6	1.6	1.9
C ₁₀ H ₁₄ converted to carbonaceous materials ^b (mole %):		4.58	
Composition of aromatic fraction after hydrogenation (mole %)			
Benzene	0.21	0.11	0.03
Toluene	0.69	0.30	0.15
Ethylbenzene	3.48	2.18	1.56
Cumene	2.93	2.18	2.01
<i>n</i> -Propylbenzene	2.22	1.10	0.77
<i>sec</i> -Butylbenzene	85.23	91.40	93.39
<i>n</i> -Butylbenzene	5.24	2.73	2.09

^a This experiment was run at 487° and an hourly liquid space velocity of 0.81.

^b The conversion to carbonaceous materials was determined at the end of the experiment.

activity of the benzoic acid was determined and compared with that of the parent hydrocarbon.

The specific activity of the starting 2-phenylbutane-2-C¹⁴ was also determined and compared with that of the benzoic acid produced after oxidation. In this manner, it was shown that all of the carbon-14 was on the α carbon of the *sec*-butylbenzene.

DISCUSSION OF RESULTS

The radioactivity data and distribution in the *n*-butylbenzene and *sec*-butylbenzene recovered from the reaction product of 2-phenyl-2-C¹⁴-butane over nonacidic chromia-alumina catalyst are summarized in Table 2.

The fact that *n*-butylbenzene retains about 60% of the carbon-14 on the α carbon suggests that both phenyl migration and methyl carbon insertion via 1,2-vinyl migration are occurring. The latter is occurring to about 60%. As the reaction proceeds, the methyl carbon insertion falls off and in the second and third cuts, nearly equals

the phenyl migration. The almost complete retention of carbon-14 on the α carbon of the recovered *sec*-butylbenzene in the first and second cuts indicates that the phenyl shift from carbon atom 2 to 3 did not occur to any appreciable extent.

TABLE 2
RADIOACTIVITY DATA AND DISTRIBUTION OF
CARBON-14 IN *n*-BUTYLBENZENE AND
sec-BUTYLBENZENE FROM THE
DEHYDROGENATION OF
2-PHENYLBUTANE-2-C¹⁴

Compound	1	2	3
<i>n</i> -Butylbenzene	1813	2140	951
Benzoic acid from <i>n</i> -butylbenzene	1082	990	464
<i>sec</i> -Butylbenzene	1492	161	173
Benzoic acid from <i>sec</i> -butylbenzene	1498	159	165
% Carbon-14 on α carbon			
<i>n</i> -Butylbenzene	59.6	46.3	48.7
<i>sec</i> -Butylbenzene	100	98.8	95.5

The large extent of methyl carbon insertion is indeed surprising, since the amount of nonconjugated terminal olefin produced would not be very large. This could be explained if the rate of vinyl migration was considerably greater than phenyl migration.

EXPERIMENTAL

2-Phenylbutane-2-C¹⁴

a. **Propionic acid-1-C¹⁴.** A 50-ml solution of 0.05 moles of ethylmagnesium bromide was carbonated by treating 3.8 g (0.036 moles) of sodium carbonate and 10.0 mc of barium carbonate-C¹⁴ with concentrated sulfuric acid by a procedure previously described (6). The reaction mixture was added to about 200 ml of crushed ice, acidified with dilute hydrochloric acid and extracted with ether (6 \times 100 ml); several milliliters of inactive propionic acid were added to the reaction mixture after the fourth extraction. The combined ether extracts were dried over anhydrous magnesium sulfate. The ethereal solution was concentrated with a rotating evaporator at

0° and water aspirator pressure. When the total volume reached about 40 ml, the remaining ether was removed by distillation at atmospheric pressure.

b. Propionyl chloride-1-C¹⁴. The crude acid (11.4 g, 0.15 moles) was treated with 8.2 g (0.06 moles) of phosphorus trichloride over a 15-min period while cooling in a cold water bath. The reaction mixture was stirred for an additional 15 min, then heated to 45° for 1.0 hr; yield, 1.5 g, 36%; b.p., 75–76°/740 mm.

c. Propiophenone-1-C¹⁴. To a mixture of 100 ml of benzene and 11.4 g (0.085 moles) of aluminum chloride maintained at 0° was added dropwise, with rapid stirring, a solution of 5.1 g (0.055 moles) of propionyl chloride-C¹⁴ in 20 ml of benzene. Following the addition, the reaction mixture was stirred at room temperature for 2 hr, then allowed to stand overnight. The reaction mixture was added to about 250 ml of crushed ice, then 25 ml of concentrated hydrochloric acid was added and, with constant stirring, the whole was heated on a hot plate for 15 min. After cooling, the layers were separated and the water layer was extracted with ether (1 × 100 ml, 2 × 50 ml). The combined ether extracts and the organic layer were washed with water, 10% aqueous sodium carbonate, and again with water. After drying over anhydrous magnesium sulfate the ether was removed *in vacuo*, and the residue was vacuum-distilled; yield, 6.5 g, 88%; b.p. 101°/18 mm.

d. 2-Phenyl-2-butanol-2-C¹⁴. The alcohol was prepared in a crude yield of 10.5 g 94%, by the reaction of 0.087 moles of methylmagnesium iodide and 10.0 g (0.075 moles) of propiophenone-1-C¹⁴.

e. 2-Phenyl-x-butene-2-C¹⁴. A mixture of 10.5 g (0.07 moles) of the crude alcohol, 16.7 g (0.14 moles) of phenylisocyanate and 2.0 g (0.025 moles) of pyridine was heated in an oil bath at 140° for 1.5 hr at total reflux. The temperature was then raised to 220° for 2.0 hr, with distillation possible. After cooling the reaction vessel, its solid contents were extracted with ether 3 × 30 ml. The ether extracts and distillate were combined, washed with dilute acetic

acid, water, and 10% sodium carbonate solution. After drying over anhydrous sodium carbonate, the ether was removed and the residue, 10 ml, passed over a column containing 30 ml of "Merck" alumina and *n*-hexane. Eluting with *n*-hexane afforded a clean separation of 2-phenyl-2-butene-2-C¹⁴ from any nitrogen-containing compounds.

f. 2-Phenyl-2-C¹⁴-butane. The *n*-hexane-phenylbutene solution was hydrogenated with palladium-on-charcoal catalyst in a Paar hydrogenation apparatus with an initial charge of hydrogen of about 3 atm. Distillation of the product gave 8.0 g, 87% yield of the 2-phenyl-2-C¹⁴-butane; b.p. 84–85°/70 mm. The purity was over 99.9% by VPC. The activity was $172 \times 10^{-1} \mu\text{c}/\text{mmole}$, or a total activity of 1.03 curies. The overall yield was 10.3%, based on the initial barium carbonate-C¹⁴.

Catalyst

The chromia-alumina catalyst was prepared according to the procedure described previously (2). The alumina was precipitated from sodium aluminate and impregnated with chromic acid. The catalyst contained 14.8 wt % of Cr₂O₃; its surface area was 89 m²/g and the average pellet weight was 0.022 g.

Apparatus and Procedure

The same apparatus and procedure was used as described previously (7).

Separation of the *n*-Butylbenzene and *sec*-Butylbenzene from the Dehydrogenation Mixture

The separation was accomplished using a Wilkins Autoprep Gas Chromatograph with a 30-ft × 3/8-inch preparative VPC column filled with 15% diethylene glycol succinate on 60/80 mesh Chromsorb W. The column temperature was 100° with a helium flow rate of 60 ml/min. Sample injection sizes were from 100–150 ml. The product was collected in a small U-tube, immersed in liquid nitrogen.

Pure *sec*-butylbenzene and *n*-butylbenzene were obtained in two separate fractions. Each was diluted with its inactive

compound and its specific activity determined before oxidation.

Oxidation of the Aromatics

The diluted aromatic compounds were oxidized to benzoic acid with hot alkaline potassium permanganate as described previously (8). The benzoic acid obtained was purified by sublimation at 100° followed by recrystallization from hot water.

Radioactive Counting

The same apparatus and procedure was used as described previously (9).

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