Alumina: Catalyst and Support. XXXVIII.[1] Dehydrogenation and Skeletal Isomerization of 2-Phenylpropane-2-^{14}C and Ethylbenzene-β-^{14}C over "Nonacidic" Chromia–Alumina[2,3]

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The dehydrogenation of 2-phenylpropane-2-^{14}C and ethylbenzene-β-^{14}C were studied over "nonacidic" chromia–alumina catalyst at 490 and 520°, respectively. From the 2-phenylpropane, α- and β-methylstyrenes were obtained; part of the starting material underwent skeletal isomerization to *n*-propylbenzene. The rearrangement of the isopropylbenzene to *n*-propylbenzene and to β-methylstyrenes occurred entirely through phenyl migration. The dehydrogenation of ethylbenzene produced styrene with about 3% phenyl migration. Part of the ethylbenzene has itself undergone molecular rearrangement. The molar ratio of the rearranged ethylbenzene to the rearranged styrene was over 4:1. The results obtained, coupled with previous observations from this laboratory, indicate that free-radical species act as intermediates in the dehydrogenation as well as in the molecular rearrangements.

As a continuation of the study of the aromatization of alkanes over chromia–alumina catalysts, the dehydrogenation of alkylbenzenes was investigated in order to shed additional light on the mechanism of dehydrogenation of hydrocarbons over these catalysts.[4] It had been observed previously that alumina may affect the course of the reaction. Alumina–chromia catalyst, in which the alumina was prepared from either aluminum isopropoxide or from aluminum nitrate and precipitated with ammonium carbonate, may cause skeletal isomerization of a cationic type to accompany the dehydrogenation reaction. Such a catalyst would dehydrogenate 1,1-dimethylcyclohexane to xylenes,[5] and dealkylate *t*-butylbenzene to benzene.[6]

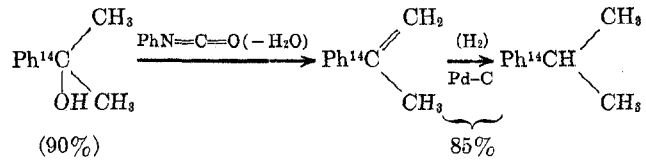
The alumina–chromia catalyst, in which the alumina has been prepared from either potassium or sodium aluminate and which contained about 0.07% of the alkali ion, will dehydrogenate *t*-butylbenzene to isobutenylbenzenes,[6] and 1,1-dimethylcyclohexane to toluene.[5] The skeletal isomerization accompanying the dehydrogenation of alkyl- and cycloalkylbenzenes, such as 2-phenylbutane-2-^{14}C,[7] 1,1-diphenylcyclohexane,[8] and 1-methyl-C^{14}-1-phenylcyclohexane,[2] had been interpreted as occurring by a radical mechanism involving a phenyl and, in the case of *sec*-butylbenzene, also a vinyl migration.

The present paper deals with the extension of this study, namely, the dehydrogenation of 2-phenylpropane-2-^{14}C and ethylbenzene-β-^{14}C.

2-Phenylpropane-2-^{14}C was synthesized in 50% yield and over 99% purity from $^{14}CO_2$ by the reactions given in Scheme I.

In order to ascertain that all the carbon-14 was on the α carbon of the 2-phenylpropane, a sample of the intermediate α-methylstyrene was ozonized and the formaldehyde produced was trapped in the form of its dimedone derivative. The lack of radioactivity of the formaldehyde–dimedone compound and the equal specific values for isopropylbenzene, and the 2,4-dinitrophenylhydrazone of the acetophenone obtained from the ozonation, showed that the radioactivity resided entirely in the α carbon of the hydrocarbon. This was further demonstrated by oxidizing the 2-phenylpropane to benzoic acid and comparing its specific radioactivity with that of the hydrocarbon.

SCHEME I



The 2-phenylpropane-2-^{14}C was passed over the "nonacidic" chromia–alumina catalyst. The experimental conditions and results are given in Table I.

TABLE I

DEHYDROGENATION AND REARRANGEMENT OF 2-PHENYLPROPANE-2-^{14}C OVER CHROMIA–ALUMINA CATALYST[a]

Aromatic product	Compn, mol %
Benzene	2.1
Toluene	1.7
Ethylbenzene	2.1
Isopropylbenzene	62.3
n-Propylbenzene	9.7
α-Methylstyrene	19.0
cis-β-Methylstyrene	0.8
trans-β-Methylstyrene	2.3

[a] Experimental conditions: catalyst, 8 cc; temperature, 490°; flow rate of 2-phenylpropane, 2.2 cc/hr.

The main product of the reaction was α-methylstyrene, amounting to 19%. The hydrocarbons resulting from the skeletal rearrangement, in a yield of about 13%, were *n*-propylbenzene and *cis*- and *trans*-β-methylstyrene. *n*-Propylbenzene was the predominant product of rearrangement. That chromia was responsible for the skeletal isomerization was demonstrated by passing isopropylbenzene over the "nonacidic" alumina and over glass beads, which were employed as spacers

(1) For paper XXXVII, see E. Blanc and H. Pines, *J. Org. Chem.*, **33**, 2035 (1968).

(2) Paper XXI in the series of aromatization of hydrocarbons. For paper XX, see W. F. Fry and H. Pines, *ibid.*, **33**, 602 (1968).

(3) This research has supported by the Atomic Energy Contract AT-(11-1)-1096; COO-1096-18.

(4) H. Pines and C. T. Goetschel, *J. Org. Chem.*, **30**, 3530 (1965); see references to previous papers.

(5) H. Pines and C. T. Chen, *J. Amer. Chem. Soc.*, **82**, 3562 (1960).

(6) H. Pines and C. T. Goetschel, *J. Catal.*, **6**, 371 (1966).

(7) H. Pines and C. T. Goetschel, *ibid.*, **6**, 380 (1966).

(8) H. Pines, W. F. Fry, N. C. Sih, and C. T. Goetschel, *J. Org. Chem.*, **31**, 4094 (1966).

in the reactor. Neither skeletal isomerization nor dehydrogenation has taken place under experimental conditions specified in Table I. The absence of catalytic acidic sites in chromia–alumina was demonstrated by passing 1,1,3-trimethylcyclohexane over this catalyst at 500°.[5] Only *m*-xylene was produced; "acidic" catalyst would have also produced trimethylbenzenes.

The dehydrogenation reaction product was collected and hydrogenated over 10% Pd/C using a microhydrogenation apparatus at atmospheric pressure. The *n*-propylbenzene and isopropylbenzene were separated from the other products by preparative gas chromatography. The *n*-propylbenzene was oxidized to benzoic acid with hot alkaline potassium permanganate. After purification, the specific activity of the benzoic acid was determined and found to be insignificant, in the range of the background readings of the radioactivity counter, this being a measure of the α-carbon-14 in the *n*-propylbenzene (Table II).

TABLE II

RADIOACTIVITY DISTRIBUTION IN *n*-PROPYLBENZENE[a] FROM THE REACTION OF 2-PHENYLPROPANE-2-^{14}C

Compd	Radioactivity, 10^{-3} μCi/mmol
n-Propylbenzene	3896
Benzoic acid from oxidation of *n*-propylbenzene	12 (background reading range)

[a] 0% α carbon-14 in *n*-propylbenzene.

Ethylbenzene-β-^{14}C.—The title hydrocarbon was synthesized in over 99% purity by the reactions given in Scheme II.

SCHEME II

$$PhCH_2MgBr \xrightarrow[2.\ H^+]{1.\ ^{14}CO_2} PhCH_2{}^{14}CO_2H \xrightarrow[2.\ H^+]{1.\ LiAlH_4} PhCH_2{}^{14}CH_2OH \xrightarrow[pyridine]{AcCl} PhCH_2{}^{14}CH_2OCOCH_3 \xrightarrow[\Delta\ 505°]{(-AcOH)} PhCH{=}{}^{14}CH_2 \xrightarrow[Pd\text{-}C]{[H_2]} PhCH_2{}^{14}CH_3$$

In order to show that all the carbon-14 was on the β carbon of the hydrocarbon, the specific activity of the benzoic acid, obtained from the oxidation of the ethylbenzene, was determined and it was found to be in the range of the background counting of radioactivity.

The dehydrogenating reactions were made using the same catalyst and procedure as in the case of the isopropylbenzene. The experimental conditions and results are given in Table III.

The ethylbenzene and the styrene were separated from the first and the last fractions by preparative gas chromatography, diluted with their inactive counterparts, and their specific activities determined. Small parts of the diluted samples of ethylbenzene and styrene were oxidized to benzoic acid with hot alkaline potassium permangante. After sublimation and purification, the specific activities of the benzoic acids were determined, as a measure of the α-carbon-14 in the styrene and recovered ethylbenzene. Table IV summarizes the radioactivity distribution of the products of the dehydrogenation reaction of ethylbenzene-β-^{14}C.

TABLE III

DEHYDROGENATION AND REARRANGEMENT OF ETHYLBENZENE-β-^{14}C OVER CHROMIA–ALUMIA CATALYST[a]

	Cut[b] 1	2	3	4
Length of cut, min	20.0	20.0	20.0	20.0
Total ethylbenzene passed, cc	2.0	2.0	2.0	2.0
Compn of aromatic products, mol %				
Benzene	0.7			0.6
Toluene	1.7			1.6
Ethylbenzene	82.7			82.2
Styrene	14.9			15.6

[a] Catalyst, 8 cc; flow rate of ethylbenzene, 6 cc/hr; temperature, 520°. [b] Cuts 2 and 3 were run with inactive material; their compositions were not determined.

TABLE IV

RADIOACTIVITY DISTRIBUTION IN ETHYLBENZENE AND IN STYRENE FROM REACTION OF ETHYLBENZENE-β-^{14}C

Compd	Cut 1	4
	Radioactivities, 10^{-3} μCi/mmol	
Ethylbenzene[a]	4830	5128
Benzoic acid from oxidation of ethylbenzene	175	134
α Carbon-14 in ethylbenzene	3.6%	2.6%
Styrene[a]	1320	2133
Benzoic acid from oxidation of styrene	43	57
α-Carbon-14 in styrene	3.3%	2.7%

[a] The difference in the radioactivities of ethylbenzene and styrene is due to the difference in the percentages of dilution of the reaction product with the nonradioactive hydrocarbons, before preparative gas chromatographic separation.

Discussion

The results summarized in Tables I and II indicate that 2-phenylpropane-2-^{14}C underwent skeletal isomerization, when passed over "nonacidic" chromia–alumina, to produce 9.7% *n*-propylbenzene and 3.1% *cis*- and *trans*-β-methylstyrene. None of the radioactivity in the isomerized product resided on the α-carbon atom, which indicates that the skeletal isomerization had occurred through a phenyl migration only.

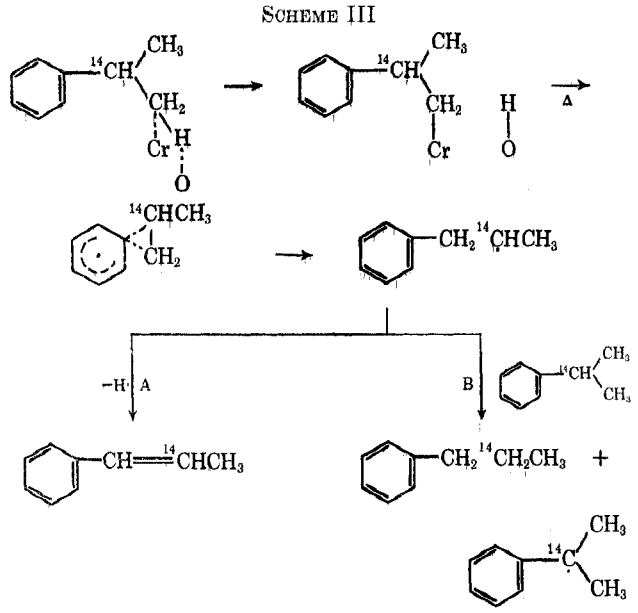
The main product of the rearrangement, 76%, was in the form of a saturated side chain, *n*-propylbenzene; the remainder consisted of β-methylstyrenes. This may suggest that the rearranged radical formed in the reaction removed preferentially a hydrogen either from the catalyst surface, or, which is more likely, from an isopropylbenzene molecule (Scheme III). The mechanism is similar to that proposed for the skeletal isomerization of 2-phenyl-2-butane-2-^{14}C[7] and in agreement with the catalytic behavior of chromia.[9,10]

The formation of *n*-propylbenzene in preference to β-methylstyrene could also be interpreted as a reverse hydrogenation of *n*-propenylbenzene produced. Although the thermodynamic equilibrium data for *n*-propylbenzene and its dehydrogenation products are not available, the concentration of the olefins would

(9) R. L. Burwell, Jr., A. B. Littlewood, M. Cardew, G. Pass, and C. T. H. Stoddart, *J. Amer. Chem. Soc.*, **82**, 6272 (1960).

(10) L. L. Van Reijen, W. M. H. Sachtler, P. Cossee, and O. M. Brouwer, *Proc. 3rd Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, 829 (1965).

SCHEME III



probably lie between the equilibrium concentration of styrene, ~15%, and α-methylstyrene ~48%.[11]

The results summarized in Tables III and IV indicate that the main reaction of ethylbenzene over chromia–alumina is not dehydrogenation but rather skeletal isomerization. The molar ratio of skeletally rearranged ethylbenzene to skeletally rearranged styrene is 6:1 and 5:1, respectively. This is based on the data given in Tables III and IV.

The skeletal isomerization and the dehydrogenation of ethylbenzene can be explained by a radical mechanism similar to the one formulated for the 2-phenylpropane-2-^{14}C.

We conclude that the dehydrogenation of alkylbenzenes over a "nonacidic" chromia–alumina catalyst is accompanied by phenyl migration.[6,7] The formation of β-phenylalkyl radical intermediates is proposed to explain the rearrangements which accompany the dehydrogenation reactions. The β-phenylalkyl radicals can either lose a hydrogen atom to the catalyst or remove a hydrogen atom from the benzylic carbon of the alkylbenzene. If a benzylic hydrogen is not available as in the case of *t*-butylbenzene,[6] only dehydrogenation occurs.

Experimental Section

2-Phenylpropane-2-^{14}C. A. Benzoic Acid-α-^{14}C.—An ethereal solution of 0.24 mol of phenylmagnesium bromide was carbonated with 0.2 mol of sodium carbonate and 20.0 mCi of barium carbonate-^{14}C as described previously.[12] The yield based on $^{14}CO_2$ was 90%.

B. Methyl Benzoate-α-^{14}C.—Benzoic acid-α-^{14}C (0.18 mol) was esterified with 2 mol of absolute methanol in the presence of 96% sulfuric acid.[13]

C. 2-Phenyl-2-propanol-2-^{14}C.—Methyl benzoate-α-^{14}C (0.14 mol) was added to 0.32 mol of ethereal solution of methylmagnesium iodide.[14]

D. 2-Phenylpropene-2-^{14}C.—The dehydration of 0.12 mol of crude 2-phenyl-2-propanol-2-^{14}C with 0.13 mol of phenyl isocyanate and 3 g of pyridine, as described previously,[15] yielded 2-phenylpropene-2-^{14}C.

E. 2-Phenylpropane-2-^{14}C.—Hydrogenation of the 2-phenylpropane-2-^{14}C with 10% palladium on charcoal in a Paar hydrogenation apparatus gave 15.2 g of 2-phenylpropane-2-^{14}C, slightly diluted with its inactive material, bp 152°. The purity was >99%. Its activity was 100.7 μCi/mmol. This corresponds to an over-all yield of 50% from barium carbonate-^{14}C.

Ethylbenzene-β-^{14}C. A. 2-Phenylacetic-1-^{14}C Acid.—An ethereal solution of 2-phenethylmagnesium bromide was carbonated with sodium carbonate and 10 mCi of barium carbonate-^{14}C as described previously.[12]

B. 2-Phenylethanol-1-^{14}C.—2-Phenylacetic acid-1-^{14}C was reduced by an ethereal solution of lithium aluminum hydride.

C. 2-Phenylethyl-1-^{14}C Acetate.—2-Phenylethanol (0.07 mol) was acylated with 0.085 mol of acetyl chloride in the presence of 0.14 mol of pyridine. The obtained material was purified by preparative gas chromatography to obtain 7.6 g of the acetate of over 99% purity.

D. 2-Phenylethylene-1-^{14}C.—The acetate was pyrolyzed over glass beads at 505° and at a flow rate of 12 drops/min; conversion was of 92–95%.

E. Ethylbenzene-β-^{14}C.—2-Phenylethylene-1-^{14}C was hydrogenated selectively with 10% palladium over charcoal in a Paar hydrogenation apparatus. After slight dilution with its inactive material, 4.9 g of ethylbenzene of >99% purity was obtained.

Catalyst.—The chromia–alumina catalyst was prepared according to the procedure described previously.[4] The alumina was precipitated from sodium aluminate and impregnated with chromic acid. The catalyst contained 14.8 wt % of Cr_2O_3; 16–20 mesh size particles were used to fill the 10-cc glass reactor tube. The activation of the catalyst has been made by passing hydrogen at 500° for several hours and checking its performance with small samples of inactive material before the radioactive run.

Apparatus and Procedure.—The apparatus and procedure used were the same as described previously.[5]

Separation of Isopropylbenzene and *n*-Propylbenzene.—The separation was accomplished using a F & M 720 dual column programmed temperature gas chromatograph with a 4.7-m-long, 3/8-in.-o.d. preparative vpc column filled with 15% silicone gum SE-30 on 60–80 mesh Chromosorb P.

Separation of Ethylbenzene and Styrene.—The separation was carried out using a 2-m-long, 3/8-in.-o.d. preparative vpc column filled with 15% Carbowax 20M on 40–60 mesh Chromosorb P.

Oxidation of Aromatics.—The alkyl- and alkenylbenzenes were oxidized to benzoic acid with hot alkaline potassium premanganate as described previously.[16]

The benzoic acid was purified by sublimation at 100°, followed by recrystallization two times from hot water, followed by drying over calcium chloride, *in vacuo*, for 24 hr.

Radiochemical Assay.—The same apparatus and procedure were used as described previously.[17]

Registry No.—2-Phenylpropane-2-^{14}C, 17949-24-5; ethylbenzene-β-^{14}C, 16510-91-1.

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(12) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. E. Yankwich, "Isotopic Carbon," John Wiley & Sons, Inc., New York, N. Y., 1949, pp 178, 179.

(13) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., New York–London 1956, p 781.

(14) J. P. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoff, and J. Smittenberg, *Rec. Trav. Chim. Pays-Bas*, **58**, 329 (1939).

(15) H. Pines and S. M. Csicsery, *J. Catal.*, **1**, 316 (1962).

(16) H. Pines, C. T. Goetschel, and S. M. Csicsery, *J. Org. Chem.*, **28**, 2713 (1963).

(17) H. Pines, and G. Benoy, *J. Amer. Chem. Soc.*, **82**, 2483 (1960).