[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Disproportionation of Alkylbenzenes. II. Rearrangement of the *n*-Propyl Group in Treatment of *n*-Propyl-β-C^{14}-benzene with Aluminum Chloride[1,2]

BY ROYSTON M. ROBERTS AND STANLEY G. BRANDENBERGER[3]

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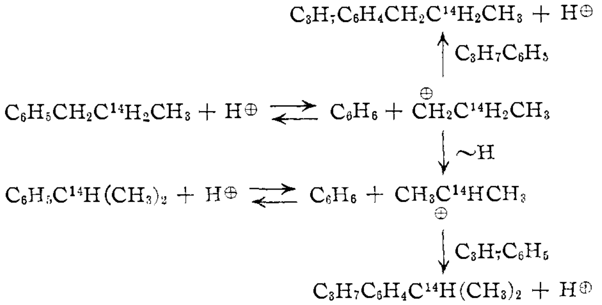
n-Propylbenzene, tagged in the β-position with C^{14}, was converted by aluminum chloride into a mixture containing benzene, propylbenzene and dipropylbenzene. These components were separated by distillation, and the propylbenzene and dipropylbenzene fractions were examined with regard to possible rearrangement of the side chains. Oxidation of these fractions to radioactive benzoic and phthalic acids, respectively, demonstrated the presence of up to 31% of the C^{14} in the α-positions of the side chains. Infrared, mass spectroscopic and vapor chromatographic analyses of the propylbenzene fraction showed it to be at least 96% *n*-propylbenzene. Degradation of the propylbenzene fraction by another route confirmed the amount of C^{14} in the α-position and showed no C^{14} in the γ-position. Thus, rearrangement of *n*-propyl-β-C^{14}-benzene to *n*-propyl-α-C^{14}-benzene was demonstrated to take place without any isotope migration to the γ-position or any appreciable rearrangement to isopropylbenzene. Possible mechanisms for the reactions are discussed.

Introduction

The rearrangement of alkyl groups during Friedel–Crafts alkylations is well known, having been first observed by Gustavson[4] only a year after the announcement of the Friedel–Crafts reaction. There has been some interest, increasing in recent years, in the behavior of alkyl groups during the disproportionation reactions which occur when alkylbenzenes are treated with Friedel–Crafts type catalysts. Heise and Töhl[5] investigated the disproportionation which *n*-propylbenzene undergoes when it is heated with aluminum chloride at 100° and found that alkyl group rearrangement did not occur; *e.g.*, the propylbenzene and dipropylbenzene among the reaction products contained only *n*-propyl groups. Their experimental evidence was not convincing, however. In 1935, Baddeley and Kenner[6] presented much better evidence that the products of the disproportionation of *p*-di-*n*-propylbenzene by aluminum chloride were *n*-propylbenzene, *m*-di-*n*-propylbenzene and 1,3,5-tri-*n*-propylbenzene. Nightingale and her co-workers[7] studied the rearrangement of 1,3-dimethyl-4-alkylbenzenes to 1,3-dimethyl-5-alkylbenzenes in the presence of aluminum chloride and reported that the migrating alkyl groups underwent rearrangement.[7a,b] However, this result was later shown to be in error,[7c,d] the alkyl groups actually being found to have the same structure after the migration. McCaulay and Lien[8] described the treatment of *n*-propylbenzene with hydrogen fluoride–boron trifluoride; they found no rearrangement of *n*-propyl groups to isopropyl groups when the disproportionations were carried out at temperatures between 5 and 25°. Kinney and Hamilton[9] found no rearrangement in the disproportionation of *n*-butylbenzene by aluminum chloride at 100°. Thus, all the evidence reported to date indicated that no rearrangement of alkyl groups occurred during the disproportionation reactions of alkylbenzenes catalyzed by aluminum chloride and other Lewis acids.

This investigation was begun before the recent publications of Nightingale and Shackelford,[7c,d] McCaulay and Lien,[8] and Kinney and Hamilton,[9] when there seemed considerable doubt as to the behavior of alkyl groups under the conditions of the disproportionation reaction. We proposed to apply the technique described in an earlier paper on ethylbenzene[1] to the reaction of *n*-propylbenzene with aluminum chloride, essentially repeating the experiment of Heise and Töhl,[5] but using modern methods of analysis and structure proof. To this end, *n*-propylbenzene, tagged in the β-position with C^{14}, was synthesized. Should rearrangement of the propyl group occur during disproportionation, it would be expected that any isopropylbenzene or diisopropylbenzene produced would have C^{14} in the α-position, and this could be simply demonstrated by oxidation of the alkylbenzenes to benzoic and phthalic acids. Radioactivity of these acids would indicate that the C^{14} was no longer exclusively in the β-positions of the chains. If the disproportionation reaction were to follow a carbonium ion mechanism analogous to that proposed[10] for Friedel–Crafts alkylations, it might be represented as



$$\begin{tikzcd}
 & C_3H_7C_6H_4CH_2C^{14}H_2CH_3 + H^{\oplus} \\
C_6H_5CH_2C^{14}H_2CH_3 + H^{\oplus} \arrow[r, rightleftharpoons] & C_6H_6 + \overset{\oplus}{C}H_2C^{14}H_2CH_3 \arrow[u, "C_3H_7C_6H_5"'] \arrow[d, "\sim H"'] \\
C_6H_5C^{14}H(CH_3)_2 + H^{\oplus} \arrow[r, rightleftharpoons] & C_6H_6 + CH_3\underset{\oplus}{C^{14}}HCH_3 \arrow[d, "C_3H_7C_6H_5"'] \\
 & C_3H_7C_6H_4C^{14}H(CH_3)_2 + H^{\oplus}
\end{tikzcd}$$

The bimolecular displacement mechanism proposed by McCaulay and Lien[8] would not allow rearrangement of the alkyl group. Whether or not such rearrangement would be possible in the localized π-complex proposed as an intermediate by Brown and Smoot[11] was not clear.

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[1] For the preceding paper, see R. M. Roberts, G. A. Ropp and O. K. Neville, THIS JOURNAL, **77**, 1764 (1955).

[2] A preliminary description of part of this work was given in *Chemistry and Industry*, 227 (1955).

[3] Taken from the Ph.D. thesis of Stanley G. Brandenberger, 1956; Celanese Corporation of America Fellow, 1955–1956.

[4] G. Gustavson, *Ber.*, **11**, 1251 (1878). For other examples, see C. C. Price, in "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 1.

[5] R. Heise and A. Töhl, *Ann.*, **270**, 155 (1892).

[6] G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935).

[7] (a) D. Nightingale and L. I. Smith, THIS JOURNAL, **61**, 101 (1939); (b) D. Nightingale and B. Carton, *ibid.*, **62**, 280 (1940); (c) D. Nightingale and J. M. Shackelford, *ibid.*, **76**, 5767 (1954); (d) D. Nightingale and J. M. Shackelford, *ibid.*, **78**, 1225 (1956).

[8] D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953).

[9] R. E. Kinney and L. A. Hamilton, *ibid.*, **76**, 786 (1954).

[10] C. C. Price, *Chem. Revs.*, **29**, 37 (1941).

[11] H. C. Brown and C. R. Smoot, THIS JOURNAL, **78**, 2176 (1956).

In addition to the application of the isotopic tracer technique, we proposed to examine the disproportionation products by means of infrared spectrophotometry, mass spectrometry and, possibly, vapor chromatography.

Experimental[12]

Synthesis of *n*-Propyl-β-C^{14}-benzene: Sodium Propionate-2-C^{14}.—Ethyl-1-C^{14} iodide (81 mg., 0.96 mc./mmole, purchased from Tracerlab, Inc.) was diluted to 16.2 g. (0.104 mole) with ordinary redistilled ethyl iodide (Eastman). To this was added 9.5 g. (0.146 mole) of potassium cyanide, 35 ml. of water and 50 ml. of 95% ethyl alcohol; this mixture was heated to reflux for 18 hours. Using an oil-bath at 150–160°, the reaction mixture was distilled to dryness. To the distillate was added 11 ml. of 20 *N* sodium hydroxide. The alkaline mixture was heated to reflux for 24 hours and then the alcohol was removed by distilling about two-thirds of the solution. The residue was diluted with water to its original volume and made acidic with 18 *N* sulfuric acid. A saturated solution of silver sulfate was added until precipitation was complete. The solution was distilled until about one-third of its volume remained, diluted with water to its original volume, and distilled again until about one-third of its volume remained. The combined distillates were neutralized (to *p*H 9) with sodium hydroxide and the solution was evaporated to dryness by heating in an oil-bath at 150°. The residue was dried in a vacuum oven at 100°. The weight of sodium propionate-2-C^{14} was 6.5 g. (65% yield, based on ethyl-1-C^{14} iodide).

Propiophenone-2-C^{14}.—To 6.5 g. (0.068 mole) of sodium propionate-2-C^{14} was added 60 ml. of benzene and 47.5 g. of anhydrous aluminum chloride. The mixture was heated and stirred under reflux for 8.5 hours. After cooling, 268 ml. of 6 *N* hydrochloric acid was added very slowly through the reflux condenser, while the reaction mixture was stirred and kept in an ice-bath. The reaction mixture was filtered and the aqueous and organic phases were separated. The aqueous phase was washed with two 20-ml. portions of benzene which were combined with the organic phase. The combined organic solution was washed with two 20-ml. portions of 10% sodium hydroxide solution, three 20-ml. portions of water, and then was dried over calcium chloride. Benzene was distilled through a short Vigreux column and propiophenone-2-C^{14} was distilled under reduced pressure; 8.20 g. was collected, b.p. 95–115° (20 mm.). This was 90% of the theoretical amount calculated from sodium propionate-2-C^{14}.

***n*-Propyl-β-C^{14}-benzene** was prepared by Clemmensen reduction of the propiophenone-2-C^{14} (8.20 g.), essentially by the procedure described by Martin.[13] It was found necessary to use a very efficient condenser, or two condensers in series, in order to avoid loss of the product by entrainment with the hydrogen. The product was worked up in the usual way except that before distillation of the ether solution, 23.6 g. of pure ordinary *n*-propylbenzene was added. The ether was removed through a Vigreux column and the product was distilled, boiling at 155–162°; 28.8 g. was obtained. The molecular radioactivity was 1.15 μc./mmole (see below). The radiochemical yield from ethyl-1-C^{14} iodide was 55%.

To make sure that the *n*-propyl-β-C^{14}-benzene did not contain propiophenone-2-C^{14} of high activity as an impurity, ordinary propiophenone (8.5 ml. per 20 ml. of *n*-propyl-β-C^{14}-benzene) was added and then recovered by fractional distillation. Radioassay of the recovered propiophenone showed an activity of only 0.01 μc./mmole.

Radioassay of the *n*-propyl-β-C^{14}-benzene was made as described previously, using wet-combustion[14] to produce carbon dioxide which was collected in an ionization chamber and counted on a vibrating-reed electrometer.[15] The liquid samples (2–10 mg.) were weighed in open-ended capillary tubes. It was found that there was some danger of incomplete oxidation when larger samples of liquids were assayed. Best results were obtained with two 3-mg. samples, weighed on a microbalance. The molecular radioactivities of the *n*-propyl-β-C^{14}-benzene samples used as starting materials in the various disproportionations are given in Table I.

Oxidation of *n*-Propyl-β-C^{14}-benzene to Benzoic Acid and Radioassay of Benzoic Acid.—To 1 ml. of *n*-propyl-β-C^{14}-benzene was added 6 g. of potassium permanganate, 1 g. of potassium hydroxide and 60 ml. of water. The mixture was refluxed with stirring for three hours. The mixture was then acidified with 18 *N* sulfuric acid and refluxed with stirring for two more hours. The mixture was made basic with sodium hydroxide pellets, heated, the manganese dioxide was filtered off, and the residue was washed with three 5-ml. portions of hot water. The filtrate was heated and acidified with 18 *N* sulfuric acid. After cooling the solution in an ice-bath, the benzoic acid was collected and washed with two 5-ml. portions of cold water. It weighed 270 mg. when dry and melted at 121.8–122.9°.

An 8.6-mg. sample of the benzoic acid was radioassayed. The sample activity was the same as the background, showing that the benzoic acid was completely inactive.

Disproportionation of *n*-Propyl-β-C^{14}-benzene.—The expt. labeled 3 in Table I will be described in detail; the other differed only in the conditions shown in Table I.

The reaction was carried out in a 500-ml. three-necked flask equipped with a sealed stirrer and a reflux condenser. To 16 ml. (13.8 g., 0.115 mole) of *n*-propyl-β-C^{14}-benzene, molecular activity 1.20 μc./mmole, was added 5.0 g. of aluminum chloride (Baker and Adamson, anhydrous, sublimed). In weighing and transferring the aluminum chloride to the reaction flask, no care was taken to exclude atmospheric moisture from the aluminum chloride. The mixture was heated on a steam-cone with stirring for 6.5 hours. The reaction flask was cooled in an ice-bath and 40 ml. of water was added slowly through the condenser. The two phases were separated and the aqueous phase was extracted with two 10-ml. portions of ether. The combined organic phases were washed with two 10-ml. portions of 5% sodium bicarbonate solution and with two 10-ml. portions of water. The ether solution was dried over 2 g. of calcium chloride.

The ether solution of the disproportionation products was fractionated through a 12-mm. × 45-cm. Vigreux column. The following fractions were obtained:

No.	B.p., °C.	Wt., g.
1	34–37	(Ether)
2	37–77	0.14
3	77–81	1.37 (benzene)
4	81–148	0.95
5	148–160	3.28 (propylbenzene)
6	160–195	1.16
7	195–210	1.60 (dipropylbenzene)
Residue		2.96
		11.46 Total

A 1.0-ml. sample of fraction 5 was *oxidized to benzoic acid* using the procedure described above. The product weighed 310 mg. It was sublimed at atmospheric pressure and the sublimed material was recrystallized from water. Assay of a 7.15-mg. sample of the purified benzoic acid gave a radioactivity of 0.372 μc./mmole, corresponding to 31.0% of the C^{14}-activity in the α-position. A second 1.0-ml. sample of fraction 5 was oxidized to benzoic acid, which was sublimed and recrystallized and then assayed as before. The radioactivity was again 0.372 μc./mmole.

A 0.5-ml. sample of fraction 7 was *oxidized to phthalic acids*.[16] One gram of potassium permanganate, 1 g. of potassium hydroxide and 60 ml. of water were added to the hydrocarbon and the mixture was heated under reflux. After each gram of permanganate was decolorized another gram was added until a total of 4 g. had been added. After the last gram had been decolorized, the mixture was acidified with 18 *N* sulfuric acid, and refluxing and stirring were continued another two hours. The mixture was made basic with potassium hydroxide pellets and filtered while hot. The hot filtrate was acidified with 18 *N* sulfuric acid, cooled in ice, and the phthalic acids were collected on a filter; 54 mg. was obtained. The product was recrystallized from 50% aqueous ethanol. A 9.2-mg. sample was assayed as before; the molecular activity was 0.744 μc./mmole.

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(12) Melting points are corrected; boiling points are not corrected.

(13) E. L. Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 164.

(14) D. D. Van Slyke, J. Plazin and J. R. Weisiger, *J. Biol. Chem.*, **191**, 299 (1951).

(15) O. K. Neville, THIS JOURNAL, **70**, 3501 (1948).

(16) Mainly *m*- and *p*-isomers, according to Heise and Töhl, ref. 5.

This corresponds to 31.0% of the C^{14}-activity in each of the two α-positions.

A *neutralization equivalent* of an 8.3-mg. sample of the phthalic acids was determined by titration in aqueous ethanol with 0.0241 *N* sodium hydroxide solution, calcd., 83.1; found, 84.3. A sample was submitted for elementary analysis.[17]

Anal. Calcd. for $C_8H_6O_4$: C, 57.84; H, 3.64. Found: C, 58.00; H, 3.65.

Degradation of Propylbenzene to Benzaldehyde, Acetaldehyde and Iodoform.—Disproportionation expt. 4 was carried out exactly like expt. 3, using *n*-propyl-β-C^{14}-benzene with an activity of 1.19 μc./mmole. Part of the propylbenzene fraction was oxidized as before to benzoic acid, which had an activity of 0.293 μc./mmole. This corresponds to 24.6% of the C^{14}-activity in the α-position.

A second portion (2 ml.) of the propylbenzene fraction was dissolved in 24 ml. of carbon tetrachloride and 1.50 g. of N-bromosuccinimide was added. The mixture was refluxed by heating with a 250-watt heat lamp placed directly beneath the flask until all the solid material floated. The succinimide was removed by filtration, and the solvent was removed from the filtrate by evaporation at aspirator pressure at room temperature. The residue was refluxed for one hour with 3 ml. of dry pyridine. The volatile material was distilled from the reaction flask and 10 ml. of 6 *N* hydrochloric acid was added to the distillate. The two layers were separated and the aqueous layer was extracted with carbon tetrachloride. The combined organic layers were dried over calcium chloride and the carbon tetrachloride was evaporated. To the residue was added 9.2 ml. of 98% formic acid and 1.17 g. of 30% hydrogen peroxide. The mixture was heated gently and stirred with a magnetic stirrer for 48 hours. The excess formic acid was removed by heating the mixture gently under reduced pressure. The residue was neutralized with 6 ml. of 3 *N* methanolic potassium hydroxide, then an excess of 6 ml. of the potassium hydroxide solution was added and the mixture was refluxed for three hours. The excess methanol was evaporated with an air stream. To the residue was added 20 ml. of water and enough 18 *N* sulfuric acid to bring the *p*H to 2. The flask was fitted with a condenser and a gas delivery tube leading from the top of the condenser to a test-tube containing 10 ml. of methanol, cooled in a Dry Ice–isopropyl alcohol bath. (The methanol had been tested and shown to give a negative iodoform test.) To the reaction mixture was added 2.5 g. of periodic acid and a magnetic stirring capsule, and the mixture was stirred at room temperature for 24 hours. The reaction mixture was then neutralized with sodium bicarbonate. The water flow through the condenser was restricted and the reaction mixture was heated so that the reflux occurred high in the condenser for 4 hours.

The methanol in the cold trap was divided into two equal portions. The first was treated with 5 ml. of a solution prepared from 20 g. of potassium iodide, 10 g. of iodine and 80 ml. of water. The mixture was decolorized with 1.5 ml. of 5% potassium hydroxide solution, and 15 ml. of water was added. The iodoform which separated was collected, dried in a desiccator under nitrogen and found to weigh 85 mg.; m.p. 118–120°. Radioassay of an 11.46-mg. sample showed no activity above background.

The second half of the methanol solution was added to 40 ml. of saturated aqueous 5,5-dimethyldihydroresorcinol solution. After cooling the mixture for 24 hours in an ice-bath, the "dimedone" derivative of acetaldehyde was removed by filtration, dried and found to weigh 95 mg. A second crop of crystals was obtained by treating the filtrate with more reagent and allowing the mixture to stand in ice for several days. The combined yield of crystals was purified by recrystallization from aqueous alcohol; m.p. 140–141°. Radioassay showed a molecular activity of 0.895 μc./mmole. This corresponds to 75.3% of the C^{14}-activity in the β-position.

Attempts to obtain the "dimedone" derivative of benzaldehyde from the reaction mixture failed on the active material, although it had been obtained in a run with non-radioactive material.

Infrared spectra were determined using a Baird double-beam spectrophotometer. The pure liquid samples were placed in sodium chloride cells of 0.021-mm. thickness. Spectrograms of pure starting material, *n*-propyl-β-C^{14}-benzene, and pure isopropylbenzene were prepared and compared with authentic spectrograms.[18] The most characteristic difference in the absorption spectra of these two compounds is in the strong absorption of *n*-propylbenzene at 13.5 μ and of isopropylbenzene at 13.1 μ. Synthetic mixtures of *n*-propylbenzene containing 1, 2, 4 and 5% of isopropylbenzene were prepared and their spectra determined; in this way it was found that as little as 1% of isopropylbenzene could be detected in *n*-propylbenzene, and larger amounts estimated, by means of the absorption at 13.1 μ. The probylbenzene fraction from expt. 5 was thus found to contain less than 1% isopropylbenzene. The spectra of the propylbenzene fractions of expts. 3 and 4 were identical, and indicated an isopropylbenzene content of about 2%.

A mass spectroscopic analysis[19] of the propylbenzene fraction of expt. 4 indicated the following composition by weight: *n*-propylbenzene, 91.0%; isopropylbenzene, 3.8%; dipropylbenzene, 3.4%; tripropylbenzene, 0.2%; "nonene," 1.6%.

Analysis by means of vapor chromatography was also made[20] on the propylbenzene fraction of expt. 3. *n*-Propylbenzene and isopropylbenzene were identified in the proportion of approximately 97 to 3%.

Discussion of Results

The synthesis of the *n*-propyl-β-C^{14}-benzene is outlined below.

$$\begin{tikzcd}
CH_3C^{14}H_2I \arrow[r, "1,\ KCN", "2,\ H_2O,\ NaOH"'] & CH_3C^{14}H_2CO_2Na \arrow[d, "C_6H_6,\ AlCl_3"] \\
CH_3C^{14}H_2CH_2C_6H_5 & CH_3C^{14}H_2COC_6H_5 \arrow[l, "Zn(Hg)_x"', "HCl"]
\end{tikzcd}$$

The over-all radiochemical yield from ethyl iodide was 55%. In order to demonstrate that none of the C^{14} was in the α-position of the side chain of the synthetic product, a sample was oxidized by permanganate to benzoic acid, which was found to be non-radioactive.

Six disproportionations of the tagged *n*-propylbenzene were carried out by treatment with aluminum chloride under the conditions described in Table I. The reaction mixtures were decomposed with water and worked up in the usual way. The products were separated into benzene, propylbenzene and dipropylbenzene fractions by distil-

TABLE I

DISPROPORTIONATION OF *n*-PROPYL-β-C^{14}-BENZENE BY ALUMINUM CHLORIDE

Expt.	M.A.,[a] μc./mmole	Temp., °C.	Time, hr.	$AlCl_3$/PrPh,[b] mole ratio	Rearrangement, % in Propylbenzene[c]	Rearrangement, % in Dipropylbenzene[d]
1	1.15	100	6.5	0.16	14	13
2	1.15	100	24	.16	13	13
3	1.20	100	6.5	.32	31	31
4	1.19	100	6.5	.32	25	
5	0.618	25	6.5	.32	1.5	0.3
6	0.618	159	0.5	.32	23	22

[a] Molecular radioactivity of the *n*-propyl-β-C^{14}-benzene starting material. [b] In all expts., 13.8 g. (0.115 mole) of *n*-propyl-β-C^{14}-benzene was used. [c] Calculated from the formula (M.A. benzoic acid)/(M.A. *n*-propyl-β-C^{14}-benzene) 100. [d] Calculated from the formula (M.A. phthalic acid/2)/(M.A. *n*-propyl-β-C^{14}-benzene) 100.

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[17] Clark Microanalytical Laboratory, Urbana, Illinois.

[18] A. P. I. Research Project 44, Serial Nos. 313, 314.

[19] We are grateful to Dr. David Medley of the Celanese Corporation of America, Clarkwood, Texas, for this analysis.

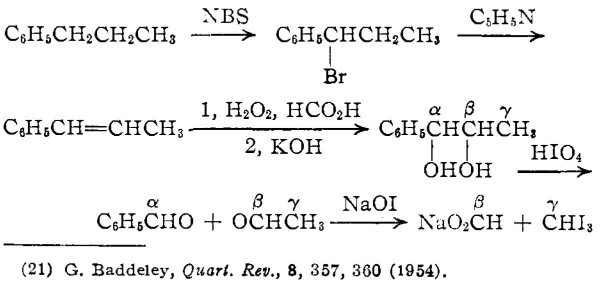
[20] We are grateful to Professor L. F. Hatch of this department for this analysis.

lation. Wide cuts were taken in the propylbenzene and dipropylbenzene ranges so as to include any isopropyl- as well as *n*-propylbenzenes present. Experiment 1 closely corresponds to that reported by Heise and Töhl in regard to temperature, time and catalyst/hydrocarbon ratio. Experiment 2 was designed to show whether a longer heating period would increase the amount of isotopic rearrangement; it did not, but gave exactly the same amount. However, doubling the catalyst/hydrocarbon ratio did increase the amount of rearrangement, as is shown by expts. 3 and 4. The discrepancy between the results of these two expts. is not understood, but may be due to the difficulty of exactly reproducing the catalyst, since its activity toward such reactions is known to depend on minor amounts of water and hydrogen chloride.[21] Disproportionation took place readily at room temperature (expt. 5), but no appreciable isotopic rearrangement occurred. This was in line with the results of McCaulay and Lien[8] with hydrogen fluoride–boron trifluoride catalyst. In order to determine whether temperatures above 100° would result in more extensive rearrangement, reaction was carried out at the reflux temperature of *n*-propylbenzene. The mixture darkened rapidly so it was heated for only one-half hour. The degree of rearrangement was not higher than that occurring at 100°, but actually was somewhat lower.

At this point in the research the authors interpreted the isotopic rearrangement as representing conversion of *n*-propylbenzene into isopropylbenzene and diisopropylbenzene. (Infrared analysis was delayed for a while due to the installation of a new instrument.) When the infrared spectra were determined, it came as a surprise that *the propylbenzene fraction shown to have undergone 31% isotopic rearrangement contained only 2% isopropylbenzene*, according to its infrared spectrum! The infrared analysis was confirmed by a mass spectroscopic analysis which indicated 4% isopropylbenzene, and smaller amounts of dipropyl- and tripropylbenzene and an unknown "nonene." Further confirmation was obtained by means of vapor chromatography which indicated approximately 97% *n*-propylbenzene and 3% isopropylbenzene. The only interpretation possible on the basis of these data is that the isotopic rearrangement involves the conversion of *n*-propyl-β-C^{14} groups into *n*-propyl-α-C^{14} groups; *e.g.*

$$\mathrm{Ar{-}CH_2C^{14}H_2CH_3} \longrightarrow \mathrm{Ar{-}C^{14}H_2CH_2CH_3}$$

This result was so unexpected that it was felt that an alternative method of degradation to confirm the isotopic distribution was desirable. The scheme adopted is outlined



$$\mathrm{C_6H_5CH_2CH_2CH_3} \xrightarrow{\text{NBS}} \underset{\displaystyle \mathrm{Br}}{\mathrm{C_6H_5\underset{|}{C}HCH_2CH_3}} \xrightarrow{\mathrm{C_5H_5N}}$$

$$\mathrm{C_6H_5CH{=}CHCH_3} \xrightarrow[\text{2, KOH}]{\text{1, }\mathrm{H_2O_2,\ HCO_2H}} \mathrm{C_6H_5}\overset{\alpha}{\underset{\mathrm{OH}}{\mathrm{CH}}}\overset{\beta}{\underset{\mathrm{OH}}{\mathrm{CH}}}\overset{\gamma}{\mathrm{CH_3}} \xrightarrow{\mathrm{HIO_4}}$$

$$\mathrm{C_6H_5}\overset{\alpha}{\mathrm{C}}\mathrm{HO} + \mathrm{O}\overset{\beta}{\mathrm{C}}\mathrm{H}\overset{\gamma}{\mathrm{C}}\mathrm{H_3} \xrightarrow{\mathrm{NaOI}} \mathrm{NaO_2}\overset{\beta}{\mathrm{C}}\mathrm{H} + \overset{\gamma}{\mathrm{C}}\mathrm{HI_3}$$

This allowed determination of C^{14}-activity not only in the α- and β-positions, but also in the γ-position. Although a benzaldehyde derivative was obtained on a practice "dead" run, it was not when the radioactive material was degraded. This was not too serious, because the same information was given by degradation of a part of the propylbenzene as before to benzoic acid, which was found to have a radioactivity corresponding to 25% of the original C^{14} in the α-position. The "dimedone" derivative of acetaldehyde was isolated and found to have a radioactivity corresponding to 75% of the original C^{14}. Since the iodoform derived from the acetaldehyde was found to be non-radioactive, all of the radioactivity of the acetaldehyde must reside in the carbonyl carbon, which corresponds to the β-position of the *n*-propyl group. Hence, the *n*-propylbenzene recovered from the disproportionation reaction contained 25% of the C^{14} in the α-position, 75% in the β-position, and none in the γ-position.

We cannot give a complete explanation of this unique rearrangement at this time, but we should like to emphasize certain facts and to postulate mechanisms to account for them as well as possible.

(1) Either the alkyl group rearrangement is independent of the disproportionation or the mechanism of the latter changes significantly in going from 25 to 100°. The fact that the degree of rearrangement of propyl groups is the same in the propylbenzene and dipropylbenzene fractions may be considered as supporting the former alternative.

(2) The failure to observe more rearrangement at 159° than at 100° must be due to the increased rate of competing reactions which involve the same intermediate as the isotopic rearrangement.

(3) The catalyst concentration, as well as the temperature, has a strong effect on the degree of rearrangement. Doubling the concentration increased the rearrangement from 13 to 31%.[22]

(4) The isotopic rearrangement involves only the α- and β-carbon atoms of the *n*-propyl group; *e.g.*, the three carbons do not become equivalent at any time.

An attempt to fit the rearrangement into the mechanism proposed by Brown and Smoot[11] for disproportionation leads to the scheme pictured. If the alkyl group is held loosely enough in the localized π-complex III, presumably it may rearrange to produce IV, which may then form rearranged *n*-propylbenzene (II). Either of the π-complexes may undergo nucleophilic attack by propylbenzene to produce benzene and the dipropylbenzenes V and VI.

However, one must ascribe to the localized π-complex the unique property of allowing a methyl shift almost to the exclusion of a hydrogen shift, which would result in isopropylbenzene. In reactions which are thought to involve propylcarbonium ions there is no such selectivity of methyl

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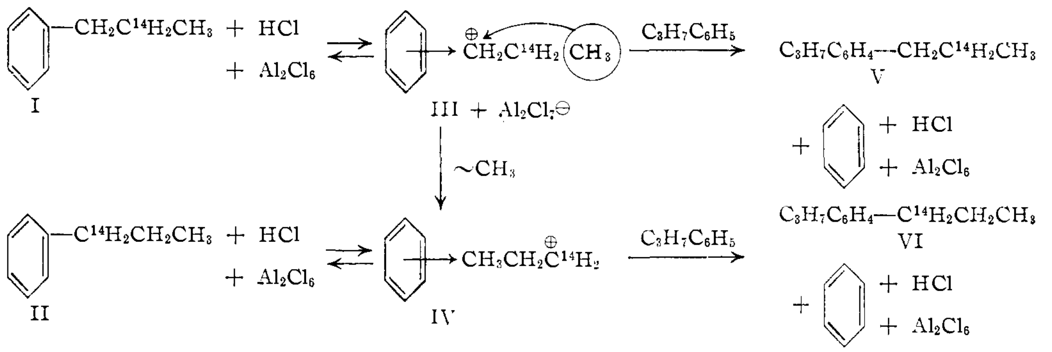
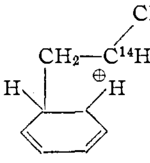
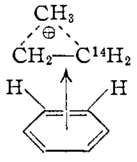
[21] G. Baddeley, *Quart. Rev.*, **8**, 357, 360 (1954).

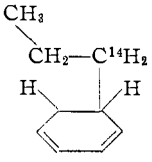
[22] We plan to investigate this effect further, but it may be difficult because of the limited solubility of aluminum chloride. It has been observed (R. M. Roberts, unpublished results) that massive amounts of aluminum chloride and hydrogen chloride result in extensive decomposition and it may become impossible to isolate propylbenzene and dipropylbenzene from other reaction products.



shift over hydrogen shift.[23] However, it is possible that the special structure of the localized π-complex may indeed set it apart from the more free carbonium ion involved as intermediate in reactions such as those mentioned in footnote 23. We propose that the rearrangement may take place in the following way. A σ-complex VII is formed first by addition of a proton from the catalyst.[24] The σ-complex VII is converted into the isomeric σ-complex IX by passing through a symmetrical localized π-complex VIII, which is either a high-energy intermediate or a transition state. We show the rearrangement as involving a 1,2-shift on the aromatic ring as well as the methyl shift.

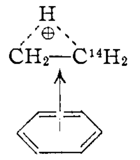

VII


VIII


IX

Although we have no direct evidence for this, it seems plausible in view of the geometry of the molecule, and the transition from VII to IX may be a concerted process. Except for the methyl shift, this mechanism is the same proposed by Baddeley[25] and Brown[26] for the well known isomerization of dialkylbenzenes (*e.g.*, *p*-xylene → *m*-xylene).[27]

It is interesting to recall that ethyl-β-C^{14}-benzene did not undergo isotopic rearrangement when treated as was *n*-propyl-β-C^{14}-benzene, but ethyl-2-C^{14} chloride did isomerize when treated with aluminum chloride in the absence of benzene.[1] The isomerization undoubtedly involves a carbonium ion intermediate, but the rearrangement of the ethyl-β-C^{14}-benzene would (according to the presently postulated theory) involve a hydrogen-bridged intermediate, as would the formation of isopropylbenzene from *n*-propylbenzene. Thus, the behavior of ethyl-β-C^{14}-benzene may be considered to support the interpretation of the present results.



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(23) For example, F. C. Whitmore and R. S. Thorpe (This Journal, **63**, 1118 (1941)) found 7% *n*-propyl alcohol and 32% isopropyl alcohol from treatment of *n*-propylamine with nitrous acid at room temperature; (b) V. N. Ipatieff, H. Pines and L. Schmerling (*J. Org. Chem.*, **5**, 253 (1940)) found 40% *n*-propylbenzene and 60% isopropylbenzene from *n*-propyl chloride, benzene and aluminum chloride at 35°.

(24) The σ-complex was omitted from the over-all scheme given above for the sake of brevity.

(25) G. Baddeley, *J. Chem. Soc.*, 994 (1950).

(26) H. C. Brown and H. Jungk, This Journal, **77**, 5579 (1955).

(27) It is, of course, quite possible that no 1,2-shift on the aromatic ring occurs, the same carbon atom of the ring becoming bonded to the β-carbon atom of the side-chain as the methyl group shifts to the α-carbon atom. We intend to determine the relationship between rearrangements of side-chains and 1,2-shifts on the ring by studying di- or tri-substituted alkylbenzenes.