solid, white neoisopinocamphylamine hydrochloride, 0.31 g. (8.1%) was obtained.

Acetylation of neoisopinocamphylamine hydrochloride with acetic anhydride in the presence of sodium hydroxide solution gave (+)-N-acetylneoisopinocamphylamine, m.p. 148.5–149.5°, $[\alpha]^{28}D$ +50.8° (chloroform *c*, 1.51).

Anal. Calcd. for $C_{12}H_{21}ON$: C, 73.79; H, 10.84; N, 7.17. Found: C, 74.26; H, 10.87; N, 7.54.

Acknowledgment.—This work was supported in part by a research grant (NSF-G-13290) from the National Science Foundation. Thanks are due to R. Sitaram Iyer for some preliminary experiments. We are very thankful to Professor W. Hückel for a sample of (+)-isomenthol and to Professor H. C. Brown and Dr. G. Zweifel for a sample of isopinocampheol.

Alkylbenzenes. IX. Equilibration of the α- and β-Carbon Atoms in C^{14}-Labeled *n*-Propylbenzenes by Lewis Acid Catalysts[1]

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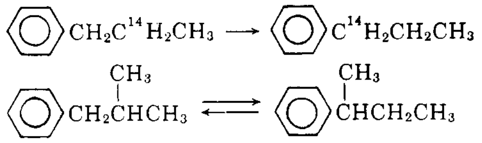
Multiple treatments with fresh aluminum chloride of *n*-propylbenzene labeled in either the α- or β-position with C^{14} led to complete equilibration of the isotopic carbon between the α- and β-positions of the side chain of recovered *n*-propylbenzene; no appreciable amount of the isotope was found in the γ-position. The effectiveness of other Lewis acid catalysts for rearrangement of C^{14}-labeled *n*-propylbenzene was tested; hydrogen bromide–aluminum bromide produced 44% rearrangement from the α- to the β-position in one treatment.

The aluminum chloride-induced rearrangement of *n*-propyl-β-C^{14}-benzene was reported to result in the appearance of up to 31% of the C^{14} in the α-position of the normal side chain, while none was found in the γ-position.[3] Subsequently it was demonstrated that either isobutyl- or *sec*-butylbenzene is converted under the same conditions into a mixture containing a 2:1 proportion of isobutyl- and *sec*-butylbenzene, respectively.[4] In a sense, the butylbenzene isomers may be considered to be β- and α-methyl-labeled propylbenzenes, so that the similarity in the rearrangement reactions is obvious.



The 2:1 "equilibrium" proportion of isobutyl- and *sec*-butylbenzene produced from either of these butylbenzene isomers is probably a result of several factors; *e.g.*, the relative thermodynamic stability of the two isomers[4,5] and their relative susceptibilities toward dealkylation and fragmentation reactions.[6]

However, α- and β-C^{14}-labeled *n*-propylbenzene molecules are chemically identical, and one would expect that the isotopic rearrangement of *n*-propyl-β-C^{14}-benzene should result in a 50:50 distribution of C^{14} between the α- and β-carbon atoms, since the γ-carbon atom is apparently not involved.[3] It occurred to us that a possible explanation of the observed incomplete rearrangement lay in deactivation of the catalyst by the di-, tri-, and polypropylbenzenes formed by disproportionation reactions which are concurrent with the rearrangement. A simple experimental test of this theory appeared to be multiple treatments with fresh catalyst; *i.e.*, α- or β-C^{14}-labeled *n*-propylbenzene would be treated with catalyst, the monopropylbenzene separated from benzene, dipropylbenzene and higher disproportionation products, degraded, and radioassayed to determine the extent of isotopic rearrangement. This recovered, partially rearranged *n*-propylbenzene would then be subjected to treatment with fresh catalyst and the separation, degradation, and radioassay of recovered *n*-propylbenzene repeated. If the theory of catalyst deactivation were correct, repetition of these procedures should result in a 50:50 distribution of C^{14} between the α- and β-carbon atoms of the side chain.

This paper describes results of such experiments and of certain other related experiments.

Discussion of Results

In previous papers we suggested two mechanisms for the rearrangement of *n*-propyl-β-C^{14}-benzene to *n*-propyl-α-C^{14}-benzene,[3,7] and Nenitzescu and coworkers[5] proposed a third which differed slightly from our second mechanism. Each of the steps in all of these mechanisms are assumed to be reversible, and hence we expected that an equal distribution of C^{14} between the α- and β-carbon atoms should be approached from starting material labeled in either position. To test the validity of these assumptions we synthesized both *n*-propyl-α-C^{14}-benzene and *n*-propyl-β-C^{14}-benzene.

Two syntheses of *n*-propyl-α-C^{14}-benzene utilizing (a) sodium cyanide-C^{14} and (b) barium carbonate-C^{14} as sources of the isotopic label are outlined in Fig. 1. A method different from that used in the earlier work[3] was used for the synthesis of *n*-propyl-β-C^{14}-benzene; it is outlined in Fig. 2.

Multiple Rearrangements of *n*-Propyl-α-C^{14}-benzene.—Treatment of *n*-propyl-α-C^{14}-benzene with aluminum chloride at 100° for 6.5 hours in three consecutive stages is outlined in Fig. 3. The procedure

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[1] A preliminary report of some of the results described fully here was given in *Chem. Ind.* (London), 1557 (1958).

[2] Taken from the Ph.D. thesis of James E. Douglass, The University of Texas, 1959. Procter and Gamble Co. Fellow, 1957–1958; University of Kentucky, Lexington, Ky.

[3] (a) R. M. Roberts and S. G. Brandenberger, *Chem. Ind.* (London), 227 (1955); (b) R. M. Roberts and S. G. Brandenberger, *J. Am. Chem. Soc.* **79**, 5484 (1957).

[4] R. M. Roberts, Y. W. Han, C. H. Schmid, and D. A. Davis, *ibid.*, **81**, 640 (1959).

[5] C. D. Nenitzescu, I. Necsoiu, A. Glatz, and M. Zalman, *Chem. Ber.*, **92**, 10 (1959).

[6] These reactions will be the subject of a subsequent paper.

[7] J. E. Douglass and R. M. Roberts, *Chem. Ind.* (London), 926 (1959).

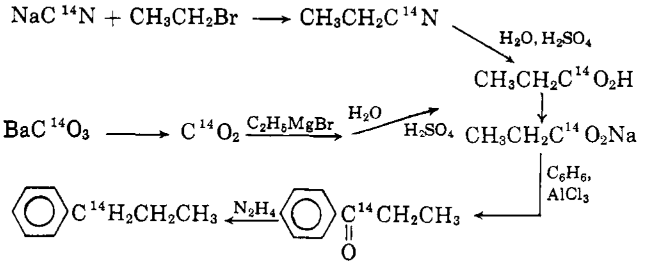

Figure 1

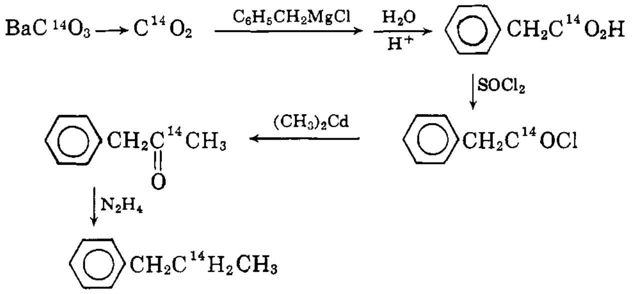

Figure 2

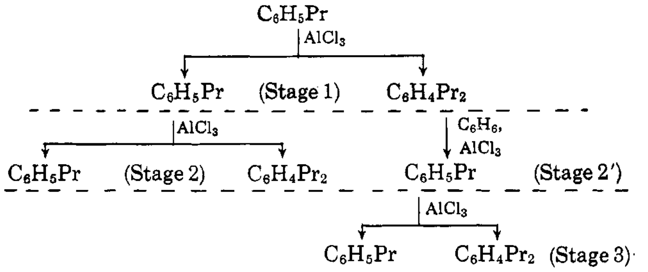

Figure 3

indicated by "stage 2′" was transalkylation of the dipropylbenzene fraction produced in stage 1, to conserve material. The propylbenzene recovered and the dipropylbenzene produced in each stage were degraded to benzoic and mixed phthalic acids by permanganate oxidation as described previously[3] and these acids were radioassayed to determine the amount of C^{14} remaining in the α-positions of the side chains. The extended degradation used in the previous work[3] was also applied to the propylbenzene recovered at each stage of this multiple rearrangement to confirm (by the benzaldehyde assay) the α-C^{14} content given by the simple oxidations, and to indicate individually the C^{14} content of the β- and α-carbon atoms (by the acetaldehyde and iodoform assays). The results are given in Table I. It can be seen that rearrangement of C^{14} from the α- to the β-carbon atom of the side chain did progress from 27 ± 1% in the first stage, to 43 ± 1% in the second stages, to 47 ± 1% in the third stage, and that no introduction of C^{14} into the γ-position occurred.[8]

A second experiment was carried out in which water-activated aluminum chloride (mole ratio $AlCl_3$:H_2O = 1:0.25) was used as catalyst. (Studies on the effect of water and other cocatalysts on the rearrangement are described in the latter part of this paper.) The starting material was *n*-propyl-α-C^{14}-benzene (2.12 μc./mmole, determined by radioassay of benzoic acid from degradation). After heating at 100° for 6.5 hours with the catalyst, a sample of the *n*-propylbenzene recovered was degraded to benzoic acid, which was found to contain radioactivity of 1.42 μc./mmole, corresponding to 33.0% rearrangement of C^{14} from the α-position. The remainder of the recovered propylbenzene was heated with a fresh portion of water-activated catalyst and the propylbenzene fraction was again recovered by distillation. Degradation of a sample afforded benzoic acid having 1.11 μc./mmole, corresponding to 47.7% rearrangement of C^{14} from the α-position. Thus, the use of water-activated aluminum chloride accomplished the same degree of rearrangement in two stages as that produced in four stages by catalyst to which no water had been added deliberately.

TABLE I

THREE-STAGE REARRANGEMENT OF *n*-PROPYL-α-C^{14}-BENZENE BY ALUMINUM CHLORIDE AT 100°[a]

Compound radioassayed	Molecular radioactivity, μc./mmole α-C	β-C	γ-C	Isotopic rearrangement, %
n-Pr-α-C^{14}-benzene[b]				
benzoic acid	0.497	0	0	...
Stage 1				
Benzoic acid	0.367	...	...	26.2
Phthalic acids	0.712	...	...	28.4
Benzaldehyde	0.362	...	...	27.2
Acetaldehyde	...	0.129[c]	...	26.0
Iodoform	...	...	0[c]	...
Stage 2				
Benzoic acid	0.281	...	...	43.5
Phthalic acids	0.558	...	...	43.8
Benzaldehyde	0.284	...	...	42.8
Acetaldehyde	...	0.206	...	41.4
Iodoform	...	...	0	...
Stage 2′				
Benzoic acid	0.286	...	...	42.3
Benzaldehyde	0.284	...	...	42.9
Acetaldehyde	...	0.214	...	43.1
Iodoform	...	...	0	...
Stage 3				
Benzoic acid	0.263	...	...	47.1
Phthalic acids	0.518	...	...	48.0
Benzaldehyde	0.265	...	...	46.6
Acetaldehyde	...	0.227	...	45.8
Iodoform	...	...	0	...

[a] The degradation schemes are outlined in ref. 3b. [b] Starting material. [c] The acetaldehyde assayed actually included both β- and γ-C atoms, but since the iodoform derived from the acetaldehyde was always nonradioactive, the radioactivity of the acetaldehyde could be attributed to the β-C alone.

Multiple Rearrangements of *n*-Propyl-β-C^{14}-benzene.—A multistage experiment was also carried out using *n*-propyl-β-C^{14}-benzene as starting material. Unfortunately the first three stages of this experiment were, like the first experiment with *n*-propyl-α-C^{14} benzene, performed before the activating effect of a cocatalyst was recognized. It may be observed in Table II that the extent of rearrangement in the fourth

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(8) After this work was completed, it was recognized that the experimental error in the radioassay of iodoform is unusually high owing to the extremely small carbon content of this compound (3.05%). Hence, although radioassays of iodoform showed no activity significantly above background, it is estimated that the iodoform could possibly have contained 2–3% of C^{14}. There is no actual evidence that it did, however, and the fact that the rearrangements of C^{14} from both α- and β-carbon atoms approached asymptotically a 50:50 distribution of the isotope between these two carbon atoms suggests that there was indeed no C^{14} in the iodoform.

TABLE II

FOUR-STAGE REARRANGEMENT OF *n*-PROPYL-β-C^{14}-BENZENE BY ALUMINUM CHLORIDE AT 100°

Compound degraded	Molecular radioactivity, μc./mmole	Isotopic rearrangement, %
n-Pr-β-C^{14}-benzene (Starting material)	β-C^{14}, 0.622[a]	..
n-Pr-α,β-C^{14}-benzene		
Stage 1	α-C^{14}, 0.109[b]	17.6
Stage 2	α-C^{14}, 0.179[b]	28.8
Stage 3	α-C^{14}, 0.226[b]	36.4
Stage 4[c]	α-C^{14}, 0.281[b]	45.2

[a] *p*-*n*-Propylbenzenesulfonamide assayed. [b] Benzoic acid assayed. [c] Water added to catalyst in molar ratio approximately $AlCl_3/H_2O = 1:0.1$.

stage, in which water was added to the aluminum chloride, was considerably greater than would have been expected on the basis of the results from the first three stages. If water-activated catalyst had been used in the first three stages, the final distribution of C^{14} between the α- and β-carbon atoms would undoubtedly have been very close to 50:50.

The results of these multiple catalyst treatments of *n*-propylbenzene labeled with C^{14} in either the α- or the β-position thus show that there is progressive equilibration of the α- and β-, but not the γ-carbon atoms of the side chain and they support the theory that deactivation of the catalyst by disproportionation products is responsible for the incomplete rearrangements produced by single catalyst treatments.

The degree of rearrangement of *n*-propylbenzene to isopropylbenzene was determined in some of these experiments, by infrared spectrophotometry or by isotope dilution analysis. For example, after the first stage of the multiple rearrangements recorded in Table I, the propylbenzene fraction was found to contain 2.1% isopropylbenzene and, after the second stage, 4.6%. The distribution of the C^{14} in this isopropylbenzene has been determined and is reported in the following paper.[9]

Studies on Effects of Water and Other Cocatalysts.—Having observed the activating effect of water on the aluminum chloride-induced rearrangement of *sec*-butyl- and isobutylbenzene,[4] we carried out a series of experiments designed to show if the propylbenzene rearrangement is similarly susceptible to cocatalysis by water. Experiments 1–9 in Table III indicate that it is. There was not a great difference in the extent of rearrangement produced by catalysts having mole ratios of $H_2O/AlCl_3$ from 0.067 to 0.500, but when the mole ratio was increased to 1.00, the activity of the catalyst toward rearrangement was greatly reduced. This is in contrast to experience with *sec*-butyl- and isobutylbenzene; catalysts having a $H_2O/AlCl_3$ mole ratio of 1.00 were found to give complete equilibration of the butylbenzenes.

An approximate measure of the rate of the rearrangement is given by experiments 6–8 and 3, in which treatments with catalyst having the optimum $H_2O/AlCl_3$ ratio were carried out for different time intervals at 100°. Experiment 9 was conducted at 80°. Since the equilibration of *sec*-butyl- and isobutylbenzene by water-activated aluminum chloride was found to be complete within one hour at 100°, it can be seen that the *n*-propylbenzene rearrangement is much slower.

Comparison of experiments 3 and 10 shows that water-activated aluminum bromide is equally as effective as the chloride.

Several experiments were carried out in which aluminum bromide saturated with hydrogen bromide was used as catalyst. At room temperature for 6.5 hours, very little rearrangement occurred (experiment 11). One experiment in which the temperature was kept at 100° for 6.5 hours gave a black product from which no propylbenzene could be recovered. When the time was cut down to one hour, propylbenzene was recovered in about 7% yield; it had undergone the most extensive rearrangement effected in one stage (experiment 12).

TABLE III

EXTENT OF REARRANGEMENT OF C^{14}-LABELED *n*-PROPYLBENZENE INDUCED BY COMPLEX CATALYSTS[a,b]

Expt. no.	C^{14c}	Catalysts, mole ratios	Time, hr.	Rearrangement, %
		$H_2O/AlCl_3$		
1	α	0.067	6.5	36.4
2	β	.125	6.5	35.5
3	α	.250	6.5	38.8
4	α	.500	6.5	31.2
5	β	1.00	6.5	11.4
6	α	.250	0.5	4.27
7	α	.250	1.5	13.5
8	α	.250	4.5	31.6
9	α	.250	6.5	9.22[b]
		$H_2O/AlBr_3$		
10	α	0.250	6.5	38.5
		$HBr/AlBr_3$		
11	β	0.500[d]	6.5	1.25[b]
12	α	0.500[d]	1.0	44.3

[a] $AlX_3/n\text{-}PrC_6H_5$ mole ratio was 0.334 in all experiments except in no. 11, 0.458, and no. 12, 0.320. [b] Temperature was 100° in all experiments except no. 9, 80°, and no. 11, 25°. [c] Position of C^{14} in starting material. [d] Reaction mixture was saturated with HBr.[9a]

Experimental

Radioassays were made either by wet-combustion[10] to carbon dioxide which was collected in an ionization chamber and counted on a vibrating-reed electrometer[11] or by employment of a liquid scintillation spectrometer (Packard "Tri-carb"). For the scintillator solution, 2,5-diphenyloxazole and 1,4-di[2-(5-phenyloxazoyl)]benzene in toluene were used[12]; in the radioassay of acetophenone-C^{14} semicarbazone it was necessary to add ethanol to the solution. Counting efficiency of the scintillometer was determined using a benzoic-1-C^{14} acid standard (5620 d.p.m.) obtained from New England Nuclear Corp.[13]

Sodium Propionate-1-C^{14}. A. From Sodium Cyanide-C^{14}.—(See Fig. 1.) Sodium cyanide-C^{14} (Tracerlab, Inc.[13]) (1.0 mmole, 1.0 mc.) was dissolved in 20 ml. water and "diluted" with 9.75 g. (199 mmoles) of ordinary sodium cyanide dissolved in 35 ml. of water. Treatment with aqueous alcoholic ethyl iodide in the manner described previously[3] resulted in 18.3 g. (93.5%) of dry sodium propionate-1-C^{14}.

B. From Barium Carbonate-C^{14}.—(See Fig. 1.) Carbonation of the Grignard reagent prepared from 210 mg. (8.8 mg.-atoms) of magnesium and 870 mg. (8.0 mmoles) of ethyl bromide was effected by modification to a small scale of the procedure de-

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(9a) D. D. Eley and P. J. King, *J. Chem. Soc.*, 2517 (1952).

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(13) On allocation from the U. S. Atomic Energy Commission.

scribed by Calvin, *et al.*,[14] using 26.23 mg. (0.133 mmole, 2.33 mc.) of barium carbonate-C^{14} (Oak Ridge National Laboratory[13]) and 377.0 mg. (1.91 mmoles) of ordinary barium carbonate; 248 mg.[15] of sodium propionate-1-C^{14} was obtained. The active material was diluted with ordinary sodium propionate before the next step.

Propiophenone-1-C^{14} was prepared by acylation of benzene by sodium propionate-1-C^{14} and excess aluminum chloride as described previously.[3b]

***n*-Propyl-α-C^{14}-benzene** was obtained by reduction of propiophenone-1-C^{14} using either the Clemmensen method[3b] or the Huang-Minlon modification of the Wolff–Kishner method.[16] The latter proved to be more reliable and simpler. The over-all radiochemical yields of the *n*-propyl-α-C^{14}-benzene by the two routes were 50% from sodium cyanide-C^{14} and 32% from barium carbonate-C^{14}. In view of a price differential of 1:9 in favor of barium carbonate-C^{14}, this is the reagent of choice in spite of the lower over-all yield.

The molecular radioactivity of the *n*-propyl-α-C^{14}-benzene was determined by oxidation to benzoic-7-C^{14} acid[3b] or by conversion to the sulfonamide[17] and radioassay of these crystalline derivatives.

***n*-Propyl-β-C^{14}-benzene** was synthesized by the steps outlined in Fig. 2. The carbonation of the benzylmagnesium chloride was carried out in the same way as that of ethylmagnesium bromide (above), using about 1 g. of benzyl chloride in a typical run. A yield of about 82% of phenylacetic-1-C^{14} acid was obtained. This was diluted with about 35 g. of phenylacetic acid and converted to the acyl chloride (93%) by the method of Truitt, *et al.*[18]; the excess thionyl chloride was removed to a cold trap under reduced pressure.[19]

Dimethylcadmium was prepared by Cason's method.[20,21] Good yields from its reaction with phenylacetyl-1-C^{14} chloride were obtained only after considerable experimentation; details of the optimum conditions are given here. A suspension of dimethylcadmium (*ca.* 0.25 mole) in benzene (*ca.* 300 ml.) was cooled to 5° and a solution of phenylacetyl-1-C^{14} chloride (0.24 mole) in dry benzene (75 ml.) was added to the stirred suspension over a period of 10 min. The mixture was then allowed to warm to room temperature with stirring during 2.5 hr. The reaction mixture was poured onto about 300 g. of cracked ice, followed by the addition of 100 ml. of 6 *N* hydrochloric acid. After stirring until all the ice had melted, the mixture was transferred to a separatory funnel and the two layers were separated. The aqueous layer was washed with two 100-ml. portions of water, 5% sodium bicarbonate solution, and water. It was then dried over anhydrous calcium chloride. Distillation afforded an 87% yield of 1-phenyl-2-propanone-2-C^{14}, b.p. 91–2° (10 mm.).

Wolff–Kischner[16] reduction of the ketone to *n*-propyl-β-C^{14}-benzene was accomplished in 73% yield. An over-all radiochemical yield of 43% was obtained (from barium carbonate-C^{14}).

For radioassay, the hydrocarbon was converted to the diacetamido derivative.[22]

Multiple Rearrangements of C^{14}-Labeled *n*-Propylbenzene.—These were carried out as described previously,[3] using in all experiments a molar ratio of aluminum chloride/hydrocarbon of 0.3.

In the experiment of Table I, 60.3 g. of *n*-propyl-α-C^{14}-benzene was taken for the first-stage reaction; 19.8 g. of propylbenzene (2% isopropylbenzene, by infrared analysis) was recovered by distillation at 140–160°. The amount remaining for the second stage treatment (after samples had been taken for degradation) was 16.9 g., from which 4.3 g. of propylbenzene (5% isopropylbenzene) was recovered by distillation. The dipropylbenzene fraction from the first stage reaction, of which 7.1 g. remained after a sample had been taken for degradation, was transalkylated by treatment with 80 ml. of dry benzene and 3.6 g. of aluminum chloride at 100° for 4.5 hr. Decomposition with water followed by the usual work-up and distillation gave 6.422 g. of propylbenzene fraction. This was diluted with 8.712 g. of nonradioactive *n*-propylbenzene. After samples were taken for degradation, the remainder, 12.9 g. was treated with aluminum chloride (the third stage). The radioactivities reported in Table I are corrected for the dilution described above.

The details of the two-stage reaction of *n*-propyl-α-C^{14}-benzene with water-activated catalyst are given in the Experimental section of the following paper[9] as experiments 2.1 and 2.2.

The four-stage reaction of *n*-propyl-β-C^{14}-benzene started with 96.2 g. of the hydrocarbon. The propylbenzene fraction recovered after the first stage of reaction was 37.4 g. After a sample was taken for degradation, 36.5 g. was subjected to reaction with aluminum chloride and 12.3 g. of propylbenzene fraction was recovered. For the third-stage treatment, 11.32 g. of this fraction was diluted with 22.54 g. of nonradioactive *n*-propylbenzene; 11.0 g. of propylbenzene fraction was recovered after the third treatment. The fourth and final reaction was carried out with 10.6 g. of hydrocarbon, from which 2.63 g. of propylbenzene fraction was recovered. The radioactivities in Table II are corrected for the dilution after stage two.

Experiments with Complex Acids.—Water was added to the hydrocarbon–aluminum halide mixtures in the proportions shown in Table III. The heterogeneous mixtures were stirred continuously for the times given in the table. The ratio of $HBr/AlBr_3$ is assumed from the finding of a complex of the approximate composition $(C_6H_6)_6 \cdot Al_2Br_6 \cdot HBr$.[9a] In our experiments, mixtures of *n*-propylbenzene and aluminum bromide were saturated with dry hydrogen bromide. Aluminum bromide was distilled directly into the reaction flask.

The molecular radioactivities of the starting materials were as follows: *n*-propyl-α-C^{14}-benzene, in experiments 10 and 12, 0.789 μc./mmole; in all others, 0.445 μc./mmole. *n*-Propyl-β-C^{14}-benzene, in experiment 2, 2.29 μc./mmole; experiment 5, 0.580 μc./mmole; experiment 11, 0.622 μc./mmole.

Extent of isotopic rearrangement was determined in all experiments by degradation to benzoic acid.

Acknowledgment.—We wish to thank The National Science Foundation for a grant (NSF-G5925) which supported this research.

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[15] This was more than the theoretical amount of sodium propionate, due probably to incomplete drying or excess alkali. It caused no difficulty; the over-all result was equally satisfactory as the results from two other runs in which 94 and 97% yields of crude sodium propionate were obtained.

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