melting point is 93°.[126] In 48 hours, 0.10 mole of acenaphthylene in 50 ml. of chlorobenzene solution absorbed 0.005 mole of oxygen in the presence of 0.1 *M* ABN. The products could not be precipitated by methyl alcohol and were not investigated further.

**Acknowledgment.**—Miss Bess Rickman, Mrs. V. N. Pemberton and Mr. Kyle Griggs assisted materially in the experimental work in papers V-IX. Mr. A. T. Tweedie carried out some preliminary work on the high temperature oxidation of α-methylstyrene and the low pressure oxidation of diisobutylene. Dr. J. R. Ladd prepared several of the compounds used. Dr. P. D. Zemany and Dr. G. P. Schacher carried out the mass spectrographic analyses for oxygen in connection with experiments in Table V. Several members of the Analytical Chemistry Unit at the General Electric Research Laboratory and of the corresponding Section at Stanford Research Institute assisted with analyses and infrared spectra. Dr. J. F. Brown, Jr., and Dr. B. I. Rowland critically reviewed this manuscript and made numerous useful suggestions.

MENLO PARK, CALIFORNIA

[126] G. Egloff, "Physical Constants of Hydrocarbons," Vol. IV, Reinhold Publ. Corp., New York, N. Y., 1947, p. 166.

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

# Disproportionation of Alkylbenzenes. III. Behavior of *n*-Butyl-α-$C^{14}$-benzene upon Treatment with Aluminum Chloride. Further Results with Ethyl-β-$C^{14}$-benzene[1]

BY ROYSTON M. ROBERTS, STANLEY G. BRANDENBERGER[2] AND STELLAKIS G. PANAYIDES

RECEIVED DECEMBER 12, 1957

*n*-Butyl-α-$C^{14}$-benzene was synthesized and subjected to treatment with aluminum chloride at 100°. With a catalyst concentration slightly higher than that which gives 31% isotopic rearrangement of *n*-propyl-β-$C^{14}$-benzene, only 5% isotopic rearrangement of *n*-butyl-α-$C^{14}$-benzene occurred. Ethyl-β-$C^{14}$-benzene was subjected to single and repeated treatments with aluminum chloride in the same concentration used with *n*-propyl-β-$C^{14}$-benzene and found to give a maximum isotopic rearrangement of 8%. The minor extent of these rearrangements, of *n*-propylbenzene to isopropylbenzene, and of *n*-butylbenzene to *sec*-butylbenzene, are compared to the extensive isotopic rearrangement of *n*-propyl-β-$C^{14}$-benzene in terms of the mechanism proposed for the latter.

In 1954, the disproportionation of *n*-butylbenzene by aluminum chloride at 100° was described.[3] Mass spectroscopic analysis of the recovered monobutylbenzene and infrared analysis of the dibutylbenzene among the products showed that there was no rearrangement of *n*-butyl groups to *sec*-butyl or other isomeric structures. When this paper appeared, we were engaged in a study of the behavior of *n*-propyl-β-$C^{14}$-benzene upon disproportionation by aluminum chloride under similar conditions. We found that although very little isomerization to isopropylbenzene occurred, up to 31% of isotopic rearrangement to *n*-propyl-α-$C^{14}$-benzene did take place.[4] It thus became of interest to determine if isotopically labeled *n*-butylbenzene could be shown to undergo a similar isotopic rearrangement. The present paper describes the synthesis of *n*-butyl-α-$C^{14}$-benzene and the treatment of this compound with aluminum chloride at 100°.

The synthesis of *n*-butyl-α-$C^{14}$-benzene involved the same sequence of reactions used for *n*-propyl-β-$C^{14}$-benzene,[4] but the source of the $C^{14}$ was labeled sodium cyanide rather than alkyl halide. The over-all yield from sodium cyanide-$C^{14}$ was 64%. The product was radioassayed in the form of benzoic acid, produced by permanganate oxidation.

$$\begin{tikzcd}
CH_3CH_2CH_2I \arrow[r, "\text{1, NaC}^{14}\text{N, KCN}", "\text{2, H}_2\text{O, NaOH}"'] & CH_3CH_2CH_2C^{14}O_2Na \arrow[d, "C_6H_6", "AlCl_3"'] \\
CH_3CH_2CH_2C^{14}H_2C_6H_5 & CH_3CH_2CH_2C^{14}OC_6H_5 \arrow[l, "Zn(Hg)_x"', "HCl"]
\end{tikzcd}$$

The *n*-butyl-α-$C^{14}$-benzene was first heated for 3 hours at 100° with the same proportion of aluminum chloride used by Kinney and Hamilton[3] ($AlCl_3/C_4H_9C_6H_5$, mole ratio 0.20). The reaction mixture was decomposed with water and worked up in the usual way, and the benzene, monobutylbenzene and dibutylbenzene fractions were separated by fractional distillation. Oxidation of the monobutylbenzene and dibutylbenzene fractions by permanganate to benzoic and phthalic acids, respectively, and radioassay of these acids showed that less than 1% of the $C^{14}$ had been lost from the α-positions of the side chains.

The isotopic rearrangement of *n*-propyl-β-$C^{14}$-benzene was found to be strongly dependent on the concentration of catalyst. With a mole ratio of $AlCl_3/C_3H_7C_6H_5$ = 0.16, 13% isotopic rearrangement occurred, while under otherwise identical conditions, except for a mole ratio of $AlCl_3/C_3H_7C_6H_5$ = 0.32, 31% rearrangement occurred. Hence, the disproportionation of *n*-butyl-α-$C^{14}$-benzene was repeated using a doubled proportion of catalyst ($AlCl_3/C_4H_9C_6H_5$, mole ratio 0.40). A total of three disproportionations were carried out using this proportion of catalyst and hydrocarbon. The degree of isotopic rearrangement calculated from the radioactivity of the benzoic acid produced from the monobutylbenzene fraction from the first two of these disproportionations was 5.0 and 4.3%, respectively. In the third disproportionation, the dibutylbenzene fraction was also oxidized, and the degree of isotopic isomerization indicated by both

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[1] Taken from the Ph.D. thesis of Stanley George Brandenberger (1956) and the M.A. thesis of Stellakis George Panayides (1957).

[2] Celanese Corporation of America Fellow, 1955–1956.

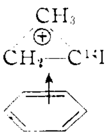
[3] R. E. Kinney and L. A. Hamilton, THIS JOURNAL, **76**, 786 (1954).

[4] R. M. Roberts and S. G. Brandenberger, *ibid.*, **79**, 5484 (1957).

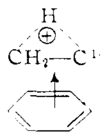
the benzoic and phthalic acid radioactivities was 4.3%. The infrared spectra of the monobutylbenzene fractions from these three disproportionations gave no appreciable evidence of anything other than *n*-butylbenzene.

Since the concentration of catalyst used in our earlier treatment of ethyl-$\beta$-C$^{14}$-benzene with aluminum chloride[5] was not quite as high as that used with *n*-propyl-$\beta$-C$^{14}$-benzene, it was thought advisable to investigate further the behavior of labeled ethylbenzene. In the first experiment, ethyl-$\beta$-C$^{14}$-benzene was subjected to treatment with aluminum chloride under exactly the same conditions of catalyst concentration, temperature and time which gave 31% isotopic rearrangement of *n*-propyl-$\beta$-C$^{14}$-benzene. The benzene, ethylbenzene and diethylbenzene fractions were separated from the reaction mixture and the latter two were oxidized to benzoic acid and phthalic acid as before. The very low radioactivity of these acids represented only 1.0% isotopic rearrangement. Another sample of ethyl-$\beta$-C$^{14}$-benzene was subjected to three consecutive treatments with fresh aluminum chloride under the same conditions described above. After each treatment the mixture was decomposed by water and the organic products were extracted into ether, the solution was dried and the ether was removed by distillation, but the benzene and alkylbenzenes were not separated before the next treatment with aluminum chloride. After the third treatment the products were separated and the ethylbenzene and diethylbenzene fractions were oxidized as before. The radioactivity of the benzoic acid and phthalic acid indicated 8% isotopic rearrangement.

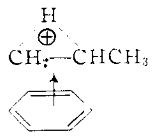
These results with *n*-butyl-$\alpha$-C$^{14}$-benzene and ethyl-$\beta$-C$^{14}$-benzene show very clearly that the extent of rearrangement of these compounds is not of the same order of magnitude as the isotopic rearrangement of *n*-propyl-$\beta$-C$^{14}$-benzene. In the preceding paper,[4] we proposed that the rearrangement of *n*-propyl-$\beta$-C$^{14}$-benzene to *n*-propyl-$\alpha$-C$^{14}$-benzene takes place *via* a methyl-bridged $\pi$-complex I.



I

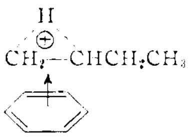


II

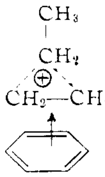


III

We speculated that any rearrangement of isotopically labeled ethylbenzene might involve a similar hydrogen-bridged intermediate II and that the rearrangement of *n*-propylbenzene to isopropylbenzene might also involve a hydrogen-bridged intermediate III. The extent of rearrangement of ethyl-$\beta$-C$^{14}$-benzene to ethyl-$\alpha$-C$^{14}$-benzene and that of *n*-propylbenzene to isopropylbenzene have been shown to be small and of the same order under comparable conditions. Any isomerization of *n*-butylbenzene to *sec*-butylbenzene might also involve a hydrogen-bridged intermediate IV. The work of Kinney and Hamilton[3] and ourselves shows that the extent of this rearrangement is negligible.



IV



V

The extent of isotopic rearrangement of *n*-butyl-$\alpha$-C$^{14}$-benzene has now been determined and shown also to be small. If we assume this rearrangement to involve an analogous $\pi$-complex intermediate V, it would in this case have a methylene bridge. Within the framework of these postulated intermediates, we may deduce from the experimental data that a methyl bridge provides a much better route for rearrangement within a $\pi$-complex than either a hydrogen bridge or a methylene bridge. We are currently studying the behavior of other alkylbenzenes, such as isobutylbenzene and *sec*-butylbenzene, which may furnish more evidence of extensive rearrangement *via* a methyl-bridged $\pi$-complex intermediate.

**Acknowledgment.**—We wish to thank Research Corporation and the University of Texas Research Institute for grants which supported this work.

## Experimental[6]

**Synthesis of *n*-Butyl-$\alpha$-C$^{14}$-benzene.**—Sodium cyanide-C$^{14}$ (49 mg., 1 millicurie, purchased from Tracerlab, Inc.) was leached from its container with 50 ml. of water in several portions and the solution was added to 13 g. (0.20 mole) of ordinary potassium cyanide. Fifty grams (0.29 mole) of *n*-propyl iodide (Eastman Kodak Co.) and 115 ml. of 95% ethanol were added and the preparation of sodium butyrate was continued in the same manner used for sodium propionate.[4] The yield of sodium butyrate-1-C$^{14}$ was 20.8 g. (94%). This material was used to alkylate benzene (170 ml.) in the presence of aluminum chloride (133 g.). The yield of butyrophenone, b.p. 114–117° (19 mm.), was 24.2 g. (86%). This product was "diluted" with 96.8 g. of ordinary butyrophenone (Matheson) and reduced by the Clemmensen method. The *n*-butyl-$\alpha$-C$^{14}$-benzene produced, b.p. 95–100° (50 mm.), weighed 86.1 g. (79%). The over-all yield from NaC$^{14}$N + KCN was 64%.

Radioassay was made as described previously[4] on an 8.2-mg. sample of *n*-butyl-$\alpha$-C$^{14}$-benzene. The radioactivity found was 1.13 $\mu$c./mmole. As mentioned in the previous paper,[4] oxidation of liquid samples is subject to some error. A better assay was made by permanganate oxidation of the hydrocarbon to benzoic acid-1-C$^{14}$ and assay of this crystalline material after sublimation. The radioactivity found was 1.17 $\mu$c./mmole.

**Disproportionation of *n*-Butyl-$\alpha$-C$^{14}$-benzene. A. Mole Ratio AlCl$_3$/C$_4$H$_9$C$_6$H$_5$ = 0.20.**—A 15-g. sample of *n*-butyl-$\alpha$-C$^{14}$-benzene (1.17 $\mu$c./mmole) was heated with 3.0 g. of aluminum chloride at 100° with stirring for 3 hours. The reaction mixture was decomposed with cold water, worked up as before and distilled. Ether and benzene were removed at atmospheric pressure through a 45-cm. Vigreux column. The higher-boiling products were fractionated through a Podbielniak column rated at a maximum of 100 plates. The following fractions were collected at 50 mm.: 1, b.p. 87–100°, 4.65 ml.; 2, b.p. 100–147°, 0.35 ml.; 3, b.p. 147–155.4°, 1.08 ml.; 4, b.p. 153.6–155.3°, 1.29 ml.

A 1.0-ml. sample of fraction 1 was oxidized with potassium permanganate and the benzoic acid produced was sublimed and radioassayed. The radioactivity was 1.18 $\mu$c./mmole, showing no loss of C$^{14}$ from the $\alpha$-position.

A 0.5-ml. sample of fraction 4 was oxidized with potassium permanganate and the phthalic acid was radioassayed. The radioactivity was 2.32 $\mu$c./mmole, or 1.16 $\mu$c./mmole per alkyl group, corresponding to less than 1% loss of C$^{14}$ from the $\alpha$-positions.

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[5] R. M. Roberts, G. A. Ropp and O. K. Neville, This Journal, **77**, 1764 (1955).

[6] Melting points are corrected; boiling points are not corrected.

B. **Mole Ratio $AlCl_3/C_4H_9C_6H_5$ = 0.40.**—Three disproportionations were run as before using $n$-butyl-$\alpha$-C$^{14}$-benzene of 1.17 $\mu$c./mmole activity. In the first two, 15 g. of hydrocarbon and 6 g. of aluminum chloride were used. The amounts of dibutylbenzene obtained by fractional distillation were too small to allow oxidative degradation and accurate radioassay, so in the third disproportionation the amounts of hydrocarbon and catalyst were doubled. After decomposition of this third reaction mixture and extraction in the usual way, the ether and benzene were distilled at atmospheric pressure and the higher-boiling products were fractionated through a 50-cm. glass helix-packed column. The following fractions were obtained.

| No. | B.p. °C. | Mm. | Reflux ratio | Wt., g. |
|---|---|---|---|---|
| 1 | 97.5–100 | 49–51 | 1/1 | 8.21 |
| 2 | 100–132 | 51 | 9/1 | 0.40 |
| 3 | 132–145 | 51 | 9/1 | 0.78 |
| 4 | 145–153 | 51 | 1/1 | 2.64 |
| Residue | | | | 3.50 |
| | | | Total | 15.53 |

Oxidation of 1 ml. of fraction 1 gave benzoic acid with an activity of 1.12 $\mu$c./mmole, after sublimation and resublimation. Oxidation of 1 ml. of fraction 4 gave phthalic acid with an activity of 2.23 $\mu$c./mmole after recrystallization and sublimation.

EXTENT OF ISOTOPIC REARRANGEMENT IN DISPROPORTIONATIONS

| Disproportionation | Isotopic rearrangement, % in Butylbenzene | Isotopic rearrangement, % in Dibutylbenzene |
|---|---|---|
| 1 | 5.0 | . . |
| 2 | 4.3 | . . |
| 3 | 4.3 | 4.3 |

**Disproportionation of Ethyl-$\beta$-C$^{14}$-benzene.**—The ethyl-$\beta$-C$^{14}$-benzene was prepared as described previously.[5] Small liquid samples (*ca.* 3 mg.) were radioassayed.[4] The activity of the material used in the disproportionations was 0.431 $\mu$c./mmole.

A. **Single Disproportionation.**—An 11.9-g. sample of ethyl-$\beta$-C$^{14}$-benzene and 4.86 g. of aluminum chloride ($AlCl_3/C_2H_5C_6H_5$, mole ratio 0.32) were heated and stirred at 100° for 6.5 hours. The reaction mixture was decomposed, extracted and distilled as before. A 50-cm. glass helix-packed column was used to separate the products. The fractions collected included benzene, b.p. 76–85°, 0.88 g.; ethylbenzene, b.p. 130–137°, 2.36 g.; and diethylbenzene, b.p. 170–183°, 1.23 g.

Oxidation of the ethylbenzene fraction gave benzoic acid with a radioactivity of $4.4 \times 10^{-3}$ $\mu$c./mmole, corresponding to 1.0% isotopic rearrangement. Oxidation of the diethylbenzene fraction gave phthalic acid with a radioactivity of $8.2 \times 10^{-3}$ $\mu$c./mmole, corresponding to 1.0% isotopic rearrangement per alkyl group.[7]

B. **Triple Disproportionation.**—The same amounts of materials used in the experiment above were heated and stirred as before for 6.5 hours at 100°. The reaction mixture was worked up as before, through the step in which ether was removed from the hydrocarbons by distillation through a 50-cm. glass helix-packed column. The hydrocarbon mixture was not distilled, however, but to it was added 4.86 g. of fresh aluminum chloride, and the mixture was heated and stirred for 6.5 hours at 100°. This procedure was repeated once more and then the hydrocarbon mixture was distilled through a 50-cm. glass helix-packed column. The fractions collected included benzene, b.p. 77–86°, 1.20 g.; ethylbenzene, b.p. 131–138°, 1.26 g.; and diethylbenzene, b.p. 176–177°, 1.40 g. (After the first disproportionation the reaction mixture was orange, after the second, purple, and after the third, black.)

Oxidation of the ethylbenzene fraction gave benzoic acid with a radioactivity of $3.44 \times 10^{-2}$ $\mu$c./mmole (32- and 47-mg. samples assayed), corresponding to 8.0% isotopic rearrangement. Oxidation of the diethylbenzene fraction gave phthalic acid with a radioactivity of $6.55 \times 10^{-2}$ $\mu$c./mmole (22- and 19-mg. samples assayed), corresponding to 7.6% isotopic rearrangement per alkyl group.

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[7] In the radioassay of these weakly radioactive products, large samples were assayed—36 to 46 mg. of benzoic acid and 26 to 38 mg. of phthalic acid—in order to increase the accuracy of the assay.

AUSTIN 12, TEXAS

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF J. T. BAKER CHEMICAL CO.]

# Preparation of Thiolmethacrylate Esters. A Study of the Reaction of Sodium Mercaptides with Methacrylyl Chloride[1]

BY GENE SUMRELL, GEORGE E. HAM AND EDWIN D. HORNBAKER

RECEIVED JANUARY 8, 1958

The usefulness of the reaction of sodium mercaptides with methacrylyl chloride as a means of preparing aryl and alkyl thiolmethacrylates has been investigated. This method was quite successful when the group attached to sulfur was phenyl, 4-chlorophenyl, pentachlorophenyl, isopropyl and $t$-butyl, but failed with methyl mercaptan and 2-mercaptobenzothiazole. The anomalous reaction which occurred in the case of the latter mercaptan is discussed. The alkyl mercaptides displayed a tendency to react at the double bond, with this tendency decreasing in the order: methyl >>> isopropyl > $t$-butyl. The reaction of the sodium mercaptides of benzenethiol and $t$-butyl mercaptan with acrylyl chloride also is reported.

The widespread usefulness which has been found for acrylic type esters led us to a desire to study the sulfur analogs of some of these compounds. The first extensive study of the thiol esters of acrylic acid was reported by Marvel and coworkers.[2] They prepared seven alkyl thiolacrylates by a method involving the reaction of 2,3-dibromopropionyl chloride with a mercaptan, followed by the removal of bromine with sodium iodide. The ease with which the mercaptans added to the double bond prevented the preparations from being carried out directly from acrylyl chloride and the mercaptans.

Recently Koton and co-workers reported the preparation of phenyl thiomethacrylate and benzyl thiolmethacrylate by a procedure involving the addition of the acid chloride to a cold solution of the mercaptan in a small excess of 5% aqueous sodium hydroxide.[3] This method appeared to be of considerable interest if generally applicable to the preparation of thiolmethacrylates and has been further investigated by us. Its shortcomings were im-

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[1] The antibacterial and antifungal properties of some of the compounds described in this paper will be reported elsewhere.

[2] (a) C. S. Marvel, S. L. Jacobs, W. K. Taft and B. G. Labbe, *J. Polymer Sci.*, **19**, 59 (1956); see also (b) S. L. Jacobs, Ph.D. Thesis, University of Illinois; *C.A.*, **49**, 10894 (1955).

[3] M. M. Koton, T. M. Kiselyeva and K. S. Podgorskaya, *Zhur, Obshchei Khim.*, **26**, 475 (1956); *C.A.*, **50**, 13815 (1956).