[Contribution from the Research Department, Phillips Petroleum Company]

PREPARATION OF 1-BUTENE LABELLED WITH C^{14} IN THE FOUR POSITION

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1-Butene labelled with C^{14} is a useful hydrocarbon for study of numerous hydrocarbon reactions. The molecule is large enough for its reactions to be typical of longer-chain olefins—for example it can undergo both double-bond and skeletal isomerization—and yet the products are in general readily analyzed by infrared absorption. Although for many purposes the position of the labelled carbon might be immaterial we elected to use a synthesis which places the C^{14} unambiguously in the 4-position.

Since the method is straightforward and simple and yields a product of high purity, the preparation is described in some detail along with data on yields and by-products.

The reactions employed are indicated in the following diagram:

$$\overset{*}{C}H_3OH \xrightarrow{HI} \overset{*}{C}H_3I \xrightarrow[\text{ether}]{Mg}$$

$$\overset{*}{C}H_3MgI \xrightarrow{CH_2{=}CH{-}CH_2Br} CH_2{=}CH{-}CH_2\overset{*}{C}H_3$$

Methyl iodide was prepared by the method of Norris (1) and the reaction yielding 1-butene was carried out following the method of Lucas (2). The over-all yield was 63%, 4 grams of material being obtained of activity such that a thick sample ($BaCO_3$) 7/8″ in diameter gave 4000 counts per minute when analyzed in the usual manner with an end-window G–M tube of window thickness 2 mg./cm². In a "cold-run" closely similar to the final preparation of labelled butene, the product was scanned with infrared and the absorption spectrum was found to be indistinguishable from that of 1-butene.[1] The impurities were, therefore, less than 1% *n*-butane, 1% isobutane, 0.5% 2-butenes, and 0.5% isobutene. Combined C_4 impurities were less than 1%. Starting material was one-quarter millicurie of labelled methyl alcohol obtained from Oak Ridge through the Atomic Energy Commission.[2]

EXPERIMENTAL

The *apparatus* is indicated diagrammatically in Fig. 1. The reaction vessel, A, was equipped with a cold finger, a modified dropping-funnel and a side-tube reaching to the bottom of the reaction flask. The latter tube could be used for introduction of inert gas or

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[1] Research Grade 1-butene, 99.7% pure, Phillips Petroleum Co.

[2] A second run has been completed with three-quarters millicurie of starting material. The yield of 1-butene and the recovery of radioactivity were about the same as in the previous run; but the product was diluted with 1-butene after distillation to provide ten ampoules of labelled material, each containing one gram of 1-butene and 0.05 millicurie of C^{14}.

for siphoning off liquid contained in the flask. Stirring was accomplished magnetically by means of a small glass-enclosed iron bar placed inside the flask and a horse-shoe magnet outside.

Methyl iodide. One ml. (0.8 g.) of methyl alcohol containing one-quarter millicurie had been transferred to tube C in a dilution carried out previously. Then 3.13 g. of additional methyl alcohol (unlabelled) was weighed into flask A which was cooled in a Dry Ice cooling-mixture and evacuated. The active methyl alcohol was then distilled into A. Finally, 76.5 g. of 57% HI (sp. gr. 1.7) was added to A through the dropping-funnel and the line was filled with dry nitrogen. Flask A was heated in a water-bath following a definite schedule arrived at in cold runs:

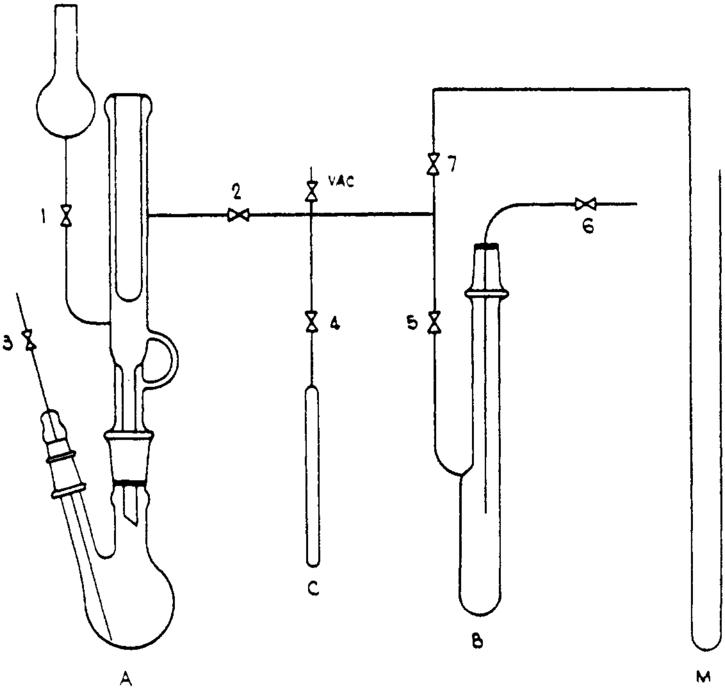

Fig. 1

0–45 minutes	50–55°	Cold finger filled with ice
45–80 minutes	55–65°	Cold finger not cooled
80–110 minutes	65–70°	Cold finger not cooled
110–140 minutes	70–100°	Cold finger not cooled

During the heating a slow stream of nitrogen was passed through the line *via* the side-tube of flask A and collected in a gas bottle attached to the outlet of B. Flask B was cooled in Dry Ice to condense methyl iodide and any unchanged methyl alcohol. On completion of the heating interval flask B was opened and 7 g. of anhydrous calcium chloride was added to absorb both water and unchanged methyl alcohol. After standing overnight the methyl iodide was distilled into tube C which was previously calibrated. The volume of CH_3I, 6.8 ml. at 20°C, indicated a yield of 88%. The residue in B was dissolved in water and siphoned into a bottle for subsequent examination.

Methyl magnesium iodide. Magnesium ribbon, free of oxide (2.8 g.) and 17.7 g. of anhydrous ether[3] were placed in flask A, which was cooled and evacuated. With Dry Ice and

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[3] Analytical reagent, Mallinckrodt Chemical Works.

acetone in the cold finger and with ice-water on A the methyl iodide was distilled into A at the rate of 6.5 grams/hour. The ice-bath was frequently removed to permit stirring. Reaction started immediately and was smooth throughout. After standing overnight the methylmagnesium iodide was siphoned off and simultaneously filtered through glass wool using another flask similar to A. Flask A was washed with three 15-ml. portions of ether.

Flask A-2, containing filtered methylmagnesium iodide, was joined to the line while a slow stream of nitrogen was passed through and the flask heated to 130° using the following schedule for boiling off ether.

0–40 minutes	65–100°
40–60 minutes	100–120°
60–80 minutes	120–130°

TABLE I

DISTILLATION OF LABELLED 1-BUTENE

FRACTION	BOILING RANGE	WT., G	MEASURED ACTIVITY OF STANDARD THICK SAMPLE ($BaCO_3$), COUNTS/MIN.
I	C_3 and lower-boiling materials	0.1	15000
II	C_4	4.4	4000
III	C_5 and higher-boiling materials	1.8	230

TABLE II

RADIOACTIVITY BALANCE

FRACTION OR RESIDUE	ASSAY, *μcuries*	PER CENT OF ORIGINAL C^{14}
HI solution with undistilled CH_3OH or CH_3I	5	2.0
$CaCl_2$ solution with CH_3OH and CH_3I	6	2.4
CH_4 from CH_3MgI	7	2.8
Fraction I from distillation	12	4.8
Fraction II (1-butene)	163	65.3
Fraction III (C_{5+}; possibly also ether and allyl bromide)	3	1.2
Loss, including errors in assays		21.5
		100.0

1-Butene. When evolution of ether became slow the reaction flask was cooled to 70°, crushed ice was placed in the cold finger, and 12.7 g. of allyl bromide[4] was added through the dropping-funnel at the rate of a few drops every half minute. The butene was collected in flask B which was cooled with a Dry Ice cooling-mixture. Pressure was maintained at atmospheric by passing a very slow stream of nitrogen into the side tube of flask A and out through flask B into a gas bottle.

The 1-butene was distilled under vacuum into an ampoule with a break-seal leaving only a trace of residue in flask B. The ampoule was sealed off and stored in a Dry Ice box for subsequent fractionation. The residue in flask A was treated with water to convert unchanged Grignard reagent to methane and the gas evolved was collected over water in a gas bottle. One hundred cc. of gas, obtained in this way, was diluted to 3 l. with methane.[5]

The 1-butene was condensed in a small distilling-apparatus and divided into three frac-

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[4] Halogen Chemicals, boiling range 69.0–70.5°.

[5] Research Grade methane, 99.6% pure, Phillips Petroleum Co.

tions using the customary procedures for light-hydrocarbon distillation. Amounts, boiling ranges and activities of the three fractions are given in Table I.

Radioactivity balance. Examination of residues and by-products yielded the information given in Table II. Calculations of absolute activity were made on the basis that a thick sample of $BaCO_3$ has measurable activity equivalent to that of 3.6 mg./cm.^{2} without self absorption. Corrections for window and air absorption and for geometry were made following Reid (3).

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SUMMARY

1-Butene of high purity has been prepared in 63% yield from methyl alcohol containing carbon-14. The method and apparatus are described in detail including examination of by-products.

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