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THE SYNTHESIS OF 1-BUTENE[1]

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Introduction

The preparation of 1-butene has been carried out in the following ways: (a) the action of zinc diethyl upon vinyl bromide,[4] (b) the action of zinc dimethyl upon allyl iodide,[5] (c) the catalytic dehydration of 1-butanol over aluminum phosphate,[6] aluminum oxide[6c] zinc chloride[7] and (d) the action of alcoholic potash upon 1-bromobutane.[8] Its formation has also been observed in the dehydration of 2-butanol over zinc chloride[9] and of 2-methyl-2-propanol over aluminum phosphate.[6a] In addition two other methods appear feasible: (e) the action of zinc upon 1,2-dibromobutane in a manner similar to the preparation of 2-pentene,[10] and (f) the action of methylmagnesium iodide upon allyl bromide, similar to the preparation of higher 1-alkenes.[10,11]

To each of the first methods certain objections can be raised, namely: in (a) and (b) the presence of the zinc halide in the reaction mixture is objectionable, since zinc salts are known to cause, at high temperatures, a shifting of double bonds; in (c) the dehydration of the alcohol leads to the production of more than one hydrocarbon; in (d) the yields are poor, due to the formation of an ether and in (e) pure 1,2-dibromobutane is best obtained from bromine and pure 1-butene. It seemed reasonable to assume that the method (f) would yield the purest product, provided the hydrocarbon could be removed from the reaction mixture as soon as formed.

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[1] This paper contains the results of one phase of an investigation on the "Preparation of Pure Typical Hydrocarbons and a Study of Their Behavior When Heated Alone and with Catalysts" listed as Project 14 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] Wurtz, *Ann.*, **152**, 22 (1869).

[5] Wurtz, *Ann.*, **144**, 234 (1867).

[6] (a) Senderens, *Compt. rend.*, **144**, 1110 (1907); (b) *Bull. soc. chim.*, (4) **1**, 689 (1907); (c) Lépingle, *ibid.*, **39**, 741 (1926).

[7] LeBel and Greene, *Compt. rend.*, **89**, 413 (1879).

[8] (a) Lieben and Rossi, *Ann.*, **158**, 164 (1871); (b) Grabowsky and Saizew, *Ann.*, **179**, 330 (1875); (c) Michael and Brunel, *Am. Chem. Jour.*, **41**, 118 (1909).

[9] Ipatiev and Sdzsitovecki, *J. Russ. Phys.-Chem. Soc.*, **39**, 897 (1907).

[10] Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926).

[11] (a) Brooks and Humphrey, THIS JOURNAL, **40**, 822 (1918); (b) Norris and Joubert, *ibid.*, **49**, 873 (1927).

The synthesis of 1-butene from methylmagnesium iodide and allyl bromide takes place according to the reaction

$$CH_2{=}CH{-}CH_2Br + CH_3MgI \longrightarrow CH_2{=}CH{-}CH_2{-}CH_3 + MgIBr$$

In carrying out this operation it was thought best to modify the original procedure[11a] in which the allyl bromide is added slowly to the ethereal solution of the Grignard reagent since first the temperature of the solution is not sufficiently high for a rapid reaction, second the hydrocarbon has a high solubility in the ether from which its separation is more or less difficult, and third the removal of the product as soon as it is formed is desirable in order to reduce to a minimum the possibility of isomeric change. Accordingly as much of the ether as possible was driven out by heating the ethereal solution of the magnesium compound in an oil-bath to 130°, after which the temperature of the bath was dropped to 70° and held there while the allyl bromide was added with constant stirring. The butene was generated immediately at a rate corresponding to the rapidity with which the bromide was added.

The purification of the hydrocarbon required the removal of the ether, allyl bromide and methyl iodide. Considerable amounts of ether were carried by the gas even after cooling to about 5°, while the amounts of the halides were much less. The high solubility of butene in methyl and ethyl alcohols, more especially in the latter, precludes the use of these two substances as wash liquids, although when diluted by water to a strength of about 30% they will remove some ether and alkyl halide. In one experiment 30% methyl alcohol effected a fair removal of these materials. It was found that perchloric acid in water has markedly different solvent powers toward ether and toward butene; for example, a 37% solution dissolves approximately two and one half times its own volume of ether on mixing, while it absorbs only 15% of its volume of gaseous 1-butene. The perchloric acid solution is thus a more satisfactory wash liquid than the dilute alcohol. However, some of the higher boiling impurities pass through and condense out with the butene, the final purification of which may be accomplished by fractional distillation through an efficient column cooled to −15° to −18°. Purification by fractional distillation through a cooled column is preferable to repeated distillations from one flask directly into another. The run-back from the column is at all times fairly large and the separation from higher boiling material is satisfactory.

Experimental

Preparation of 1-Butene.—The Grignard reagent was prepared in the three-necked, 3-liter flask (A, Fig. 1) in the usual manner from 51 g. (2.1 moles) of magnesium turnings, 300 g. (4.0 moles) of absolute ether and 284 g. (2.0 moles) of methyl iodide, b. p. 41.5–0.6° at 744 mm. The contents were agitated by the mercury sealed stirrer B and the ether was refluxed back by the bulb condenser C.[12] Stirring was continued for some time after the iodide had been added and the resulting material allowed to stand overnight in an atmosphere of nitrogen. The next day the liquid was carefully decanted from the unchanged magnesium into a flask similar to A. This was connected to the apparatus, a condenser was attached for down distillation and the flask was heated rapidly in an oil-bath with stirring until the temperature of the bath reached 130°. When the rate with which the ether distilled became slow a stream of nitrogen was passed into the flask,[13] the heating was discontinued and the flask was attached to the absorbing train as shown in Fig. 1. As soon as the bath temperature dropped to 70°, 232 g. (1.92 moles) of allyl bromide, b. p. 69–70° C., [14] was introduced slowly through the dropping funnel D with stirring. The gas, which was evolved at once,[15] passed through the bulb condenser C cooled by water at 5°, next through four glass-stoppered wash bottles E of 200cc. capacity, the first containing 30% methyl alcohol and the other three containing 100 cc. of 37% perchloric acid to remove ether, then through a tower F filled to about three-fourths of its capacity with anhydrous calcium chloride and one-fourth with soda lime and finally into G, surrounded by a Dewar flask filled with a cooling bath below −15°.[16] The butene which condensed out in G was purified by fractional distillation (see Fig. 2).

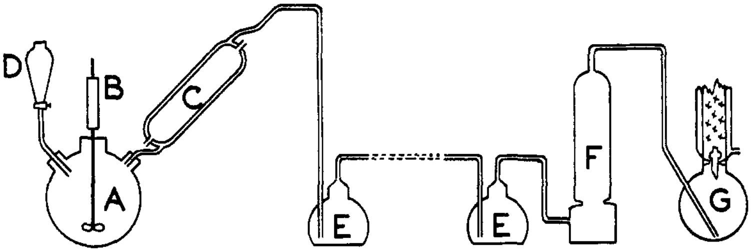

Fig. 1.—Apparatus for preparation and purification of 1-butene; A, reaction flask, 3 liter; B, mercury sealed stirrer; C, bulb condenser; D, dropping funnel; E, four wash bottles; F, drying tower; G, distilling flask, kept at −15 to −25°.

Fractional Distillation of 1-Butene.—As soon as the generation of the hydrocarbon was over, a flow of salt solution at −15 to −17° was started through the jacket H (Fig. 2). G was now warmed by water first at 0 to +5° and later at higher tempera-

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[12] The inner water-containing bulb of the condenser C was 24 cm. long and 7.3 cm. in diameter, and had therefore a condensing surface of 550 sq. cm. This is equivalent to the condensing surface of a Liebig condenser the inner tube of which has an inside diameter of 1.0 cm. and the jacket of which is 175 cm. long. The distance between the inner and outer walls was made small, 3 mm. in fact, in order to have a small gas space. This is desirable when the condenser is used in a gas stream as the loss of gas for obvious reasons is minimized.

[13] After removal of the ether the Grignard reagent is a thick, viscous mass and readily absorbs oxygen and carbon dioxide. An inert atmosphere is desirable.

[14] The allyl bromide was prepared from allyl alcohol (b. p. 80–95°), sodium bromide and sulfuric acid by the method described in "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 15. The bromide was twice fractionally distilled.

[15] An excess of allyl bromide is indicated by immediate cessation of gas evolution.

[16] Suitable cooling baths are alcohol–solid carbon dioxide, ice–60% sulfuric acid and ice–concentrated hydrochloric acid mixtures.

tures. As the butene boiled it refluxed from the fractionating column of 5 × 5 mm. cut-glass rings in the tube I. This column, which was 22 cm. long and 2.5 cm. in diameter, was supported by the hollow glass nipple J.[17] The thermometer K graduated in $^1/_{10}$ degree registered the temperature of the gas at the top of the column. The gas was further purified by passing it through four wash bottles L, one containing 30% methyl alcohol to remove organic halides and three containing 37% perchloric acid to remove ether and methyl alcohol, next through a tower M containing soda lime and calcium chloride and finally into N, similar in construction to G and kept below −15°. The gas was again fractionally distilled from N and sealed off in suitable tubes. When 30% methyl alcohol was used as the wash liquid instead of perchloric acid, the product was distilled between the temperature ranges of −6.6 to −6.3° and −6.8 to −6.5° at 748 mm. in the first and second distillations, respectively. In the experiment in which perchloric acid was the wash liquid the temperature recorded during the first distillation was high due to the fact that the thermometer bulb was so far up in the apparatus that liquid was not condensing upon it. In the second distillation the range was −6.7 to −6.5°. The difference in the character of the residues remaining after these distillations indicates that perchloric acid removes impurities from the butene better than does dilute methyl alcohol. The time taken for the preparation, starting with the heating of the Grignard reagent, was about eighteen hours. This could be shortened considerably by using a more efficient purifying train since a more rapid flow of gas would then be possible. The yield is about 43 g. or 40% of the theoretical. The smallness of the yield may be ascribed in part to the fact that in the interest of purity a considerable amount of butene was discarded at the beginning and at the end of the distillations.

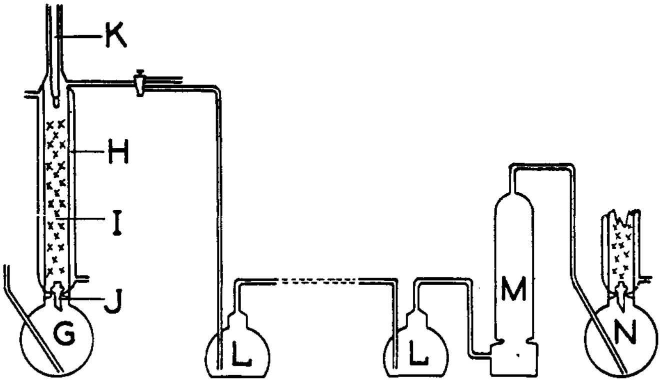

Fig. 2.—Apparatus for distillation of 1-butene; G, distilling flask, 300 cc.; H, jacket, for circulation of brine at −15 to −17°; I, column of cut glass rings; J, hollow glass nipple; K, thermometer, graduated in 1/10°; L, four wash bottles; M, drying tower; N, distilling flask, similar to G.

The absence of 2-butene in the final product is indicated by the purity of the dibromide obtained by the addition of bromine at −5 to −10°. The dibromide was fractionally distilled through a column of cut-glass rings which was 70 cm. long, 2 cm. in diameter, and surrounded on the outside by a packing of mineral wool 5 cm. thick. This column had previously served for the separation of a mixture of 1,2- and 2,3-dibromo-

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[17] Lucas, *Ind. Eng. Chem.*, 19, 680 (1927).

butanes. The dibromide from the synthetic 1-butene distilled almost entirely at 80.5–80.7° under 50.0 mm. and gave no indication that 2,3-dibromobutane was present. Its refractive index, n^{20}_{D}, was 1.5171. These constants were unaffected by subsequent distillation.

Summary

The hydrocarbon, 1-butene, is conveniently and rapidly prepared by adding allyl bromide to methylmagnesium bromide at 70° with stirring. The Grignard reagent should be previously heated in a bath at 130° in order to remove as much ether as possible. Dilute perchloric acid is effective in removing ether from the gas stream.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

EQUILIBRIUM IN THE REACTION $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$[1]

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It has been shown by Sabatier[4] that the hydrogenation of carbon dioxide to produce methane and steam is effected in the presence of catalytic nickel at 200–350°. By employing the free energy equations of Lewis and Randall,[5] it may be calculated that the reverse reaction, $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$, should proceed to the extent of 28.6% at 500° and 1 atmosphere, using a stoichiometric (1 CH_4 : 2 H_2O) mixture. In view of the fact that little data are available on this reverse reaction, and that a determination of the position of equilibrium allows of an independent calculation of the free energy of methane, which is at present based solely on dissociation experiments conducted chiefly at high temperatures (1200–1600°), some further study of the reaction seemed desirable. We have, therefore, carried out both forward and reverse reactions at 500° and have determined the equilibrium position at this temperature. Since the result is in excellent agreement with the value calculated from the Lewis and Randall equations, we have considered that further work was unnecessary. This report deals with the above mentioned measurements.

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[4] Sabatier and Senderens, *Compt. rend.*, 134, 689 (1902).

[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 485, 571, 576.