[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ETHYL GASOLINE CORPORATION]

Hexamethylethane

BY DONAL T. FLOOD AND GEORGE CALINGAERT

The synthesis of paraffin hydrocarbons by condensation of a Grignard reagent with an alkyl halide has been used for years in this Laboratory. Two examples of this type of synthesis have been published.[1] Among several other hydrocarbons, hexamethylethane was also prepared by this method, but the directions for its synthesis have never been published. In view of the renewed interest in this hydrocarbon,[2] a short investigation was carried out to determine a satisfactory set of conditions for its preparation. A brief study of several of the variables involved disclosed the following facts.

(a) The hydrocarbon can be prepared by the interaction of *t*-butyl chloride with *t*-butylmagnesium chloride. The course of the reaction is markedly affected by the conditions, particularly of concentration, under which it is carried out. In particular, conditions which give the highest yields of Grignard reagent give very poor yields of hexamethylethane. The addition of salts such as mercuric chloride does not appear to increase the yield.

(b) The highest yields are obtained by a modification of the conventional procedure for the preparation of a Grignard solution, *i. e.*, by adding magnesium directly to the solution of the halide in ether instead of observing the reverse procedure.

(c) The chief products obtained by both of the above methods are isobutene and isobutane, and if the temperature of the reaction mixture be kept below that of refluxing (*e. g.*, at 10–15°) the accumulation of isobutene in the ether solution leads to the formation of appreciable quantities of diisobutylene and higher polymers.

(d) There is formed in addition a small amount of a saturated hydrocarbon which has been tentatively identified as 2,2,4-trimethylpentane.

The yields reported below could no doubt be improved by a systematic study, bearing in mind the points stated above. In its present state the chief advantages of the method are that the synthesis is a one-step reaction and uses only inexpensive materials.

Preparation

In a three-liter three-necked flask, fitted with a reflux condenser and a mechanical stirrer, are placed 740 g. (8 moles) of *t*-butyl chloride, 1000 cc. of dry ether and a few flakes of iodine. About 4–6 g. of thin magnesium turnings, crushed into a ball in the palm of the hand (a rubber glove may be worn to prevent the introduction of moisture) is introduced through the free neck of the flask which is then closed with a rubber stopper. The reaction usually starts spontaneously after stirring for a short time, or it may be induced by heating the flask so that the ether refluxes gently. The magnesium dissolves with vigorous refluxing and the separation of a white suspension in the reaction mixture. The remainder of 97 g. (4 moles) of magnesium turnings is added in quantities of about 3–4 g. (*i. e.*, sufficient to form a convenient sized ball) and at such a rate that the mixture is kept steadily refluxing. The addition is completed in about six hours. The mixture is heated to maintain steady refluxing for about one hour and is left to stand overnight. It has then turned to a solid white cake, which is hydrolyzed with water, followed by dilute hydrochloric acid. The ether layer is separated, washed with a 5% sodium bicarbonate solution and combined with an ether washing of the aqueous layer similarly treated. After drying by shaking with crushed calcium chloride, the ether is removed by fairly rapid distillation through an efficient column until the thermometer reads 60°. The unsaturated hydrocarbons present in the residue (which is dissolved in a minimum amount of ether) are brominated with bromide–bromate solution, and the small excess of bromine is removed with potassium iodide followed by sodium thiosulfate. After washing and drying, the product is distilled rapidly (see note below) through a short column until the thermometer reads 120° (residue about 23 g.). A piece of sodium and a piece of potassium are added to the liquid in the receiver, which is then distilled through a Widmer column, fitted with a dephlegmator. When most of the ether has distilled off, the residue is left boiling, under reflux from the column, until the molten alloy shows an untarnished surface. Fractionation is then continued.

In a typical preparation the following fractions were collected at 748 mm.: (1) b. p. 60–103°, 0.5 g.; (2) b. p. 103–104°, 1.5 g.; (3) 104–105.2°, 39 g.; crystalline residue, 7 g. (recovered by subliming on a small water-cooled test-tube inserted in the flask); total yield 47.5 g. (10%).

The melting point of hexamethylethane appears to be very susceptible to traces of impurity. By recrystallizing several times from ether, a product of m. p. 100.7–101.4° was obtained.

Note.—Whenever pure or nearly pure hexamethylethane is distilled, it is necessary to heat electrically the delivery tube of the column and to insert between the column and the Liebig condenser a receiver cooled in running water. The solid condenses at that point and does not clog the condenser.

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(1) Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1487 (1929).

(2) Whitmore, Stehman and Herndon, *ibid.*, **55**, 3807 (1933).

Summary

Hexamethylethane can be prepared readily in 10% yield by adding magnesium to a refluxing ether solution of *t*-butyl chloride.

DETROIT, MICH. RECEIVED FEBRUARY 8, 1934

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. V. The Addition of Hydrogen Bromide to Butene-1

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Introduction

It has been stressed in previous communications from this Laboratory[1] that the direction of addition of hydrogen bromide to some unsaturated compounds is controlled by the peroxide content of the material. Of particular importance was the observation that the product of the reaction of hydrogen bromide and propylene in the presence of peroxides (benzoyl peroxide, ascaridole, etc.) was normal propyl bromide, a product never heretofore obtained under any experimental conditions. Under peroxide-free conditions isopropyl bromide was obtained in quantitative yields. The latter product was therefore called by us the normal product and the normal propyl bromide was considered the abnormal (peroxide catalyzed) product.

The necessity of further extension of these studies in the aliphatic field is self-evident. This paper records our observations on the addition of hydrogen bromide to butene-1.

Previous Work.—It was surprising to the authors to find so little in the literature about the addition of halogen acids to butene-1. Except for the recent work of Lucas and collaborators,[2] the only other observations recorded are those of Saytzeff[3] and of Lieben and Rossi.[4] The early investigators are in accord that the addition of hydrogen iodide to butene-1 leads to the formation of secondary butyl iodide. Mental reservation regarding the value of these results is in order, however, for undoubtedly these investigators used mixtures of butene-1 and butene-2 of various compositions.

Lucas and his collaborators, in a search for a method of analysis of mixtures of butene-1 and butene-2, investigated the addition of hydrogen bromide to butene-1 in glacial acetic acid. In view of the fact, however, that secondary butyl bromide was the only product, the reaction could not be employed as an analytical method, for both isomeric butenes yielded the same product.

Factors Influencing the Addition of Hydrogen Bromide to Butene-1.—Our results on the directed addition of hydrogen bromide to butene-1 indicate that this compound may be added to the list of compounds previously described in which the addition of hydrogen bromide is profoundly affected by the peroxide content of the material. Thus Table I proves quite conclusively that the addition of hydrogen bromide to butene-1 in air leads to practically quantitative yields of the secondary butyl bromide. The same results are obtained in solvents such as glacial acetic acid, nitrobenzene, dilute acetic acid, etc. The same product results also if the additions are carried out *in "vacuo"*[5] with samples of butene-1 from which air has been excluded rigorously during the preparation of the material. The effect of antioxidants of the type of diphenylamine and thiocresol is also to produce secondary butyl bromide.

The fact that in the presence of air and under antioxidant conditions the same product is obtained, can be correlated on the basis that butene-1 either is not sensitive to the peroxide effect, or the total amounts of peroxides present in butene-1 are very small. The correctness of this latter assumption can be demonstrated most readily by the ordinary peroxide test,[1] which shows that if air or oxygen is allowed to bubble through butene-1 at −80° for two hours, the material still fails to give any appreciable per-

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[1] Kharasch and collaborators, THIS JOURNAL, **55**, 2468, 2521, 2531 (1933); **56**, 712 (1934).

[2] Lucas, Dillon and Young, *ibid.*, **52**, 1949 (1930).

[3] Saytzeff, *J. prakt. Chem.*, **111**, 88 (1871).

[4] Lieben and Rossi, *Ann.*, **158**, 164 (1871).

[5] By "vacuo" we imply that the reagents were held at liquid air temperature while the residual gases in the bomb tubes were removed before the tubes were sealed off. Naturally as the tubes containing the addition mixture were sealed and allowed to come to room temperature, there is considerable pressure developed.