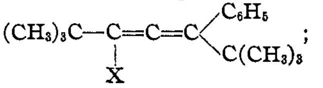
experiment described above. Hence the tetramethylethylene bromide apparently was not concerned in the reaction.

Action of Other Metals on the Bromide.—Silver and copper had no effect on solutions of the bromide. Lithium reacted with an ether solution of the bromide to give the same products that were obtained by the action of sodium amalgam. Reduction of the bromide with zinc dust in alcohol also gave the same mixture of hydrocarbons.

Properties of the Hydrocarbons $C_{34}H_{46}$.—Neither the pure hydrocarbon (m. p. 147–148°) nor the mixture (m. p. 115–125°) showed any sign of cleavage with alkali metals. Neither hydrocarbon could be converted to the other isomer by the action of heat. Neither hydrocarbon showed the property of absorbing oxygen. Both products showed signs of slow oxidation when heated in boiling xylene in the air, but no definite products were isolated. Attempts to ozonize these hydrocarbons gave only tarry products similar to the products previously obtained by the ozonization of other rearranged polyynes.

Summary

1. The Grignard reagent prepared from phenyl-*t*-butyl-*t*-butylethynylbromomethane reacts with water, methyl chlorocarbonate and carbon dioxide to give allene derivatives of the type



$$(CH_3)_3C—\underset{\displaystyle X}{\underset{|}{C}}=C=C\begin{cases} C_6H_5 \\ C(CH_3)_3 \end{cases};$$

where X represents the group introduced into the organic molecule by the reaction.

2. Phenyl-*t*-butyl-*t*-butylethynylbromo-methane reacts with 40% sodium amalgam but does not give a stable sodium alkyl. Instead some of the bromide is reduced to the allene and some of it is coupled to give two isomeric hydrocarbons of the composition $C_{34}H_{46}$ which are thought to be diallenic hydrocarbons.

URBANA, ILLINOIS RECEIVED AUGUST 26, 1935

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

The Action of Sulfuric Acid on Butanol-2[1]

BY NATHAN L. DRAKE AND FLETCHER P. VEITCH, JR.

In continuation of our study of the conversion of alcohols to higher olefins by acid catalysts, we have examined the effect of sulfuric acid on butanol-2.

When treated with 75% sulfuric acid under conditions which were found to be most favorable for converting methylisopropylcarbinol into a mixture of decenes,[2] butanol-2 yielded no octene. It was likewise impossible to obtain appreciable yields of octene by use, at atmospheric pressure, of any concentration of acid from 50 to 100%, although time of heating was varied from twenty minutes to forty-eight hours, and reaction temperature from 25 to 100°. Acid of higher than 90% concentration caused the formation of a quantity of high boiling material, probably a mixture of substances of the composition $(C_4H_8)_x$ where x is greater than 2.

The failure to obtain any octene in the experiments cited is unquestionably due to the fact that at the temperatures investigated the formation of butene takes place more readily than does its polymerization, with the consequence that the butene produced escapes before it has had the opportunity to polymerize.

It seemed logical, therefore, to study the effect of operating in a closed system, and preliminary experiments demonstrated that if the butene formed was not allowed to escape, but held in contact with the acid, slow formation of octene took place. Various conditions for effecting the polymerization under pressure were studied, and it was found that with our particular apparatus (see experimental part) the best yield of octene was obtained by the action of 75% sulfuric acid at 80° for forty-eight hours.

The formation of higher polymers from the dimer takes place very readily; distillation of the octene in the presence of a very small quantity of acid results in the formation of substances of higher molecular weight.

A quantity (2.5 kg.) of product having a boiling range which would include any octenes formed, (110–125°) was prepared and subjected to fractional distillation, from which it became apparent that there were at least two chemical individuals present.

Ozonolysis of several fractions of nearly constant refractive index yielded acetaldehyde and methyl *s*-butyl ketone. From these facts it became apparent that the octene present in the fractions ozonized was 3,4-dimethylhexene-2.

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[1] From the Ph.D. dissertation of Fletcher P. Veitch, Jr.

[2] Drake, Kline and Rose, THIS JOURNAL, **56**, 2076 (1934).

When a quantity of a higher boiling fraction was subjected to ozonolysis, it was found that only a very small quantity of unsaturated material was present. This unsaturated material (3,4-dimethylhexene-2) was removed by ozonolysis, and the resulting substance subjected to fractional distillation. The physical properties of the product indicated that it was di-*s*-butyl ether. Further investigation left no doubt as to the identity of the ether.

Exploratory ozonolyses of various other fractions failed to yield any evidence of the presence of any unsaturated substance other than 3,4-dimethylhexene-2.

Experimental

Apparatus and Method.—A lead-lined, steel autoclave of about four liters capacity was used. The desired temperature was maintained by means of an electrically heated water jacket controlled by a thermostat. Because of mechanical difficulties it was impossible to stir the charge. The temperature of the reaction mixture was determined by means of a thermometer located in a well which extended some distance below the surface of the charge.

Sixteen hundred and sixty grams of 75% sulfuric acid and 800 g. of *s*-butyl alcohol were heated at 80° for forty-eight hours. These conditions had been found to give the best yield of product of the desired boiling range. The autoclave was then allowed to cool, opened and the hydrocarbon layer siphoned off. A considerable quantity of butene escaped when the autoclave was opened and during the purification of the product. After treatment to remove the acid and water the product was distilled through a short column and the fraction from 110 to 125° (188 g.) collected for investigation as described below. An additional 100 g. of distillate boiling above 125° was also collected.

Purification and Fractionation of Reaction Products.—Two and a half kilograms of material (boiling range 110–125°), prepared from 6 kg. of *s*-butyl alcohol, was refluxed over sodium for fifty hours; the mixture was distilled from the sodium and 2 kg. of distillate was collected between 116 and 125°. A careful fractionation[3] of this mixture yielded 32 fractions of approximately 50 ml. each and a residue of 300 ml. The total volumes, b. p. (barometer varied from 751 mm. to 762 mm.) and $n^{25}\text{D}$ were as follows: Nos. 1–6, 355 ml., to 114.5°, 1.4065–1.4145; Nos. 7–14, 468 ml., to 116.6°, 1.4152 to 1.4156; Nos. 15–23, 560 ml., to 121.6°, 1.4142 to 1.4017; Nos. 24–32, 496 ml., to 122.5°, 1.3992–1.3931; residue, 300 ml., above 122.5°, 1.4118.

Ozonolysis of Fractions 7–14.—These fractions were ozonized in portions of 56 g. each dissolved in 180 ml. of ethyl acetate. The ozonizer furnished ozone at the rate of 0.03 to 0.04 mole/hr. when oxygen was supplied at the rate of 16.3 liters/hour; the temperature of the olefin was maintained between −15 and −25°. Only the amount of ozone theoretically required was supplied. The ozonide was decomposed[4] without removal of the solvent. The water layer from the decomposed ozonide gave a strong aldehyde reaction with fuchsin reagent, but a negative test for formaldehyde using resorcinol. The presence of acetaldehyde was demonstrated by the formation of a *p*-nitrophenylhydrazone which showed no depression of melting point when mixed with the *p*-nitrophenylhydrazone of acetaldehyde. The ethyl acetate layer was dried over anhydrous sodium sulfate and fractionated through a 50-cm. Widmer column to remove the ethyl acetate. The residue (250 ml.) was then subjected to careful fractionation in a Podbielniak[5] column. A considerable quantity of acetic acid was found in all fractions of the distillate, but after the removal of this acid by treatment with alkali, approximately 100 g. of a substance (A) boiling at 116.2° at 758 mm. was obtained.

Identification of A as Methyl *s*-Butyl Ketone.—(A) gave no color with Schiff's reagent, but gave a positive haloform reaction when tested in dioxane solution.[6] It was apparent, therefore, that (A) was a methyl ketone. The physical properties of (A) correspond very closely with those recorded[7] for methyl *s*-butyl ketone, and differ considerably from those of the other possible six carbon methyl ketones: for (A) b. p. 116.2°, d^{25} 0.812, $n^{18}\text{D}$ 1.4000; for methyl *s*-butyl ketone b. p. 117.8, d^{20} 0.815, $n^{20}\text{D}$ 1.3990.

Product (A) yielded a 2,4-dinitrophenylhydrazone which melted at 71.2°. No depression of melting point was observed when this product was melted mixed with the 2,4-dinitrophenylhydrazone prepared from pure methyl *s*-butyl ketone obtained synthetically via an acetoacetic ester synthesis.

Conversion of (A) to Methylethylacetic Acid.—In order to confirm our belief in the identity of (A) and methyl *s*-butyl ketone, (A) was degraded in the usual way by alkaline hypobromite to an acid whose amide agreed in melting point (110.9°) with that described for the amide of methylethylacetic acid, and whose *p*-phenylphenacyl ester possessed the composition required; 10 g. of (A) yielded 7 g. of acid.

The 2,4-Dinitrophenylhydrazone of (A).—This product which is not described in the literature melts at 71.2°.

Anal. Calcd. for $C_{12}H_{16}N_4O_4$: C, 51.42; H, 5.71. Found: C, 51.31, 51.56; H, 5.60, 5.86.

The *p*-Phenylphenacyl Ester of Methylethylacetic Acid.—The ester, prepared in the usual way, melts at 70.6°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.03; H, 6.75. Found: C, 76.76, 76.98; H, 6.93, 6.83.

Purification of Fractions 24–31.—Five hundred milliliters of material representing fractions 24–31 inclusive was ozonized until no more ozone was absorbed. After decomposition of the ozonide the water-insoluble layer was dried and distilled; 435 ml. was distilled and 395 ml. of distillate (B) whose $n^{25}\text{D}$ varied from 1.3927 to 1.3930 was

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[3] We wish to express our thanks to S. Schicktanz and the others of the Petroleum Research Section of the Bureau of Standards for their valuable assistance in fractionating this mixture; see Schicktanz [*Bur. Standards J. Research*, **11**, 89 (1933)] for a description of the still used; *cf.* also *ibid.*, **7**, 851 (1931).

[4] Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

[5] Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 119 (1933).

[6] Fuson, *Chem. Rev.*, **15**, 775 (1934).

[7] "Int. Crit. Tables," Vol. I, pp. 203, 276; Beilstein, 4th Ed. Julius Springer, Berlin, 1918, Vol. I, p. 694.

obtained. The density of the distillate was 0.759 at 25° and its boiling point 121° at 760 mm.

Anal. Calcd. for $C_8H_{18}O$: C, 73.84; H, 13.84; mol. wt. 130. Found: C, 73.86; H, 13.84; mol. wt. 126.

From the analytical data and the fact that (B) did not react with sodium, it seemed likely that (B) was a dibutyl ether.

Conversion of (B) to *s*-Butyl Bromide.—Forty grams of (B) was saturated with hydrogen bromide and heated under reflux for three hours. The product was washed with water and saturated sodium bicarbonate solution, dried and distilled; 68.5 g. of a bromide with the following physical properties was obtained (81.2%): b. p. 90–91° at 757 mm.; $n^{25}\text{D}$ 1.4341; d^{25} 1.250. From these physical constants[8] it is apparent that the bromide formed is probably *s*-butyl bromide.[8]

This conclusion is strengthened by a comparison of densities and boiling points of the three known di-butyl ethers with those of (B).[9]

Preparation of the 3,5-Dinitrobenzoate of *s*-Butyl Alcohol from (B).—One milliliter of (B) was mixed with 0.5 g. of 3,5-dinitrobenzoyl chloride and 0.15 g. of anhydrous zinc chloride and refluxed for one hour. After purification 0.1 g. of ester melting at 75.5° was obtained. This dinitrobenzoate was shown by the method of mixed melting points to be identical with the ester obtained directly from *s*-butyl alcohol and 3,5-dinitrobenzoyl chloride.

Discussion

The theory of the mechanism of the polymerization of olefins by acid catalysts suggested by Whitmore[10] would predict the formation of 3,4-dimethylhexene-2 and 3,4-dimethylhexene-1 from *s*-butyl alcohol under the conditions studied, with the latter olefin present in smaller quantity than the former. We have been unable to detect the presence of formaldehyde after ozonization of any of the fractions of the reaction product, and must conclude that 3,4-dimethylhexene-1 is not formed under the condition studied.

The theory of the mechanism of polymerization of olefins suggested by Kline[11] would likewise lead to the prediction of two products only one of which was found. In this case, however, the product expected in greatest abundance, *viz.*, 4,5-dimethylhexene-2 is not the one actually produced.

Summary

1. The formation of 3,4-dimethylhexene-2 and di-*s*-butyl ether by the action of 75% sulfuric acid on *s*-butyl alcohol at 80° under pressure has been demonstrated.

2. The theory of the mechanism of polymerization by acids suggested by Whitmore explains the observed facts better than that of Kline.

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[8] "Int. Crit. Tables," Vol. I, pp. 188, 276, 277.

[9] "Int. Crit. Tables," Vol. I, p. 204.

[10] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

[11] Kline and Drake, *Bur. Standards J. Research*, **13**, 705 (1934).

COLLEGE PARK, MD. RECEIVED SEPTEMBER 27, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF ST. JOHN'S UNIVERSITY AND WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Studies in the Synthesis of Certain Alkyl and Aryl Cryptophenols[1]

BY MARTIN E. MCGREAL AND JOSEPH B. NIEDERL

Introduction

Since *p*-*t*-octylphenol (*p*-(2,2,4,4-tetramethyl)-butylphenol)[2] has a rather high phenol coefficient (150), it was one of the objects of this investigation to prepare and study the yet unreported *p*-*t*-hexyl and *p*-*t*-heptylphenols. These phenols were prepared by condensing dimethylisopropylcarbinol (I) (b. p. 116–120°) and dimethyl-*n*-butylcarbinol (II) (b. p. 130–130.5°) with phenol in the presence of zinc chloride, utilizing the method of Liebmann, Fischer and Gruetzner.[3]

The condensation of diisobutyl alcohol (2,2,4-trimethylpentanol-4) (b. p. 145–149°) with phenol under identical reaction conditions, however, did not yield the expected *p*-*t*-octylphenol, but *p*-*t*-butylphenol as the main reaction product.[4]

The second object was to investigate the applicability of these condensations to primary, secondary and tertiary aromatic alcohols, and the following carbinols were therefore studied: phenyl (VI), phenylmethyl (VII), benzyl (VII), phenylmethylethyl (VIII) and phenylmethylisopropyl (IX). The last was prepared by the action of isopropylmagnesium bromide on acetophenone.[5]

The condensation products with phenol (VIII

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[1] Presented before the Division of Organic Chemistry at the New York meeting of the American Chemical Society, April, 1935.

[2] J. B. Niederl, U. S. Patent 2,008,337 (1935); British Patent 431,487 (1935); Niederl, Natelson and Beekman, THIS JOURNAL, **55**, 2571 (1933).

[3] (a) A. Liebmann, *Ber.*, **14**, 1842 (1881); (b) Fischer and Gruetzner, *ibid.*, **26**, 1646 (1893).

[4] P. W. Hodges, M.Sc. Thesis, New York University, 1935.

[5] B. Gutchin, M.Sc. Thesis, New York University, 1935.