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SOME DERIVATIVES OF *n*-HEPTANE

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Introduction

Following the line of reasoning previously employed in the case of 2-pentene and hydrogen bromide[1] it would be predicted that the addition of hydrogen bromide to 3-heptene should yield 3-bromoheptane largely, whereas on the basis of an alternately polarized carbon chain the product should be 4-bromoheptane. The test of this question necessitated first the preparation of these two compounds and they have been found to be so similar in physical properties that unfortunately no differentiation could be made between them. It was not considered profitable to make use of any addition reaction which would necessitate subjecting the products to a subsequent reaction, such for example as the addition of sulfuric acid and the hydrolysis of the resulting hydrogen alkyl sulfate to the alcohols, since this would necessitate a separate and complete study of each of the reactions. In the accompanying table are given the physical constants of pairs of isomers which might be of possible use in solving the problem.

TABLE I

PHYSICAL CONSTANTS

Compound	B. p., °C. (corr.)	M. p., °C.	Density, d_4^{25}	Refractive Index n_D^{20}	n_D^{25}
3-heptanol	152.7–154 (745)	...	0.8159	1.4201	1.4175
4-heptanol	153.4–154.3 (745)	−41.5 to −37.2	.8175	1.4199	1.4173
3-chloroheptane	143.4–144.4 (751)	...	...	1.4237	....
4-chloroheptane	143.1–144.4 (751)	...	...	1.4237	....
3-bromoheptane	84.5–85.5 (74)	...	...	1.4507	....
4-bromoheptane	84.0–85.5 (72–73)	...	...	1.4506	....

The compounds were slowly fractionated from flasks with attached side arms of the Eastman type until the boiling range was that indicated and the refractive index, taken with an Abbé refractometer, suffered no further change. The heating curves were obtained by allowing each substance, surrounded by a carbon dioxide–alcohol bath in a Dewar flask, to warm slowly while agitation was carried on. Temperatures read by means of a thermocouple were plotted against time. In only one case, 4-heptanol, was a freezing point value obtained. The other substances formed glasses which, even when cooled with liquid air over a period of several days, failed to crystallize.

The closeness with which the pairs of isomers approximate each other as far as the boiling points and refractive indices are concerned indicate that

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[1] Lucas and Moyse, THIS JOURNAL, **47**, 1459 (1925).

the 3- and 4-positions in *n*-heptane are practically equivalent, a condition which renders the analysis of mixtures of isomers difficult. It was hoped that the melting points would be quite dissimilar since the 3-derivatives are the less symmetrical and should on that account possess lower melting points. The failure to obtain other than glasses with all but the 4-heptanol, and the four degree range of the latter may point to the presence of impurities in the compounds. If small amounts of impurities prevent crystallization, the prospect of crystallizing a mixture of any of the above pairs of heptyl derivatives would appear to be remote. The conversion of the isomeric halides to solid compounds and the analysis of the resulting mixture through separation of the solids does not appear feasible since the quantitative conversion of secondary halides to solid compounds is a difficult matter, due to the ease with which the unsaturated hydrocarbon is produced. This was found to be the case when they were allowed to react with the silver salt of 3,5-dinitrobenzoic acid.

The synthesis of the two alcohols by means of magnesium alkyl halides and ethyl formate led to the observation that only symmetrical disubstituted methanols can be obtained by this means. This conclusion could almost be predicted from the observation that a two-fold excess of ethyl formate over the magnesium alkyl halide is necessary in preparing aldehydes.[2] In the attempted synthesis of 3-heptanol the ethyl formate was allowed to react first with ethyl magnesium bromide and then with butyl magnesium bromide. The products of the reaction were diethylmethanol and dibutylmethanol, with hardly a trace of the desired ethylbutylmethanol.

Experimental

Preparation of 4-Heptanol.—This alcohol was prepared in a 63% yield by using 370 g. (3 moles) of *n*-propyl bromide[3] (b. p. 68.2–69.2°), 72 g. (3.1 moles) of magnesium turnings (Eastman), 110 g. (1.5 moles) of ethyl formate (distilling at 52.0–53.4° from phosphorus pentoxide) and 650 g. (9 moles) of anhydrous ether. After two fractionations at 745 mm. pressure, the alcohol distilled at 153.4–154.4° (corr.) and had the following constants:[4] m. p. −37.2 to −41.5°; d_4^{25} = 0.8175; n_D^{20} = 1.4199; n_D^{25} = 1.4173.

Preparation of 3-Heptanol.—The attempted synthesis of this alcohol from 109 g. (1 mole) of ethyl bromide, 54 g. (2.24 moles) of magnesium, 74.1 g. (1 mole) of ethyl formate, 184 g. (1 mole) of *n*-butyl iodide and 444 g. (6.0 mole) of ether in accordance with the following reactions

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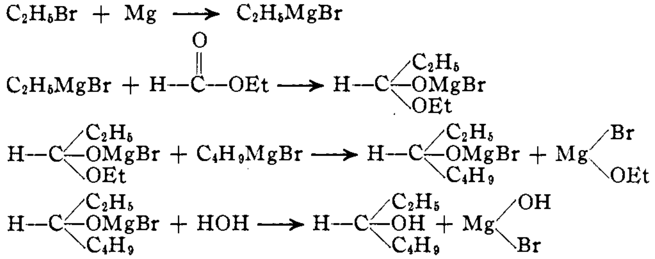
[2] Gattermann and Maffezzoli, *Ber.*, **36**, 4152 (1903); Williams, *J. Chem. Soc.*, **89**, 273 (1906).

[3] Prepared in 76% yield from *n*-propyl alcohol (Eastman's, b. p. 96–98°), sodium bromide and concentrated sulfuric acid, similar to the preparation of butyl bromide, "Organic Syntheses," Vol. I, John Wiley and Sons, Inc., New York, **1921**.

[4] Values previously given are: b. p. 149–150°, Kurtz, *Ann.*, **161**, 212 (1872); 154–155°, Willcox and Brunel, THIS JOURNAL, **38**, 1838 (1916); 155°, Brunel, *ibid.*, **45**, 1338 (1923); d_4^{25} = 0.8129 (B); d_{25}^{25} = 0.814 (K); n_D^{25} = 1.4178 (B).



$$C_2H_5Br + Mg \longrightarrow C_2H_5MgBr$$

$$C_2H_5MgBr + H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OEt \longrightarrow H{-}C\begin{array}{l}{\diagup}C_2H_5\\{-}OMgBr\\{\diagdown}OEt\end{array}$$

$$H{-}C\begin{array}{l}{\diagup}C_2H_5\\{-}OMgBr\\{\diagdown}OEt\end{array} + C_4H_9MgBr \longrightarrow H{-}C\begin{array}{l}{\diagup}C_2H_5\\{-}OMgBr\\{\diagdown}C_4H_9\end{array} + Mg\begin{array}{l}{\diagup}Br\\{\diagdown}OEt\end{array}$$

$$H{-}C\begin{array}{l}{\diagup}C_2H_5\\{-}OMgBr\\{\diagdown}C_4H_9\end{array} + HOH \longrightarrow H{-}C\begin{array}{l}{\diagup}C_2H_5\\{-}OH\\{\diagdown}C_4H_9\end{array} + Mg\begin{array}{l}{\diagup}OH\\{\diagdown}Br\end{array}$$

gave, instead of the expected alcohol, a mixture of diethylmethanol (3-pentanol) and dibutylmethanol (5-nonanol). In order to avoid an excess of the Grignard reagent the ethereal solution of the ethylmagnesium bromide was added to the ethyl formate and then the butylmagnesium bromide added to the resulting product. Two fractional distillations of the final product gave no 3-heptanol but yielded instead 27.4 g. (0.311 mole) of impure 3-pentanol, b. p. 105–120°, and 49.5 g. (0.345 mole) of impure 5-nonanol, b. p. 76–80.6° at 10 mm., corresponding to yields of 62 and 69%, respectively, calculated on the basis of separate reactions. Some pure 5-nonanol was prepared from ethyl formate and *n*-butylmagnesium bromide and was found to distil at 77–79.5° under a pressure of 10 mm.[5]

The desired alcohol was obtained in 40% yield from 155 g. (1.1 moles) of butyl bromide, b. p. 99.1–100°, 27.5 g. (1.1 moles) of magnesium turnings (Eastman), 65.6 g. (1.1 moles) of propionic aldehyde,[6] b. p. 45.5–50.5°, and 500 g. (6.8 moles) of ether. After three fractionations there was obtained a total of 53 g. of product (40% yield) having the following characteristics: b. p. = 152.3–156° (corr.) at 745 mm.; d_4^{25} = 0.8159; n_D^{20} = 1.4197; n_D^{25} = 1.4185. When this was still further purified by subsequent distillations the properties were changed as follows:[7] b. p. = 152.7–154° (corr.) at 745 mm. and n_D^{20} = 1.4201.

Preparation of the Heptyl Halides.[8]—The 3-chloro- and 4-chloroheptanes were prepared from the corresponding alcohols by the method of Norris and Taylor[9] in yields of 30 and 35%, respectively, and the bromo derivatives were obtained by heating each alcohol with four times the calculated quantity of hydrobromic acid (sp. gr. = 1.49) under a reflux cooler for one and one-half hours and then distilling the bromide. The yields were 30 and 40%, respectively. In each case the halide, after washing with cold, concd., sulfuric acid and water, was dried with anhydrous potassium carbonate, first by shaking with a small amount and removing the heavier aqueous phase which developed, and then by letting it stand with an additional amount of the solid. Since the isomeric chlorides and bromides have almost identical properties, and on that account cannot be easily distinguished, the preparation of 3-heptene and its reaction with a hydrogen halide was not attempted.

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[5] Malengreau, *Chem. Cent.*, **1907**, I, 1398, states that 5-nonanol distils at 193° under a pressure of 766 mm.

[6] Obtained in 30% yield by the oxidation of *n*-propyl alcohol with sodium dichromate and sulfuric acid, drying the product with potassium carbonate and fractionating three times.

[7] Blaise and Picard, *Ann. chim. phys.*, [8] **26**, 287 (1912), report the boiling point as 156.5–157°, and Pickard and Kenyon, *J. Chem. Soc.*, **103**, 1943 (1913), as 150–2°.

[8] Subsequent to the completion of this work it has been noted that the chloride and bromide of 4-heptanol have been prepared by Mathus and Gibon, *Bull. soc. chim. Belg.*, **34,** 303 (1925).

[9] Norris and Taylor, THIS JOURNAL, **46,** 753 (1924).

Summary

Some physical properties of the pairs of isomers, 3- and 4-heptanol, 3- and 4-chloroheptane and 3- and 4-bromoheptane have been determined. The boiling points and refractive indices of any pair are very similar, while of only one substance, 4-heptanol, could a freezing point be obtained. The reaction of ethyl formate with butyl magnesium bromide and ethylmagnesium bromide gave 2-pentanol and 4-nonanol but no 3-heptanol.

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A METHOD FOR THE QUANTITATIVE ANALYSIS OF LEAD IN ORGANIC COMPOUNDS

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In connection with studies on organolead compounds a need was felt for a convenient method for the quantitative estimation of total lead in compounds having an aryl group attached directly to lead. None of the present methods was found satisfactory for our purposes. The method described here consists essentially in the decomposition of the sample by sulfuric and nitric acids, and estimation as lead sulfate. It has been used successfully by different workers in this Laboratory for the analysis of various aryl and aryl-alkyl lead compounds.

Polis[1] analyzed his organolead compounds, as lead sulfate, after decomposition by concentrated sulfuric acid and oxidation by potassium permanganate. Grüttner and Krause[2] decomposed their compounds with a 30% solution of bromine in carbon tetrachloride, and estimated the lead as lead bromide. They also used the Carius method of decomposition for volatile compounds. Calingaert[3] modified the method of decomposition by bromine, and obtained highly satisfactory results with *alkyl* lead compounds. This method, with our compounds, has not given acceptable analyses, very probably because of the greater firmness of attachment of *aryl* groups to lead.[4] Treadwell and Hall[5] recommend decomposition in a crucible by concentrated sulfuric acid and weighing as lead sulfate. We have not obtained consistent results by this method,

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[1] Polis, *Ber.*, **19**, 1024 (1886); **20**, 718 (1887).

[2] Grüttner and Krause, *Ber.*, **49**, 1125 (1916).

[3] Calingaert, *Chem. Reviews*, **2**, 43 (1925).

[4] Dr. Calingaert has found that the aryl lead compounds submitted by us to him for a comparative rating of their antiknock effectiveness can be analyzed satisfactorily by heating with concentrated nitric acid subsequent to treatment with bromine in carbon tetrachloride.

[5] Treadwell and Hall, "Analytical Chemistry" (5th English edition), John Wiley and Sons, Inc., New York, 1919, Vol. II, p. 175.