NOTE

The Decomposition of Methyl-2-hexanol-2.—Recently, Edgar, Calingaert and Marker[1] have described the preparation of methyl-2-hexanol-2. The olefin formed by slow distillation of this tertiary alcohol with a trace of iodine was stated to be methyl-2-hexene-2, but the isomeric methyl-2-hexene-1 may also have been present. Hydrogenation of either of these heptenes would produce 2-methylhexane, and since this was the desired product no study was directed to identify the olefins which may have been produced.

In 1927 we studied this problem and obtained evidence to show that a single olefin, presumably methyl-2-hexene-2 (later called "Heptene-A"), was formed when the alcohol was refluxed without catalyst for several hours. This decomposition always occurs to a small extent during distillation at atmospheric pressure (139–141°). Apparently, methyl-2-hexanol-2 does not undergo scission into "acetone + butane" or into "methyl butyl ketone + methane," since no ketones could be isolated from the distillate. This type of scission is known to occur in similar cases at more elevated temperatures.[2] At 58–60° and 20 mm., methyl-2-hexanol-2 may be distilled repeatedly without decomposition. When purified in this way the index of refraction was n_D^{20} 1.4187.

With a small amount of iodine as catalyst, as in the work of Edgar, Calingaert and Marker, the extent of the dehydration was found to be much greater and the nature of the "Heptene-B" thus produced differed from Heptene-A. This difference displayed itself in the refractive index and in the properties of the respective heptene dibromides. Both heptenes boiled at 92–95°.

The index of refraction values for Heptene-B were: 18.5°, 1.4098; 19.0°, 1.4091; 20.5°, 1.4088; 23.5°, 1.4054. The corresponding values for Heptene-A at 17.5 and 20.5° were 1.4049 and 1.4040, respectively. This difference is certainly large enough to be significant. The density of Heptene-B at 20° was found to be 0.7089.

The dibromides were prepared by adding the calculated quantity of pure bromine drop by drop to each of the heptenes. The reaction flasks were cooled in ice water during this addition. The dibromide of Heptene-A distilled at 99–100° (27 mm.) and the pure compound gave the following values for n_D: 18°, 1.5020; 19°, 1.5014; 19.8°, 1.5010; 22°, 1.5001.

Anal. Calcd. for $C_7H_{14}Br_2$: Br, 62.0. Found, 62.6.

This dibromide boiled with decomposition at 187–188° at ordinary pressure.

The dibromide of Heptene-B, similarly prepared, and fractionally distilled *in vacuo*, yielded a fraction boiling at 65–70° (18–19 mm.) with

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[1] Edgar, Calingaert and Marker, This Journal, **51**, 1485 (1929).

[2] See Grignard and co-workers, *Compt. rend.*, **176**, 1860 (1923); **182**, 299 (1926); *Ann. chim.*, **2**, 298 (1924).

$n_D^{17.5}$ 1.4700, and 1.6 times as much of a higher fraction, b. p. 93–97° (17–18 mm.), with $n_D^{17.5}$ 1.5022. Of these two fractions, the latter seemed identical with the dibromide from Heptene-A.

To explain these data, it is suggested that "Heptene-A" is largely or entirely methyl-2-hexene-2, and that "Heptene-B" is a mixture of methyl-2-hexene-2 and methyl-2-hexene-1, the former predominating.

Summary.—Methyl-2-hexanol-2 slowly undergoes dehydration into methyl-2-hexene-2 by refluxing. With iodine as a catalyst, the dehydration reaction proceeds more readily but methyl-2-hexene-1 also appears to be formed.

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ADDITIONS AND CORRECTIONS

1921. VOLUME 43

Indirect Method of Preparation of Organic Mercuric Derivatives and a Method of Linking Carbon to Carbon, by Morris S. Kharasch.

Page 2243. The author writes as follows: ". . . Lines 22 and 34 should read '2,2′,4,4′,6,6′-hexanitro mercury diphenyl' instead of '2,2′,4,4′,6,6′-hexanitro diphenyl.' It is unfortunate that this omission of the word 'mercury' has occurred. The author intended to call attention to the very interesting fact that if the molecule of 2,4,6-trinitrophenyl mercuric chloride is treated with potassium periodide at room temperature, two simultaneous reactions take place. The first reaction is a substitution of the —HgX radical by iodine and the second reaction is a 'bridging' effect due to the potassium iodide.

"This is believed to clear up the apparent discrepancy in the article and results recorded in a recent publication [Whitmore and Thurston, THIS JOURNAL, **51**, 1502 (1929)], except that since these authors refluxed the sample of 2,4,6-trinitrophenyl mercuric chloride with iodine for *eight* hours and did not employ potassium iodide at all, they could not have noted the formation of the 2,2′,4,4′,6,6′-hexanitro mercury diphenyl, as observed by the first author. It is the unusual speed of formation of this latter compound from 2,4,6-trinitrophenyl mercuric chloride and potassium iodide at ordinary temperature that was deemed worthy of mention."—M. S. KHARASCH.

1928. VOLUME 50

The Analysis of Mixtures of Ethyl Alcohol, Ethyl Acetate, Acetic Acid and Water, by S. Poznanski.

Page 986. Line 3 from the end should read: ". . . This method has the advantages that the unknown acid and standard dissociate equally in solution, . . ."

Page 988, line 4 from the end, insert "of a per cent." after "thousandths."—S. POZNANSKI.

The Iodide, Iodine, Tri-iodide Equilibrium and the Free Energy of Formation of Silver Iodide, by Grinnell Jones and B. B. Kaplan.

Page 1856. In Table IIA the second entry in the last column should read "0.0011364" instead of "0.001364."—GRINNELL JONES.