[Contribution from the Houston Refinery Research Laboratory Shell Oil Company, Inc.]

Vapor Phase Dehydration of 1-Heptanol over Activated Alumina

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Introduction

The vapor phase dehydration of alcohols over activated alumina has been one of the standard methods for the preparation of olefins of low molecular weight. However, very little work has been done with this method for compounds containing five or more carbon atoms and there is disagreement as to the products obtained. Goldwasser and Taylor[1] reported the production of a large amount of branched chain olefins from the vapor phase dehydration of 6 to 8 carbon aliphatic alcohols over activated alumina and also indicated that a large amount of chain-branching isomerization is obtained from the passage of olefins over activated alumina. However, their method of analysis has been shown to be greatly in error.[2] In contrast, Egloff, Morrell, Thomas and Bloch[3] dehydrated 2-octanol by the same method and reported 1-octene and 2-octene as their chief products, with very little, if any, isomerization. Also Ewell and Hardy[4] found that no chain-branching isomerization was obtained with pentenes over activated alumina.

1-Heptene was prepared in this Laboratory by the vapor phase dehydration of 1-heptanol. Since there is disagreement in the literature as to the products obtained when dehydrating high molecular weight alcohols, the product was carefully tested in order to establish unequivocally its identity.

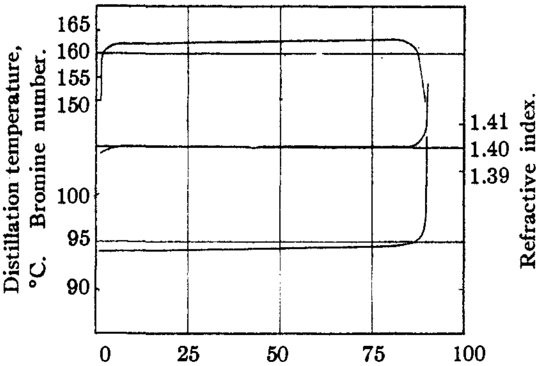

Fig. 1.—Distillation of products from dehydration of *n*-heptyl alcohol over activated alumina.

Experimental

Harshaw Grade A activated alumina, $^1/_8$ inch pellets, was placed in a 28-mm. i. d. glass tube to a depth of 40 cm. The alumina was supported on a plug of glass wool and covered with a 5-cm. layer of $^1/_{16}$ inch glass beads to serve as a preheating section. The reaction tube was supported in a vertical tube furnace held in the temperature range 380–400° and a fraction from Eastman Kodak Co. *n*-heptanol,[5] boiling point 175.5°, $d^{20}{}_4$ 0.8224, n^{20}D 1.4241, was passed through at the rate of 0.6–0.7 volume of liquid per volume of catalyst space per hour. The product was passed through a condenser at 25° and the two liquid layers were separated and the volumes measured. The gases produced in the reaction were passed through a wet test meter and samples were analyzed by a multiple isothermal distillation method.[6] These gases represented 0.4% by weight of the charge. The analysis showed the presence of 68% H_2, 7% CO, 13% CH_4 and 12% heavier hydrocarbon gases. The formation of aldehydes was thought to be a possible source of the relatively large amount of hydrogen in the gas, but a test of the liquid products with Schiff reagent indicated only a trace of aldehyde. Decomposition to coke on the catalyst can also be ruled out as a source of the hydrogen since after thirty hours only a very slight darkening (less than 0.1% by weight of carbon) of the catalyst was observed.

The volumes of the two liquid layers agreed with the stoichiometric ratio of heptene and water from the dehydration of heptanol. A determination of the bromine number of the hydrocarbon layer gave a value of 150, which is lower than the theoretical (163), indicating the presence of high boiling polymer having a lower bromine number.

The hydrocarbon layer was dried over calcium chloride and then distilled at a 49:1 reflux ratio in a column having 60 theoretical plates at total reflux. Figure 1 shows the variation in boiling point, corrected to 760 mm., refractive index n^{20}D, and bromine number (grams bromine per 100 g. of sample) of the overhead product during the distillation. For about the first 87% (by weight) of the distillation, the values of refractive index and bromine number were constant, while the boiling range extended from 93.6 to 94.4°. This fraction of the product was shown to be 1-heptene. The distillation also indicated 2% of unconverted heptanol, about 8% of a residue boiling above 230° and the possible presence of about 3% of 2-heptene. No proof of the the presence of 2-heptene other than the trend of the distillation data can be given, however.

Since a number of branched chain heptenes boil within a few degrees of 1-heptene and would not be definitely distinguishable by such physical properties as density, refractive index and bromine number, a sample from the first 87% overhead was hydrogenated over Raney nickel catalyst at 24° and 1 atmosphere pressure of hydrogen to produce heptanes corresponding to the heptenes. The product from the hydrogenation was then distilled at a 24:1 reflux ratio in a column of 60 theoretical plates. The initial boiling point was 98.7° and distillation continued to the end at 98.9°. This indicates that no branched chain heptenes were originally present since this is definitely above the boiling points of ethylpentane at 95.5° or 3-methylhexane at 92.0°, which are the heptane isomers having boiling points closest to *n*-heptane at 98.4°.[7] The refractive index, n^{20}D 1.3874, of the hydrogenated sample also agrees with the value of 1.3876 for *n*-heptane.[7]

In order to obtain a still more positive check on the composition of our product, infrared absorption spectra were obtained on three cuts from the heptene distillation, at 2.3, 15.4 and 60.1% distilled. These spectra are plotted in Fig. 2 and show very good agreement, indicating that the

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(1) Goldwasser and Taylor, This Journal, 61, 1751, 1762 (1939).

(2) Whitmore, Fenske, *et al.*, *ibid.*, 62, 795 (1940).

(3) Egloff, Morrell, Thomas and Bloch, *ibid.*, 61, 3571 (1939).

(4) Ewell and Hardy, *ibid.*, 63, 3460 (1941).

(5) "The Handbook of Chemistry and Physics," 28th ed., 1944, lists values of b. p. 176°, n^{20}D 1.4241, $d^{20}{}_4$ 0.8219 for 1-heptanol.

(6) To be published.

(7) M. P. Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Company, 4th ed., New York, N. Y., 1943.

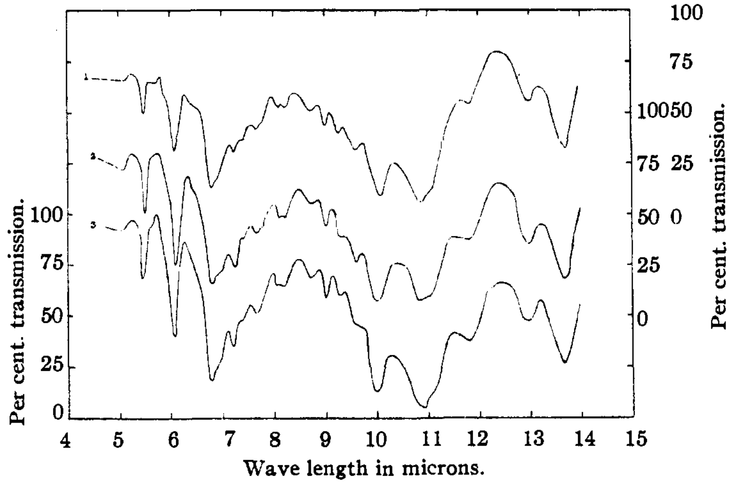

Fig. 2.—Comparison of the spectra of cuts from the heptene distillation.

product composition remained constant during the distillation. No spectra for 1-heptene were available for comparison, but those of Fig. 2 are consistent with the spectra of 1-octene and show no correspondence with the spectra of 2-octene, 3-octene or 4-octene.[8] Also, the spectrum for the hydrogenated heptene, shown in Fig. 3, agrees with that for *n*-heptane.[9]

These tests conclusively show that 1-heptene is the primary product obtained by the dehydration of 1-heptanol over activated alumina. The true boiling point of the heptene which distilled in the range from 93.6 to 94.4°, measured in a Cottrell type boiling point apparatus using a Bureau of Standards calibrated thermometer, was 93.6°. This is somewhat higher than the value of 92.8° reported in M. P. Doss' compilation of physical constants of hydrocarbons[7] or the value 93.1° given as best by Egloff.[10] There is also a slight disagreement as to refractive index and density, our values being n^{20}_D 1.4003 and d^{20}_4 0.6971 as compared to 1.3991 and 0.6968 for Doss' compilation[7] and 1.3999 and 0.6976 according to Egloff.[10] However, Egloff also lists a large number of values of boiling point, refractive index and density from the literature which cover a much wider range than those reported above, but in no case was a comparably careful analysis made to show the presence of pure 1-heptene.

It had been thought that the high boiling residue from the heptene distillation was heptene polymer. The boiling range, as determined from a vacuum distillation, and the molecular weight, from the freezing point lowering with benzene, corresponded to those for heptene dimer. However, the bromine number indicated only about 60% of olefinic hydrocarbons. The composition of the remainder of the material could not be definitely established, but the presence of aromatic hydrocarbons was indicated by the high value for the specific dispersion, 114.3, and the high percentage of hydrogen in the gas.

The indicated production of 2-heptene, mentioned earlier, is in agreement with the findings of Ewell and Hardy,[4] who showed that pentenes are isomerized by double bond shifting when passed over activated alumina. Since the contact time in the present experiment was much shorter, only a small amount of isomerization should be expected.

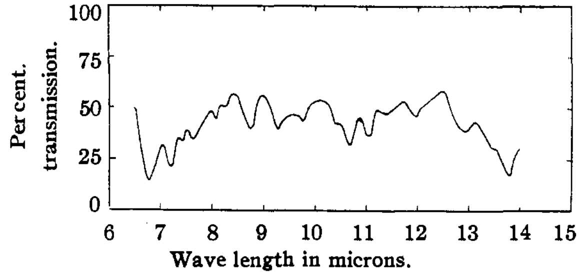

Fig. 3.—Spectrum of hydrogenated heptene.

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Summary

1-Heptene has been shown to be the principal product of dehydration of 1-heptanol over activated alumina at 380–400°.

Physical properties of the 1-heptene so obtained are compared with existing literature values.

No evidence of any chain-branching isomerization of 1-heptene over alumina was obtained.

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(8) Infrared Absorption Spectrograms, API Research Project 44, Serial Nos. 29, 31, 33, 35, November 30, 1943.

(9) Infrared Absorption Spectrograms, API Research Project 44, Serial No. 49, November 30, 1943.

(10) Gustav Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1939.