

The Hydration of Mixtures of 1-Heptyne and 1-Heptene

KENNETH N. CAMPBELL and EDWARD J. TOMCIK,
University of Notre Dame

In the course of our studies on the reduction of alkyl and dialkyl acetylenes, it became desirable to find a method whereby the amounts of acetylene and olefin present in the reduction mixture could be determined. Unfortunately, the boiling points of acetylenes and olefins of the same carbon skeleton lie too close together to permit of efficient separation by fractional distillation. Index of refraction measurements can be used to analyze a two-component mixture, but since it was possible that our reduction mixtures also contained some of a third component, the saturated hydrocarbon, this method did not seem promising. Terminally bonded acetylenes can, of course, be separated from olefins and saturated hydrocarbons by virtue of the acidic hydrogen atom, through formation of a copper, mercury or silver salt, but this method is of no value with disubstituted acetylenes, and a general procedure was desired.

It seemed reasonable to hope that a selective hydration method could be developed which would permit of hydration of either the acetylene or the olefin, but not of both. Such a method might also be used for the purification of olefins and acetylenes. With this in mind, a study of the hydration of mixtures of acetylenes and olefins was undertaken, using 1-heptyne and 1-heptene.

There is comparatively little information in the literature on the hydration of higher unsaturated compounds. The lower olefins, ethylene, propylene and the butylenes, are converted to alcohols by treatment with sulfuric acid of various strengths; sometimes the reaction mixture is heated, but more frequently the reaction occurs in the cold (1, 2). No studies have been made, apparently, on the conditions necessary to bring about hydration of higher, straight-chain olefins. Acetylenes, in the absence of a catalyst, are not as readily hydrated as are the lower olefins; Behal (3) found it necessary to use concentrated sulfuric acid in the cold, and Favorski (4) used dilute sulfuric acid, with heating in a bomb tube, to hydrate acetylenes. By the use of a mercuric salt as catalyst, however, hydration of an acetylene can be accomplished under much milder conditions; Campbell, Thomas and Hennion (5) showed that 1-hexyne could be hydrated at 60° in aqueous methanol, acetone or acetic acid by the use of small amounts of sulfuric acid and mercuric sulfate.

In the present work an attempt was made to find conditions which would permit of hydration of the olefin and not the acetylene, and vice-versa. When an equimolar mixture of 1-heptyne and 1-heptene was heated at 70° in 60% aqueous acetic acid, in the presence of a little mercuric sulfate and sulfuric acid, distillation of the reaction product showed that 1-heptyne had been hydrated but not the heptene. The

yield of methyl *n*-amyl ketone of constant boiling point was about 85% of the theoretical, but only about half of the 1-heptene used was recovered. Since there was only a small amount of tarry residue formed, the loss of olefin was probably due to solubility or volatility.

When an equimolar mixture of 1-heptyne and 1-heptene was treated at 0° with 60% sulfuric acid, no hydration of either hydrocarbon could be detected, and 80% of the hydrocarbon mixture was recovered. Since hydration sometimes occurs better at higher temperatures (4), the heptyne-heptene mixture was treated with 60% sulfuric acid at 60°, but here again no high-boiling product was obtained and the mixed hydrocarbons were recovered. The use of 85% phosphoric acid in place of 60% sulfuric acid, at 75° was of no avail; no hydration occurred. An attempt was made to use a 1:1 mixture of sulfuric and acetic acids as hydration medium, but this resulted in charring and polymerization of the hydrocarbons.

It is possible, from this work, to convert the acetylene in an acetylene-olefin mixture to the corresponding ketone in good yields; since, however, the olefin is not recovered quantitatively, the method is not suitable for analysis of such mixtures. No conditions have been found so far which will cause the olefin to be hydrated, and not the acetylene.

Experimental

Reagents. 1-Heptyne, b.p. 99°, n_D^{20} : 1.4088, was prepared from sodium acetylide and amyl bromide in liquid ammonia solution (6), and 1-heptene, b.p. 94-95°, n_D^{20} : 1.3973, was made by the catalytic hydrogenation of the acetylene in the presence of Raney nickel, by the procedure of Campbell and Eby (7). The sulfuric and phosphoric acids used were reagent grade, as was the mercuric sulfate.

Hydration in 60% acetic acid. A mixture of one-fourth mole (24 g.) of 1-heptyne and one-fourth mole (24.5 g.) of 1-heptene was added dropwise, with stirring, over a period of an hour, to a solution of 1 g. of mercuric sulfate and 1 g. of sulfuric acid in 50 g. of 60% acetic acid. The reaction mixture was maintained at 70° during the addition and for three hours thereafter. It was then cooled to room temperature and treated with a solution of 28 g. of sodium carbonate in 75 cc. of water. Sodium chloride was added to salt out any organic material held in the water, and the organic layer was separated, washed with saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. It was then distilled through a Whitmore-Fenske total-condensation, partial-take-off column packed with glass helices. There was thus obtained 24 g. of material of b.p. 87-89°/50 mm., 150°/747 mm., n_D^{20} : 1.4093; 12.3 g. of 1-heptene, b.p. 92°/740 mm., n_D^{20} : 1.3970-1.3979, and about 3 g. of residue. A comparison of the main product with methyl *n*-amyl ketone shows they are the same; methyl *n*-amyl ketone has b.p. 150°, n_D^{20} : 1.4083, while for methylamylcarbinol the values are: b.p. 160-162°, n_D^{20} : 1.4209.

Hydration in 60% sulfuric acid. A mixture of one-fourth mole of heptyne and one-fourth mole of heptene was added, dropwise and with stirring, to 50 g. of 60% sulfuric acid. The mixture was kept at 0° during the addition, and for three hours thereafter. It was then poured onto ice and the acid neutralized with sodium carbonate. The entire mixture distilled at 93-99° at atmospheric pressure, n_D^{20} : 1.3998-1.4058, showing that no hydration of either component had occurred. The weight of distillate was 39.1 g., and there was a residue of about 3 g.

When the hydration temperature was kept at 60° instead of 0°, the results were similar; no hydration occurred, but less material was recovered, due to polymerization.

Hydration in phosphoric acid. A mixture of one-fourth mole of acetylene and one-fourth mole of olefin was added to 50 g. of 85% phosphoric acid, kept at 55°. When addition was complete, the mixture was heated at 55° for two hours and then at 75° for two hours. When it was worked up in the usual way the entire product boiled at 94-100°, n_D^{20} : 1.3979-1.4068, and weighed 39.2 g.

Summary

When a mixture of 1-heptyne and 1-heptene is treated with 60% acetic acid in the presence of mercuric sulfate and sulfuric acid, the acetylene is converted to methyl amyl ketone, and part of the olefin is recovered.

Treatment of a mixture of the two unsaturated hydrocarbons with 60% sulfuric acid at 0° and at 60°, or with 85% phosphoric acid at 75°, causes no hydration of either component.

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