1-Propyl-2-iodoacetylene

By Thomas H. Vaughn

When the densities and indices of refraction of the alkyl iodoacetylenes are plotted against molecular weight it becomes apparent that the values for these constants reported for propyl iodoacetylene by Grignard and Perrichon [*Ann. chim.*, **5**, 5–36 (1926)] are seriously in error.

This compound has been prepared in this Laboratory in 77% yield by the action of iodine on pentinylmagnesium bromide according to the procedure outlined by Grignard and Perrichon and has been found to possess the following properties: b. p. 67.0–67.5° at 35 mm.; 75–77° at 51 mm.; γ_{25} 34.22 dynes/cm. (maximum bubble pressure method); [P], obs., 283.3; calcd., 281.3; n^{25}_{D} 1.52231, n^{10}_{D} 1.5310; d_{25} 1.6557; MR'_{D} calcd., 36.54; obs., 35.73. These values for the index of refraction and density lie on their curves as determined from the other members of the series.

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Received January 11, 1933
Published March 7, 1933

COMMUNICATIONS TO THE EDITOR

HYDROGENOLYSIS OF ALCOHOLS TO HYDROCARBONS

Sir:

Recently we have found a method for the preparation of certain hydrocarbons which were not readily available. The reaction involved is the hydrogenolysis of a primary alcohol according to the equation $RCH_2OH + 2H_2 = RH + CH_4 + H_2O$. The reaction proceeded smoothly with duodecanol-1, tetradecanol-1, octadecanol-1 and 3-cyclohexylpropanol-1, from which were obtained *n*-undecane [b. p. 189–190° (740 mm.), n^{25}_{D} 1.4164], *n*-tridecane [b. p. 84–85° (3 mm.), n^{25}_{D} 1.4250, m. p. −7–8°], *n*-heptadecane [b. p. 290–292° (738 mm.), n^{25}_{D} 1.4360, m. p. 20–21°], and ethylcyclohexane [b. p. 127–128° (738 mm.), n^{25}_{D} 1.4310]. Similarly the diprimary glycol, decanediol-1,10, by the removal of both carbinol groups was converted into *n*-octane [b. p. 121–123° (742 mm.), n^{25}_{D} 1.3975].

Hydrogenolysis was accomplished by subjecting 40 to 50 g. of the alcohol or glycol for about five hours to the action of hydrogen (100 to 200 atmospheres) at 250° over a nickel catalyst. The reaction proceeded almost quantitatively and no product other than the indicated hydrocarbon was found in any case. In some experiments a small amount of the original alcohol or glycol was recovered. [The catalyst and apparatus have been described in THIS JOURNAL, **54,** 4116 (1932), and *Ind. Eng. Chem., Anal. Ed.*, **4,** 342 (1932).]

Secondary alcohols also undergo hydrogenolysis but in this case the reaction involves the cleavage of a carbon to oxygen rather than a carbon to carbon bond, *i. e.*, $R_2CHOH + H_2 = R_2CH_2 + H_2O$. This type of reaction giving a hydrocarbon of the same carbon content as the alcohol is not novel; in fact it has been regarded as the normal reaction for primary as well as secondary and tertiary alcohols. The reaction proceeds smoothly under the conditions described above. For example, cyclohexane (m. p. 4–5°, n_D^{25} 1.4260) and *n*-octane were the only hydrocarbons obtained by the hydrogenolysis of cyclohexanol and octanol-2.

The primary–secondary glycol octadecanol-1,12, $CH_3(CH_2)_5CHOH(CH_2)_{10}CH_2OH$, as would be anticipated from the results stated above, underwent carbon to oxygen cleavage at the secondary carbinol, and carbon to carbon cleavage at the primary carbinol, with the formation of *n*-heptadecane, $C_{17}H_{36}$. The glycol [293 g., m. p. 67–69°, b. p. 200–208° (4 to 5 mm.)] was obtained by hydrogenation of castor oil (500 g.) over copper–chromium oxide catalyst (35 g.) for nine hours at 250° under 200–300 atmospheres pressure. The product so obtained was not completely homogeneous, as evidenced by its physical constants and the fact that in addition to the main product, *n*-heptadecane, a small amount of an unidentified hydrocarbon was obtained in its hydrogenolysis.

The primary alcohols and decanediol-1,10 subjected to hydrogenolysis were prepared from the ethyl esters of the corresponding acids through the action of hydrogen over a copper–chromium oxide catalyst [THIS JOURNAL, **54,** 4678 (1932)]. Both of the steps in the conversion of an ester to a hydrocarbon containing one less carbon atom than the acyl group of the ester can be accomplished by using a mixture of the two catalysts, *i. e.*, copper–chromium oxide and nickel. However, our experience indicates that it is preferable to carry out the operation in two stages since the water formed in the second step prevents the completion of the first reaction.

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RECEIVED JANUARY 23, 1933 PUBLISHED MARCH 7, 1933

A NEW CONDENSATION REACTION OF THE THIOPHENOLS

Sir:

In view of the recent increase of interest in mercaptan chemistry, both in this country and abroad, we should like to report briefly upon a new reaction of the thiophenols, the investigation of which has been carried forward in this Laboratory during the past two years.

We have found that phenyl mercaptan itself, and many substituted