solved in chloroform and the extract washed free of acid. The sirup obtained on solvent removal from the dried extract was crystallized from absolute ethanol, from which it separated as long, distinct needles. Pure material was obtained on further recrystallization from the same solvent; m. p. 86–87°, spec. rot. +84° (20°, *c* 3.3, U. S. P. $CHCl_3$). Karrer and Büchi[8] record an analysis and a melting point of approximately 86° for a product which they characterized as a "nicht deutlich krystallines Pulver." Our preparation was very soluble in chloroform and acetone; soluble in benzene; moderately soluble in hot ethanol; very moderately so in ether; practically insoluble in water.

Anal. Calcd. for $C_{12}H_{15}O_{11}(CH_3CO)_9$: C, 49.86; H, 5.86; CH_3CO, 12.45 cc. 0.1 *N* NaOH per 100 mg. Found: C, 49.76; H, 5.78; CH_3CO, 12.2 cc.

We are indebted to Mr. S. H. Nichols, Jr., for the preparation of the melibiose used in this work.

Summary

1. Melibiotol has been synthesized in crystalline form by the high pressure catalytic reduction of melibiose and further characterized as a crystalline nonabenzoate.
2. The structure of melibiotol was demonstrated by its lack of reduction and by its hydrolysis to sorbitol and *d*-galactose, both of which were characterized as crystalline derivatives.
3. The work of Karrer and Büchi on the reduction of maltose has been repeated and the amorphous maltitol produced has been characterized as a crystalline nonaacetate and both hydrolytic components (sorbitol and *d*-glucose) of the maltitol preparation have been identified by crystalline derivatives.

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The Partial Reduction of Acetylenes to Olefins Using an Iron Catalyst

BY A. F. THOMPSON, JR., AND S. B. WYATT[1]

The problem of reduction of acetylenic compounds to the corresponding olefins has engaged the attention of many workers. Palladium has come to be accepted as a catalyst whose selective action can be utilized for this type of partial reduction. Recently, Campbell and O'Connor[2] have reported that Raney nickel exhibits similar selective properties, and have used it as a catalytic agent in the preparation of numerous olefins from the corresponding acetylenes.

Both palladium and Raney nickel are unsatisfactory, however, to the extent that both are excellent catalysts for the reduction of olefins, and the reduction must therefore be watched constantly and stopped at the proper moment. Therefore, the announcement by Paul and Hilly[3] of an iron catalyst, similar to Raney nickel, but unable to effect the reduction of olefins, was of considerable importance. It was decided to investigate the properties of this catalyst in this Laboratory, since certain synthetic studies being carried on here involve reduction of triple bonds to double bonds, in the presence of conjugated systems of carbon–carbon double bonds. Moreover, Paul and Hilly[3] worked exclusively with liquids and it was considered desirable to work with solid substances in order to be able to characterize the reaction products more effectively.

Diphenylacetylene was chosen as the first substance to be investigated. It proved to be an unfortunate choice, since it behaved abnormally, being reduced quantitatively to diphenylethane by hydrogen and the iron catalyst at 100° and 1000 lb. per sq. in. This happened in each of three separate experiments. It was especially surprising in view of the results of Campbell and O'Connor,[2] who obtained isostilbene by persistent reduction of diphenylacetylene with Raney nickel.

To avoid any special effect of phenyl groups, an aliphatic acetylene with appropriate properties was sought, and 2,5-dimethylhexyne-3-diol-2,5 was chosen. It proved more resistant to reduction, but at 150° and 1400 lb. per sq. in. it was reduced nearly quantitatively to the beta form of the olefin, m. p. 67–69°. The corresponding acetylene and ethane both melt above 90°. The unsaturation of the product was confirmed by quantitative

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[1] From the thesis submitted by S. B. Wyatt in partial fulfilment of the requirements for the degree of Bachelor of Science.

[2] Campbell and O'Connor, THIS JOURNAL, **61**, 2897 (1939). This paper includes numerous references to earlier investigations of partial hydrogenation.

[3] Paul and Hilly, *Bull. soc. chim.*, [5] **6**, 218 (1939).

hydrogenation with PtO catalyst. These results were repeated and indicated the specific nature of the catalyst.

To test the specific action of the catalyst on triple bonds when a conjugated carbon–carbon double bond system was present, a vinyl-acetylene derivative was chosen. 2-Methyl-butene-1-yne-3 was reduced in the bomb with the iron catalyst at 100° and 1000 lb. per sq. in. The shaking was allowed to continue overnight, although the absorption of hydrogen was complete in two hours. The liquid obtained was highly unsaturated as measured by quantitative hydrogenation with Adams catalyst, but gave no test for acetylenic hydrogen. On treatment with maleic anhydride the characteristic isoprene addition product was obtained, m. p. 62–63°. These results indicated applicability of the catalyst to the reduction of triple bonds in the presence of conjugated systems. It is planned to extend these investigations to 1,6-systems since these also will be met with in projected synthetic work. Also, it will be of interest to carry out the reductions on a larger scale and seek for allenes in the reduction products.

Experimental

The active iron catalyst was prepared from an iron–aluminum alloy according to the directions of Paul and Hilly.[3] The alloy was prepared[4] by melting the iron in a magnesia-lined induction furnace, and adding four times its weight of aluminum rod to make a 20% iron alloy. One hundred and fifty grams of alloy was pulverized, and added in small portions to a solution of sodium hydroxide (250 g. per liter). The reaction was very vigorous, and three hours were necessary for the addition. At the end, the temperature was held at 80–90° until evolution of hydrogen had ceased. The treatment with alkali was then repeated, after which the iron was washed repeatedly with boiling water, by decantation. It was fully washed free of alkali with absolute alcohol and stored under alcohol.

Reduction of Diphenylacetylene.—Five grams of diphenylacetylene was dissolved in 50 cc. of absolute alcohol and 1 g. of the iron catalyst (in alcohol) was added. The mixture was shaken overnight in a bomb at 100° under 1000 lb. per sq. in. hydrogen pressure. On filtration and evaporation 5 g. of the substance was obtained, m. p. 49–51°. One recrystallization from ligroin yielded a product melting at 51–52°. The m. p. of pure diphenylethane is 52°.

Reduction of 2,5-Dimethylhexyne-3-diol-2,5.—Five grams of the acetylenic glycol prepared according to Froning and Hennion[5] was dissolved in 50 cc. of absolute alcohol and 1 g. of the iron catalyst was added. The mixture was shaken overnight in a bomb at 150° and 1400 lb. per sq. in. initial hydrogen pressure. A marked absorption of hydrogen occurred. On filtration and evaporation about 4 g. of substance was obtained, m. p. 67–69°. On recrystallization from petroleum ether the melting point was unchanged, indicating the substance to be the beta form of the 2,5-dimethylhexene-3-diol-2,5; recorded m. p. 69.5°.

Reduction of 2-Methylbutene-1-yne-3.—The acetylene derivative was prepared by dehydration of the condensation product of acetylene and acetone as described by Carothers and Coffman.[6] 15 g. of the acetylenic hydrocarbon, b. p. 35–36°, was mixed with 1 g. of the iron catalyst in absolute alcohol and shaken with hydrogen at 1000 lb. per sq. in. at 100° for eighteen hours. The hydrogen was strongly absorbed during the first two hours. The strongly cooled reaction mixture was filtered and carefully fractionated. On refractionation, 8 g. of substance was obtained, b. p. 32–33°. The substance gave no precipitate with alkaline silver nitrate, indicating complete reduction of the acetylenic bond. One hundred fifteen mg. of substance shaken with PtO in an atmosphere of hydrogen absorbed 65 cc. out of a theoretical 85 cc., corresponding to at least 50% of diene in the reaction product, since it was shown no acetylene was present. On heating with maleic anhydride the addition product was obtained, m. p. 62–63°; recorded 63°. This indicated the presence of isoprene and established that the 1–4 system was not attacked readily under the conditions used for hydrogenation.

Summary

The usefulness of an iron catalyst in the reduction of acetylenes to olefins has been demonstrated. It has been shown that such reductions can be carried out even in the presence of a conjugated system of carbon–carbon double bonds without having to stop the reduction, if this iron catalyst is used.

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(5) Froning and Hennion, THIS JOURNAL, **62**, 654 (1940).

(6) Carothers and Coffman, *ibid.*, **54**, 4071 (1932).