Notes

Condensation of Acetylene with Aldehydes

HARRY A. STANSBURY, JR., AND WILLIAM R. PROOPS

Received July 17, 1961

The condensation of acetylene with aldehydes to form secondary acetylenic alcohols has been studied extensively. The most widely used method is the reaction of sodium acetylide with the aldehyde in liquid ammonia.[1,2]

A more convenient and simpler method involves the reaction of acetylene with the aldehyde in a suspension of potassium hydroxide in nonhydroxylic ethers, such as acetals and ethylene glycol dialkyl ethers[3,4] The formation of a loose complex between potassium hydroxide and the ethereal oxygens has been suggested as the reason that the aldehyde did not form exclusively self-condensation products, as might be expected. However, the yields were good (60–71%) only when aldehydes more resistant to alkali, such as isobutyraldehyde and 2-ethylhexanal, were employed.[4] The surprisingly beneficial effect of small amounts of aliphatic alcohols on the reaction under five to ten atmospheres of acetylene pressure has been reported. Using 85% potassium hydroxide suspended in ethyl ether as the medium for the condensation of acetaldehyde with acetylene under a pressure of ten atmospheres at 0°, the addition of about 1% ethanol to the reaction mixture increased the yield of 3-butyn-2-ol from 20% to 43%.[5] In a subsequent article, these workers reported that even under twenty atmospheres of acetylene pressure, the yield of 3-butyn-2-ol was only about 40%.[6] The hazards of handling acetylene under pressure have long been recognized. We have now found that even higher yields of 3-butyn-2-ol may be obtained by operation at atmospheric pressure in the presence of potassium hydroxide suspensions in certain solvents. Very mobile and stable suspensions were prepared by grinding the potassium hydroxide at 0–10° in a cooled Waring Blendor. This procedure is more rapid and convenient than cooling the molten base from 150° while stirring in the solvent, as described by Bergmann *et al.*[4] Under optimum conditions using 85% potassium hydroxide (reagent grade) suspended in 1,2-dimethoxyethane, we were able to obtain 3-butyn-2-ol in 51% yield based on acetaldehyde. With 91.5% potassium hydroxide (technical grade) in 1,2-dimethoxyethane-dioxane mixture, the yield was 61%. Dimethylformamide and *N*-methylpyrollidone were each ineffective as solvents for this reaction.

This procedure was used to condense other aldehydes with acetylene. Other aldehydes employed and the yields of acetylenic carbinols were as follows: propionaldehyde (81%), butyraldehyde (82%), isobutyraldehyde (87%), 3-cyclohexenecarboxaldehyde (92%), 3,4-dihydro-2,5-dimethyl-2-formyl-2*H*-pyran (56%), 2-methylbicyclo[2.2.1]-5-hepten-2-carboxaldehyde (53%), 2-ethyl-2-hexenal (37%) and crotonaldehyde (22%). The following unsaturated aldehydes were condensed with acetylene under these conditions but no acetylenic alcohol could be isolated from the polymeric product: methacrolein, phenylacetaldehyde, cinnamaldehyde, and 2,4-hexadienal.

EXPERIMENTAL

A mixture of equal weights of potassium hydroxide and 1,2-dimethoxyethane was ground in a Waring Blendor at −5° for 0.5 hr. The resulting suspensions were transferred to a creased reaction flask and diluted with solvent to obtain a mixture containing 6.67 moles of potassium hydroxide and 1600 g. of 1,2-dimethoxyethane. After 11 g. of ethanol was added, the rapidly stirred suspension was saturated with acetylene at −10 to 0°. Then 3.33 moles of the aldehyde (containing 11 g. of ethanol) was added dropwise over a period of 2 hr. followed by an 0.5 hr. soaking period at −10 to 0°. A slight excess of acetylene was fed all during the reaction period. Ice water (894 g.) was added rapidly and the resulting aqueous layer was extracted with ethyl ether. The oil layer and extracts were combined, neutralized with carbon dioxide, filtered and fractionated to obtain the acetylenic alcohol.

UNION CARBIDE CHEMICALS CO.
RESEARCH DEPARTMENT
SOUTH CHARLESTON W. VA.

---

[1] K. N. Campbell, B. K. Campbell, and L. T. Eby, *J. Am. Chem. Soc.*, **60**, 2882–4 (1938).

[2] E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 733–5 (1942).

[3] P. Seguin, *Bull. Soc. Chim.*, **12**, 948–9 (1945).

[4] E. D. Bergmann, M. Sulzbacher, and D. F. Herman, *J. Appl. Chem.*, **3**, 39–42 (1953).

[5] I. N. Nazarov, I. L. Kotlyarevsky, and V. F. Ryabchenko, *J. Gen. Chem. U.S.S.R.*, **23**, 2011 (1953).

[6] I. N. Nazarov, I. L. Kotlyarevsky, and V. F. Ryabchenko. *Bull. Acad. Sci. U.S.S.R., Div. Chem Sci.*, 980 (1956).

A Convenient General Method for the Preparation of Aldehydes. II

ANTHONY SISTI, JULIA BURGMASTER, AND MURRAY FUDIM

Received May 5, 1961

In a previous publication[1] a new and general synthesis for the preparation of aldehydes was

---

[1] M. Stiles and A. Sisti, *J. Org. Chem.*, **25**, 1691 (1960).