Oxidative Coupling of Acetylenic Alcohols

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The oxidative coupling of compounds containing acetylenic hydrogen represents a very useful laboratory method to form a carbon to carbon bond and double the size of the molecule. Acetylenic alcohols have been oxidized with oxygen or air to form the corresponding diacetylenic glycol in aqueous cuprous chloride–ammonium chloride solution[1] and in aqueous amine–amine hydrochloride media.[2]

Although it has been established that cuprous chloride functions as a catalyst for the oxidative coupling, at least 0.25 mole of cuprous chloride per mole of 3-butyn-2-ol was required to obtain the diacetylenic glycol in good (70%) yield after a reaction period of fourteen hours. Similar large requirements for cuprous chloride in the oxidative coupling of propargyl alcohol have also been reported.[2]

Improvements in this technique were desired because (1) large amounts of aqueous cuprous chloride–ammonium chloride solution were employed and (2) some water-insoluble acetylenic alcohols were slow to oxidize. Therefore, a brief study has been made of the use of truly catalytic quantities of cuprous chloride in a pyridine-methanol medium. When 2-methyl-3-butyn-2-ol in pyridine-methanol was oxidized for four hours with air and using 0.025 mole of cuprous chloride per mole of acetylenic alcohol, 2,7-dimethyl-3,5-octadiyne-2,7-diol was formed in 87% yield. Under similar conditions except that only 0.012 mole of cuprous chloride was employed per mole of acetylenic alcohol and air was replaced by oxygen, the diol was isolated in 90% yield after a reaction period of only two and one-half hours. Propargyl alcohol (1 mole) was oxidized with oxygen using only 0.016 mole of cuprous chloride to form 2,4-hexadiyne-1,6-diol in 75% yield. Under similar conditions, 4-hexen-1-yn-3-ol was coupled to produce 2,10-dodecadiene-5,7-diyne-4,9-diol in 66% yield. These results show that a primary secondary and tertiary acetylenic alcohol can each be oxidatively coupled in good yield using truly catalytic amounts of cuprous chloride.

The oxidation of 1-methoxy-1-butene-3-yne to form 1,8-dimethoxy-1,7-octadiene-3,5-diyne has been accomplished with small amounts of cuprous chloride in the presence of pyridine.[3] Acetylenic hydrocarbons have also been coupled under similar conditions.[4,5]

EXPERIMENTAL

The following procedure illustrates the method employed to obtain the results summarized above.

A mixture of 2-methyl-3-butyn-2-ol (84 g., 1.00 mole), pyridine (20 g., .25 mole), methanol (78 g.) and cuprous chloride (1.2 g., .012 mole) was stirred at 30–35° for 2.5 hr. while oxygen was passed through the liquid at the rate of 10 l./hr. The oxygen absorption had ceased by this time and a total of 7 l. (0.28 mole) of oxygen had been absorbed. The mixture was poured into 400 ml. of saturated ammonium chloride solution and extracted with ethyl ether. The extract was washed with sodium carbonate solution, dried with magnesium sulfate and evaporated to dryness on the steam bath. The crude diol (77g.) was crystallized from 1200 ml. of benzene to obtain 75 g. (90% yield) of 2,7-dimethyl-3,5-octadiyne-2,7-diol of m.p. 127–129°.

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Attempted Preparation of 2-Azabicyclooctatriene[1]

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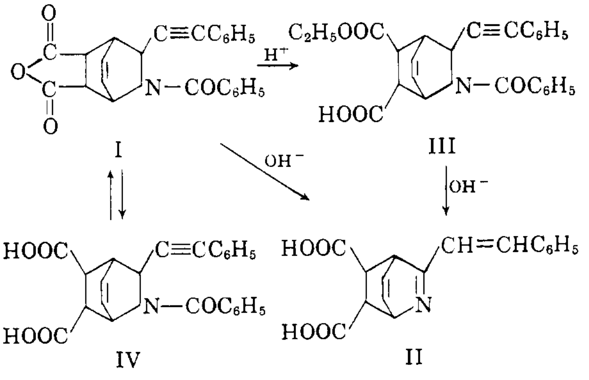
Recent interest in barrelene, bicyclo[2.2.2]octatriene, prompted us to seek analogs containing nitrogen.[4] In several exploratory experiments we failed to dehydrogenate 1,4-diazabicyclo[2.2.2]-octane. More extensive work with 2-azabicyclo compounds[5] indicated that if an octatriene (VII) was obtained, it fell apart under the conditions of the experiments.



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