Oxidation of o-Hydroxyphenylacetylene and o, o′-Dihydroxydiphenyldiacetylene by Copper Ion

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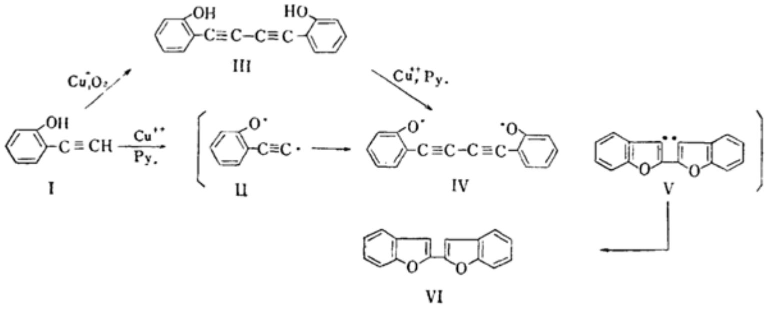
Previously the present authors have reported the quantitative formation of 2, 2′-dibenzofuranyl (VI) by the intramolecular cyclization of *o*, *o*′-dihydroxydiphenyldiacetylene (III) on treatment with basic reagents[1]. It has been found that VI is also formed quantitatively by the photodecomposition of the silver salt of III[2]. It is apparent that the former reaction involves an intramolecular nucleophilic addition of a phenoxide anion to the triple bond and the latter reaction proceeds through a radical intermediate.

The present paper deals with the formation of VI from *o*-hydroxyphenylacetylene (I) or III by the action of cupric acetate in pyridine. The treatment of I with the conventional cuprous chloride-ammonium chloride coupling reagent in an atmosphere of oxygen yielded the expected product III in a reasonable yield[1]. Unexpectedly, however, an evolution of heat was observed when I was added to a solution of cupric acetate in pyridine which is an excellent reagent of oxidative coupling of ethynyl compound proposed by Eglinton[3], and VI was isolated in a yield of 30% from the reaction mixture together with fairly large amount of an unidentified neutral oily material. A similar treatment of III with the Eglinton's reagent gave VI in quantitative yield. No change was observed when III was treated with pyridine without cupric acetate, in spite of the intramolecular cyclization of III could be caused by a weak base such as sodium carbonate or sodium hydrogen carbonate. Therefore, the presence of cupric ion is essential for the cyclization of III to VI.

Transitory formation of ethynyl radical during the course of oxidation of terminal acetylene by aqueous solution of cupric salt was postulated by Klebanski et al[4]. One electron oxidation of an ethynyl anion by cupric ion results in a transitory radical. Rapid combination of two of the ethynyl radicals forms diacetylenic product. The formation of the ethynyl radical VII seems to be probable in the course of the photochemical transformation of silver acetylide of I into coumarone[5]. Also the appearance of the phenoxyl radical IV seems to be highly probable in an intermediate stage of transformation of the silver salt of III into VI by irradiation[2]. More recently the appearance of phenoxyl radical was confirmed in several instances[6].

From the above-mentioned consideration, it appears likely that we may conclude that the reaction of I with cupric ion proceeds through the formation of free radical II. The coupling of two of II results in the new radical IV which is the same with the intermediate of the photochemical formation of VI from the silver salt of III. The oxidation of I with cupric ion may produce other radicals such as VII



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[1] F. Toda and M. Nakagawa, This Bulletin, 32, 514 (1959).

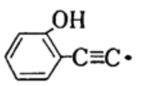
[2] F. Toda and M. Nakagawa, ibid., 33, 1287 (1960).

[3] G. Eglinton and A. R. Galbraith, *Chem. & Ind.*, **1956**, 737; *J. Chem. Soc.*, **1959**, 889.

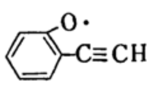
[4] A. L. Klebanski, I. V. Grachev and O. M. Kustretsova, *Zhur. Obshchei Khim.*, **27**, 2977 (1957).

[5] V. Prey and G. Pieh, *Monath. Chem.*, **80**, 790 (1949).

[6] A. S. Hay, H. S. Blanchard, G. F. Endres and J. W. Enstance, *J. Am. Chem. Soc.*, **81**, 6335 (1959); G. D. Staffin and C. C. Price, ibid., **82**, 3632 (1960).



VII



VIII

and VIII. Coupling two of VII and subsequent oxidation of the hydroxyl groups may be another route leading I to IV. Cyclization or other side reactions of II, VII and VIII which occur prior to the coupling reaction leading to IV may be responsible for the low yield of VI and the formation of a neutral oily by-product in the reaction of I with Eglinton's reagent.

The great difference between the mode of oxidation of I by the conventional coupling technique employing cuprous salt and that of the one by the Eglinton's procedure is remarkable, because cupric ion produced by the aerial oxidation of cuprous ion is regarded as the oxidizing agent in the former reaction[3] and also the oxidizing agent in the latter process is undoubtedly the same cupric ion. Quite recently, Hay[7] has reported that phenylacetylene and diethynylbenzenes can be coupled rapidly at room temperature with oxygen or air in a pyridine solution containing catalytic amount of cuprous chloride. He pointed out also that cupric carboxylates are catalysts for the reaction but they have far inferior catalytic activity as compared with cuprous salts. The copper ion in these coupling reagents must exist in some form of complex and it seems to be highly possible that the ethynyl compound takes the part of the ligand of the copper complex. Therefore, the marked difference of the oxidizing power of these coupling reagents is associated with the difference of the structure of copper complex formed in the particular reaction mixture.

Experimental

Oxidative Coupling of *o*-Hyroxyphenylacetylene by the Eglinton's Method.—A solution of *o*-hydroxyphenylacetylene (I, 5.0 g.) in ethanol (10 ml.) was added to a deep blue solution of cupric acetate monohydrate (30 g.) in pyridine (65 g.). An appreciable elevation of the temperature of the mixture was observed and the color of the mixture rapidly changed to green. The reaction mixture was stirred for 2 hr. under cooling with running water. Stirring was continued for further 2 hr. at 50°C. After removal of the solvent under reduced pressure the residue was mixed with water and extracted with ether. The ether extract was washed with aqueous solution of cupric acetate and water, successively and dried over sodium sulfate. Tiny colorless needles suspended in an oily liquid were obtained after evaporating the solvent. The crystals were filtered, washed with ethanol and recrystallized from benzene using active charcoal giving colorless needles, m.p. 194.5∼195.5°C, 1.5 g. (30%). The substance showed no depression of the melting point on admixture with a genuine sample of 2,2′-dibenzofuranyl (VI)[1].

Oxidation of *o, o′*-Dihydroxydiphenyldiacetylene with the Eglinton's Reagent.—A mixture of *o, o′*-dihydroxydiphenyldiacetylene (III, 0.50 g.), cupric acetate monohydrate (3.0 g.) and pyridine (20 g.) was stirred for 3 hr. at 60°C. The solvent was distilled in vacuo. The residue was mixed with water and extracted with ether. The extract was washed with aqueous cupric acetate and water, successively. The dried solution (over magnesium sulfate) was concentrated, yielding crude crystals, m. p. 194.5∼195.5°C, 0.5 g. The crude material was recrystallized from benzene employing active charcoal to give colorless needles, m. p. 194.5∼195.5°C, 0.45 g. (90%). This was identified as 2,2′-dibenzofuranyl (VI) by the mixed melting point determination with an authentic specimen of VI[1].

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[7] A. S. Hay, *J. Org. Chem.*, **25**, 1276 (1960).