

OXIDATION OF ETHYNYL-2-FURYLCARBINOL WITH ACTIVE MANGANESE OXIDE. (STUDIES ON HETEROAROMATICITY V)

Tadashi Sasaki and Yasushi Suzuki

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

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It is well known that ethynylcarbinols (I) are oxidized to the corresponding ethynyl ketones (II) either by chromic acid in an acidic medium (1) and in pyridine (2), or by active manganese oxide in inert organic solvents (3). Though the oxidation by chromic acid in sulfuric acid medium is the convenient method for alkyl- and aryl-ethynylcarbinols from the preparative aspect (1), this method is entirely inapplicable to the oxidation of ethynyl-furylcarbinols because of the instability of the furan ring towards acids. Recently Vereshchagin and Korshunov (2) reported that the secondary bromofuryl-acetylenic carbinols (III) were oxidized to the ketones (IV) by using active manganese oxide in chloroform or chromic acid-pyridine complex in pyridine, but there has been no report described on the oxidation of unsubstituted ethynyl-2-furylcarbinol (V).

We carried out the oxidation of V by using several kind of oxidants in various inert solvents, and as shown in Table I, any attempt was unsuccessful except when active manganese oxide was used in chloroform or in benzene. In this case we could separate two oxidation products, VI of mp. 51° and VII of mp. 198-199°.

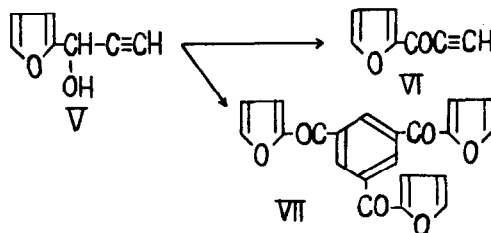
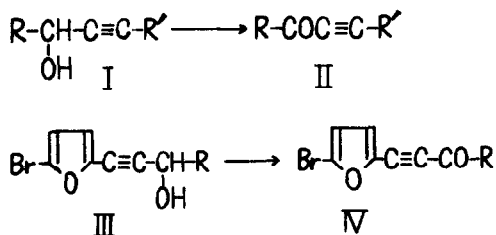


TABLE I. OXIDATION OF ETHYNYL-2-FURYL CARBINOL (V)

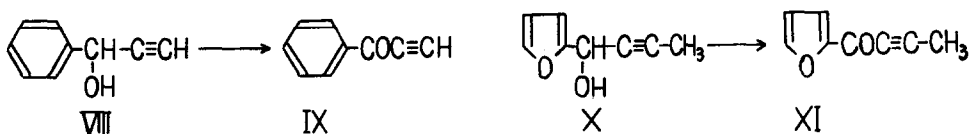
OXIDANT	SOLVENT	REACTION CONDITION	PRODUCTS & YIELDS, %
active MnO ₂	C ₆ H ₆	reflux for 5 hr.	VI 3%, VII 20%
* "	CHCl ₃	at room temp. for 3 hr.	VI 5%, VII 20%
commercial MnO ₂	CHCl ₃	"	recovering of V
CrO ₃ -AcOH	CH ₃ COCH ₃	at 0° for 24 hr.	"
CrO ₃ -H ₂ SO ₄	"	at room temp. for 24 hr.	resinified
CrO ₃ -C ₅ H ₅ N	"	"	"

* Here, one of the experiments is described: 3 g of V (4) was dissolved in 300 ml of chloroform and 30 g of active manganese oxide (3, 5) was added to this solution under stirring at room temperature and stirring was continued for 3 hr.. Manganese oxide was filtered off and the filtrate was washed thoroughly with chloroform. After removal of chloroform, the residual yellow masses were recrystallized from benzene to give VII as thin yellow crystals in the yield of 20%. Benzene filtrate was chromatographed on a silica gel column by using chloroform as an eluent. An oily substance separated from the first fraction after removing the solvent was identified to be unreacted V by comparison of IR and T.L.C. with a specimen. A crystalline product from the second fraction was recrystallized from benzene to give VI as colorless needles in the yield of 5%.

Both compounds, VI and VII, have the same empirical formula, C₇H₄O₂, by their microanalyses but show different behavior in their IR and UV spectra; in the IR spectra, VI shows sharp absorptions at 3320 cm⁻¹ (ν≡CH), 2120 cm⁻¹ (νC≡C) and 1633 cm⁻¹ (νC=O), all of which afford good evidences that VI is ethynyl 2-furyl ketone, the normal oxidation product, but VII only at 1645 cm⁻¹ (νC=O) and no absorption due to any triple bond. The UV of VI in ethanol shows no absorption in a range from 210 mμ to 700 mμ, but VII in the same solvent at 235 mμ (log ε, 4.55) and 294 mμ (log ε, 4.65). The NMR of VII in CDCl₃ (6) shows a singlet (1H) at 1.17τ besides three signals (each 1H) at

2.22, 2.26 and 3.33 τ , assignable to three protons of the furan ring (7). If the structure of VII is assumed to be 1,3,5-trifuroylbenzene, a cyclic trimer of V, 1.17 τ might be reasonably assigned to three phenyl protons of symmetrically tri-substituted benzene. This assumption is further confirmed by its mass spectrum, by which the molecular weight of VII is determined to be 360.

In order to investigate the mechanism of this oxidation reaction, VI was treated with active manganese oxide under the same condition as the above-mentioned oxidation, but only the starting material was recovered. This fact shows that the oxidative cyclization of V to VII and the normal oxidation of V to VI have occurred simultaneously as parallel reactions. It is known that 3-phenylpropyn-3-ol, VIII, the corresponding phenyl compound, and 1-(2-furyl)-but-2-yn-1-ol, X, the methyl analog of V, have been oxidized exclusively both to the ketones, IX and XI, under the same conditions in the yields of 15% (8) and 90% (9), respectively. For the purpose of cyclotrimerization of acetylenes many transitional metal complexes have been used since the discovery of the Keppe catalyst (10) and recently Makovetskii et al. have reported on the cyclotrimerization of 2-ethynylfuran and also on the co-cyclotrimerization of 1-hexyne with 2-ethynylfuran by using an $\text{Al}(\text{iso-C}_4\text{H}_9)_3\text{-TiCl}_4$ system as the catalyst (11), none has been reported on the same reaction by using active manganese oxide and this paper is the first example of it. It is certain that in this oxidative cyclization reaction active manganese oxide plays a very important role, for which the presence of ethynyl linkage is necessary, but about the detailed mechanism we are uncertain, which is under investigation.



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