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Synthesis of (4-Pyridyl)-1,2-ethanediol and α-Acetoxy-4-vinylpyridine

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Aaron *et al.*[1] synthesized (4-pyridyl)-1,2-ethanediol as an intermeidate compound in the process of obtaining 3-quinuclidiol using 4-vinylpyridine and potassium permanganate. Haas *et al.*[2] similarly carried out the synthesis and obtained (4-pyridyl)-1,2-ethanediol as a pasty mass which could not be readily purified. They produced α-acetoxy-4-vinylpyridine by the reaction of (4-pyridyl)-1,2-ethanediol with acetic anhydride[2] and polymerized it with azobisisobutyronitrile as an initiator. Both the above procedures gave a low yield of the compound.

The present authors investigated the synthetic process of (4-pyridyl)-1,2-ethanediol and α-acetoxy-4-vinylpyridine, and found a very much improved route in comparison with the above synthetic methods[1,2]. By our process the polymeriaztion grade of α-acetoxy-4-vinylpyridine is easily obtained. The α-acetoxy-4-vinylpyridine was polymerized with γ-rays, and its physical properties were studied. Results of the polymerization have been presented elsewhere[3].

Results and Discussion

It is known that glycol synthesis from a $C=C$ double bond with permanganates proceeeds favorably in an alkaline condition[4]. If the synthesis is carried out in

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[1] H. S. Aaron, O. O. Owens, P. D. Rosenstock, S. Leonard, S. Elkin, and J. I. Miller, *J. Org. Chem.*, **30**, 1331 (1965).

[2] H. C. Haas, H. S. Kolesinski, and N. W. Schuler, *J. Polym. Sci., Part B*, **3**, 879 (1965).

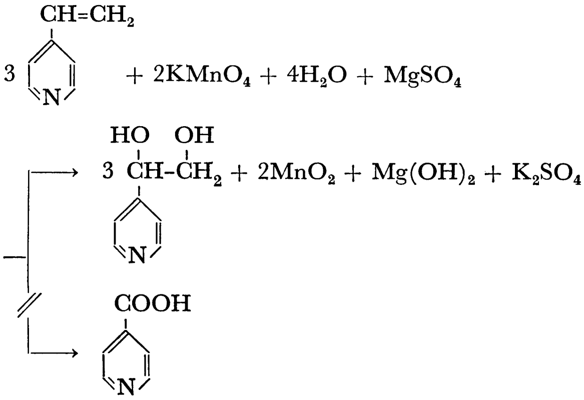
[3] T. Furuyama, K. Mori, and R. Wakasa, *J. Polym. Sci., Part A*, **9**, 3411 (1971).

[4] Y. Ogata, "Oxidation and Reduction", Nankodo, Tokyo (1963), pp. 348—403.

either acidic or neutral conditions, the main product turns out to be an oxidized material which could be produced by cleavage of the C=C[4].

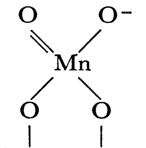
In the initial experiments we carried out glycol synthesis with a potassium hydroxide solution (alkaline condition), and, contrary to expectation, obtained isonicotinic acid as the main product. When we used water as a solvent (neutral condition), potassium hydroxide formed from the consumed potassium permanganate facilitated the formation of isonicotinic acid. It can be concluded that the methods of Aaron *et al.* and Haas *et al.* give an appreciable amount of isonicotinic acid together with (4-pyridyl)-1,2-ethanediol.

We used magnesium sulfate as a scavenger of the potassium hydroxide formed, as shown in reaction scheme (1), and obtained (4-pyridyl)-1,2-ethanediol in an exceptionally high yield, 84% or quantitatively.



(1)

As regards the mechanism of the reaction of potassium permanganate with a C=C, Wiberg and Saegabarth[5] discussed a mechanism based upon the formation of a cyclic ester between the permanganate ion and the C=C[6], as shown in (I).



(I)[5,6]

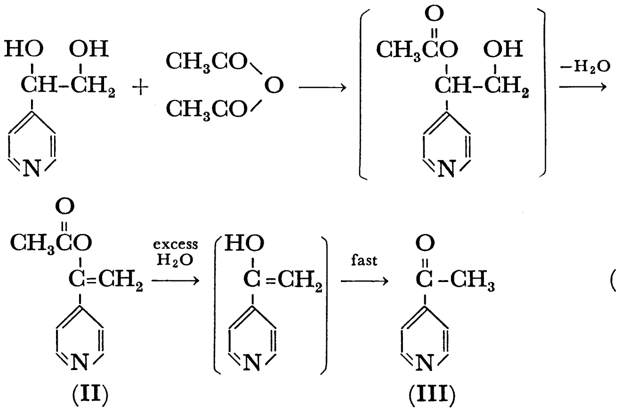
In 4-vinylpyridine, the proton abstraction reaction may easily take place with the attack of the hydroxyl ion on a similar cyclic ester, which may lead to the formation of isonicotinic acid, the cleavage product.

The solubility of (4-pyridyl)-1,2-ethanediol is summarized in Table 1 against Hildebrand's solubility parameter. (4-Pyridyl)-1,2-ethanediol seems to dissolve in solvents with a solubility parameter greater than 12.7. Our results make us doubtful of those given by Aaron *et al.*[1] with respect to the solubility and melting point of (4-pyridyl)-1,2-ethanediol. Haas *et al.*[2] also indicated a similar doubt.

With respect to the synthesis of α-acetoxy-4-vinylpyridine (II), we carried out a method similar to that of Haas *et al.*[2] except for one difference, removal of contaminated water. This water seems to facilitate the formation of the by-product 4-acetylpyridine (III) according to reaction scheme (2):

Table 1. Solubility of (4-pyridyl)-1,2-ethanediol

Solvents		Hildebrand's solubility parameters
Diethyl ether	insoluble	7.4
Carbon tetrachloride	insoluble	8.6
Benzene	insoluble	9.2
Chloroform	insoluble	9.3
Acetone	insoluble	9.9
Acetonitrile	insoluble	11.9
Ethanol	soluble	12.7
Methanol	soluble	14.5
Water	soluble	23.4



(2)

Repetition of azeotropic removal of water elevates the yield of α-acetoxy-4-vinylpyridine to a great extent. In the NMR spectrum of α-acetoxy-4-vinylpyridine, the coupling constant of the vinyl protons indicates that the acetoxy group is on α-carbon.

Experimental

(4-Pyridyl)-1,2-ethanediol. 25.2 g (0.24 mol) of 4-vinylpyridine was dissolved in 300 m*l* of acetone. The resulting solution was maintained at 2—5°C under strong magnetic stirring. 25.3 g of potassium permanganate (0.16 mol) and 9.6 g of anhydrous magnesium sulfate (0.08 mol) were dissolved in 500 m*l* of water. The solution was added dropwise from a dropping funnel onto the above acetone solution over a period of 20 min. Mechanical agitation was continued for an additional 10 min and the temperature of the reaction system was raised to room temperature. After addition of a very small amount of hydroquinone, the mixture was filtered with a glass filter. The solid material, manganese dioxide and magnesium hydroxide, was discarded. The clear pale yellow filtrate was concentrated under nitrogen atmosphere with a bath temperature of 50°C under reduced pressure. When the amount of the concentrate became approximately 50 m*l*, 200 m*l* of ethanol was added to the precipitate potassium sulfate, and the solution was kept in a refrigerator overnight. After filtration of the resulting potassium sulfate, (4-pyridyl)-1,2-ethanediol was condensed from the ethanol solution as a pale yellow viscous liquid. Yield, 84% or quantitative. NMR (60 MHz, DSS reference, in D_2O at 80°C): $H_{(a)}$, $\delta 3.83$; $H_{(b)}$, 4.40; $H_{(c)}$, 4.90; $H_{(d)}=H_{(d')}$, 7.50; $H_{(e)}=H_{(e')}$, 8.57.

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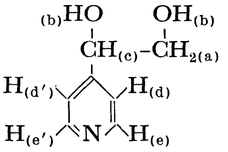
[5] K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 2822 (1957).

[6] G. Wagner, *J. Russ. Phys. Chem. Soc.*, **27**, 219 (1895).



α-Acetoxy-4-vinylpyridine. 100 g of (4-pyridyl)-1,2-ethanediol was dissolved in 300 m*l* of ethanol and 100 m*l* of benzene was added. The ethanol and benzene were removed under reduced pressure. The azeotropic procedure was repeated three times. 500 g of acetic anhydride was added to the dried (4-pyridyl)-1,2-ethanediol and the mixture was subjected to gentle boiling overnight. Acetylation was exothermic and no external heating was required at the initial stage of the reaction. Excess acetic anhydride was removed under reduced pressure. The following high vacuum distillation gave α-acetoxy-4-vinylpyridine. In order to obtain the polymerization grade of α-acetoxy-4-vinylpyridine, high vacuum distillation was repeated twice. The yield of polymerization grade material was 50%. Bp 80°C/0.58 mmHg. Found: C, 66.3; H, 5.6; N, 8.4%. Calcd for $C_9H_9O_2N$: C, 66.2; H, 5.6; N, 8.6%. NMR (60 MHz, TMS reference, in $CDCl_3$ at room temperature): $H_{(a)}$, δ2.25; $H_{(b)}$, 5.28; $H_{(c)}$, 5.80; $H_{(d)}=H_{(d')}$, 7.42; $H_{(e)}=H_{(e')}$, 8.70; $|J_{(b)(c)}|$, 2.5 Hz.