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4-(1,2-Diacetoxyethyl)pyridine and Its Chemical Properties

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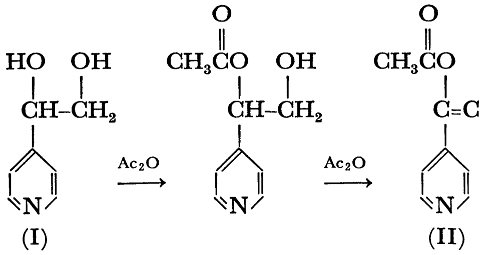
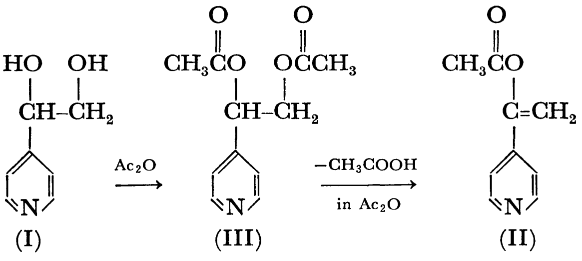
A new compound 4-(1,2-diacetoxyethyl)pyridine was synthesized from reaction of (4-pyridyl)-1,2-ethanediol (I) with acetic anhydride. It was converted into α-acetoxy-4-vinylpyridine (II) (yield, 85%) on being heated in acetic anhydride. The compound shows a characteristic NMR spectrum with respect to its methylene splitting, indicating that the two protons on methylene are not chemically equivalent.

Haas *et al.*[1] treated (I) with acetic anhydride and obtained α-acetoxy-4-vinylpyridine. They stated that the formation of 4-(1,2-diacetoxyethyl)pyridine (III) was unlikely since the deacetylation of the analogous compound, 2-(1,2-diacetoxyethyl)pyridine, seldom affords α-acetoxy-2-vinylpyridine. Their proposed mechanism which involves an intermediate compound of a half acylated diol is shown.



Scheme (1)

Having succeeded in synthesizing α-acetoxy-4-vinylpyridine (II) from 4-(1,2-diacetoxyethyl)pyridine in an 85% yield, we propose a mechanism which involves the formation of (III) as follows.



Scheme (2)

Results and Discussion

The formation of III from I is fast and the yield is quantitative. 4-(1,2-Diacetoxyethyl)pyridine, bp. 112 °C/0.28 mmHg, mp. 46.5 °C (DSC method) and $n_D^{25.5}$ 1.4908, can be distilled from the reaction solution by the removal of the acetic acid formed and excess acetic anhydride just after I is dissolved into acetic anhydride. In this case the molar ratio of I to acetic anhydride is 1 : 7.5. The reaction (exothermic) was carried out at inner temperature of *ca.* 40 °C for 30 min under occasional water cooling.

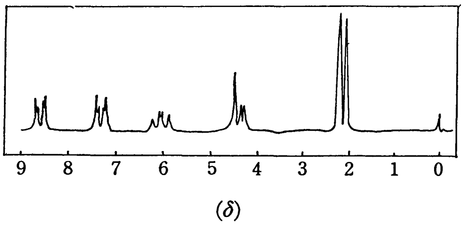
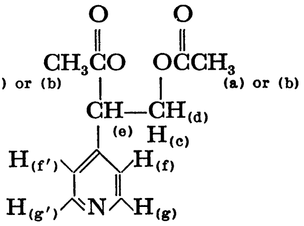
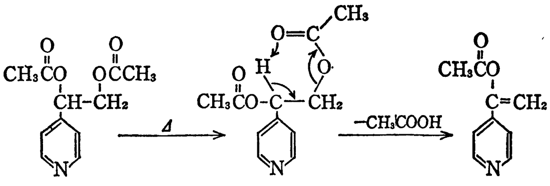


Fig. 1. 60 MHz NMR spectrum 4-(1,2-diacetoxyethyl)pyridine in $CDCl_3$.

The NMR spectrum of III at 60 MHz in deuterochloroform at room temperature is shown in Fig. 1. The methylene peaks ($H_{(c)}$, 4.33 δ; $H_{(d)}$, 4.37 δ) appear as three peaks ($|J_{(c)(e)}|$, 7 cps; $|J_{(d)(e)}|$, 4.5 cps; $|J_{gem}|$, 12 cps), and the methine peaks ($H_{(e)}$, 6.03 δ) were four peaks.



This indicates that the methylene protons are not chemically equivalent. A similar example of aspartic acid in D_2O, was reported by Silverstein and Bassler,[2] where methylene protons adjacent to the asymmetric carbon appear as a triplet. However, the possibility that 4-(1,2-diacetoxyethyl)-pyridine takes a specific conformation cannot be ruled out, since the deacetylation of 4-(1,2-diacetoxyethyl)pyridine *via* a six membered transition state easily takes place to form α-acetoxy-4-vinylpyridine (scheme (3)).



Scheme 3.

A kinetic study for the deacetylation reaction of III was carried out in acetic anhydride at 130 °C (Fig. 2). The deacetylation obeys a first order reaction.

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

[2] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Japanese Ed. translated by S. Araki and Y. Mashiko, Tokyo Kagakudojin, Tokyo (1969), p. 135.

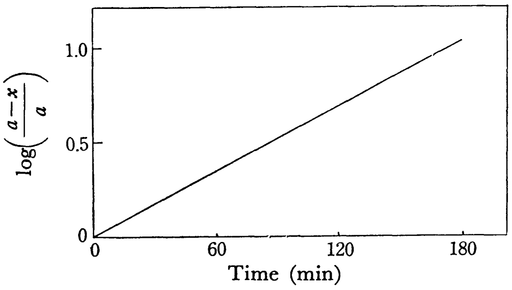


Fig. 2. The deacetylation reaction of 4-(1,2-diacetoxyethyl)-pyridine at 130°C.
a : initial 4-(1,2-diacetoxyethyl)pyridine (mol)
x : product formed (mol)

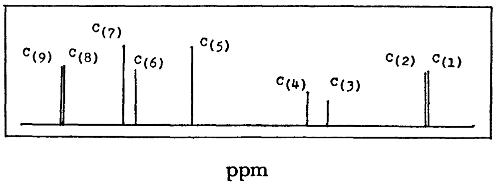


Fig. 3. Carbon-13 NMR spectrum of 4-(1,2-diacetoxyethyl)-pyridine in D_2O.

The yield of deacetylation is as high as 50%, according to the Haas method[1] or the improved Haas method,[3] in contrast to the present method (85% yield) which involves III as an intermediate compound.

A carbon-13 NMR spectrum of III proves the formation of 4-(1,2-diacetoxyethyl)pyridine (Fig. 3).

α-Acetoxy-4-vinylpyridine which was synthesized by the present method can be crystallized with mp of 12.6 °C, and be polymerized with both γ-rays and radical initiators.[4]

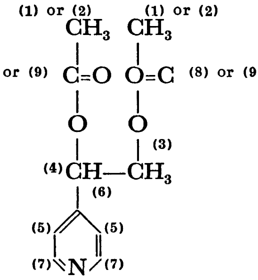
Experimental

4-(1,2-Diacetoxyethyl)pyridine. To 10 g (0.07 mol) of pyridyl)-1,2-ethanediol was added 55 g (0.54 mol) acetic anhydride. The reaction started exothermally, pasty (4-pyridyl)-1,2-ethanediol being gradually dissolved. The system was maintained at approximately 40 °C for 30 min by occasional water cooling. Acetic acid and the excess acetic anhydride were removed under reduced pressure. The subsequent vacuum distillation gave 4-(1,2-diacetoxyethyl)pyridine in a quantitative yield: bp. 112°C/0.28 mmHg. mp. 45.6°C (DSC method). $n_D^{25.5}$ 1.4908. Found: C, 59.2; H, 5.9; N, 6.3%. Calcd for $C_{11}H_{13}O_4N$: C, 59.2; H, 5.9; N, 6.3%.

Deacetylation. A mixture of 10 g (0.045 mol) of 4-(1,2-diacetoxyethyl)pyridine and 35 g (0.343 mol) of acetic anhydride was maintained at 130°C for 6 hr in thermobath. The subsequent fractional distillation under reduced pressure gave α-acetoxy-4-vinylpyridine, yield 85%, mp 12.6°C. The results for bp and elemental analysis for C, H, and N are the same as described previously.[3] Kinetic study was carried out by taking small portion of the reaction mixture and measuring the decreasing methylene protons with a 60 MHz NMR instrument.

Carbon-13 NMR Spectrum. This was measured with JEOL 100 MHz spectrometer (JNM-PET-100) in heavy water at room temperature by the pulse Fourier transform NMR method.[5]

Carbon-13 NMR: $C_{(1)}$ or $C_{(2)}$, ppm 20.9 or 21.1; $C_{(3)}$ 66.2; $C_{(4)}$, 73.3; $C_{(5)}$, 122.6; $C_{(6)}$, 147.2; $C_{(7)}$, 149.9; $C_{(8)}$ or $C_{(9)}$ 173.3 or 173.9 (TMS reference).



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[3] T. Furuyama, K. Mori, and R. Wakasa, This Bulletin, **45**, 1924 (1972).

[4] T. Furuyama, K. Mori, and R. Wakasa, *J. Polym. Sci.*, *A*-1, **9**, 3411 (1971).

[5] E. Breitmaier, G. Jung, and W. Voelter, *Angew. Chem. Intern. Ed.*, **10**, 673 (1971).