BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3900—3901 (1973)

The Solvent Effect on the Stability of α-Pyridoin

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(Received July 23, 1973)

α-Pyridoin is known to take an endiol form (1,2-di-2-pyridylethenediol-1,2) from its infrared absorption spectrum,[1,2] dipole moment,[1] chemical reactivity,[3,4] and crystal analysis.[5] This is in contrast to the case of benzoin.

Recently, in our laboratory the endiol-form compound of benzoin, 1,2-diphenylethenediol-1,2, has been produced photochemically from benzil in particular solvents, but it is too unstable to be isolated.[6] On the other hand, α-pyridoin is relatively stable in some solvents at room temperature.

In this paper, we wish to report about the solvent effect on the stability of α-pyridoin.

Experimental

The α-pyridoin was obtained commercially (Aldrich Chemical Co., Inc.); mp 154.5 °C (lit,[7] 154—155 °C). The solvents used here were purified by the ordinary procedures for each solvent. The ultraviolet absorption spectra were recorded on a Shimadzu Spectrophotometer UV-200, using 1-cm quartz cells. The infrared spectra were measured with a Hitachi Infrared Spectrophotometer EPI-G3, using a 0.025 mm cell.

Results and Discussion

α-Pyridoin has its ultraviolet absorption band around 380 nm in various solvents. Its stability can be seen from the decrease in the absorbance of this band with the time elapsing after the preparation of the solution. The results are shown in Fig. 1. Nitrogen was flushed into the solvent while dissolving the α-pyridoin, except when cyclohexane, benzene, and *N,N*-dimethylformamide were used as solvents. In a mixed solvent of ethanol, for example, the absorption spectrum changed as is shown in Fig. 2. Thirty min after the preparation of the solution, the α-pyridoin was almost completely changed into 2,2′-pyrizil. The product was identified on the basis of the ultraviolet[4] and infrared spectra.[8] Therefore, α-pyridoin was oxidized by a trace of oxygen in the solution.

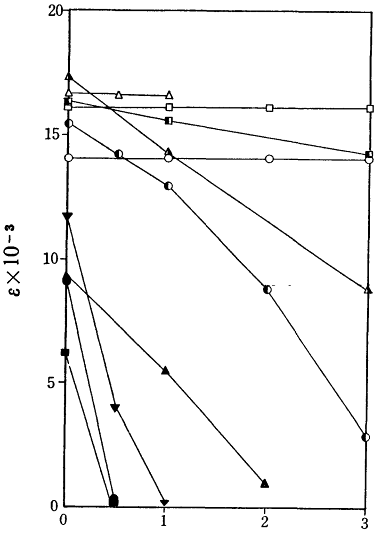

Fig. 1. Change in absorbance of the 380 nm band with time after the preparation of solution.
○: cyclohexane, □: benzene, △: *N,N*-dimethylformamide, ◐: ethanol, ◧: 2-propanol, ◭: di-*n*-butylamine, ●: ethanol+H_2O (1:1), ■: *n*-butylamine, ▲: formamide, ▼: 2-propanol+H_2O (1:1)

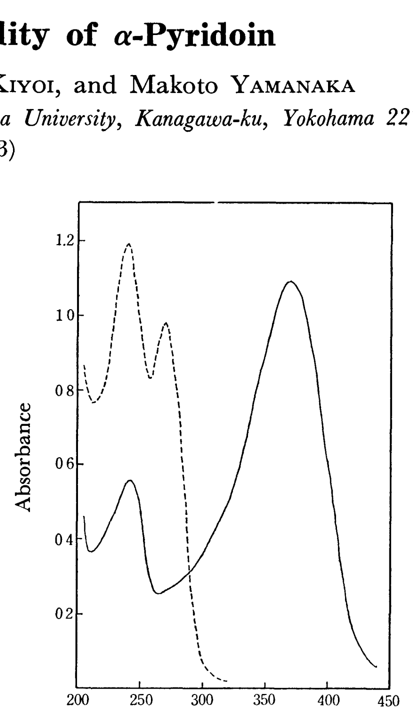

Fig. 2. Spectral change of α-pyridoin in mixed solvent of ethanol and water (1:1).
—— measured immediately after the preperation of the solution, ---- after being allowed to stand for 30 min in contact with the atmosphere.

As may be seen from Fig. 1, the solvents can be grouped into three classes with respect to the stability of α-pyridoin. The results are summarized in Table 1, in which the positions of the long-wavelength band of the α-pyridoin in each solvent are also presented. It can be seen from this table that, in a solvent containing water, α-pyridoin is unstable, Therefore, water seems to play a role in making α-pyridoin unstable. Further-

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1) W. Lüttke and H. Marsen, *Z. Elektrochem.*, **57**, 680 (1953).
2) H. R. Hensel, *Angew. Chem.*, **65**, 491 (1953).
3) F. Cramer and W. Krum, *Chem. Ber.*, **86**, 1586 (1953).
4) B. Eistert and H. Munder, *ibid.*, **88**, 215 (1955).
5) T. Ashida, S. Hirokawa, and Y. Okaya, *Acta Crystallogr.*, **18**, 122 (1965).
6) H. Inoue, S. Takido, T. Somemiya, and Y. Nomura, *Tetrahedron Lett.*, **1973**, 2755.
7) W. Mathes, W. Sauermilch, and Th. Klein, *Chem. Ber.*, **84**, 452 (1951).
8) C. J. Pouchert, "The Aldrich Library of Infrared Spcetra," Aldrich Chemical Co. (1970), p. 978.

Table 1. Solvent effect of stability of α-pyridoin and the position of the long wavelength band

Class A[a]		Class B[b]		Class C[c]	
Solvent	λ_{max} (nm)	Solvent	λ_{max} (nm)	Solvent	λ_{max} (nm)
Cyclohexane	387	Di-*n*-butylamine	385	*n*-Butylamine	380
Benzene	383	Ethanol	377	Ethanol+H_2O (1 : 1)	370
N,N-Dimethylformamide	378			Formamide	374
		2-Propanol	378	2-Propanol+H_2O (1 : 1)	372

a) In this solvent α-pyridoin is stable when allowed to stand in contact with the atmosphere. b) In this solvent α-pyridoin is gradually oxidized when allowed to stand in contact with the atmosphere, but is stable when nitrogen is flushed into solution. c) In this solvent α-pyridoin is oxidized even when nitrogen is flushed into solution.

more, it can be said that, in a solvent with a primary amino group, α-pyridoin is less stable than in the corresponding alkylated solvent, *i.e.*, formamide—*N,N*-dimethylformamide, *n*-butylamine—di-*n*-butylamine. In the cases of *n*-butylamine and formamide, α-pyridoin is oxidized to picolinic acid.

It is noteworthy that the position of the long wavelength band shifts to the blue upon the addition of water to an alcohol solution or upon going from *N,N*-dimethylformamide and di-*n*-butylamine to formamide and *n*-butylamine respectively. Moreover, the position of the band is at a relatively longer wavelength in non-polar solvents such as cyclohexane and benzene than in a polar solvent. This is in contrast to the ordinary behavior of a π-π^* band. The absorption intensity is significantly lower in each solvent of Class C than in the solvents of Classes A and B. Accordingly, it is considered that an intermolecular interaction of α-pyridoin with water and primary amines takes place, thus resulting in the lability of α-pyridoin. It has been presumed that α-pyridoin is stabilized through two intramolecular hydrogen bonds between the enolic OH groups and the heterocyclic nitrogen atoms.[5]

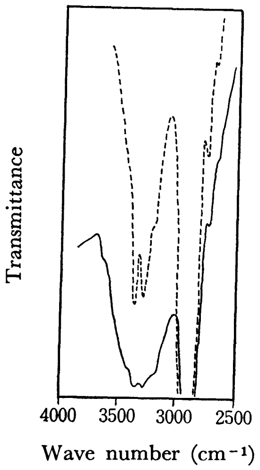
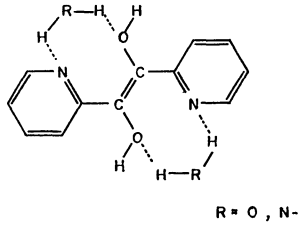


Fig. 3. Infrared absorption spectra of α-pyridoin. —— in *n*-butylamine, ---- *n*-butylamine



Consequently, the solvent effect on the stability and on the position of the band can be interpreted as being due to the breaking of the intramolecular hydrogen bonds, because of the formation of intermolecular hydrogen bonds between α-pyridoin and each solvent of Class C. That is to say, α-pyridoin may form a hydrogen-bonded complex with solvent molecules as is illustrated below. This is clearly indicated by the infrared spectra presented in Fig. 3. In carbon tetrachloride, the OH stretching band appears at a very low wave number (2740 cm^{-1}) because of the intramolecular hydrogen bondings,[1] whereas in *n*-butylamine the OH band appears at 3300 cm^{-1}, though there is some overlapping with the NH band of *n*-butylamine.

That α-pyridoin is gradually oxidized in each solvent of Class B may be interpreted as a result of weak hydrogen bonding between the heterocyclic nitrogen atoms and the NH or OH group of the solvent molecule, because no solvent of Class A has the ability to form such a hydrogen bond.