Method C (Aromatic Solvents).—Approximately 3-g aliquots of a 10–20% solution of allyl *p*-tolyl ether in the aromatic solvent were sealed in test tubes, and the tubes were thermostated for various periods of time. The tube was then weighed and the contents were quantitatively transferred to a volumetric flask and diluted with carbon disulfide to give a solution with an easily measurable absorbance at 12.91 μ. The empty tube was weighed and the sample size was obtained by difference. The absorbance values were normalized, using the sample weight, to eliminate variations due to sample size. The absorbance at infinite time was available from the known concentrations of the solutions and the extinction coefficients of the solvent and 2-allyl-4-methylphenol at 12.91 μ. Plots of log $(D_\infty - D_t)$ *vs.* t were excellent straight lines.

Preparation of Allyl-^{14}C *p*-Tolyl Ether.—In a small distillation flask equipped with an efficient magnetic stirrer were placed 0.605 g (0.1 mC: 10.5 mmol) of allyl-1-^{14}C alcohol and 1.40 g (24.2 mmol) of ordinary allyl alcohol (a total of 34.7 mmol of allyl alcohol). After the addition of 8.0 ml (69.0 mmol) of 48% hydrobromic acid, the mixture was warmed to 70°. Then 3.8 ml (69.0 mmol) of concentrated sulfuric acid was added over a period of 20 min, and the product was allowed to distil as it was formed. The distillate was collected in a receiver immersed in an ice bath and containing 3 g of solid potassium carbonate. There was obtained 3.15 g (75%) of allyl-^{14}C bromide.

To the flask containing the allyl-^{14}C bromide were added an additional 4 g of potassium carbonate, 5.6 g (52.0 mmol) of *p*-cresol, and 30 ml of dry acetone. The slurry was stirred and refluxed for 24 hr. After cooling, 30 ml of water was added, and the mixture was extracted twice with 60-ml portions of ether. The combined ether extracts were washed twice with 20-ml portions of 10% sodium hydroxide solution and once with 20 ml of brine and then dried over magnesium sulfate. The ether was removed and the residue was taken up in a small volume of Skellysolve B and chromatographed on a 15 × 120 mm column of Woelm activity grade I alumina, using Skellysolve B as eluent. After evaporation of the solvent, the residue was distilled, giving 3.37 g (88%) of allyl-^{14}C *p*-tolyl ether, bp 89–91° at 12 mm (lit.[1a] bp 97.5–98.5° at 17 mm), or a 66% overall yield based on allyl alcohol.

Preparation of 2-Allyl-4-methylphenyl 3,5-Dinitrobenzoate.—Using the procedure of Phillips and Kennan,[10] crude 2-allyl-4-methylphenyl 3,5-dinitrobenzoate was prepared. The air-dried solid was taken up in a small volume of 10% ether–benzene and chromatographed on a 15 × 125 mm column of activity grade I alumina, using the same solvent as eluent. After evaporation of the solvent, the residue was recrystallized three times from 1:1 benzene–Skellysolve B and three times from 1:1 chloroform–Skellysolve B. Colorless needles of 2-allyl-4-methylphenyl 3,5-dinitrobenzoate, mp 141.2–142.4°, were obtained.

Anal. Calcd for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.88; H, 4.12; N, 7.93.

Identification of Reaction Product and Determination of Yield.—An accurately weighed sample of 25–50 mg of allyl-^{14}C *p*-tolyl ether was dissolved in 0.5–3.2 g of solvent and sealed in a small test tube. The tube was thermostated for a period of either two or ten half-lives. The contents of the tube were then quantitatively rinsed with 30 ml of 10% sodium hydroxide solution into a flask containing a carefully weighed sample (1.2–1.8 g) of normal 2-allyl-4-methylphenol. The resulting mixture was thoroughly stirred, acidified with hydrochloric acid, and extracted with 30 ml of ether. The solution was dried over magnesium sulfate and then evaporated. The residue was taken up in 20 ml of pyridine and the 3,5-dinitrobenzoate was prepared and purified as described directly above. The melting point and mixture melting point showed the material was 2-allyl-4-methylphenyl 3,5-dinitrobenzoate.

The specific activities of the samples were obtained by converting the samples to carbon dioxide which was collected in an ionization chamber and analyzed for activity with a vibrating reed electrometer.[11]

The activity of the orginal allyl-^{14}C *p*-tolyl ether was obtained by converting it to 2-allyl-4-methylphenyl 3,5-dinitrobenzoate after dilution with the normal ether.

Registry No.—Allyl *p*-tolyl ether, 23431-48-3; 2-allyl-4-methylphenyl 3,5-dinitrobenzoate, 24454-16-8.

(10) M. Phillips and G. L. Keenan, *J. Amer. Chem. Soc.*, **53**, 1926 (1931).
(11) O. K. Neville, *ibid.*, **70**, 3501 (1958); V. F. Raaen and G. A. Ropp, *Anal. Chem.*, **35**, 174 (1953).

Kinetics of the Condensation of 2-Picoline with Aromatic Aldehydes in Acetic Anhydride[1]

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Condensation of 2-picoline with *p*-nitrobenzaldehyde to give *trans*-2-(4′-nitrostyryl)pyridine has been studied kinetically in acetic anhydride, acetic acid, or N,N-dimethylformamide as solvent. The rate in acetic anhydride is shown by the third-order equation $v = k_3$[2-picoline][*p*-nitrobenzaldehyde][acetic acid], where k_3 is 2.4×10^{-5} M^{-2} sec^{-1} at 135°. Acetic acid is formed in the reaction in acetic anhydride and acts as a catalyst. The catalytic ability of carboxylic acids increases with increasing acidity of the acid, the order being as follows: $CH_3CO_2H <$ $PhCO_2H <$ $ClCH_2CO_2H$. The intermediate alcohol, 1-(4′-nitrophenyl)-2-(α-pyridyl)ethanol (1), was obtained from the reaction in N,N-dimethylformamide or dimethyl sulfoxide in the presence of acetic acid. Dehydration of 1 occurs readily both in acetic acid and in acetic anhydride; the rate of dehydration in N,N-dimethylformamide with acetic anhydride is higher than that with acetic acid. Therefore, dehydration of 1 may proceed *via* the acetate, followed by the elimination of acetic acid. Only a little olefin and intermediate alcohol were obtained in the reaction of 2-picoline with benzaldehyde in the presence of basic catalyst such as potassium hydroxide, tributylamine, or potassium acetate by refluxing for 100 hr. The results are explicable by a mechanism involving rate-determining addition of 2-picoline to aromatic aldehyde, where acetic acid acts as an acid catalyst.

The condensation of 2- or 4-picoline with benzaldehyde to give styrylpyridine is satisfactory *via* ethyl pyridylacetate, picoline methiodide, or its N-oxide with basic catalysts,[2] but with picoline itself no basic condensation has been reported, though 2- and 4-picolines are convertible to their conjugate bases by the action of ordinary bases.[3] On the other hand, the condensation of picoline with benzaldehyde is successful

(1) Contribution No. 144.
(2) (a) D. R. Bragg and D. G. Wiberly, *J. Chem. Soc.*, 5074 (1961); (b) L. Pentimalli, *Tetrahedron*, **14**, 151 (1961); (c) H. C. Beyerman, J. Enshnistra, E. Eveleens, and A. Zweistra, *Rec. Trav. Chim. Pays-Bas*, **78**, 43 (1959); (d) K. Raniaiah and V. R. Srinivasan, *Indian J. Chem.*, **1**, 351 (1963); [*Chem. Abstr.*, **60**, 500*g* (1963)]; (e) A. P. Phillips, *J. Org. Chem.*, **12**, 332 (1947).
(3) (a) D. A. Brown and M. J. S. Dewar, *J. Chem. Soc.*, 2406 (1953); (b) H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser., A*, **207**, 121 (1951); (c) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin Inc., New York, N. Y., 1964, p 1003; (d) L. A. Daquette, "Principles of Modern Heterocyclic Chemistry," W. A. Benjamin Inc., New York, N. Y., 1968 pp 245, 293.

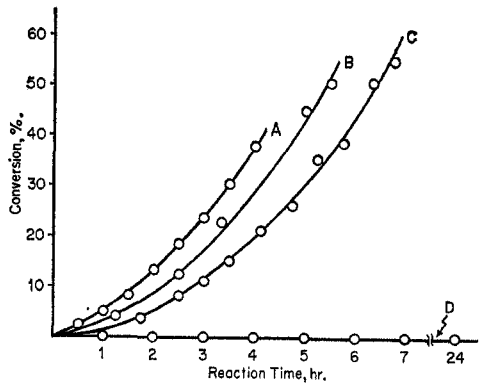


Figure 1.—Effect of acetic anhydride on the condensation of 2-picoline with *p*-nitrobenzaldehyde at 135° in xylene. Initial concentration: *p*-nitrobenzaldehyde, 0.779 *M*; 2-picoline, 2.381 *M*; acetic anhydride, (A) 4.613 *M*, (B) 2.307 *M*, (C) 0.923 *M*, (D) 0 *M*.

by using acetic anhydride as a solvent[4] or zinc chloride as a catalyst.[4a,5] Isolation of 1-phenyl-2-(α-pyridyl)-ethanol as an intermediate has been reported.[4a] The present paper is a summary of our data of kinetic studies on the condensation of 2-picoline with *p*-nitrobenzaldehyde together with the effect of acetic anhydride and carboxylic acids to enable the mechanistic speculation.

Results and Discussion

The condensation of 2-picoline with benzaldehyde gave 2-styrylpyridine by refluxing a mixture in acetic anhydride at 140°. The rate is too slow for the convenient measurement (10% in 30 hr). The rate with *p*-nitrobenzaldehyde is much faster than with benzaldehyde; this acceleration with an electron-withdrawing substituent in benzaldehyde, which has been observed also by Shaw[4a] and Williams,[4b] agrees with a positive Hammett constant ($\rho = +1.2$) for the zinc chloride catalyzed condensation in dimethyl sulfoxide.[6] The product was identified by melting point and uv and ir spectra as *trans*-2-(4′-nitrostyryl)pyridine. No appreciable amount of *p*-nitrobenzaldiacetate could be isolated, but the diacetate was formed on the addition of sulfuric acid, as will be stated later. In the absence of acetic anhydride or acetic acid the condensation failed. 2-(4′-Nitrostyryl)pyridine in a methanolic solution (10^{-5} *M*) showed rapid *trans–cis* photoisomerization (λ_{max} 338 mμ → 323 mμ for 6 hr), which was avoided by interception of a diluted sample solution from light until the uv measurement (see Experimental Section).

Rate Law.—The reaction in acetic anhydride shows a S-shaped conversion curve, suggesting an autocatalysis. An apparent induction period is 1–2 hr as shown in Figure 1. In xylene as a solvent, the rate increased with an increasing amount of added acetic anhydride without disappearance of the apparent induction period. On addition of acetic acid the rate of reaction in acetic anhydride increased with increasing initial concentration of acetic acid and the apparent induction period is shortened. As a limiting case, the reaction in neat acetic acid solvent showed no induction. The reaction follows third-order kinetics, where k_3 is 2.4 × 10^{-5} M^{-2} sec^{-1} at 135°. Here, *a*, *b*, and *c* are initial

$$dx/dt = k_3 (a - x)(b - x)(c + 2x) \quad (1)$$

concentrations of *p*-nitrobenzaldehyde, 2-picoline, and acetic acid, respectively, and *x* is the concentration of formed 2-(4′-nitrostyryl)pyridine at time *t*. The kinetic data are shown in Table I.

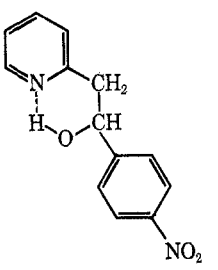
TABLE I

THIRD-ORDER RATE CONSTANT, k_3, FOR THE REACTION OF 2-PICOLINE WITH *p*-NITROBENZALDEHYDE IN ACETIC ANHYDRIDE AT 135°

Initial concentration, *M*			Rate constant, M^{-2} sec^{-1},
p-Nitrobenzaldehyde	2-Picoline	Acetic acid	$10^5 k_3$
0.779	2.381	0	2.4
0.779	2.381	0.515	2.8
0.779	2.381	0.773	2.5
0.779	2.381	1.030	2.4
0.779	2.381	1.803	1.9
1.177	1.177	0.585	2.3
		Average	2.4

The results indicate a catalysis by acetic acid. Even without addition of acetic acid, the reaction is started by a trace of acetic acid which is contained in the original system. The reaction in acetic anhydride should produce 2 molar equiv of acetic acid, and so the rate tends to increase gradually as the reaction proceeds. An alternative possibility that styrylpyridine should promote the reaction as a basic catalyst is excluded, because the basicity of styrylpyridine is lower than that of 2-picoline and because the kinetics is only first order in 2-picoline.

Intermediates.—The following facts present evidence that 1-(4′-nitrophenyl)-2-(α-pyridyl)ethanol (**1**) is an intermediate and that acetic acid and anhydride act as dehydrating agents. Heating a mixture of 2-picoline and *p*-nitrobenzaldehyde in N,N-dimethylformamide or dimethyl sulfoxide in the presence of acetic acid gave **1** (18%) but not 2-(4′-nitrostyryl)pyridine. Its uv spectrum shows a resemblance to that of 2-picoline. A broad OH band at 3100 cm^{-1} in its ir spectrum suggests a chelation as shown in **1**. 1-(4′-Nitrophenyl)-2-(α-pyridyl)ethanol (**1**) was converted readily to 2-(4′-nitrostyryl)pyridine (64 and 58% at 2 hr by heating at 115° in acetic acid and acetic anhydride, respectively), but neither *p*-nitrobenzaldehyde nor 2-picoline was obtained. This is evidence that **1** is an intermediate. It has been reported that **1** is a main product at 130–



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(4) (a) B. S. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, 77 (1933); (b) J. L. Williams, R. E. Adel, J. M. Carlson, G. A. Reynolds, D. G. Borden, and J. A. Ford, Jr., *J. Org. Chem.*, **28**, 387 (1963); (c) W. Baker, K. M. Buggle, J. F. W. McOmie, and D. A. M. Watkins, *J. Chem. Soc.*, 3594 (1958); (d) R. Royer, *ibid.*, 1803 (1949).

(5) (a) G. Langer, *Ber.*, **38**, 3704 (1905); (b) K. Katsumoto, *Bull. Chem. Soc. Jap.*, **33**, 242 (1960); (c) W. H. Mills and J. L. B. Smith, *J. Chem. Soc.*, **121**, 2724 (1922).

(6) S. Matsuo and K. Onishi, Meeting of Tokai Branch of Chemical Society of Japan, Nagoya, 1968.

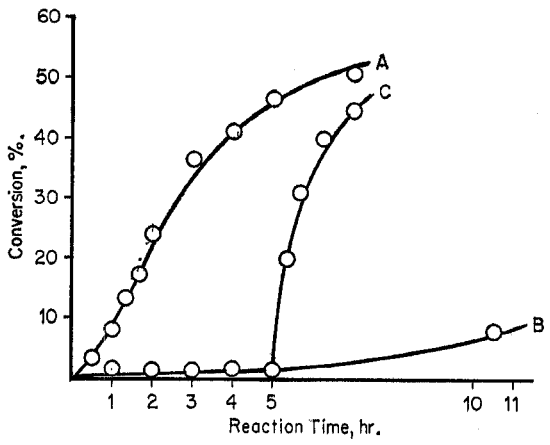


Figure 2.—Conversion curves for the reaction of 2-picoline with *p*-nitrobenzaldehyde at 135° in N,N-dimethylformamide in the presence of (A) 1.730 *M* of acetic anhydride; (B) 1.030 *M* of acetic acid; (C) 1.030 *M* of acetic acid at first and on further addition of 1.730 *M* of acetic anhydride after 5 hr. Initial concentration: *p*-nitrobenzaldehyde, 0.779 *M*; 2-picoline, 2.381 *M*.

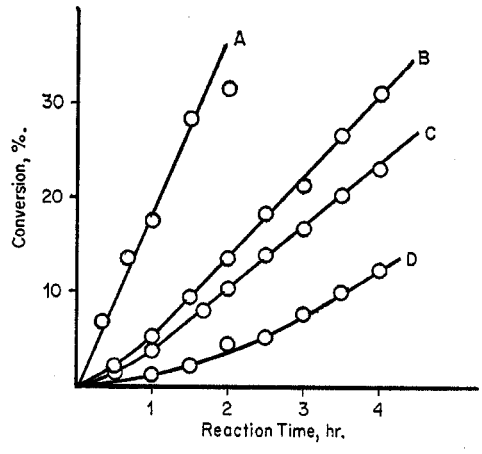


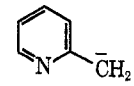
Figure 3.—Effect of carboxylic acids on the conversion of 2-picoline to 2-styrylpyridine in acetic anhydride at 135°. Initial concentration: carboxylic acid, 0.585 *M*; *p*-nitrobenzaldehyde, 1.177 *M*; 2-picoline, 1.177 *M*, (A) $ClCH_2CO_2H$, (B) $PhCO_2H$, (C) CH_3CO_2H, (D) no carboxylic acid.

150° in the presence of water and that **1** is converted in part to 2-picoline and aromatic aldehyde by heating in the presence of water at 140–200°. Therefore, the formation of **1** is reversible.[4b] The rate of dehydration of the intermediate alcohol (**1**) is much faster than that of decomposition at least in acetic anhydride or acetic acid. The conversion curves for the formation of 2-(4′-nitrostyryl)pyridine in N,N-dimethylformamide are shown in Figure 2. Although the formation of 2-(4′-nitrostyryl)pyridine proceeds smoothly in the presence of excess acetic anhydride (curve A in Figure 2), the reaction is very slow in the presence of acetic acid (curve B in Figure 2). On addition of acetic anhydride to the latter system, represented by curve B after 5 hr, 2-(4′-nitrostyryl)pyridine is formed rapidly (curve C in Figure 2) to the corresponding conversion in the former system (A). The higher rate in C than that in A suggests accumulation of a considerable amount of the intermediate alcohol **1** in B in agreement with the isolation of **1** from system B. As **1** is formed either in the presence of acetic acid or acetic anhydride, the rate of formation of 2-(4′-nitrostyryl)pyridine is controlled by the dehydration (or elimination) step of **1** at least in N,N-dimethylformamide in the absence of acetic anhydride. The superior ability of acetic anhydride to that of acetic acid suggests that the formation of 2-(4′-nitrostyryl)pyridine from **1** proceeds not by a simple dehydration but *via* acetate, followed by elimination of acetic acid.

Acid Catalysis.—Acetic acid and some other carboxylic acids show catalysis in acetic anhydride (Figure 3). The order of catalytic power is in the order of acidity, *i.e.*, $ClCH_2CO_2H > PhCO_2H > CH_3CO_2H$.

However, the reaction stopped at *ca.* 40% conversion on addition of hydrochloric acid instead of carboxylic acid; little olefin, together with a large amount of *p*-nitrobenzaldiacetate, was obtained with sulfuric acid. *p*-Nitrobenzaldiacetate was obtained in a 66% yield with hydrochloric acid in a reaction system without 2-picoline. Accordingly, for the reaction with mineral acids in acetic anhydride, the suppression of the olefin formation is due to a side reaction, *i.e.*, the rapid formation of unreactive *p*-nitrobenzaldiacetate.

A weak base catalysis was observed, since the yield of a mixture of olefin and intermediate alcohol was only below 10% with potassium hydroxide (3.5%), tributylamine (9.6%), or potassium acetate (1%) for the attempted condensation of 2-picoline with benzaldehyde by refluxing for 100 hr. These observations suggest that the conjugate base of 2-picoline, **2**, is not important as a reactive species for the condensation in acetic anhydride.



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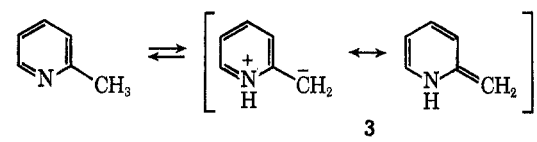
The Mechanism.—The observed facts are summarized as follows. (i) The condensation in acetic anhydride was overall third order; *i.e.*, $v = k$[2-picoline][*p*-nitrobenzaldehyde][acetic acid]. (ii) Only a little base catalysis was observed. (iii) The condensation proceeds *via* 1-(4′-nitrophenyl)-2-(α-pyridyl)ethanol (**1**) (or its acetate). (iv) The elimination of intermediate **1** to 2-(4′-nitrostyryl)pyridine was faster with acetic anhydride than with acetic acid. These facts



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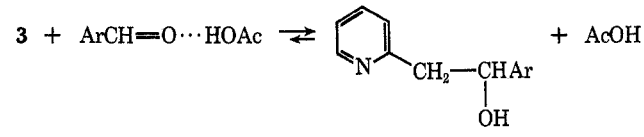

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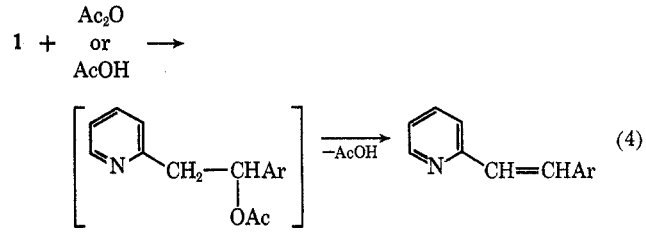
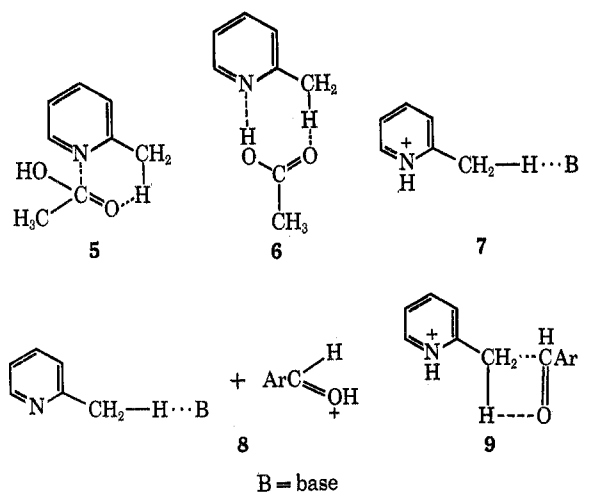


(4)

and the observation described below suggest the preceeding mechanism as the most probable one.

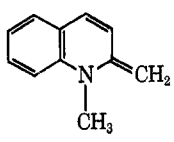
The rate-determining step is the formation of intermediate alcohol **1** (addition step), since the dehydration of **1** was rapid in acetic anhydride and the rate showed first-order dependence on acetic acid but not on acetic anhydride, whereas acetic anhydride in N,N-dimethylformamide was more efficient than acetic acid as a dehydrating agent. The fact that *p*-nitrobenzaldehyde reacts much faster than unsubstituted benzaldehyde supports the rate-determining attack of **3** on benzaldehyde. For the specific acid-catalyzed condensation of substituted benzaldehydes with acetophenone a small negative ρ value of -0.25 has been reported,[7] while for the general acid catalyzed condensation of substituted acetophenones with semicarbazide a positive ρ value of $+0.91$ has been reported.[8] Hence, the present mechanism involving association between benzaldehyde and the general acid catalyst prior to the rate-determining step is acceptable. The acceleration by electron-withdrawing substituents in benzaldehyde has been reported for the zinc chloride catalyzed condensation of substituted benzaldehydes with 2-picoline in dimethyl sulfoxide ($\rho = 1.2$)[6] and for the condensation in acetic anhydride.[4,5a] Conversely, the elimination of 1-phenylethyl chloride ($\rho^+ = -1.36$)[9] and acetate ($\rho^+ = -0.64$)[10] and 1-aryl-2-phenylethanol ($\rho^+ = -3.9$)[11] is retarded by an electron-withdrawing substituent.

An alternative possibility of the intermediacy of **5**, **6**, **7**, **8**, or **9** might be implied in view of the rate equation, but they are less plausible because of the following reasons. (i) The observed kinetics is not first order in acetic anhydride (excluding **5**). (ii) 4-Picoline, which cannot have such a cyclic mechanism, reacts more rapidly than 2-picoline (excluding **5** and **6**). (iii) The condensation of 4-picoline was also promoted by acetic acid (excluding **5** and **6**). (iv) No general base catalyzed addition of the saturated C—H bond to the C=O group for aldol-type reactions has been reported (excluding **7** and **8**). (v) No four-centered mechanism with saturated C—H bond has been reported (excluding **9**).



B = base

In view of the observed acid catalysis and weakness of base catalysis, the participation of the conjugate base of 2-picoline (**2**) is less plausible; the methyl group of 2-picoline is not so acidic as to transfer its proton to an ordinary base. The probable reactive species may be **3**. An intermediate similar to **3** has been reported in base-catalyzed condensation of picoline methiodide and picoline N-oxide and in the hydrogen–deuterium exchange at methyl group of quinaldine with deuterated alcohols.[12] Moreover, it has been reported that 1-methyl-2-methylene-1,2-dihydroquinoline (**10**) is isolated.[13]



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Intermediate alcohols are obtained even in the absence of acid catalyst in water for the condensation of benzaldehydes with 2-picoline,[4a] while intermediate alcohols (adducts) were obtained without an acid catalyst in a reaction with neat quinaldine, where an uncatalyzed reaction has been observed by kinetic study in acetic anhydride.[14] These facts support the participation of **3** as a reactive species.

Since eq 2 does not require the acetic acid catalysis, the first-order dependence of the rate on acetic acid suggests that acetic acid acts as shown in **4**. The catalysis is more effective with stronger carboxylic acids, *i.e.*, $ClCH_2CO_2H > PhCO_2H > CH_3CO_2H$.

The formation of intermediate **1** is reversible, because **1** is known to produce the parent aldehyde and 2-picoline by heating at 200°.[4a] Dehydration of **1** proceeds probably *via* its acetate, since (i) acetic anhydride was more effective than acetic acid in N,N-dimethylformamide (in Figure 2), and (ii) an acyloxy group is a better leaving group than a hydroxy group.[15a] 2-Styrylquinoline is also known to be formed through the acetate intermediate.[16]

Xanthates (the Chugaev reaction) and carboxylate esters are known to undergo *cis* elimination,[15b] and this may be applied to this case. Consideration of the steric course of the elimination implies that the predominant product would be *trans* olefin in view of the steric requirement for the transition state and this is the case.

Experimental Section

Materials.—Benzaldehyde and 2-picoline were purified by distillation under nitrogen atmosphere; boiling points were 87.0° (41.5 mm) and 49.8° (40.3 mm), respectively. *p*-Nitrobenzaldehyde was prepared from *p*-nitrotoluene,[17] mp 105–106° (lit.[17] 106°). Ordinary purification was applied to acetic acid, bp 108°, and acetic anhydride, bp 140°.

Products. 2-Styrylpyridine.—A mixture of 2-picoline (0.33 mol), benzaldehyde (0.33 mol), and acetic anhydride (190 ml)

(7) D. S. Noyce and W. A. Pryor, *J. Amer. Chem. Soc.*, **81**, 618 (1959).

(8) (a) R. P. Cross and P. Fugassi, *ibid.*, **71**, 22 (1949); (b) Y. Ogata, A. Kawasaki, and N. Okumura, *Kagaku Kagaku*, **21**, 63 (1966).

(9) M. R. Bridge, *J. Chem. Soc., B*, 805 (1968).

(10) R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, **84**, 4817 (1962).

(11) G. M. London and D. S. Noyce, *ibid.*, **91**, 1433 (1969).

(12) (a) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 169 (1963). (b) A. I. Shatenshtein and E. N. Zuyagintseva, *Dokl. Akad. Nauk SSSR*, **117**, 852 (1957).

(13) (a) E. Rosenhauer, H. Hoffmann, and H. Unger, *Ber.*, **59B**, 946 (1926); (b) F. W. Bergstrom, *Chem. Rev.*, **35**, 77 (1944).

(14) Unpublished data.

(15) E. S. Gould, "Structure and Mechanism in Organic Chemistry," Henry Holt Co., New York, N. Y., 1959: (a) p 261; (b) p 500.

(16) A. F. Walton, R. S. Tipson, and L. H. Cretcher, *J. Amer. Chem. Soc.*, **67**, 1501 (1945).

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was refluxed at 140° for 30 hr. The mixture was steam distilled and the distillate was made alkaline by aqueous NaOH to give precipitate of 2-styrylpyridine, which was recrystallized from aqueous ethanol: 10 g (18.1%), mp 90.0–90.5° (lit.[4a] 90.0–91.0°).

2-(4′-Nitrostyryl)pyridine.—A mixture of *p*-nitrobenzaldehyde (0.033 mol), 2-picoline (0.051 mol), and acetic anhydride (0.053 mol) was refluxed for 10 hr and further heated without the reflux condenser for 30 min to remove any acetic acid, which was produced, 2-picoline, and acetic anhydride. The filtered product was washed with water and recrystallized from aqueous ethanol, yielding yellow crystals (81.5%): mp 134–135° (lit. 126°,[18] 136°,[4a] 142°[19]); ir (KBr disk) 960 ~ 970 cm^{-1} (characteristic to *trans* –CH=CH– group); uv λ_{max} (MeOH) 338 mμ (log ε 4.50), λ_{max} (protonated by 1 or 2 drops of concentrated HCl in a methanolic solution) 340 mμ (log ε 4.50) [lit.[4b] 355 mμ (log ε 4.48) in MeOH].

Effect of Light on *trans–cis* Isomerization of *trans*-2-(4′-Nitrostyryl)pyridine.—It is known that irradiation causes the *trans–cis* isomerization[20] of 2-styrylpyridine derivatives under nitrogen atmosphere, and also dimerization[20,21] and cyclization[22] *via* the *trans–cis* isomerization in the presence of oxygen. We also observed that 2-(4′-nitrostyryl)pyridine suffered *trans–cis* photoisomerization in methanol or dioxane (10^{-5} *M*) by standing in the diffused light in a room. The change in its uv spectra is listed in Table II. Irrespective of the presence or absence of oxygen the photoisomerization which disturbs the precise rate measurement was avoided by the interception of light with aluminum foil.

TABLE II
EFFECT OF DIFFUSED LIGHT IN A ROOM ON *cis–trans* ISOMERIZATION OF 2-(4′-NITROSTYRYL)PYRIDINE

Solvent	At the moment of dilution, λ_{max} (log ε)	Interception from light (after 6 hr), λ_{max} (log ε)	Standing in diffused light (after 6 hr), λ_{max} (log ε)
Methanol	338 (4.52)	338 (4.54)	323 (4.20)
Dioxane	345 (4.41)	344 (4.43)	330 (4.07)

Rate Measurement.—The rate of reaction was measured by following the extinction at 338 mμ (log ε 4.50) of *trans*-2-(4′-nitrostyryl)pyridine. The reaction was carried out in a 100-ml two-necked flask furnished with a Dimroth condenser, at 135°. Aliquots were taken out at appropriate intervals of time, diluted with methanol, and kept standing in a test tube covered with aluminum foil in the dark; extinctions at 338 mμ were determined. The third-order rate constant, k_3, in eq 1 was calculated by the following equation, $k_3 = 2.303A/(2a + c)(2b + c)(a - b)$, if $a \neq b$, where A is the slope in a plot of $[(2b + c) \log (a - x) + (a + c) \log (b - x) + 2(a - b) \log (c + 2x)]$ *vs.* time, or $k_3 = B/(2a + c)_2$, if $a = b$, where B is a slope in a plot of $[-2 \ln (a - x) + (2a + c)/(a - x) + 2x \ln (b + 2x)]$ *vs.* time. a, b, c, and x are defined in eq 1. The third-order plot showed a good linearity except at an early stage of the reaction at low concentration of acetic acid ($c \sim 0$).

Intermediate Criterion. 1-(4′-Nitrophenyl)-2-(α-pyridyl)ethanol (1).—A mixture of *p*-nitrobenzaldehyde (1 g), 2-picoline (2 ml), acetic acid (0.5 ml), and N,N-dimethylformamide or dimethyl sulfoxide (5 ml) was heated at 135° for 4–5 hr. The reaction mixture was poured into water, made alkaline by aqueous NaOH, and precipitated. The precipitate was dissolved in benzene, treated with saturated $NaHSO_3$ to remove aldehyde, and dried (Na_2SO_4), and the solvent was evaporated. The residue was recrystallized from aqueous methanol, giving yellow crystals (18%), mp 154–160°. The uv spectrum showed a strong resemblance to that of 2-picoline; ir spectrum (KBr) 3140 (OH···N chelation as shown in 1), 2920, 2850, 1465 (CH_2), 1094 cm^{-1} (α-phenyl OH).

Dehydration of 1-(4′-Nitrophenyl)-2-(α-pyridyl)ethanol (1) in Acetic Acid or in Acetic Anhydride.—1 (10 mg) in acetic acid (1 ml) or acetic anhydride (1 ml) was heated at 115° for 2 hr. The reaction mixture was made alkaline with aqueous NaOH, the products being filtered and dried (Na_2SO_4). The yield was 64% (in acetic acid) and 58% (in acetic anhydride): mp 133–133.5°; uv λ_{max} (MeOH) 338 mμ; ir (KBr disk) 960–970 cm^{-1} (*trans* –CH=CH–). The product was *trans*-2-(4′-nitrostyryl)pyridine alone.

Attempted Condensation of 2-Picoline with Benzaldehyde by a Basic Catalyst.—A mixture of 2-picoline (0.1 mol), benzaldehyde (0.1 mol), and tri-*n*-butylamine (0.01 mol) was refluxed for 100 hr. The mixture, after being treated with water, was extracted with benzene. The benzene solution was treated with aqueous HCl and the aqueous layer was neutralized with K_2CO_3 to give precipitate of a mixture of 2-styrylpyridine and 1-phenyl-2-(α-pyridyl)ethanol, 1.7 g (9.2%).

Registry No.—2-Picoline, 109-06-8; acetic anhydride, 108-24-7; *p*-nitrobenzyldehyde, 555-16-8; 1, 20151-01-3; *trans*-2-(4′-nitrostyryl)pyridine, 24470-06-2.

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Acid-Catalyzed Decarboxylation of Glycidic Acids. "Abnormal" Products

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The acid-catalyzed decarboxylation of α-phenylglycidic acids yields carbonyl compounds in which the carbonyl is at the original β carbon of the starting material, and the accepted concerted mechanism for the decarboxylation of glycidic acids must therefore be revised. Consideration of the energy of the two carbonium ions formed by isomerization of the oxirane-protonated species explains the "normal" as well as the "abnormal" behavior of the glycidic acids. The energy of a benzylic carbonium ion adjacent to a carboxyl group is lower than that of a primary or secondary β-alkyl carbonium ion, but is comparable with that of a tertiary β-alkyl carbonium ion since 9 yielded the "normal" as well as the "abnormal" product (11). This latter conversion represents the first example of group migration in the decarboxylation of glycidic acids.

A classical preparative method for aldehydes and ketones utilizes sodium glycidates prepared by Darzens synthesis,[2] followed by Claisen saponification. Decarboxylation and epoxide ring opening take place after acid treatment, usually in the presence of heat. The method has been particularly reliable since no group migration has ever been detected,[3] and the carbonyl in the final product has always been found at the carbon atom bearing the carboxyl in the starting material. The accepted mechanism for the reaction[4,5] involves a *concerted* process in which decarboxylation and epoxide ring opening occur simultaneously, yielding an enol which finally ketonizes. The reacting species

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