

same manner as described for conversion of 20 to 14. The spectral and vpc retention time on a 250-ft UCON 50HB2000 capillary column of vpc-purified material were identical with those of the hydrocarbon prepared from 19.

distal-4-Methyl-1-spiropentane (24).—Reduction of 5 to *distal-4-methyl-1-spiropentane* (24) was accomplished as described above for reduction of 17 to 20: ir (CCl₄) 3620, 3370 (broad), 3050, etc., 1380, and 1022 cm⁻¹; nmr (100 MHz) (CCl₄) δ 0.23 (broad singlet, 1 H), 0.44 (unsymmetrical triplet, 1 H), 1.01 (broad singlet) superimposed on a multiplet between 0.75 and 1.44 (total of 7 H), 2.53 (broad singlet, 1 H), and 3.40 (doublet, *J* = 7 Hz 2 H).

Anal. Calcd for C₇H₁₂O: C, 74.95; H, 10.79. Found: C, 74.84; H, 10.61.

distal-1,4-Dimethylspiropentane (14) from 24.—The alcohol 24 was converted to *distal-1,4-dimethylspiropentane* (14) in the same manner as described for conversion of 20 to 14. The spectral properties and vpc retention time on a 250-ft UCON 50-

HB2000 capillary column of vpc purified hydrocarbon were identical with those of the hydrocarbon prepared from 30.

Registry No.—3, 24298-73-5; 4, 24298-74-6; 5, 24298-75-7; 6, 24299-28-3; 7, 6142-68-3; 8, 24299-29-4; 9, 24299-30-1; 10, 24299-31-8; 11, 24299-32-9; 12, 24299-33-0; 13, *medial*, 24299-34-1; 14, 24299-35-2; 15, 24299-36-3; 16, 24299-37-4; 17a, 24375-89-1; 18, 24299-39-6; 19, 24299-40-9; 20, 24343-79-1; 21, 24299-41-0; 22, 24299-42-1; 23, 24343-80-4; 24, 24299-43-2.

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The *ortho* Claisen Rearrangement. VIII. Solvent Effects^{1,2}

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The rates of rearrangement of allyl *p*-tolyl ether in the gas phase and in 17 solvents of different polarities have been determined. The rates varied over a 300-fold range, indicating a considerable solvent effect. The normal rearrangement product was formed in every case. The results cannot be explained solely on the basis of the hydrogen-bonding ability of the solvent and it is necessary to invoke other solvent properties to account for the findings.

The Claisen rearrangement has often been cited as a reaction insensitive to solvent effects, in spite of the fact that early studies³ indicated that this was probably not so. A couple of more recent investigations^{1a,4} have also indicated that the reaction is influenced by the nature of the medium. A more complete evaluation of solvent effects and their origin was attempted in this investigation.

Results

The rates of rearrangement of allyl *p*-tolyl ether in the gas phase and in 17 solvents of differing polarities were determined. The specific rate constant was measured in one of three different ways, depending on the nature of the solvent. If the solvent had negligible absorption in the ultraviolet-visible range, aliquots of the reaction mixture were dissolved in aqueous or alcoholic base and the formation of product was followed through the absorption of the 2-allyl-4-methylphenoxide ion. The reaction in solvents that have significant absorption in the ultraviolet-visible region was monitored by observing the change in a band at 12.91 μ that appears in the infrared spectrum of allyl *p*-tolyl ether. In the gas phase runs, samples of the

ether were sealed in evacuated tubes and thermostated for various intervals. The sample size was such that all of the reactant and/or product was in the gas phase at the reaction temperature. The extent of reaction was determined from the ultraviolet spectrum of a solution of the partially reacted sample in alcoholic sodium hydroxide solution. The absence of a wall effect in the gas phase reaction was obvious from the constancy of per cent reaction in normal tubes and in tubes packed with glass wool. The rate constants obtained by these methods are listed in Table I. These values were used to obtain rate constants at 170° by extrapolation or interpolation (Table II).

The reaction product in all of the solvents was shown to be 2-allyl-4-methylphenol by isotope dilution analysis. A solution of allyl-C¹⁴ *p*-tolyl ether in the solvent under study was rearranged; *n*-2-allyl-4-methylphenol was mixed in and then was converted into the 3,5-dinitrobenzoate for isolation and purification. The per cent yield of 2-allyl-4-methylphenol was calculated from the specific activity of the purified product. The yields in the various solvents are shown in Table III. The expected product, 2-allyl-4-methylphenol, was formed in greater than 80% yields in all of the solvents except 2-aminoethanol, 2-octanol, propylene carbonate, sulfolane, and *p*-chlorophenol. Because of the possibility for decomposition of the product during the long reaction period, the rearrangement in these five solvents was carried out for a shorter period. In all cases, the yields were improved indicating that the product was being destroyed by prolonged heating.

Discussion

As is evident from the data listed in Table II, the rate of the *ortho* Claisen rearrangement is significantly

(1) Previous papers in this series: (a) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. K. Fife, *J. Amer. Chem. Soc.*, **80**, 3271 (1958); (b) W. N. White and B. E. Norcross, *ibid.*, **83**, 1968 (1961); (c) W. N. White and B. E. Norcross, *ibid.*, **83**, 3265 (1961); (d) W. N. White and W. K. Fife, *ibid.*, **83**, 3846 (1961); (e) W. N. White and C. D. Slater, *J. Org. Chem.*, **26**, 3631 (1961); (f) W. N. White and C. D. Slater, *ibid.*, **27**, 2908 (1962); (g) W. N. White and E. F. Wolfarth, *ibid.*, **26**, 3509 (1961); (h) W. N. White, C. D. Slater, and W. K. Fife, *ibid.*, **26**, 627 (1961).

(2) This investigation was supported by Grants G-7345 and GP-1970 from the National Science Foundation.

(3) J. F. Kincaid and D. S. Tarbell, *J. Amer. Chem. Soc.*, **61**, 3085 (1939), found that the rate of rearrangement of allyl *p*-tolyl ether in the absence of solvent increased about fourfold as the reaction progressed implying that the reaction occurred faster in the phenolic product than in the original ether.

(4) H. L. Goering and R. R. Jacobsen, *ibid.*, **80**, 3277 (1958).

TABLE I
 REARRANGEMENT RATES OF ALLYL *p*-TOLYL ETHER IN VARIOUS SOLVENTS

Solvent	Method ^a	T ^b °C	10 ⁶ k (sec ⁻¹)	Solvent	Method ^a	T ^b °C	10 ⁶ k (sec ⁻¹)
Gas phase	A	185.3	0.309	1-Decanol	B	160.3	0.501 ± 0.003
		199.7	1.63			180.3	2.41 ± 0.01
		217.3	5.96			199.7	9.48 ± 0.03
		231.9	12.2				
Tetradecane	B	160.3	0.123 ± 0.002	Et(OCH ₂ CH ₂) ₂ OH	B	160.3	0.784 ± 0.004
		180.3	0.728 ± 0.002			180.3	3.94 ± 0.05
		199.7	3.30 ± 0.02			199.7	15.7 ± 0.7
<i>n</i> -C ₄ H ₉) ₂ O	B	170.3	3.27 ± 0.2	<i>n</i> -C ₇ H ₁₅ COOH	B	170.3	24.2 ± 0.3
<i>n</i> -C ₁₀ H ₂₁ NH ₂	B	160.3	0.187 ± 0.001	HOCH ₂ CH ₂ NH ₂	B	160.3	1.22 ± 0.01
		180.3	1.05 ± 0.01			180.3	5.79 ± 0.03
		199.7	4.64 ± 0.01			199.7	24.2 ± 0.3
(EtOCH ₂ CH ₂) ₂ O	B	170.3	5.33 ± 0.4	HOCH ₂ CH ₂ OH	B	155.3	2.06 ± 0.02
						170.3	6.73 ± 0.15
						185.3	20.4 ± 0.1
Propylene carbonate	B	160.3	0.392 ± 0.008	<i>p</i> -MeC ₆ H ₄ OH	C	150.3	1.90
		180.3	2.18 ± 0.06			170.3	7.31
		199.7	8.59 ± 0.14			190.3	21.6
2-Octanol	B	160.3	0.411 ± 0.003	C ₆ H ₅ OH	C	150.3	2.42
		180.3	2.18 ± 0.05			165.3	7.11
		199.7	8.15 ± 0.04			180.3	20.4
NC(CH ₂) ₄ CN	B	160.3	0.436 ± 0.003	28.5% EtOH-H ₂ O	B	148.7	2.23 ± 0.01
		180.3	2.42 ± 0.01			159.7	5.13 ± 0.03
		199.7	10.4 ± 0.3			170.3	10.7 ± 0.3
Sulfolane ^c	B	160.3	0.459 ± 0.002	<i>p</i> -ClC ₆ H ₄ OH	C	148.2	7.47
		180.3	2.36 ± 0.02			158.8	13.2
		199.7	11.0 ± 0.1			170.3	30.3

^a Method A—gas phase, ultraviolet spectrophotometric analysis; method B—solution, ultraviolet spectrophotometric analysis; method C—solution, infrared spectrophotometric analysis. ^b Temperature maintained to within ±0.1°. ^c Tetramethylene sulfone.

 TABLE II
 RATE CONSTANTS AND ACTIVATION PARAMETERS FOR
 REARRANGEMENT OF ALLYL *p*-TOLYL ETHER IN
 VARIOUS SOLVENTS

Solvent	10 ⁶ k (sec ⁻¹) ^a	ΔH ^{‡b,c}	ΔS ^{‡c,d}	Z
Gas phase	1.01	35.1	-7.7	
Tetradecane	3.01	33.1	-9.8	60.1
<i>n</i> -Butyl ether	3.27			60.1
<i>n</i> -Decylamine	4.52	32.4	-10.7	
Ethylcarbitol ^d	5.33			65.2
Propylene carbonate	9.42	31.0	-12.4	72.4
2-Octanol	9.65	29.3	-16.2	78.6
Adiponitrile	10.5	32.0	-10.0	70.7
Sulfolane ^e	10.7	32.0	-9.8	76.9
1-Decanol	11.1	29.6	-15.2	78.0
Carbitol ^f	17.9	30.1	-13.1	78.1
Octanoic acid	24.2			77.6
2-Aminoethanol	27.1	30.1	-12.2	84.4
Ethylene glycol	67.3	28.9	-13.1	85.1
<i>p</i> -Cresol	73.1	22.9	-26.6	88.8
Phenol	103	26.3	-18.2	
28.5% ethanol-water	107	26.2	-18.5	91.9
<i>p</i> -Chlorophenol	303	22.9	-23.8	

^a Rate constants at 170°. ^b In kcal/mol. ^c cal/deg mol. ^d EtOCH₂CH₂OCH₂CH₂OEt. ^e Tetramethylene sulfone. ^f EtOCH₂CH₂OCH₂CH₂OH. ^g The average error of ΔH[‡] is ±0.2 kcal/mol and that of ΔS[‡] is ±0.3 eu (calculated by the procedure of E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *J. Amer. Chem. Soc.*, **77**, 837 (1955)).

affected by the nature of the solvent. The rate was found to vary by a factor of 100 in going from the least polar to the most polar solvent studied, and a factor of 300 in going from the gas phase to the most polar solvent. It is interesting to compare these rate factors with those observed in well-established polar reactions.

 TABLE III
 YIELDS OF 2-ALLYL-4-METHYLPHENOL FROM REARRANGEMENT
 OF ALLYL *p*-TOLYL ETHER IN VARIOUS SOLVENTS

Solvent	Reaction time, half-lives	% yield
Ethylene glycol	10	101
2-Aminoethanol	10	17
	2	58 ^b
Carbitol ^a	10	91
1-Decanol	10	94
2-Octanol	10	81
<i>n</i> -Decylamine	10	77
Adiponitrile	10	95
Propylene carbonate	10	25
	2	87 ^b
Sulfolane ^e	10	55
	2	81 ^b
Tetradecane	10	90
Octanoic acid	10	86
Ethylcarbitol ^d	10	92
<i>n</i> -Butyl ether	10	94
28.5% ethanol-water	10	93
<i>p</i> -Chlorophenol	10	5
	2	68 ^b
Phenol	10	86
<i>p</i> -Cresol	10	88
Gas phase	10	96

^a EtOCH₂CH₂OCH₂CH₂OH. ^b Based on an expected 75% yield. ^c Tetramethylene sulfone. ^d EtOCH₂CH₂OCH₂CH₂OEt.

One of the few reactions of this type which has been carried out in both polar and nonpolar solvents is the Menshutkin reaction. The rate of formation of tetraethylammonium iodide from ethyl iodide and triethylamine at 100° is very solvent sensitive; the rate in methanol is 290 times as great as that in hexane⁵

(5) N. Menshutkin, *Z. Phys. Chem. (Leipzig)*, **6**, 41 (1890).

and the difference in rates in nitrobenzene and in hexane⁶ is even greater, 2800-fold. On the other hand, the solvent effects in the reaction between pyridine and methyl iodide are much smaller; the reaction is only 5.4 times faster in 56% ethanol-water than in benzene⁷ and 25 times as fast in nitrobenzene as in benzene.⁷

A cursory examination of the data of Table II leaves the impression that hydrogen bonding between the solvent and substrate or acid catalysis may influence the rate of the Claisen rearrangement. Thus, the solvents in which the reaction was fastest are hydroxylic while those in which it was slowest are, in general, nonhydroxylic. Furthermore, the phenols, which are actually weak acids, were about the most accelerative (with *p*-chlorophenol, the strongest acid of the three phenols, showing this effect the most and *p*-cresol, the least acidic, showing it the least).

However, closer scrutiny of the data shows several inconsistencies in this interpretation. For one thing, the rate effects of the solvents do not fall in exactly the order expected from their room-temperature acid dissociation constants. Thus, the rate in octanoic acid was 2.8 times slower than in *p*-chlorophenol. Likewise, aqueous ethanol promoted the reaction to about the same extent as phenol. Furthermore, the reaction was as fast in some nonhydroxylic solvents as in certain hydroxylic ones (compare propylene carbonate, adiponitrile, and tetramethylene sulfone with 2-octanol and 1-decanol). Clearly, factors other than hydrogen bonding must be involved in solvent effects on the Claisen rearrangement.

This conclusion is reinforced by the existence of a good correlation ($r = 0.97$) between the ΔH^\ddagger 's and ΔS^\ddagger 's for the rearrangement in different solvents. Such an isokinetic correlation has been assumed to imply that there is no change in mechanism on passing from one system to another. Thus, the same mechanism must be operating in each solvent studied. This would tend to rule out the operation of any special effects (*e.g.*, hydrogen bonding, acid catalysis, etc.) that might be associated with some solvents but not with others.

One feature generally associated with hydroxylic solvents that might be the cause of their effectiveness in facilitating the Claisen rearrangement is their high polarity. Solvent polarity is a rather nebulous term depending as it does on many different solvent properties (dipole moment, polarizability, hydrogen-bonding ability, etc.). The best definitions of solvent polarity are empirical. Kosower⁸ has established a measure of solvent polarity based on the charge-transfer absorption maxima of 1-ethyl-4-carbomethoxy-pyridinium iodide in various solvents. Absorption wave-lengths were converted to their equivalents in kilocalories/mole and designated as solvent polarity or *Z* factors.

The qualitative parallelism of the rates of the Claisen rearrangement in several solvents with the polarities of the solvents suggested that a correlation of the rates might be obtained by use of the empirical *Z* factors.⁸ The following equation was obtained

$$Z = 15.93(\log k + 6) + 58.79$$

(6) H. G. Grimm, H. Ruf, and H. Wolff, *Z. Phys. Chem.* (Liepzig), **B13**, 301 (1931).

(7) R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937); K. J. Laidler and C. N. Hinshelwood, *ibid.*, 858 (1938).

($r = 0.892$, $s = 13.93$). Three of the solvents in which rates were determined are not included in this correlation because their *Z* values could not be ascertained (*n*-decylamine reacted with the pyridinium iodide and phenol and *p*-chlorophenol absorbed in the charge-transfer region). It is evident that the fit is not perfect. However, it appears to be about as good as the correlations of the rates of iodide-ion exchange, of the rates of the Menshutkin reaction (pyridine and methyl iodide), and of the rates of solvolysis of *t*-butyl chloride; all cases cited and treated by Kosower⁸ in support of the usefulness of *Z* values. Thus, there is a reasonably good correlation between the *Z* values and the rates of rearrangement of allyl *p*-tolyl ether in different solvents. It should be noted that, while the rates were determined at 170°, the *Z* values for each solvent were measured at 25°. In an attempt to measure *Z* as a function of temperature, it was observed that the 1-ethyl-4-carbomethoxy-pyridinium iodide decomposed below 70°.

Since the *Z* value of a solvent is a measure of the interaction between a dipolar ion pair and the solvent, the correlation between the *Z* values and the rates of rearrangement suggests that a dipolar or charge-separated transition state must also be formed during the Claisen rearrangement. Such an activated complex has been previously proposed.^{1d,f,h}

In conclusion, the sensitivity of the rate of rearrangement of allyl *p*-tolyl ether to the nature of the reaction medium can be attributed either to the hydrogen-bonding abilities or to the polar character of the solvent.⁹ Both of these interpretations leave much to be desired, but correlation in terms of solvent polarities seems to involve the fewest inconsistencies.

Experimental Section

Preparation of Allyl *p*-Tolyl Ether.—This compound, bp 90.0–90.5° at 12 mm (lit.⁶ bp 97.5–98.5° at 17 mm), was prepared as previously described^{1a} with one minor modification. Before final distillation, the ether was chromatographed on a 15 × 120 mm column of activity grade I alumina using Skellysolve B as eluent. The solvent was then removed and the residue distilled.

Purification of Solvents.—All of the solvents except the ethanol-water mixture were commercially available. They were purified by slow distillation through a 45-cm Vigreux column. A centercut with a boiling range of a degree or less was selected for the kinetic work.

The ethanol-water mixture was prepared by pipetting 30 ml of grain alcohol into a 100-ml volumetric flask and diluting to volume with distilled water to give a 28.5% ethanol-water mixture.

Kinetic Measurements. Method B (Nonaromatic Solvents).—The spectrophotometric procedure outlined in a previous paper^{1a} was employed with those reaction solvents which had negligible light absorption in the visible and ultraviolet region.

Method A (Gas Phase).—About 15 mg of allyl *p*-tolyl ether was placed in a 25-ml Pyrex test tube and frozen. The tube was evacuated to 0.4–0.9 mm, and sealed off. At the reaction temperature, this amount of ether would be completely in the gas phase at a pressure of 95–105 mm. The tubes were immersed in a constant-temperature bath for varying intervals and then removed and cooled. The contents of the sample tube were dissolved in a measured quantity of alcoholic sodium hydroxide solution and the absorbance of the resulting solution was determined at 278 m μ (allyl *p*-tolyl ether) and 301 m μ (2-allyl-4-methylphenoxide ion). The concentration of each of these substances was obtained by solution of a set of simultaneous equations.

(8) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958).

(9) Referee I suggests that a multiparameter equation may fit the data better than a single parameter correlation.

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-¹⁴C *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-1-¹⁴C 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-¹⁴C bromide.

To the flask containing the allyl-¹⁴C 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-¹⁴C *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 C₁₇H₁₄N₂O₆: 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-¹⁴C *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 original allyl-¹⁴C *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.*, **25**, 174 (1953).

Kinetics of the Condensation of 2-Picoline with Aromatic Aldehydes in Acetic Anhydride¹

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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 $v = k_3[2\text{-picoline}][p\text{-nitrobenzaldehyde}][\text{acetic acid}]$, where k_3 is $2.4 \times 10^{-5} M^{-2} \text{sec}^{-1}$ 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: $\text{CH}_3\text{CO}_2\text{H} < \text{PhCO}_2\text{H} < \text{ClCH}_2\text{CO}_2\text{H}$. 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-picoline 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. Enshnstra, 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**, 500g (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.