base.[12] Compound IV may rearrange, lose water and form N-methyl-α-pyridone (VI) by a similar mechanism. The over-all reaction at *p*H values 7 to 13 is given by equation VII.

The presented mechanism may account for three observations made by this Laboratory: (a) the presence of a green color in commercial preparations of the oxime I; compound VI turns green on exposure to light; (b) the formation of two spots when commercial samples of I were chromatographed on paper; (c) the presence of traces of cyanide ion in I, even after three recrystallizations from ethyl alcohol.

Experimental

2-Cyanopyridine Methiodide (II).—A solution of 5.2 g. of 2-cyanopyridine and 10.5 g. of methyl iodide dissolved in 80 ml. of ethyl alcohol was heated under reflux for 4 hours. A double condenser was used to prevent excessive evaporation of methyl iodide. On cooling, the solid methiodide was filtered and washed with dry ether. Two recrystallizations from absolute ethyl alcohol gave 4.5 g. of yellow crystals, m.p. 183–184°.

Anal. Calcd. for $C_7H_7N_2I$: C, 34.14; H, 2.85. Found: C, 33.9; H, 2.8.

Pyridine-2-carboxylic Acid Methiodide (III).—A solution of 6.0 g. of pyridine-2-carboxylic acid and 12 g. of methyl iodide dissolved in 75 ml. of ethyl alcohol was heated under reflux for four hours as above. Concentration of the solvent to 30 ml. gave 5.5 g. of yellow crystals. The solid product was recrystallized from propanol, m.p. 164.5–166°.

Anal. Calcd. for $C_7H_8O_2NI$: C, 31.70; H, 3.02. Found: C, 31.6; H, 3.0.

Isolation of N-Methyl-α-pyridone from 2-Cyanopyridine Methiodide.—Add 100 ml. of 0.1*N* NaOH to 0.5 g. of 2-cyanopyridine methiodide dissolved in a minimum of water. The mixture was placed in a water-bath at 87° for 1.5 hours. After cooling, the solution was extracted with two 25-ml. portions of chloroform. On evaporation of the chloroform a colorless oil remained. The oil was identified as N-methyl-α-pyridone by its picrate derivative.

Isolation of N-Methyl-α-pyridone from Pyridine-2-aldoxime Methiodide (I).—Dissolve 0.5 g. of pyridine-2-aldoxime methiodide in a minimum of water, add 100 ml. of 0.1 *N* NaOH and proceed as above. On evaporation of the chloroform, an oil was isolated and identified as N-methyl-α-pyridone by its picrate derivative.

Picrate of N-Methyl-α-pyridone.—Ten ml. of a saturated solution of picric acid was added to 0.5 ml. of synthetic N-methyl-α-pyridone dissolved in 10 ml. of 95% ethanol. The solution was heated to boiling for a few minutes, cooled and the yellow crystals filtered. The picrate was recrystallized from ethyl alcohol, m.p. 145°. The melting point was not depressed on admixture with the picrates prepared above.

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[12] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 579.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Mechanism of the Reaction of 2-Picoline N-Oxide with Acetic Anhydride[1]

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Both free radical and ionic mechanisms have been proposed for the formation of 2-pyridylmethyl acetate from 2-picoline N-oxide and acetic anhydride. In this work evidence is reported for the presence of free radicals in the reaction mixture; however, these radicals do not appear to be involved in the origin of 2-pyridylmethyl acetate. Thus the alternative ionic path seems most likely with data presented to support an intramolecular rearrangement of the anhydro base II.

In recent years several groups of investigators have described reactions of heterocyclic N-oxides with acid anhydrides. When pyridine N-oxide[2] or 3-picoline N-oxide[3] was employed, the reaction with acetic anhydride resulted in the introduction of an acetoxy group into the 2-position of the pyridine ring; however, with 2- and 4-alkylpyridine N-oxides[3–9] the reaction followed an alternate course which led to 2- and 4-(α-acetoxyalkyl)-pyridines. A specific example of the latter process[3] is the formation of 2-pyridylmethyl acetate from 2-picoline N-oxide and acetic anhydride. Similar reactions have been reported in the quinoline[10–13] and isoquinoline[14] series. The subject of this report deals with reactions of 2-picoline N-oxide and acid anhydrides which may be used to elucidate the mechanism of this process.

Both ionic and free radical mechanisms have been proposed for this reaction; each involves as the initial step the formation of 1-acetoxy-2-methylpyridinium (I) acetate. The ionic path was suggested by Pachter[12] to explain a similar rearrangement with quinaldine N-oxide and extended to the pyridine system by others.[3,5,6] This proceeds through the anhydro base II which results from I by abstraction of an acidic hydrogen from the 2-methyl group by acetate anion. At least two paths are available for the conversion of II to 2-pyridylmethyl acetate (III): (a) by an intramolecular cyclic rearrangement and (b) by a nucleophilic attack of acetate anion on the methylene carbon with elimination of acetate anion.

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[1] Presented at the 133rd Meeting of the American Chemical Society at San Francisco, Calif., in April, 1958.

[2] M. Kataka, *J. Pharm. Soc. Japan*, **67**, 51 (1947); *C. A.*, **45**, 9537e (1951).

[3] V. Boekelheide and W. J. Linn, THIS JOURNAL, **76**, 1286 (1954).

[4] G. Kobayashi and S. Furukawa, *Pharm. Bull. Japan*, **1**, 347 (1953); *C. A.*, **49**, 10948e (1955).

[5] O. M. Bullitt, Jr., and J. T. Maynard, THIS JOURNAL, **76**, 1370 (1954).

[6] J. A. Berson and T. Cohen, *ibid.*, **77**, 1281 (1955).

[7] G. Kobayashi, S. Furukawa and Y. Kawada, *J. Pharm. Soc. Japan*, **74**, 790 (1954); *C. A.*, **49**, 1164c (1955).

[8] S. Furukawa, *Pharm. Bull. Japan.*, **3**, 413 (1955); *C. A.*, **50**, 13926a (1956).

[9] F. Cislak, U. S. Patent 2,718,141, May 29, 1956; *C. A.*, **51**, 2878e (1957).

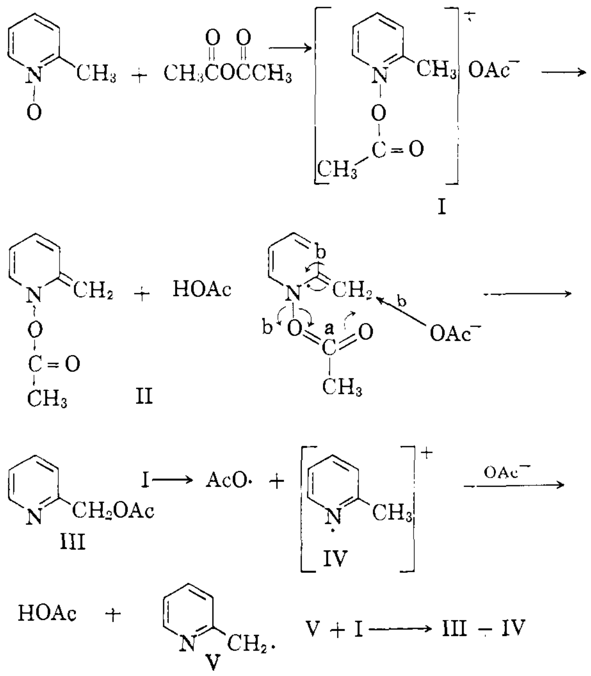
[10] K. Oda, *J. Pharm. Soc. Japan*, **64**, No. 8A, 6 (1944); *C. A.*, **45**, 8523i (1951).

[11] T. Itai, *J. Pharm. Soc. Japan*, **65**, 70 (1945); *C. A.*, **45**, 8525h (1951).

[12] I. J. Pachter, THIS JOURNAL, **75**, 3026 (1953).

[13] F. Montanari and A. Risaliti, *Gazz. chim. ital.*, **83**, 278 (1953).

[14] M. M. Robison and B. L. Robison, *J. Org. Chem.*, **21**, 1337 (1957); THIS JOURNAL, **80**, 3143 (1958).



The free radical mechanism was proposed by Boekelheide and Harrington[15] and involves a homolytic cleavage of the nitrogen oxygen bond in I to give the radical ion IV and an acetoxy radical. After acetate anion removed a proton from the 2-methyl group of IV, the resulting 2-picolyl radical (V) upon collision with I produced the compound III and regenerated the radical ion IV.

Our first concern was to determine whether the mechanism was free radical. One piece of evidence presented by Boekelheide for the free radical path was the demonstration of the presence of radicals by isolation of polystyrene when the reaction was performed in the presence of styrene. These experiments were repeated. After 21.8 g. of 2-picoline N-oxide, 21 g. of acetic anhydride and 14 g. of styrene were allowed to react in 20 g. of acetic acid, the following products were isolated: 8.3 g. (60%) of polystyrene, identified by comparison of the infrared spectrum to that of an authentic sample, 2.1 g. (15%) of styrene and 23 g. (75%) of 2-pyridylmethyl acetate. Some control experiments were performed to demonstrate that styrene in acetic anhydride will undergo free radical catalyzed polymerization and that this polymerization can be inhibited by the addition of *p*-benzoquinone. Also a mixture of styrene and acetic anhydride was subjected to the reaction conditions and only 4% polystyrene was found, while 2-picoline N-oxide and styrene gave less than 1% polystyrene. These results which are in agreement with the report by Boekelheide strongly suggest the presence of radicals.

Additional evidence for the presence of radicals was obtained by analysis of the gases evolved from the reaction of 2-picoline N-oxide and acetic anhydride. The products from this reaction, which was carried out in an atmosphere of nitrogen, were 2-pyridylmethyl acetate (87%), 2-picoline (0.14%) identified by preparation of its picrate (m.p. 163-164°, lit.[16] m.p. 164°) which showed no depression in melting point of a mixture with an authentic sample and gave an infrared spectrum identical with that of the authentic sample, and 370 ml. of gas which was analyzed mass spectrometrically. The major components of this gas mixture were carbon dioxide and methane. In addition to a strong peak at mass number (*m/e*) 44 which suggested carbon dioxide, chemical evidence for its presence was obtained by precipitation of barium carbonate when a barium hydroxide solution was exposed to the gas mixture. After the contribution of carbon dioxide and nitrogen, which was present since the reaction was performed in an atmosphere of nitrogen, was subtracted from the mass spectrum of the mixture, methane was identified by its pattern. Among the minor components suggested by certain mass numbers were air (mass number 32 for oxygen and 40 for argon), acetic acid (mass number 60) and methyl acetate (mass number 43). When the percentage composition based on these six components was calculated by the usual methods,[17] the analysis showed no residual peaks at the mass numbers used for the calculation and either small or no residuals for all other mass numbers. The results of this determination are listed in Table I.

TABLE I

MASS SPECTRUM ANALYSIS OF THE GAS FROM 2-PICOLINE N-OXIDE AND ACETIC ANHYDRIDE REACTION

Gas	M/e^b	H^c	H'^d	P^e	Mmol.^{a}	Mole, %
Methane	16	510.0	364.9	5.28	3.81	0.93
Carbon dioxide	44	1410.0	1409.7	14.37	10.36	2.53
Methyl acetate	43	15.3	14.3	0.88	0.638	0.16
Acetic acid	60	1.0	1.0	0.44	0.319	0.08
Nitrogen	28	307.5	164.7	1.80		
Air	32	1.6	1.5	0.04		

[a] Calculation was based on the volume corrected to standard temperature. [b] M/e = mass number of "100" peak for the pure compound. [c] H = peak height for the mixture. [d] H' = contribution to peak height of pure component. [e] P = partial pressure for each component; $P_{\text{calcd}} = 22.30$, $P_{\text{obsd}} = 22.81$.

The presence of carbon dioxide and methane can be rationalized on the basis of acetoxy radicals. These may arise as suggested by Boekelheide and Linn by homolytic cleavage of I or another possibility would be the homolytic cleavage of II. The acetoxy radicals decompose into carbon dioxide and methyl radicals which upon abstraction of a hydrogen atom from either reactants or products give methane. The origin of 2-picoline from the 2-picolyl radical could be explained in a similar manner. Thus the formation of carbon dioxide, methane and 2-picoline, along with the polymerization of styrene under reaction conditions, strongly support the conclusion that radicals are formed; however, the question remains whether

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(15) V. Boekelheide and D. L. Harrington, *Chemistry & Industry*, 1423 (1955).

(16) E. J. Constam and J. White, *Am. Chem. J.*, **29**, 38 (1903).

(17) H. W. Washburn, in W. G. Berl, "Physical Methods in Chemical Analysis," Vol. I, Academic Press, Inc., New York, N. Y., 1950, pp. 612-618.

these radicals are responsible for the formation of the major product III.

The approach to this problem was to add free radical scavengers to the reaction mixture and observe its effects on the yield of 2-pyridylmethyl acetate and the products known to be derived from free radicals such as polystyrene and methane. The results illustrating the effect of *p*-benzoquinone and *m*-dinitrobenzene on the reaction of 2-picoline N-oxide and acetic anhydride in the presence of styrene are given in Table II.

TABLE II

REACTION OF 2-PICOLINE N-OXIDE AND ACETIC ANHYDRIDE IN STYRENE

Product		Yield, % *p*-Benzoquinone	*m*-Dinitrobenzene
Polystyrene	60	11	0
Styrene	15	83	89
2-Pyridylmethyl acetate	75	70	61

Since the inhibitor removed radicals sufficiently to drastically decrease or stop polymerization of styrene, the absence of an effect of the radical acceptors upon the yield of ester III makes a free radical chain mechanism for the formation of III seem unlikely. Additional support for this conclusion was obtained from a study of the effect of various amounts of *m*-dinitrobenzene upon the yield of 2-pyridylmethyl acetate and methane. The data presented in Table III clearly demonstrate a sharp decrease in the yield of methane with increasing quantities of inhibitor while the yield of III is unaltered. The results of these two approaches indicate that two reactions are in progress, a minor one giving rise to radicals and the major path which leads to ester III.

TABLE III

EFFECT OF *m*-DINITROBENZENE ON REACTION OF 2-PICOLINE N-OXIDE AND ACETIC ANHYDRIDE

		Yield, % with *m*-dinitrobenzene		
Product		2.2%	10%	20%
Methane	0.93	0.59	0.40	0.31
Carbon dioxide	2.53	2.39	2.37	2.42
Methyl acetate	0.16	0.26	0.25	0.98
2-Pyridylmethyl acetate	87	88	88	87
Decrease in methane, %	...	37	57	67

This evidence leaves the alternative ionic mechanism as the most likely rationalization. Two modes of reaction have been suggested in this category, one an intramolecular process (path a) and the other (path b) a bimolecular attack of an anion on the exocyclic methylene group of II. One could test the possibility of path b by the addition of foreign anions into the reaction medium and analysis for products resulting from them. Two experiments of this type were investigated. The first involved the reaction of 2-picoline N-oxide and acetic anhydride in pyridine with lithium chloride added. Although the only products isolated from this reaction were III (53%) and lithium chloride (99%), this experiment leaves some doubt in excluding path b because of a difference in nucleophilic character of chloride ion and acetate ion. In the second experiment the reaction of 2-picoline N-oxide and butyric anhydride in the presence of sodium acetate was studied. The butyric anhydride–sodium acetate system was used since Michael and Hartmann[18] have demonstrated that the equilibrium mixture at 100° and 150° (well above our reaction temperature) contained no acetic anhydride and sodium butyrate but was essentially butyric anhydride and sodium acetate. Thus if 2-pyridylmethyl acetate were found, it would not be attributed to the presence of acetic anhydride, which with 2-picoline N-oxide would give III, but could be explained by attack of acetate anion according to path b. The result of this reaction was the isolation of 2-pyridylmethyl butyrate (69%) only. Prior to this experiment with added sodium acetate, the reaction of 2-picoline N-oxide and butyric anhydride was performed and gave 2-pyridylmethyl butyrate (64%). The structure was assigned on the basis of analysis and hydrolysis to 2-pyridinemethanol and butyric acid which were identified by preparation of appropriate derivatives (Experimental section).

The results of these last two experiments are in support of an intramolecular process. This process may involve shifts of electron pairs in II as illustrated by path a; however, two alternate possibilities involve first the cleavage of the nitrogen oxygen bond, either homolytically to give a radical pair or heterolytically to give an ion pair, and then recombination of the two parts to give the ester III.

Experimental[19]

The Reaction of 2-Picoline N-Oxide and Acetic Anhydride.—A three-necked round-bottom flask fitted with a gas inlet tube, dropping funnel with a pressure equalizer and a condenser connected to a gas buret by glass tubing which contained a gas sampling bulb was charged with acetic anhydride (56.5 g., 0.55 mole) and the system flushed out thoroughly with dry nitrogen. Freshly distilled 2-picoline N-oxide (45.0 g., 0.41 mole), b.p. 132° (15 mm.), m.p. 46–47° (sealed tube), was added dropwise to gently refluxing acetic anhydride over a period of 2 hours. The mixture became reddish-brown and was maintained at gentle reflux for 1.5 hours after addition was completed. The gas produced during the reaction was collected in the gas buret over mercury at pressures slightly greater than atmospheric and measured 370 ml.[20] When the reaction was completed, a gas sample was taken for mass spectrometric analysis (Table I). After the acetic acid and acetic anhydride were removed at atmospheric pressure, distillation of the residue gave 55.1 g. (87.4%) of 2-pyridylmethyl acetate, b.p. 108–109° (10 mm.), n^{21}D 1.4985. A pure sample of this ester, b.p. 117.5–118° (22 mm.), n^{20}D 1.4990, was obtained by careful fractionation through an electrically heated 0.8 × 25 cm. column packed with $^1/_{16}$ in. glass helices and equipped with a variable take-off head.

The acetic acid–acetic anhydride distillate was added to 50 ml. of water and saturated with potassium carbonate. After the alkaline solution was shaken with ether, the extract was dried over sodium sulfate and the ether distilled. The residue was impure 2-picoline (0.51 g., 0.14%) which was converted to its picrate, m.p. 163–164°, in the usual way. The melting point of a mixture with an authentic

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(18) A. Michael and R. N. Hartmann, *Ber.*, **34**, 918 (1901).

(19) All melting points and boiling points are uncorrected. The microanalysis are by Midwest Microlab Inc., Indianapolis, Ind. Mass spectra were recorded by Mr. George Young on a Consolidated 21-103A analytical mass spectrometer, Radiation Project, University of Notre Dame. Infrared spectra were determined with a Perkin–Elmer model 21 or a Baird Associates infrared spectrophotometer by Mr. R. F. Love and Mr. A. Saraceno.

(20) The volume was measured at 25° and was corrected to standard temperature for the calculations.

sample was not depressed and the infrared spectra of the above and of an authentic sample were identical.

Using the same quantities of reactants as above, three experiments were carried out in the presence of *m*-dinitrobenzene (1.0 g., 0.006 mole, 2.2% by weight of 2-picoline N-oxide; 4.5 g., 0.027 mole, 10% by weight; 9.0 g., 0.054 mole, 20% by weight). By the procedure described, distillation gave 2-pyridylmethyl acetate: 55.7 g. (88.4%), b.p. 99–101° (7 mm.), $n^{21}\text{D}$ 1.4978; 55.2 g. (87.6%), b.p. 93–95° (5 mm.), $n^{20}\text{D}$ 1.4984; 55.1 g. (87.4%), b.p. 96–99° (4.8 mm.), $n^{20}\text{D}$ 1.4977, respectively. The volume of gas[20] for each experiment was 345, 315 and 285 ml., respectively. The analysis was by mass spectrometry (Table II).

The Reaction of 2-Picoline N-Oxide and Acetic Anhydride in the Presence of Styrene.—2-Picoline N-oxide (21.8 g., 0.200 mole) was added dropwise over a period of 10 minutes to a refluxing solution of acetic acid (20.0 g.), acetic anhydride (21.0 g., 0.206 mole) and freshly distilled styrene (14.0 g.) in a 200-ml. three-necked flask which was fitted with a mechanical stirrer, a reflux condenser, dropping funnel, and which had been thoroughly flushed with dry nitrogen. After addition of the N-oxide was completed, the dark brown reaction mixture was cooled, some sulfur added and distilled through a 10-in. Vigreux column. The colorless distillate, b.p. 30–60° (30 mm.), a mixture of acetic acid, acetic anhydride and unreacted styrene, was added to 20 ml. of water and the acetic acid neutralized with potassium carbonate. After the solution was shaken with ether, the extract was separated, dried and the ether distilled. A residue of 2.1 g. (15%) of unreacted styrene remained. The residue from the initial distillation was poured into 300 ml. of methanol and a pink solid precipitated. The solid (polystyrene) was isolated by filtration, dried *in vacuo* and weighed 8.3 g. (59.3%). The infrared spectra of this solid and an authentic sample of polystyrene were identical. The methanol was removed from the above solution at atmospheric pressure and distillation of the residue gave 22.9 g. (75.1%) of 2-pyridylmethyl acetate, b.p. 95–96° (4.5 mm.), $n^{20}\text{D}$ 1.4991. A tarry residue of 4 g. remained.

Using the same procedure and conditions described above, the reaction of 2-picoline N-oxide (20.0 g., 0.183 mole), acetic anhydride (40.0 g., 0.392 mole) and freshly distilled styrene (20.0 g., 0.197 mole) was carried out in the presence of *p*-benzoquinone (1.0 g. 0.0093 mole, 5% by weight of 2-picoline N-oxide). The products isolated were styrene, 16.6 g. (83%), b.p. 50–55° (30 mm.); polystyrene, 2.3 g. (11.5%); and 2-pyridylmethyl acetate, 19.6 g. (70%), b.p. 109–110° (10 mm.), $n^{20}\text{D}$ 1.4980.

In a third experiment identical to the one above, 2-picoline N-oxide (20.0 g., 0.183 mole), acetic anhydride (40.0 g., 0.392 mole), freshly distilled styrene (14 g. 0.13 mole) and *m*-dinitrobenzene (2.0 g., 0.012 mole, 10% by weight) gave styrene, 12.4 g. (88.6%), b.p. 50–54° (30 mm.); 2-pyridylmethyl acetate, 17.0 g. (60.7%), b.p. 109–110° (10 mm.); and unreacted 2-picoline N-oxide, 4.2 g. (21%), b.p. 125° (10 mm.).

Polymerization Control Experiments. Styrene and Acetic Anhydride.—Freshly distilled styrene (14.0 g., 0.13 mole, b.p. 54° (30 mm.)) and 40 g. of acetic anhydride were refluxed for 2 hours under an atmosphere of nitrogen and then distilled through a 12-in. Vigreux column. The distillate was added to 50 ml. of water, the acetic acid neutralized with potassium carbonate and the mixture extracted with ether. After the extract was dried over sodium sulfate, the ether was removed and the residue upon distillation gave 10.2 g. (73%) of styrene, b.p. 50–55° (30 mm.). The residue from the first distillation was dissolved in 5 ml. of benzene and the solution added to 300 ml. of methanol. Polystyrene, which precipitated, was filtered, washed with methanol, dried and weighed 0.6 g. (4%). This compound was identified by comparison of its infrared spectrum with that of an authentic sample.

Styrene and 2-Picoline N-Oxide.—A mixture of 2-picoline N-oxide (20.0 g., 0.183 mole), freshly distilled styrene (22.7 g., 0.22 mole) and 100 ml. of benzene was refluxed for 2 hours under an atmosphere of nitrogen. Some sulfur was added to the reaction mixture and after the benzene was removed, distillation under reduced pressure gave 19.5 g. (86%) of styrene, b.p. 50–55° (30 mm.). The residue was poured into methanol and the precipitate which formed was filtered and dried. This solid was identified as polystyrene by its infrared spectrum and weighed about 50 mg. (0.2%).

Polymerization of Styrene in Acetic Anhydride.—The procedure described above under the styrene and acetic anhydride experiment was employed. Using the same quantities of materials as described in that experiment with the addition of benzoyl peroxide (0.2 g., 0.0008 mole), the products isolated were 2.5 g. (18%) of polystyrene and 9.9 g. (71%) of styrene.

In a second experiment styrene (20.0 g., 0.206 mole), acetic anhydride (10.2 g., 0.100 mole), benzoyl peroxide (0.2 g., 0.00083 mole), *p*-benzoquinone (1.0 g., 0.0091 mole) and 50 ml. of dry benzene were refluxed one hour under nitrogen. After the benzene was removed, isolation according to the above procedure gave 17.8 g. (89%) of styrene, b.p. 54° (30 mm.), while no polystyrene was found.

The Reaction of 2-Picoline N-Oxide and Acetic Anhydride in the Presence of Lithium Chloride.—Acetic anhydride (24.5 g., 0.24 mole) was added dropwise with stirring over a period of 2 hours to a solution of 2-picoline N-oxide (21.8 g., 0.20 mole) and lithium chloride (10.3 g., 0.24 mole) in 50 ml. of pyridine. The mixture was refluxed for one hour, cooled and poured into 500 ml. of acetone. The yellow-brown solid which precipitated was filtered, washed with acetone and dried. The yield of lithium chloride (identified by a flame test for lithium and precipitation of silver chloride) was 10.2 g. (99%). After acetone and pyridine were removed, the residue was distilled and gave a crude liquid boiling over a 10° range. A second distillation gave 16.1 g. (53%) of pure 2-pyridylmethyl acetate, b.p. 113–115° (14 mm.), $n^{22}\text{D}$ 1.4982.

The Reaction of 2-Picoline N-Oxide and Butyric Anhydride.—The apparatus described in the second experiment was charged with butyric anhydride (31.8 g., 0.20 mole) and placed in an oil-bath at 130°. 2-Picoline N-oxide (10.9 g., 0.10 mole) was added dropwise, with stirring, over a 15-minute period and the resulting mixture heated for 35 minutes. The dark brown reaction mixture was cooled, added to 50 ml. of water and the butyric acid neutralized with potassium carbonate. After the mixture was extracted with ether, the ether solution was dried over sodium sulfate. The ether was removed and distillation of the residue gave 11.5 g. (64%) of 2-pyridylmethyl butyrate, b.p. 105–106° (3.9 mm.), $n^{20.2}\text{D}$ 1.4912. Careful redistillation gave a series of colorless fractions, b.p. 97–98° (2.0 mm.), $n^{20}\text{D}$ 1.4920.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.13. Found: C, 66.81; H, 7.27.

Using the same conditions and quantities of reactants as described above, a second experiment was carried out in the presence of sodium acetate (8.2 g., 0.10 mole). The only ester isolated was 12.3 g. (69%) of 2-pyridylmethyl butyrate, b.p. 92–93° (1.6 mm.), $n^{20.2}\text{D}$ 1.4907.

Hydrolysis of 2-Pyridylmethyl Butyrate.—2-Pyridylmethyl butyrate (3.0 g.) was refluxed with concentrated hydrochloric acid (15 ml.) for 9 hours. After the solution was neutralized with sodium carbonate and concentrated, the precipitated salts were filtered and the alkaline layer extracted with chloroform. This solution was dried over sodium sulfate and the solvent removed leaving 1.0 g. of high boiling residue. This was converted to the picrate of 2-pyridylmethanol, m.p. 157–158° (lit.[3] m.p. 160–161°), by the usual method. A mixture melting point with an authentic sample was not depressed. The above salts were added to concentrated hydrochloric acid. After sodium chloride was removed by filtration, the solution was extracted with ether. Removal of the ether left 0.5 g. of high boiling material which gave the *p*-bromophenacyl ester of butyric acid, m.p. 57–60° (lit.[21] m.p. 63°).

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NOTRE DAME, IND.

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(21) W. L. Judefind and E. E. Reid, THIS JOURNAL, **42**, 1055 (1920).