

saturated NaCl solution, dried (Na_2SO_4), and evaporated to give 4.9 g of yellow oil which on trituration with ether gave pale yellow crystals of octahydrophenazine N,N-dioxide (VIIa) (30% yield). Recrystallization from methylene chloride-pentane afforded white crystals: mp 230°; ir (CHCl_3), 3000, 1720 (w), 1580 (w), 1470, 1360, 1340, and 1100 cm^{-1} (s); nmr (CDCl_3) δ 2.9 (m, 8, $\text{CH}_2\text{C}=\text{C}$) and 1.9 ppm (m, 8, CH_2). *Anal.* Calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_2$: C, 65.43; H, 7.32; N, 12.72; mol wt, 220. Found: C, 64.76; H, 7.13; N, 12.70; mol wt, 250.

In like manner, VIIb was prepared in 50% yield from 2-hydroxylaminocyclooctane oxime (IVb).² White crystals, mp 248° (from methylene chloride-pentane), were obtained: ir (CHCl_3) 3000, 1730 (w), 1610 (w), 1460, 1340 (s), 1290, and 1100 cm^{-1} (s); nmr (CDCl_3) δ 3.2 (m, 8, $\text{CH}_2\text{C}=\text{C}$), 1.9 (m, 8, CH_2), and 1.5 ppm (m, 8, CH_2). *Anal.* Calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_2$: C, 69.53; H, 8.75; N, 10.14; mol wt, 276. Found: C, 69.67; H, 8.83; N, 10.04; mol wt, 295.

Treatment of VIIa (0.5 g) with 0.5 g of selenium at 350° under nitrogen for several hours gave a condensate which on extraction with methylene chloride and evaporation provided 50 mg of orange oil. Vacuum distillation of this residue in a Kugelrohr tube afforded 5 mg of sublimate which was identical in mixture melting point and vpc properties with phenazine.

Registry No.—IIa, 2567-33-1; IIb, 21205-24-3; IIIa, 24707-22-0; IIIb, 24707-24-2; IVa, 13757-09-0; VIIa, 24716-05-0; VIIb, 24716-06-1; 2-nitrocyclohexanone (2,4-dinitrophenylhydrazone), 10269-95-1; phenylglyoxal (dioxime), 4589-97-3; dimethylglyoxime, 95-45-4.

Acknowledgment.—The author is indebted to Mr. J. J. Porcelli for experimental assistance.

Aromatic N-Oxides. VI. Anhydro Base Intermediate and the Rate-Controlling Step in the Reaction of 4-Alkylpyridine N-Oxide with Acid Anhydrides¹

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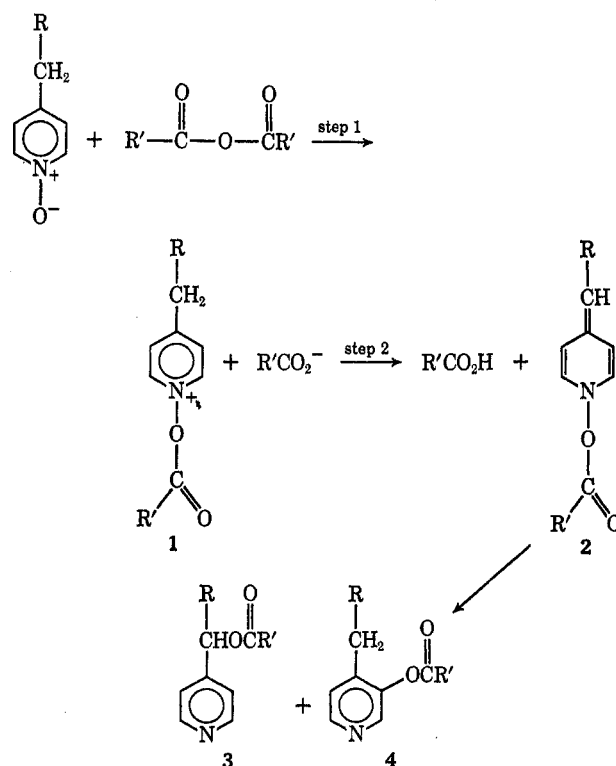
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Evidence for the first step of the reaction of 4-alkylpyridine N-oxides with acid anhydrides was obtained by isolation of 1-acetoxy-4-methylpyridinium and 1-acetoxy-4-benzylpyridinium perchlorates and their conversion by triethylamine in acetonitrile to the corresponding rearranged esters. The reaction of 1-acetoxy-4-benzylpyridinium perchlorate (1) and triethylamine was also examined spectroscopically and provided uv evidence for the intermediate anhydro base, 1-acetoxy-4-benzal-1,4-dihydropyridine (2), whose absorption spectrum resembled 1-methyl-4-benzal-1,4-dihydropyridine. The absence of deuterium exchange in the reaction of 1-acetoxy-4-(α,α -dideuteriobenzyl)pyridinium perchlorate with sodium acetate in acetic acid-acetonitrile and the dependence of the conversion of 1 to 2 on base strength support the assignment of this step as rate controlling.

The generally accepted mechanism for the reaction of 4-alkylpyridine N-oxides and acid anhydrides has been reviewed in several places.^{1,3} In this report we offer evidence in support of the formation of the 1-acyloxy-4-alkylpyridinium cation (1) in step 1, of the anhydro-base intermediate (2), and of the rate-controlling step 2.

The isolation of cation 1 was accomplished as the perchlorate salt from the reaction of 4-methyl- and 4-benzylpyridine N-oxides and acetic anhydride in the presence of perchloric acid. Structural assignments for these salts were based on elemental analysis, a characteristic carbonyl frequency (1825–1830 cm^{-1}),^{4,5} and the reaction of these salts with triethylamine in acetonitrile to produce the esters: 4-pyridylmethyl acetate (3, R = H, R' = CH_3) and 3-acetoxy-4-methylpyridine (4, R = H, R' = CH_3) (both esters identified spectroscopically) from 1-acetoxy-4-methylpyridinium (1, R = H, R' = CH_3) perchlorate, and phenyl-4-pyridylmethyl acetate (3, R = C_6H_5 , R' = CH_3) from 1-acetoxy-4-benzylpyridinium (1, R = C_6H_5 , R' = CH_3) perchlorate. Identification of phenyl-4-pyridylmethyl acetate was achieved by comparison with an authentic sample, saponification of the ester to the known phenyl-4-pyridylmethanol,⁶ and isolation of the



(1) For paper V in this series see V. J. Traynelis and Sr. A. I. Gallagher, *J. Amer. Chem. Soc.*, **87**, 5710 (1965).

(2) (a) Department of Chemistry, West Virginia University, Morgantown, W. Va. (b) Abstracted from the Ph.D. dissertation of A. I. G.

(3) V. J. Traynelis in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Interscience Publishers, New York, N. Y., 1969, pp 31–37.

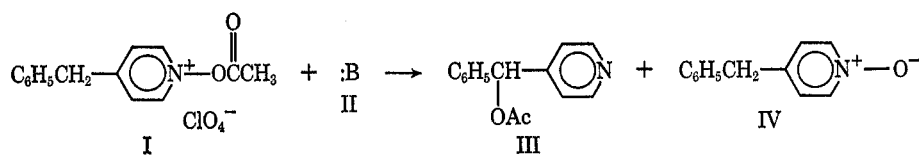
(4) C. W. Muth and R. S. Darlak, *J. Org. Chem.*, **30**, 1909 (1965).

(5) V. J. Traynelis and P. L. Pacini, *J. Amer. Chem. Soc.*, **86**, 4917 (1964).

(6) A. E. Tschitschibabin, *Chem. Ber.*, **37**, 1371 (1904).

ester from the reaction of 4-benzylpyridine N-oxide and acetic anhydride. These conversions of the perchlorate salts of 1 by triethylamine in acetonitrile to the same esters as obtained from the corresponding 4-alkylpy-

TABLE I
REACTION OF 1-ACETOXY-4-BENZYLPIYRIDINIUM PERCHLORATE AND BASE



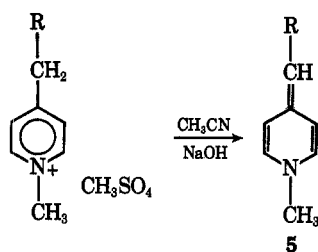
I, mol	CH ₃ CN, ml	Base	II, mol	CH ₃ CN, ml	Time	Temp, °C	Procedure	% yield	
								II	IV
0.012 ^a	100	Et ₃ N	0.012 ^a	100	1 hr	0	A	60	
0.018	75	Et ₃ N	0.018	25	<5 min ^b	0	B	26	
					25 min ^{b,c}	0	B	40	
0.012	37		0.012	5	2.25 hr ^d	0	B	54	
0.012 ^e	20	NaOAc	0.012 ^e	10	15 min	87	C	0	93
0.014 ^f	25	NaOAc	0.014 ^f	13	1 hr	87	D	32	24
0.012 ^e	20	NaOAc	0.012 ^e	10	1.33 hr	87	D	38	
0.017 ^e	25	NaOAc	0.017 ^e	10	3 hr	87	D	50	6

^a Reactants were precooled to 0° and added simultaneously to the reaction flask. ^b Data taken from one reaction, one-half was processed immediately after addition (<5 min), the other half after 25 min. ^c This reaction was followed by ir and visible spectroscopy and is reported in the Experimental Section. ^d Progress of the reaction was followed by ir; the 1-acetoxy carbonyl at 1825 cm⁻¹ slowly disappeared while the ester carbonyl at 1739 cm⁻¹ appeared and increased. The reaction was quenched when the 1825 cm⁻¹ absorption was absent. ^e Acetic acid (10 ml) was added to the 1-acetoxy salt while sodium acetate was dissolved in 14 ml of acetic acid. ^f Same as ^e except the acetic acid volumes were 13 and 15 ml, respectively. ^g Same as ^e except the acetic acid volumes were 10 and 25 ml.

ridine N-oxide acetic anhydride reaction led to the conclusions that cation 1 is a reasonable intermediate in this reaction and that rearrangement to ester products requires the action of base on 1.

A spectral study of the reaction of 1-acetoxy-4-benzylpyridinium perchlorate and triethylamine in acetonitrile provided information regarding the intermediacy of the anhydro base 2. The model system used which corresponded to 2 was the known 1-methyl-4-benzal-1,4-dihydropyridine (5, R = C₆H₅), prepared *in situ* by the reaction of 1-methyl-4-benzylpyridinium methosulfate in acetonitrile and aqueous NaOH.

The uv-visible spectrum of 5, R = C₆H₅, in CH₃CN-H₂O, 90:10 (v/v), showed an absorption maximum at 370 mμ (357 mμ in anhydrous CH₃CN) which reached



maximum intensity in 2 hr (ϵ 18,900 assuming complete conversion of salt to anhydro base 5 in 2 hr) and then began to decay. When a precooled solution of equimolar amounts of 1-acetoxy-4-benzylpyridinium perchlorate in CH₃CN and triethylamine in CH₃CN were mixed at 0°, a band appeared rapidly at 352 mμ (absorbance 0.780) and remained constant for at least 10 min (absorbance 0.775) but by 25 min had decreased markedly (absorbance 0.145). If one assumes that the molar extinction coefficient for 1-acetoxy-4-benzal-1,4-dihydropyridine (2, R = C₆H₅, R' = CH₃) is comparable to that of 1-methyl-4-benzal-1,4-dihydropyridine and that these solutions obey Beer's Law, the concentration of the acetoxy anhydro base (2, R = C₆H₅, R' =

CH₃) in the first two aliquots would be approximately 4×10^{-4} molar. This concentration of anhydro base compared to the concentration of reactants (0.18 M) reflects a 0.2% conversion to the intermediate anhydro base 2. Thus the low conversion to anhydro base along with the constant concentration is suggestive of a steady-state situation. Aliquots also taken upon mixing, after 10 and 25 min were subjected to infrared spectral measurements and showed that the first spectrum after mixing had a more intense band for $>\text{C}-\text{OOCCH}_3$ (1739 cm⁻¹) than $>\text{N}^+-\text{OOCCH}_3$ (1825 cm⁻¹). Spectra taken after 10 and 25 min showed continued increase in intensity of the 1739-cm⁻¹ band with a concurrent decrease in the 1825-cm⁻¹ band. The infrared spectra clearly demonstrate the rapid conversion of the cation 1 (R = C₆H₅, R' = CH₃) to phenyl-4-pyridylmethyl acetate, while the appearance of a chromophore with λ_{max} 352 mμ upon mixing the reactants and eventual disappearance of this band supports an anhydro base 2 for the intermediate leading to ester products. Additional evidence in support of the anhydro base intermediate has been reported recently by Oae⁷ employing the lepidine N-oxide benzoyl chloride reaction and deuterium labeling; however, the major products in this reaction had the benzoate in the C-3 position rather than attached to the side-chain methyl group.

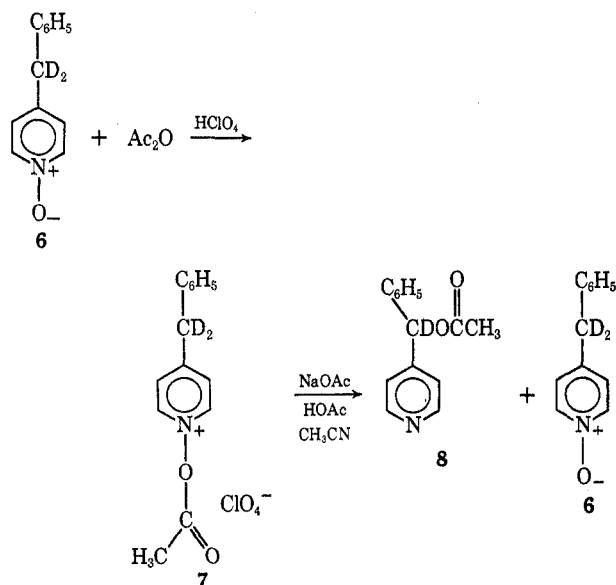
Application of the above approach to detect the presence of anhydro base in the reaction of 1-acetoxy-4-methylpyridinium perchlorate and triethylamine was unsuccessful. The reaction of 1,4-dimethylpyridinium methosulfate and base slowly produced an absorption maximum at 310 mμ which slowly disappeared; however, the reaction of 1-acetoxy-4-methylpyridinium perchlorate and triethylamine showed no absorption in the 310-mμ region but revealed the disappearance of the band at λ_{max} 254 mμ (N-acetoxy cation) and the appearance of absorption maxima at 276 and 265 mμ cor-

(7) S. Oae, S. Tamagaki, and S. Kozuka, *Tetrahedron Lett.*, 1513 (1966).

responding to a mixture of 4-pyridylmethyl acetate and 3-acetoxy-4-methylpyridine.

A study of the reaction of 1-acetoxy-4-benzylpyridinium perchlorate with a variety of bases is summarized in Table I. These results show the need for base to promote the conversion of cation 1 to ester products *via* anhydro base 2. In the reactions performed with sodium acetate in acetonitrile-acetic acid the nature of the reactants is less certain since the cation 1 ($R = C_6H_5$) can react with acetate ion to generate acetic anhydride and 4-benzylpyridine N-oxide. These conditions thus represent the standard N-oxide acetic anhydride reactants in acetonitrile-acetic acid solution with sodium perchlorate.

Oae and coworkers⁸ have previously presented support for step 2 as rate determining by their deuterium kinetic isotope effect study which gave a value of $K_H/K_D = 4.6$ at 30° for the reaction of 4-picoline N-oxide and acetic anhydride. Additional support for step 2 as rate controlling was obtained from deuterium exchange studies similar to those reported for the 2-benzylpyridine N-oxide system.⁵ 4-(α,α -Dideuterio-benzyl)pyridine N-oxide (6) was prepared by an exchange reaction of 4-benzylpyridine N-oxide in deuterium oxide catalyzed by triethylamine. The replacement of the two α,α -benzyl hydrogens by deuterium was complete (Calcd: 18.18 atom % excess deuterium. Found: 21.00%) and the nmr spectrum showed the absence of proton resonance in the region of the benzyl hydrogens. The excess deuterium incorporated into the molecule involves the partial exchange with the α -hydrogens of the pyridine ring.⁹ The deuterated N-oxide 6 was converted to 1-acetoxy-4-(α,α -dideuterio-benzyl)pyridinium perchlorate (7). When 7 was



treated with sodium acetate in the presence of acetic acid and acetonitrile under conditions which led to approximately 50% reaction (see Table I, entry 5, for conditions and results with undeuterated compounds), no deuterium loss was found in the rearranged ester 8 (Calcd: 7.69 atom % excess deuterium. Found:

9.05%) and the N-oxide 6 (Found: 21.80 atom % excess deuterium) formed from 7 by hydrolysis. Also the nmr spectrum of ester 8 showed no absorption in the region of the benzylic proton.

The absence of deuterium exchange in the above experiments requires that the rate of conversion of anhydrobase 2 to products 3 and 4 is more rapid than the protonation of 2 to regenerate the cation 1. The rapid conversion of 1 ($R = C_6H_5$, $R' = CH_3$) by triethylamine to ester 3 ($R = C_6H_5$, $R' = CH_3$) and the low concentration of anhydrobase 2 ($R = C_6H_5$, $R' = CH_3$) (what appears to be a steady-state concentration) generated in this reaction both point to a more rapid disappearance of 2 in contrast to its formation from 1. These exchange experiments are consistent with the assignment of step 2 as rate controlling and thus lend further support to this mechanism.

The above spectral observation of the anhydrobase 2 intermediate in the 4-alkylpyridine N-oxide system is in contrast to similar attempts to detect the anhydrobase in the 2-alkylpyridine studies. This may be rationalized by considering that the rearrangement reaction in the 4 system appears to be slower than in the 2-system. Thus the generation of anhydro base 2 reaches a concentration limit that permits its observation. The remaining question in the 4-alkylpyridine N-oxide system is the nature of the rearrangement of anhydrobase 2 to ester products 3 and 4. This will be discussed in the subsequent paper.

Experimental Section¹⁰

4-Benzylpyridine N-oxide [mp 104–105° (lit.¹¹ mp 151°); nmr ($CDCl_3$) τ 6.03 (s, 2, $-CH_2C_6H_5$), 2.98 (d, $J = 7.4$ Hz, partially hidden under the phenyl multiplet, β -hydrogens on pyridine ring), 2.76 (sharp peak of multiplet, phenyl hydrogens, total intensity of 2.98 and 2.76 peaks is 7), 1.95 (d, 2, $J = 7.4$ Hz, α -hydrogens in pyridine); uv max (CH_3CN) 281 m μ (ϵ 18,900)] was prepared by oxidation of 4-benzylpyridine¹² by the procedure of Hands and Katritzky.¹¹

Phenyl-4-pyridylmethyl Acetate.—A solution of 1.9 g (0.01 mol) of phenyl-4-pyridylmethanol, mp 125° (lit.⁶ mp 126°), prepared by a photochemical reduction of 4-benzylpyridine in alkaline isopropyl alcohol, and 1.53 g (0.015 mol) of acetic anhydride was heated for 2 hr. After the acetic acid and excess acetic anhydride were removed *in vacuo*, distillation of the residue gave 1.7 g (75%) of phenyl-4-pyridylmethyl acetate: bp 137–139° (0.75 mm); n_D^{20} 1.5617; nmr ($CDCl_3$) τ 7.94 (s, 3, $-OOCCH_3$), 3.18 (s, 1, C_6H_5CHOAc), 2.74 (m, 7, phenyl hydrogens and the β -hydrogens in pyridine), 1.55 (d, 2, α hydrogens in pyridine); uv max (CH_3CN) 256 m μ (ϵ 2410), 264 (sh).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76. Found: C, 73.97; H, 5.69.

A picrate which was extremely light sensitive was prepared and recrystallization from ethanol gave an analytical sample, mp 124–125°.

Anal. Calcd for $C_{20}H_{16}N_4O_6$: C, 52.64; H, 3.53. Found: C, 52.94; H, 3.94.

Reaction of 4-Benzylpyridine N-Oxide and Acetic Anhydride.—A solution of 4-benzylpyridine N-oxide (9.26 g, 0.05 mol) in acetic acid (25 ml) was added over a 2-hr period to refluxing acetic anhydride (10.5 g, 0.102 mol) under nitrogen. Distillation

(10) The microanalysis were carried out by Midwest Microlab, Inc. Indianapolis, Ind., or Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., while the deuterium analysis was performed by J. Nemeth, Urbana, Ill. Infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer, the uv-visible spectra were recorded on a Bausch and Lomb Spectronic 505 instrument and the nmr spectra were determined by D. Schifferl or W. E. Hunter with a Varian Associates 60 Mc high resolution nmr spectrometer Model V-4300B.

(11) A. R. Hands and A. R. Katritzky, *J. Chem. Soc.*, 1754 (1958).

(12) The authors wish to thank Dr. F. A. Cislak, Reilly Tar and Chemical Co., Indianapolis, Ind., for a generous gift of 4-benzylpyridine.

(8) S. Oae, S. Tamagaki, T. Negoro, K. Ogino, and S. Kozuka, *Tetrahedron Lett.*, 917 (1968).

(9) Sr. A. I. Gallagher, I. H. M., B. A. Lalinsky, and C. M. Cuper, *J. Org. Chem.* **35**, 1175 (1970).

of the reaction mixture gave 8.44 g (75%) of phenyl-4-pyridylmethyl acetate, bp 164–166° (3.75 mm), n_D^{20} 1.5618. The infrared spectrum of the ester was identical with that of the authentic sample.

The ester was saponified with KOH in water and gave phenyl-4-pyridylmethanol (80% yield), mp 121–122°. A mixture melting point with an authentic sample was not depressed.

1,4-Dimethylpyridinium Methosulfate.—Dimethyl sulfate (6.8 g, 0.054 mol) in anhydrous ether (5 ml) was added slowly to a stirred solution of 4-methylpyridine (5.0 g, 0.054 mol) in anhydrous ether (5 ml). The initial white emulsion slowly solidified and gave 11.0 g (96%) of 1,4-dimethylpyridinium methosulfate as very hygroscopic white solid. Recrystallization from dry acetonitrile–ether gave an analytical sample: mp 66–69° (sealed tube); uv max (CH₃CN) 255 m μ (ϵ 4500), 260 and 262 (sh).

Anal. Calcd for C₈H₁₂N₂O₄S: C, 43.82; H, 5.98. Found: C, 43.56; H, 6.33.

1-Methyl-4-benzylpyridinium Methosulfate.—Using the above procedure 4-benzylpyridine (5.0 g., 0.03 mol) and dimethyl sulfate (3.7 g., 0.03 mol) in 10 ml ether gave 7.8 g (90%) of 1-methyl-4-benzylpyridinium methosulfate as a clear oil which could not be induced to crystallize: uv max (CH₃CN) 254 m μ (ϵ 5450), 261 (sh).

1-Acetoxy-4-methylpyridinium perchlorate [mp 84–86° (sealed tube) (lit.⁴ 84.5–86°); ir (CH₃CN) 1831 cm⁻¹ (ν N⁺-OOCCH₃); uv max (CH₃CN) 254 m μ (ϵ 4800), 261, 275 (sh)] was prepared in 72% yield according to the procedure of Muth and Darlak.⁴

1-Acetoxy-4-benzylpyridinium Perchlorate.—The reaction of 4-benzylpyridine N-oxide (3.7 g, 0.02 mol) in acetic acid (10 ml) and acetic anhydride (25 ml) with perchloric acid (0.5 M, 40 ml) gave 5.7 g (87%) of 1-acetoxy-4-benzylpyridinium perchlorate: mp 136–141°; uv max (CH₃CN) 253 m μ (ϵ 6200), 275 m μ (sh); ir (Nujol mull) 1825 cm⁻¹ (ν N⁺-OOCCH₃). An analytical sample, mp 140–141°, was obtained by recrystallization from CH₃CN–ether.

Anal. Calcd for C₁₄H₁₄ClNO₆: C, 51.31; H, 4.31. Found: C, 51.52; H, 4.55.

Reaction of Pyridinium Salts with Base, Spectral Study.

A. 1-Methyl-4-benzylpyridinium Methosulfate.—A solution of 1-methyl-4-benzylpyridinium methosulfate (0.05 ml of 0.01 M soln in CH₃CN) and 1 ml of 10% NaOH was diluted to 10 ml with acetonitrile (5 \times 10⁻⁵ M in 1-methyl-4-benzylpyridinium methosulfate) and the uv-visible spectrum observed over several hr. An absorption maximum appeared shortly at 370 m μ , reached a maximum intensity after 2 hr, then began to decay. Assuming complete conversion to 1-methyl-4-benzal-1,4-dihydropyridine in 2 hr, the molar extinction coefficient has the value ϵ 18,900 [lit.¹³ $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ 350 m μ (ϵ 8900); λ_{max} 388 m μ (ϵ 7950)].

Addition of 10% NaOH to an aqueous solution of 1-methyl-4-benzylpyridinium methosulfate gave a red-brown oil¹⁴ which was extracted into acetonitrile and showed an absorption maximum at 370 m μ . After removal of the solvent, the brown oil was dried, redissolved in acetonitrile and showed an absorption maximum at 357 m μ .

B. 1-Acetoxy-4-benzylpyridinium Perchlorate.—A solution of triethylamine (1.85 g, 0.0183 mol) in acetonitrile (25 ml) cooled to 0° was added rapidly to a stirred solution of 1-acetoxy-4-benzylpyridinium perchlorate (6.00 g, 0.0183 mol) in acetonitrile (75 ml) precooled to 0°. Aliquots were removed immediately upon mixing, 10 and 25 min after addition and the ir and uv-visible spectra recorded for each aliquot. The uv-visible spectra were measured on solutions prepared by diluting a 1-ml aliquot to 10 ml of solution with acetonitrile. The ir spectrum taken of the aliquot removed immediately upon mixing showed a sharp decrease in the N-acetoxy carbonyl band at 1825 cm⁻¹ and the appearance of the ester product carbonyl band at 1739 cm⁻¹. After 25 min of reaction time the 1825-cm⁻¹ band was very small. The uv-visible spectrum of the aliquot taken immediately upon mixing had an absorption maximum $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 352 m μ (absorbance 0.780) which showed no change in λ_{max} or absorbance value after 10 min (0.775) but after 25 min the λ_{max} had an absorbance of 0.145. Product isolation and identification will be reported in a later section.

C. 1,4-Dimethylpyridinium Methosulfate.—An aliquot (0.1 ml) from a 1.12 \times 10⁻² molar solution of 1,4-dimethylpyridin-

ium methosulfate in acetonitrile was mixed with 0.25 ml of 10% sodium hydroxide solution and diluted to 10 ml with acetonitrile to give a solution 1.12 \times 10⁻⁴ M in 1,4-dimethylpyridinium methosulfate. The uv spectrum recorded immediately upon preparation of the above solution was identical with that of 1,4-dimethylpyridinium methosulfate in acetonitrile. After 0.5 hr a broad absorption began to appear at about 300 m μ and developed into an intense absorption maximum at 310 m μ . This band began to decrease with the appearance of other absorption bands at longer wavelengths. After 15 hr the 310-m μ band had essentially disappeared.

D. 1-Acetoxy-4-methylpyridinium Perchlorate.—A cold solution of 1-acetoxy-4-methylpyridinium perchlorate and triethylamine (1 \times 10⁻⁴ M in each reactant) in acetonitrile was observed spectroscopically. The absorption band due to the salt (λ_{max} 254 m μ) slowly disappeared; however, no band appeared in the 310-m μ region. The final uv curve showed absorption maxima at 276 and 265 m μ which corresponded to a mixture of 4-pyridylmethyl acetate and 3-acetoxy-4-methylpyridine. The ir of the reaction mixture had the carbonyl stretching frequency at 1739 cm⁻¹.

Reaction of 1-Acetoxy-4-benzylpyridinium Perchlorate with Base.—A solution of the base in acetonitrile was added rapidly to a solution of 1-acetoxy-4-benzylpyridinium perchlorate in acetonitrile and subjected to the conditions in Table I. The reaction mixture was processed by one of the following procedures. (a) The reaction mixture was concentrated, *in vacuo*, to one-half volume, diluted with water and extracted with ether. After the extract was dried and the solvent removed, the residue was identified as phenyl-4-pyridylmethyl acetate by comparison of its infrared spectrum with that of an authentic sample. The picrate, mp 121–122°, was prepared and a mixture melting point with an authentic sample was not depressed. (b) The reaction mixture was poured into water, extracted with chloroform, and the extract was washed with saturated sodium bicarbonate, dried and the solvent was removed. The residue was chromatographed on Florisil (25 g/g of residue). Elution with benzene–chloroform (90–10) gave phenyl-4-pyridylmethyl acetate while 4-benzylpyridine N-oxide was eluted with a chloroform–methanol (90–10) solution. The ester was identified as in method a and the recovered N-oxide identified by melting point and a mixture melting point with an authentic sample. (c) The reaction mixture was quenched in ice and basified with solid sodium bicarbonate. The alkaline solution was extracted with chloroform, the extract dried and solvent removed. The residue was identified as 4-benzylpyridine N-oxide. (d) Same procedure as in c except the aqueous layer was made strongly alkaline and the chloroform extract was processed as in (b).

Deuterium Label Experiments. 4-(α,α -Dideuteriobenzyl)pyridine N-Oxide.—Using the procedure of Traynelis and Pacini⁵ a 91% yield of recrystallized (ethyl acetate Skelly B) 4-(α,α -dideuteriobenzyl)pyridine, mp 105–107° (sealed tube), nmr (CDCl₃) τ 2.97 (d, J = 7.2 Hz) as part of a multiplet with a sharp peak at 2.78 (total intensity 7, β hydrogens of pyridine and phenyl hydrogens), 1.94 (d, 2, J = 7.2 Hz, α hydrogens in pyridine), was obtained. The region of the benzylic hydrogens τ 6.03 was completely blank.

Anal. Calcd for C₁₂H₈D₂O:¹⁵ C, 76.97; H, 5.92; D, 18.18 atom % excess. Found: C, 76.41; H, 6.10; D, 21.00 atom % excess.

1-Acetoxy-4-(α,α -dideuteriobenzyl)pyridinium Perchlorate.—Employing the procedure described earlier, 6.3 g (89%) of 1-acetoxy-4-(α,α -dideuteriobenzyl)pyridinium perchlorate, mp 143–144°, was obtained from the reaction of 4-(α,α -dideuteriobenzyl)pyridine N-oxide (4.00 g, 0.024 mol) in acetic acid (10 ml) and acetic anhydride (25 ml) with perchloric acid (48 ml, 0.5 M). The ir had a carbonyl absorption at 1825 cm⁻¹.

Reaction of 1-Acetoxy-4-(α,α -dideuteriobenzyl)pyridinium Perchlorate and Sodium Acetate in the Presence of Acetic Acid.—Sodium acetate (1.38 g, 0.017 mol) in acetic acid (25 ml) and acetonitrile (10 ml) was added rapidly to a stirred solution of 1-acetoxy-4-(α,α -dideuteriobenzyl)pyridinium perchlorate (5.50 g, 0.017 mol) and the mixture was refluxed 1 hr. The reaction was processed according to procedure B described for the undeuterated salt. Column chromatography gave upon elution

(13) L. C. Anderson and N. V. Seeger, *J. Amer. Chem. Soc.*, **71**, 343 (1949). The extinction coefficients listed above were estimated from the curve reported in the literature.

(14) H. Decker, *Chem. Ber.*, **38**, 2493 (1905).

(15) The % H was calculated using the formula weight of the deuterated molecule and the number of hydrogen atoms \times 1.008 of the undeuterated molecule. The conversion factor for regular water was used for the combustion water collected in the absorption tube.

with benzene-chloroform (90-10) 0.99 g (26%) of phenyl-(4-pyridyl)-1-deuteriomethyl acetate: n_D^{20} 1.5621; nmr (CDCl_3) τ 7.94 (s, 3, acetate methyl protons), a hint of a peak at 3.15 (benzylic proton), 2.82 (doublet) partially hidden under the multiplet with a sharp peak at 2.73 (total intensity 7, β protons in pyridine and phenyl protons), 1.47 (d, 2, α protons in pyridine).

Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{DNO}_2$:¹⁵ C, 73.67; H, 5.74; D, 7.69 atom % excess. Found: C, 74.03; H, 5.85; N, 9.05 atom % excess.

Continued elution with chloroform-methanol (90-10) gave 0.80 g (25%) of 4-(α,α -dideuteriobenzyl)pyridine N-oxide: mp 103-105°; nmr (CDCl_3) identical with that of the authentic sample. A sample was recrystallized from ethyl acetate for analysis, mp 105-106°.

Anal. Calcd for $\text{C}_{12}\text{H}_9\text{D}_2\text{NO}$:¹⁵ C, 76.97; H, 5.92; D, 18.18 atom % excess. Found: C, 76.58; H, 6.03; D, 21.80 atom % excess.

Registry No.—Phenyl-4-pyridylmethyl acetate, 24929-18-8; phenyl-4-pyridylmethyl acetate picrate, 24866-72-6; 1,4-dimethylpyridinium methosulfate, 24866-73-7; 1-acetoxy-4-benzylpyridinium perchlorate, 24866-74-8; 4-(α,α -dideuteriobenzyl)pyridine N-oxide, 24866-75-9; phenyl-(4-pyridyl)-1-deuteriomethyl acetate, 24866-76-0.

Photochemistry of Unsaturated Nitrogen Containing Compounds.

VII. Photolysis of Phenylhydrazones¹

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The photochemistry of benzaldehyde phenylhydrazone (1), benzophenone hydrazone (2), benzaldehyde diphenylhydrazone (3), benzophenone phenylhydrazone (4), and benzophenone diphenylhydrazone (5) has been investigated. The products formed from these irradiations indicate that hydrazones are capable of two types of reaction. First, the nitrogen-nitrogen bond of the hydrazone system may be cleaved in a process which results in the formation of an amine and an imine (isolated in most cases as the corresponding aldehyde or ketone). In cases where the hydrazone is derived from an aldehyde, this same reaction pathway also produces a nitrile. The second type of reaction, observed only for benzaldehyde phenylhydrazone (1) and benzophenone hydrazone (2), is one which reduces the hydrazone system to a hydrocarbon; hence, this latter reaction type is a photochemical analog of the Wolff-Kishner reduction. Possible mechanisms for these two reaction processes are proposed and discussed.

As a part of a continuing study of the photochemistry of unsaturated systems containing nitrogen,² the light-induced reactions of a series of five hydrazones (1-5) have been investigated. Interest in these molecules was stimulated by recent findings arising from the photochemistry of a related group of compounds, the azines (6). Several studies during the past few years³⁻⁵ have indicated that the photolysis of azines leads either to cleavage of the nitrogen-nitrogen bond in the azine system, the major reaction pathway, or complete loss of nitrogen from the molecule, a minor process. The structural similarity between the azine (6) and hydrazone (7) systems suggested a possible similarity in their photochemical reaction.

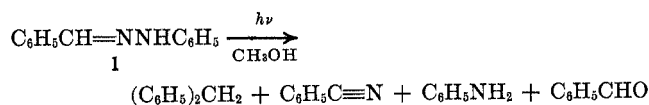


Of the five compounds studied, only benzaldehyde phenylhydrazone (1) has been mentioned previously in the chemical literature as a reactant in light-initiated processes. In these earlier reports the interest in 1 centered around the observation that it is photochromic^{6,7} and that it may undergo a photochemical *cis*-

trans isomerization;⁸ however, in no case was a general study of the photochemistry of this compound conducted. Thus, in order to establish and extend the knowledge of the photochemical reactions of hydrazones as well as to compare hydrazone (7) and azine (6) photochemistry, the following results from the photolyses of hydrazone systems 1-5 are reported.

Results

Vycor-filtered irradiation of a methanol solution of benzaldehyde phenylhydrazone (1) under nitrogen produced upon solvent removal a reddish-brown oil. Chromatography on Florisil separated the reaction mixture into five fractions, one of which was unreacted starting material. The other four were diphenylmethane (14%), benzonitrile (8%), benzaldehyde (15%), and aniline (17%). [The identity of the photo-



products in this and subsequent reactions was established in each case by comparison of the spectral properties (ir, nmr, uv) of the photoproducts with those of independently obtained samples; where possible, mixture melting point comparisons were also made.] The remainder of the reaction mixture stayed as a dark brown band at the top of the chromatography column. Elution with several different solvents failed to move

(1) For paper VI, see J. I. Sarkisian and R. W. Binkley, *J. Org. Chem.*, **35**, 1228 (1970).

(2) Part of this work has been reported in a preliminary form; see R. W. Binkley, *Tetrahedron Lett.*, 1893 (1969).

(3) R. K. Brinton, *J. Amer. Chem. Soc.*, **77**, 842 (1955).

(4) J. F. Ogilvie, *Chem. Commun.*, 359 (1965).

(5) R. W. Binkley, *J. Org. Chem.*, **33**, 2311 (1968).

(6) G. Wettermark and A. King, *Photochem. Photobiol.*, **4**, 417 (1965).

(7) M. Padoa and T. Minganti, *Atti. Accad. Naz. Lincei, Mem., Cl. Sci. Fis. Mat. Natur. Sez. 2a*, **22**, 500 (1914).

(8) G. Condorelli and L. L. Costanzo, *Boll. Sedute Accad. Gioenia Sci. Natur. Catania*, **8** [4], 753 (1969).