sodium acetate was sealed in four test tubes under nitrogen and heated for 48 hr at 100°. The cooled tubes were opened, and the solution was neutralized with sodium bicarbonate and extracted with ether. The ethereal solution was washed with saturated sodium chloride solution, dried (MgSO₄), and concentrated. The product was purified by chromatography on silica gel column, eluting with 20% ether in petroleum ether affording 82 mg (64%) of a mixture of 1413 (65%) and 7-OAc (35%). The exo-tosylate (7-OTs, 67.8 mg) was solvolyzed at 50° to give 25 mg (58%) of 14.

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Registry No.-1-OTs, 41326-96-9; 2-OTs, 41326-98-1; 4, 1072-77-1; 5-OH, 53555-56-9; 5-OPNB, 53555-57-0; 6-OH, 53585-67-4; 6-OPNB, 53585-68-5; 7-OTs, 53585-69-6; p-nitrobenzoyl chloride, 122-04-3.

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- and Mrs. S. Yoshida for measurement of the temperature-dependent nmr spectra of these alcohols. (12) In our study of 1-OTs, we suggested the possible existence of an initial
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Aromatic N-Oxides. VII. The Reaction of Diphenyl-2-pyridylmethane **N-Oxide with Acetic Anhydride**¹

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The rearrangement of diphenyl-2-pyridylmethane N-oxide (8) with acetic anhydride in acetonitrile was investigated. The product was identified as diphenyl-2-pyridylmethyl acetate (10). An intramolecular pathway was elucidated by a combination of oxygen-18 labeling studies and the conversion of 1-acetoxy-2-benzhydrylpyridinium perchlorate (14) to product by a base (Dabco) other than added acetate ion.

The reactions of aromatic N-oxides with acid anhydrides have been studied extensively since the first report in 1947 that pyridine N-oxide was converted to 2-pyridyl acetate when heated in acetic anhydride.³ Twenty years ago several groups observed that alkyl substituents at C-2 of pyridine N-oxide altered the pathway to afford 2-pyridylmethyl acetates.⁴⁻⁶ Since that time mechanistic aspects of these reactions have been thoroughly investigated and excellent reviews are available.^{7,8} The generally accepted mechanism for side chain rearrangement is represented in eq 1-3, the key feature of which is the generation of an anhydrobase intermediate (3), which rearranges intramolecularly via an ion pair to product (4).⁹

The present work stemmed from our observation that nearly all reported examples of this rearrangement with 2alkylpyridine N-oxides (1) involved structures with an α methylene group. At the time this work was commenced we were aware of only two cases in which disubstitution at the α position of the side chain was involved; both compounds, 5^5 and 6,¹⁰ were reported to undergo no rearrangement in acetic anhydride. Since the failure to observe the anticipated reaction with 5 and 6 could be attributed to an intramolecular interaction between the N-oxide moiety and the α -acetoxy group, it seemed desirable to test a simpler case



of disubstitution such as 7. The choice of diphenyl-2-pyridylmethane N-oxide (8) was based on product considerations. Side chain rearrangement of 7 (R = alkyl) to a tertiary acetate would, upon acid hydrolysis, afford an alcohol capable of undergoing an undesirable dehydration. Subse-



quent to the completion of this study Schnekenburger reported that 7 (R = p-acetoxyphenyl) rearranged in acetic anhydride to give 93% of 9. Although no mechanistic stud-



ies were carried out, it was assumed that the pathway involved a "concerted" rearrangement of the anhydrobase.

Results and Discussion

The reaction of 8 with excess acetic anhydride in refluxing acetonitrile yielded 94% of diphenyl-2-pyridylmethyl acetate (10) under optimum conditions. The initial struc-

8
$$\frac{Ac_2O}{MeCN}$$
 (4)
ACO HO HO
 10 H

tural assignment was based on spectroscopic evidence: the presence of an acetate ester (ir, nmr), the presence of H-6, and the absence of the benzylic proton (nmr). If ring substitution had occurred, hydrolysis during work-up would have afforded an α -pyridone compound.¹² The identity of the previously unreported 10 was confirmed by hydrolysis to the known carbinol 11 and by comparison with an authentic sample of 10 prepared independently (eq 5).

$$\begin{array}{cccc}
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With the product structure established, our attention was focused on the mechanism for this rearrangement. Although the anhydrobase route (eq 1-3) was assumed to be applicable, the details of the final step were not secure. Ion pair 13, derived from anhydrobase 12 (eq 6), could afford 10 either intramolecularly (eq 7) or intermolecularly (eq 8). The latter step would involve diffusion from the solvent cage and reaction of the diphenyl-2-pyridylmethyl cation with acetic acid. Our attempts to resolve this ambiguity were patterned after the elegant studies of Oae,¹³ Traynelis,¹⁴ and Muth.¹⁵

The reaction of 8 (no oxygen isotope enrichment) was carried out with uniformly labeled (>90 atom %) oxygen-18 acetic anhydride. Mass spectral analysis of the crude tertiary acetate showed the presence of three species of product 10 with molecular ions of m/e 303, 305, and 307 in relative



proportions of 12, 51, and 37, respectively.¹⁶ Since the m/evalues corresponded to an isotopic composition for 10 of zero, one, and two atoms of ¹⁸O, the anticipated distinction between eq 7 and eq 8 could not be based on these data alone. The most abundant of the three species (m/e 305)was clearly produced by an intramolecular process, while the doubly labeled product $(m/e \ 307)$ appeared consistent with an intermolecular pathway. An alternate interpretation, however, was possible for the latter species. The reaction of 8 with labeled acetic anhydride produced 1 equiv of acetic acid uniformly labeled with oxygen-18, and it was therefore possible that trityl ester 10 had undergone dissociation and exchange in the reaction medium. That this process could occur was demonstrated by a control experiment in which unlabeled 10 was refluxed in acetonitrile with labeled acetic acid. The mass spectrum of the recovered ester exhibited molecular ions only at m/e 303 and 307. Thus the isotopic labeling studies indicated that the major, if not the exclusive, pathway was the intramolecular process (eq 8).

Additional mechanistic inferences were drawn from the ¹⁸O experiments. Mild alkaline hydrolysis of labeled 10 (from 8 and labeled acetic anhydride) afforded diphenyl-2-pyridylcarbinol (11) whose mass spectrum contained molecular ions at m/e 261 and 263 in relative proportions of 51 and 49, respectively.¹⁶ The m/e values corresponded to species of 11 unlabeled and labeled with one ¹⁸O atom. When adjustments were made for the generation of 11 from unlabeled and doubly labeled 10, it was estimated that singly labeled 10 produced the species at m/e 261 and 263 in a ratio of ca. 3:1. This result indicated that complete equilibration of the oxygen atoms did not occur for the acetate ion within the ion pair. Such a preference for ¹⁶O bond formation at the side chain may be caused by steric effects within the anhydrobase 12; similar interpretations have been proposed by Oae.¹³ Supporting evidence for this assignment of the ¹⁸O distribution was obtained from the infrared spectra of the esters. The carbonyl stretching frequency of unlabeled 10 occurred at 1742 cm^{-1} , whereas labeled 10 exhibited a medium shoulder at 1748 and a strong doublet at 1727 and 1709 cm^{-1} . The greater intensity of the lower frequency doublet was consistent with ¹⁸O as the predominant oxygen isotope of the carbonyl group.¹⁷

The intramolecular nature of the rearrangement was corroborated by studies with 1-acetoxy-2-benzhydrylpyridinium perchlorate (14). Thus, treatment of 14 with base

$$8 \xrightarrow[MeCN]{hase} Ph \xrightarrow[AcO]{Ph} Ph \xrightarrow[MeCN]{hase} [12] \rightarrow 10 \quad (9)$$

yielded a product mixture composed of 8 and 10. A variety of bases was investigated and 1,4-diazabicyclo[2.2.2]octane (Dabco) proved to be the reagent of choice. The reaction (eq 9) was monitored by nmr spectroscopy, and the product composition was deduced from ir analysis. The conversion of analogous 1-acetoxypyridinium ions to mixtures of starting N-oxides and rearranged acetates has been observed primarily with added triethylamine or acetate ion,^{14,15,18} although Dabco has effected a similar "back reaction."19 High-pressure liquid chromatography of the reaction mixture confirmed the presence of 8 and 10. This analytical procedure also showed that trace amounts of diphenyl-2pyridylmethane (15) were produced. Similar deoxygenations have been observed with picoline N-oxides.²⁰ The process, which is always a minor pathway, involves free radical intermediates.

Experimental Section

Melting points, uncorrected, were determined on a modified Hershberg apparatus with total-immersion Anschutz thermometers. Spectra were recorded on the following instruments: Perkin-Elmer 237B ir spectrophotometer (polystyrene film calibration); Beckman DB-G uv spectrophotometer; Perkin-Elmer R12B nmr spectrometer at 60 MHz, chemical shifts in ppm from an internal TMS reference; AEI MS-9 mass spectrometer at an ionizing voltage of 70 eV. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials. Triethylamine was refluxed over acetic anhydride and distilled, and a middle cut was stored over solid potassium hydroxide and then redistilled from barium oxide: middle cut bp 87.5–88° (736 mm). Dabco from Houdry Process and Chemical Co. was recrystallized from methanol-diethyl ether and vacuum sublimed: mp 156–157° (sealed tube).

The following reagents were used without further purification: acetic anhydride (99.2%) from J. T. Baker; acetonitrile (<0.01% water, stored over molecular sieves) from Eastman Kodak; uniformly labeled oxygen-18 acetic anhydride and acetic acid (min 90 atom %) from Bio-Rad Laboratories; 15 from Aldrich.

Diphenyl-2-pyridylmethane *N***-Oxide** (8). To a solution of diphenyl-2-pyridylmethane (10 g, 0.041 mol) in acetic acid (75 ml) was added 30% hydrogen peroxide (5.5 ml) and the solution was heated at 70–80°. After 3 hr additional 30% H₂O₂ (4.0 ml; total 9.5 ml, 0.12 mol) was added, and the solution was heated an additional 9 hr. The reaction solution was concentrated at reduced pressure to 15 ml and the yellow residue, which solidified upon cooling, was triturated with diethyl ether to give 8.9 g (83%) of white crystals, mp 161.0–161.8°. The product was recrystallized from benzene to give 8.5 g (80%) of 8: mp 161.6–162.1° (lit.²¹ mp 164–166°); ir (HCCl₃) 1245 and 835 cm⁻¹ (*N*-oxide); uv (CH₃CN) max 276 nm (ϵ 10,500); nmr (CD₃CN) δ 6.18 (s, 1, benzylic H), 8.15 (m, 1, H-6).

Diphenyl-2-pyridylmethyl Chloride. A magnetically stirred solution of diphenyl-2-pyridylmethane (2.2 g, 9.0 mmol) and N-chlorosuccinimide (2.7 g, 20 mmol) in 90 ml of CCl₄ was heated and irradiated 4.5 hr with a 275-W sunlamp. Insoluble succinimide was removed by gravity filtration from the cooled reaction mixture, and the filtrate was concentrated on a rotary evaporator at reduced pressure to give 2.4 g of a viscous residue which crystallized, mp 60-65°. The crude product was recrystallized twice from ligroin (charcoal decolorization) to give 0.44 g (17%) of diphenyl-2-pyridylmethyl chloride, mp 72.2-73.2°.

Anal. Calcd for $\rm C_{18}H_{14}NCl:$ C, 77.28; H, 5.04; N, 5.01; Cl, 12.67. Found: C, 77.12; H, 5.04; N, 4.96; Cl, 12.74.

Diphenyl-2-pyridylmethyl Acetate (10). A magnetically stirred mixture of diphenyl-2-pyridylmethyl chloride (2.0 g, 7.2 mmol) and silver acetate (1.5 g, 9.3 mmol) in 30 ml of cyclohexane was refluxed 3 hr under a nitrogen atmosphere, cooled, and filtered by suction. The filtrate was concentrated on a rotary evaporator under reduced pressure to give 2.0 g (92%) of a crystalline residue, mp 78-82°. The crude product was recrystallized from isooctane (charcoal decolorization) to give 1.3 g (60%) of 10: mp 84.2-85.6°; ir (HCCl₃) 1742 cm⁻¹ (C=O); uv (CH₃CN) max 259 nm (ϵ 4070); nmr (CD₃CN) δ 2.12 (s, 3 H, acetate), 8.47 (m, 1, H-6).

Anal. Calcd for $C_{20}H_{17}O_2N$: C, 79.18; H, 5.65; N, 4.62. Found: C, 79.07; H, 5.61; N, 4.57.

Rearrangement of 8. A solution of 8 (1.3 g, 5.0 mmol) and acetic anhydride (5.1 g, 50 mmol) in 100 ml of acetonitrile was refluxed 24 hr, concentrated on a rotary evaporator under reduced pressure, neutralized with 0.1 N NaOH, and extracted four times with 30-ml portions of diethyl ether. The combined ethereal extract was washed three times with 5% NaHCO₃, dried (MgSO₄), and concentrated as above to yield 1.4 g (94%) of a semicrystalline yellow oil whose ir and nmr spectra were identical with those of authentic 10. The crude product was recrystallized from isooctane (charcoal decolorization) to give 0.56 (37%) of 10, mp 83.6–85.0°, mixture melting point undepressed. Variations over the following ranges defined the above optimal conditions: temperature, ambient or reflux; time, 3–120 hr; molar ratio of Ac₂O:8, 2:1 to 10:1.

Similarly, the rearrangement of 8 (0.072 g, 0.28 mmol) was carried out with uniformly labeled (>90 atom % ¹⁸O) acetic anhydride (0.28 g, 2.6 mmol) in 6 ml of acetonitrile to afford 0.086 g (100%) of a viscous yellow oil, whose identity as uncontaminated 10 was confirmed by ir and nmr spectra. The isotopic composition of the crude product was determined by mass spectral analysis.

Diphenyl-2-pyridylcarbinol (11). A solution of rearrangement product 10 (1.4 g, 4.6 mmol) and KOH (0.42 g, 7.5 mmol) in 5 ml of methanol was refluxed 4 hr, diluted with 60 ml of water, neutralized with 2 N HCl, extracted with three 30-ml portions of diethyl ether, dried (MgSO₄), and concentrated under reduced pressure to give 0.99 g (83%) of a semicrystalline residue. A portion of the crude product was recrystallized from 95% ethanol (charcoal decolorization) to afford 11, mp 102.8-103.5° (lit.²¹ mp 105°), mixture melting point was undepressed with an authentic sample prepared by the reaction of 2-benzoylpyridine with phenylmagnesium bromide.²²

Similarly, the hydrolysis of ¹⁸O-labeled **10** (70 mg, 0.023 mmol) was carried out with KOH (20 mg, 0.3 mmol) in 2 ml of 50% aqueous methanol at reflux for 20 min. Work-up as above gave 34 mg (57%) of semicrystalline product; the isotopic composition of the crude product was determined by mass spectral analysis.

Acetolysis of 10. A solution of 10 (51 mg, 0.17 mmol) and uniformly labeled (>90 atom % ¹⁸O) acetic acid (0.11 g, 1.7 mmol) in 4 ml of acetonitrile was refluxed 24 hr and worked-up as above to give quantitative recovery of 10, whose identity was confirmed by ir and nmr spectra. The isotopic composition of the crude product was determined by mass spectral analysis.

1-Acetoxy-2-benzhydrylpyridinium Perchlorate (14). A solution of 8 (2.5 g, 9.6 mmol) and acetic anhydride (10 ml) in 125 ml of 0.1 N perchloric acid in acetic acid was refrigerated overnight. The crystalline product was collected, washed twice with cold Ac₂O-AcOH solution (12:1), and three times with cold diethyl ether, and dried *in vacuo* over P₂O₅ to give 3.4 g (88%) of 14: mp 184.5-185.2° dec; ir (CH₃CN) 1842 cm⁻¹ (C=O); nmr (CD₃CN) δ 2.20 (s, 3, acetate), 6.18 (s, 1, benzylic).

Anal. Calcd for $C_{20}H_{18}$ ClNO₆: C, 59.49; H, 4.49; N, 3.47; Cl, 8.78. Found: C, 59.42; H, 4.52; N, 3.33; Cl, 8.94.

Reaction of 14 with Base. A solution of 14 (133 mg, 0.33 mmol) and 1,4-diazabicyclo[2.2.2]octane (37 mg, 0.33 mmol) in 10 ml of acetonitrile was refluxed for 24 hr, concentrated on a rotary evaporator at reduced pressure, diluted with 10 ml of water, made slightly alkaline with NaHCO₃, and extracted with three 10-ml portions of CH₂Cl₂. The combined extract was washed with saturated NaCl solution, dried (MgSO₄), and evaporated to dryness as above to give 87 mg of residual oil whose composition as a mixture containing 8 and 10 was deduced from ir and nmr spectra.

The mixture was analyzed by high-pressure liquid chromatography on a Waters Associates ALC 202/401 instrument fitted with a 2 mm \times 4 ft Bondapak C₁₈/Corasil column and with acetonitrile: water (1:1) as the mobile phase. Compared to authentic samples of 8, 10, 15, and 11, the product mixture was shown to contain the first three of these compounds, but not the fourth.

The reaction of 14 with various bases in acetonitrile was analyzed by ir ($\nu_{C=0}$ 1742 cm⁻¹ for 10) and nmr (appearance of 8.47 for H-6 of 10 and disappearance of δ 6.18 for benzylic proton of 14) spectra. The generation of 10 was not observed with the following bases: sodium acetate, pyridine, triethylamine, 1,5-diazabicyclo-[4.3.0]nonene-5, 1,5-diazabicyclo[5.4.0]undecene-5, and 1,8-bis(dimethylamino)naphthalene. In some cases product mixtures were obtained which exhibited frequencies at 1718 or 1661 cm⁻¹, but these structures were not investigated further. Control experiments established that 10 was stable to Dabco under the reaction conditions.

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Registry No.-8, 21883-34-1; 10, 53608-48-3; 11, 19490-90-5; 14, 53608-50-7; diphenyl-2-pyridylmethane, 3678-72-6; diphenyl-2pyridylmethyl chloride, 53608-51-8; N-chlorosuccinimide, 128-09-6; acetic anhydride, 108-24-7; 1,4-diazabicyclo[2.2.2]octane, 280-57-9.

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Acetylenedicarbonyl Fluoride. I. Its Physical Properties and Reaction with Nucleophilic Reagents

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Acetylenedicarbonyl fluoride (3) has been prepared by (a) reaction of SF₄ with the monopotassium salt of acetylenedicarboxylic acid and (b) by reaction of phenylsulfur trifluoride with acetylenedicarboxylic acid. The physical and spectral properties including a mass spectral analysis of 3 have been determined. The diacyl fluoride reacts with alcohols, phenols, and aliphatic primary and secondary amines to give the respective esters and diamides in good yield. With ethanethiol and 3, a mixture of α -ethylthiofumaroyl and maleoyl fluorides, is produced.

The properties and reactions of acetylenedicarbonyl halides have not been reported. Only two disclosures on their synthesis have been documented. The synthesis in low yield of acetylenedicarbonyl chloride (1) by a Diels-Alder displacement reaction involving maleic anhydride was reported in 1938.² Attempts to prepare 1 from acetylenedicarboxylic acid (2) or its salts by more direct routes^{4a} give only addition products and tars.^{3a,4b,c} Acetylenedicarbonyl fluoride (3) has been prepared by the controlled fluorination of 2 with $SF_{4.5}$ Its properties and experimental details, however, were not reported.

$$\begin{array}{cccccccc} O_2CC \equiv CCO_2H + 2SF_4 \longrightarrow & & \\ 2 & & & O & \\ & & & & \\ FCC \equiv CCF + 2HF + 2SOF_2 \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

H

The diacyl halides of 2 are potentially reactive intermediates for the preparation of acetylenic compounds which cannot be conventionally prepared from 2 or its diesters. Acetylenedicarbonyl fluoride has been prepared by two additional routes⁶ in moderate to good yields. We report here on these modified routes as well as a survey of its physical properties and reactions with alcohols, phenols, a thiol, and amines.

Synthesis

The fluorination of the monopotassium salt of 2(4) in dimethylcyclohexane with SF_4 at 60° for 15 hr produced 3 in yields ranging from 48 to 70%, depending upon the purity of the SF_4 employed. The substitution of 2 by 4 alleviated the problem of having excess HF which is always a potential source of side reactions in the product mixture. The HF

$$HO_2CC \equiv CCO_2K + SF_4 \longrightarrow 3 + KHF_2 + 2SOF_2$$
4

produced in the fluorination is thus scavenged by the KF generated. Alternatively, 3 could be prepared in the laboratory and in glass equipment from 2 and phenylsulfur trifluoride⁷ in 1,2-dibromoethane⁸ at 10°. The latter preparation required a catalytic amount of HF to initiate the fluorination as evidenced by a short induction period at the onset of the phenylsulfur trifluoride addition. The yield of 3 using this route was ca. 50%.

$$2 + 2C_{e}H_{5}SF_{3} \rightarrow 3 + 2C_{e}H_{5}SOF + 2HF$$

Physical Properties of 3

Acetvlenedicarbonyl fluoride has a bp of 46° and a fp of -51° (DTA). From -15 to 41° the vapor pressure obeyed the relation log $P_{\text{Torr}} = -(1688 \pm 41)/T^{\circ} \text{ K} + 8.19 \pm 0.16$