Aromatic *N*-Oxides. VII. Nature of the Rearrangement Step in the Reaction of 4-Alkylpyridine *N*-Oxides and Acid Anhydrides[1-3]

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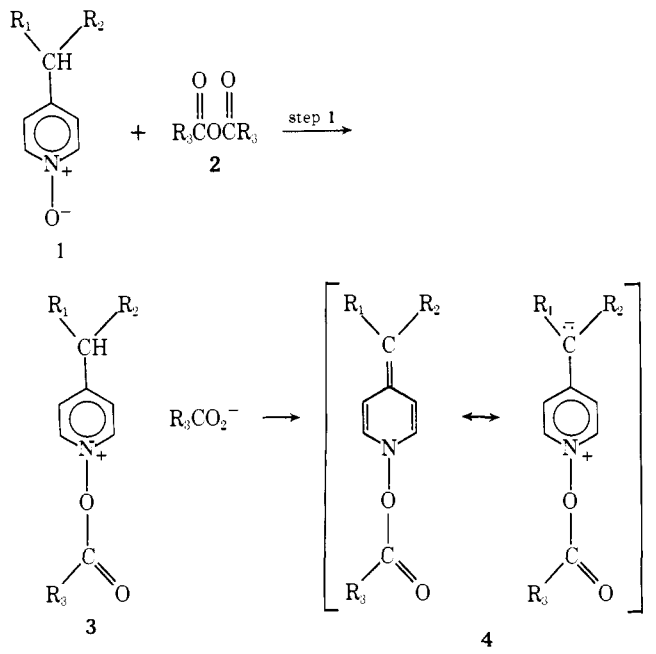
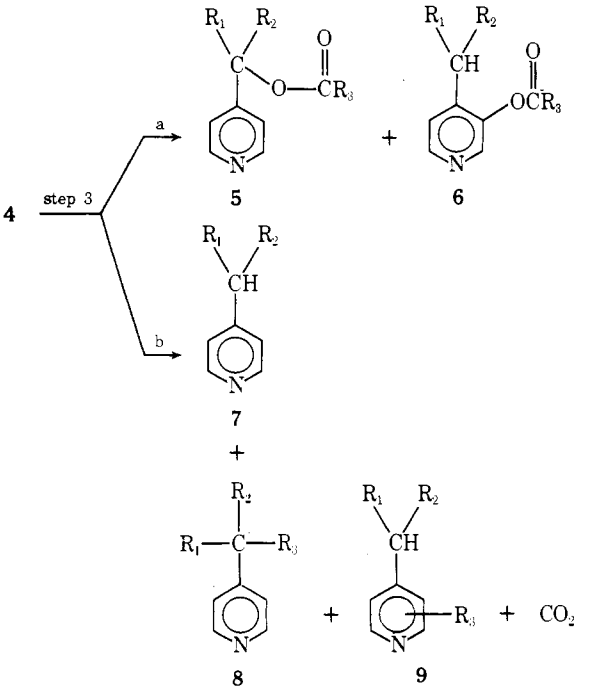
Abstract: The reactions of 4-diphenylmethylpyridine 1-oxide (**1**, $R_1 = R_2 = C_6H_5$), 4-(1-phenylethyl)pyridine 1-oxide (**12**, R = C_6H_5), 4-isopropylpyridine 1-oxide (**12**, R = CH_3), 4-(2-phenylethyl)pyridine 1-oxide, and 4-neopentylpyridine 1-oxide with acetic anhydride are described. The reaction with **12**, R = C_6H_5, and **12**, R = CH_3, produced 1-phenyl-1-(4-pyridyl)ethene (**14**, R = C_6H_5) (62%) and 2-(4-pyridyl)propene (**14**, R = CH_3) (42%), respectively, along with 1-phenyl-1-(4-pyridyl)ethyl acetate (**13**, R = C_6H_5) (16%) and 2-(4-pyridyl)-2-propyl acetate (**13**, R = CH_3) (27%), respectively. The reaction of **1**, $R_1 = R_2 = C_6H_5$, formed diphenyl-(4-pyridyl)methyl acetate (**5**, = $R_1 = R_2 = C_6H_5$; $R_3 = CH_3$) in 94% yield. 4-Neopentylpyridine 1-oxide and acetic anhydride gave 2-(4-pyridyl)-3-methyl-2-butene (**19**) (54%) and 1-(4-pyridyl)-2,2-dimethyl-1-propyl acetate (**20**, 31%). The appearance of these alkenes (40–60%) as major reaction products are discussed in terms of an ion pair fragmentation of an anhydrobase intermediate which leads to both ester **13** and alkenes **14** and **19** *via* carbonium ions. When **1**, $R_1 = R_2 = C_6H_5$, and **12**, R = C_6H_5, were treated with pivalic anhydride, the formation of free radical derived products (CO_2, 30–35% and alkylpyridines, 28%) increased, but the expected esters **5**, $R_1 = R_2 = C_6H_5$, $R_3 = (CH_3)_3C$ (68%), and **13**, R = C_6H_5, $R_3 = (CH_3)_3C$ (18%), and alkene **14**, R = C_6H_5 (26%), respectively, remained as the major ion pair process. The effect of varying structure on these reactions is discussed.

The general mechanistic scheme for the reaction of 4-alkylpyridine *N*-oxides and acid anhydrides, as outlined below, is well established and has been reviewed in several places.[1,5,6] Isolation of the 1-acyloxy-4-alkylpyridinium ion (**3**) as the perchlorate salt and its base-catalyzed conversion to esters **5** and **6**,[1] spectral evidence for the anhydrobase **4**,[1] and identification of step 2 as rate determining[1,7] have been reported recently and strengthen the proposed mechanistic pathway.

The nature of the rapid rearrangement of **4** to esters **5** and **6** (step 3a) has been controversial, while the formation of the alkylpyridines **7**, **8**, and **9** and carbon dioxide are generally acknowledged to involve radical precursors; however, the origin of these radicals has not been experimentally established. Both intermolecular and intramolecular pathways have been proposed for the conversion of **4** to ester. Oae and coworkers[8-10] invoked an intermolecular pathway to explain complete scrambling of all oxygens in the reactions of 4-picoline *N*-oxide with ^{18}O-labeled acetic anhydride or butyric anhydride in the presence of their respective acids. When equal molar amounts of 4-picoline *N*-oxide and these acid anhydrides were studied in aromatic solvents,[9,10] an intramolecular pathway appeared to be operative. The concerted intramolecular rearrangement of **4** to esters **5** and **6** has been excluded;[8,11,12] however, the alternative fragmentation of **4** at the N–O bond into radical pairs **10**[9-11,13] or into ion pairs **11**[6,14,15] followed by recombination to esters has received considerable attention. Most recently, Cohen and Deets[6,14] have reported trapping the





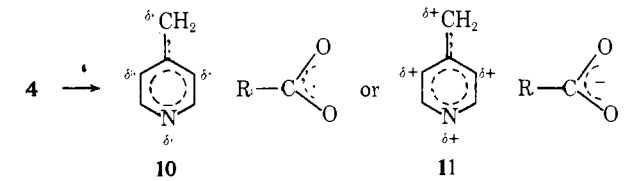


Table I. Reaction of 4-Alkylpyridine *N*-Oxides with Acid Anhydrides

$[RC(=O)]_2$–O R, mol	R′, mol	Temp, °C	CO_2, % yield	(ester) R″, % yield	(olefin) R‴, % yield	(alkylpyridine) % yield
1. CH_3, 0.083	$(C_6H_5)_2CH$–, 0.030	~140	0.69	$(C_6H_5)_2C(OAc)$, 94[a]		
2. CH_3, 0.097	$C_6H_5C(CH_3)H$–, 0.023	~137	0.76	$C_6H_5C(OAc)(CH_3)$–, 16	$C_6H_5C(=CH_2)$–, 62	
3. CH_3, 0.093	$(CH_3)_2CH$–, 0.022	~136	1.66	$(CH_3)_2C(OAc)$–, 27	$CH_3C(=CH_2)$–, 42	
4. CH_3, 0.26	$C_6H_5[(CH_2)_2]$–, 0.054	~140	1.28	$C_6H_5CH_2C(OAc)H$–, 75[b]	$C_6H_5CH=CH$–, 11	
5. CH_3, 0.212	$(CH_3)_3CCH_2$–, 0.015	~140	2.93	$(CH_3)_3CC(OAc)H$–, 31[c]	$(CH_3)_2C=C(CH_3)$–, 54	4[d]
6. $(CH_3)_3C$–, 0.10	$(C_6H_5)_2CH$–, 0.033	176	31	$(C_6H_5)_2C[OC(=O)C(CH_3)_3]$–, 68[e]		28
7. $(CH_3)_3C$–, 0.073	$(C_6H_5)_2CH$–, 0.0234	135	27	$(C_6H_5)_2C[OC(=O)C(CH_3)_3]$, 69[f]		17
8. $(CH_3)_3C$–, 0.042	$C_6H_5C(CH_3)H$–, 0.015	176	35	$C_6H_5C[OC(=O)C(CH_3)_3](CH_3)$–, 18	$C_6H_5C(=CH_2)$–, 26	28

[a] This yield represents 88% ester and 6% of the corresponding alcohol. [b] This yield represents 40% ester and 35% of the corresponding alcohol. [c] This yield represents 21.5% ester and 9.5% of the corresponding alcohol. [d] A fourth reaction product 4-neopentyl-2(1*H*)-pyridone was also isolated in 5% yield. [e] This yield represents 65% ester and 3% of the corresponding alcohol. [f] This yield represents 67% ester and 2% of the corresponding alcohol.

picolyl cation by reaction with anisole and with benzonitrile, both used as solvents in the reaction of 4-picoline *N*-oxide with acetic anhydride. The yield of trapped products ranged from 11 to 20% and clearly demonstrated the presence of picolyl cations in the reaction medium. Ion pair intermediates have also been used to explain the ^{18}O scrambling results, cited earlier, *via* solvent (RCO_2H) capture of the picolyl cation.[6] The free radical pair route to esters emerged from evidence for the presence of radicals in the reaction medium[9,11] and the effect of structure on the formation of radical products (alkylpyridines and carbon dioxide) *vs.* esters.[13] Recently, Iwamura and coworkers[16] obtained support for at least a portion of the ester production *via* radical pairs by observation of the CIDNP effect in the formation of 4-pyridylmethyl acetate from the reaction of 4-picoline *N*-oxide with acetic anhydride. This report deals with the rearrangement (step 3) of **4** to esters and provides further support for the ion pair intermediate **11**. The effect of structure variation of reactants on the formation of ester products *vs.* alkylpyridines is also presented.

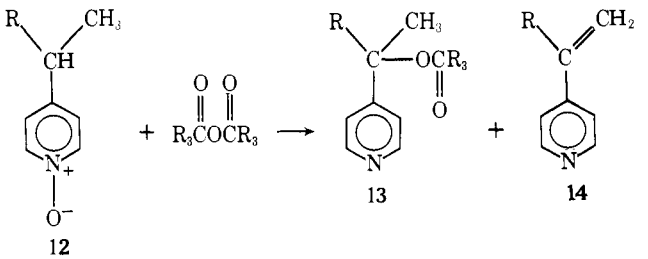
Results

A series of 4-alkylpyridines, either available commercially or prepared according to the literature, were converted by 30% H_2O_2 into the corresponding *N*-oxides: 4-diphenylmethylpyridine 1-oxide (89%), 4-(1-phenylethyl)pyridine 1-oxide (90%), 4-isopropylpyridine 1-oxide (63%), 4-(2-phenylethyl)pyridine 1-oxide (quant), and 4-neopentylpyridine 1-oxide (76%). The reaction of each of these 4-alkylpyridine 1-oxides with acetic anhydride and the reaction of 4-diphenylmethylpyridine 1-oxide and 4-(1-phenylethyl)pyridine 1-oxide with pivalic anhydride have been studied, and the results are summarized in Table I.

In all these reactions, the only esters formed were **5** with the acyloxy group attached to the side chain α carbon. Identification of these esters entailed comparison with authentic samples (Table I, entries 2, 3, 5, 7) obtained by esterification of the corresponding alcohols prepared by an independent route and/or saponification of the esters to their corresponding alcohols. The ir and nmr spectral properties of these esters and corresponding alcohols were consistent with the assigned structures. Authentic samples of 1-phenyl-1-(4-pyridyl)ethene and 2-phenyl-1-(4-pyridyl)ethene were prepared and were used to identify these same alkenes formed in entries 2, 8, and 4, Table I. Structural assignments for 2-(4-pyridyl)propene (entry 3, Table I) and 2-(4-pyridyl)-3-methyl-3-butene (entry 5, Table I) were made on the basis of characteristic ir and nmr spectra. In the latter case, this new alkene was isolated and characterized as a picrate, which also showed the expected spectral properties. The 4-alkylpyridines formed in these reactions were identified by comparison of ir and nmr spectra with those of an authentic sample. The yields reported in Table I were obtained by isolation, glc, and/or nmr analysis.

For those reactions where both ester and alkene products were formed (entries 2–5, 8, Table I), each product was individually subjected to the reaction conditions, except 2-phenyl-1-(4-pyridyl)ethene and 2-(4-pyridyl)-3-methyl-2-butene. In each control experiment, the individual ester or alkene was stable to the reaction conditions which precludes the concern that the alkene may have been formed from the expected ester in a subsequent elimination reaction.

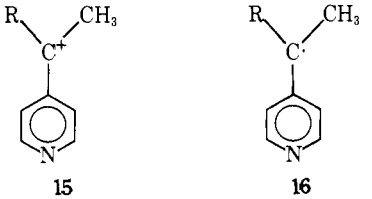
The reaction of 4-diphenylmethylpyridine 1-oxide (**1**, $R_1 = R_2 = C_6H_5$) with acetic anhydride produced diphenyl(4-pyridyl)methyl acetate (**5**, $R_1 = R_2 = C_6H_5$) in high yield (94%) with only 0.7% carbon dioxide evolved. However, reactions of 4-(1-phenylethyl)pyridine 1-oxide (**12**, R = C_6H_5) and 4-isopropylpyridine 1-oxide (**12**, R = CH_3) with acetic anhydride proceeded in high conversion to products (70–80%) but gave alkenes (**14**, R = C_6H_5, and **14**, R = CH_3, respectively) as the major component in a 2–4:1 ratio over the expected ester **13**. Again the production of carbon dioxide in these reactions was minimal.



12 13 14

Discussion

The origin of the alkenes is best explained *via* carbonium ion intermediate **15** which, in an E1 type process, transfers

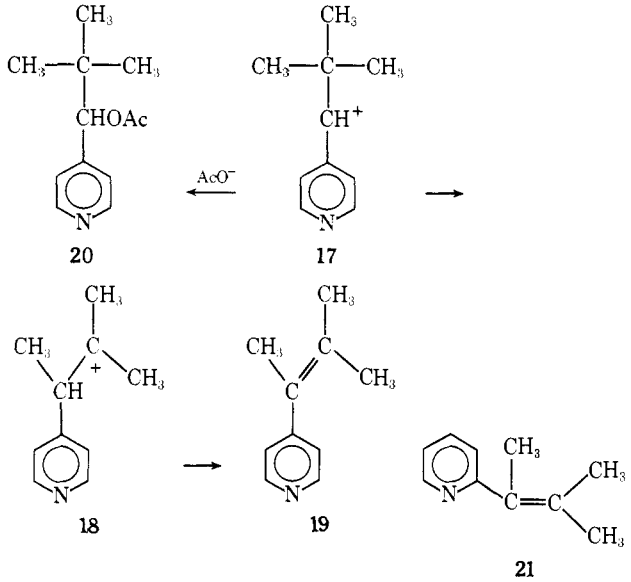


15 16

a proton to some base (alkylpyridine or acid anion). The alternative free radical intermediate **16** is less attractive as a source of alkenes in view of its preference to dimerize.[17] In bimolecular self reactions, radicals do undergo disproportionation to alkenes and alkanes, but elimination to alkenes between two different radicals does not appear to be common.[18] The absence of 4-(1-phenylethyl)pyridine and 4-isopropylpyridine in the reactions of the corresponding *N*-oxides with acetic anhydride (entries 2 and 3, Table I) removes the radical disproportionation route as a possible avenue to the alkenes **14.**

The high yields of alkenes (40–60%) require that a substantial amount of the reaction proceed *via* carbonium ions. These carbonium ions may also combine with acid anions to produce esters **13.** Thus the reaction products (both alkenes and esters) are readily rationalized *via* ion pair intermediate **11** as the pathway for rearrangement step 3.

The most convincing evidence for carbonium ion intermediates was found in the reaction of 4-neopentylpyridine 1-oxide and acetic anhydride where 54% of the reaction underwent carbon skeletal rearrangement and elimination to form 2-(4-pyridyl)-3-methyl-2-butene (**19**). Ester **20** was



present in 31% yield; however, no ester resulting from the rearranged carbonium ion **18** was observed. Whereas rearrangements of neopentyl carbonium ions are commonplace and well established, the vicinal shift of an alkyl group in a radical reaction has not been observed even though numerous attempts have been reported.[19] A similar carbon skeletal rearrangement in the reaction of 2-neopentylpyridine 1-oxide and acetic anhydride was reported by Bodalski and Katritzky.[15c] The rearranged alkene, 2-(2-pyridyl)-3-methyl-2-butene (**21**), was formed in only 3% yield, while the expected acetate ester [1-(2-pyridyl)-2,2-dimethyl-1-propyl acetate] was isolated in 54% yield. The marked difference in yields between the rearranged alkenes **19** and **21** most likely reflects the proximity of the reaction sites of the ion pair in the 2-neopentylpyridine 1-oxide–acetic anhydride system. Thus recombination of ion pairs to produce the ester in the 2-system appears more favorable than the carbon skeletal rearrangement and elimination to **21.** In the 4-neopentylpyridine 1-oxide case, rearrangement of carbonium ion **17** is more prevalent owing to separation of reaction centers which upon recombination would form ester **20.**

In the reaction of 4-alkylpyridine 1-oxides with acid anhydrides, the amount of carbon dioxide or alkylpyridines formed has been used as a measure of the minimum amount of radical intermediates present. An earlier report in the literature[13] described the effect of varying the structure of the acid anhydride on the product distribution in the reaction with 4-methylpyridine 1-oxide. As one proceeded through the series acetic, butyric, isobutyric, and pivalic anhydride, the yields of carbon dioxide and alkylpyridines increased while ester yields decreased. Thus the more labile pivaloxyloxy radical [$(CH_3)_3CCO_2\cdot$] decomposed to the more stable *tert*-butyl radical and governed the course of the reaction (52% CO_2, 35% alkylpyridines, and only 7% esters). In this report, we observed a contrasting structural effect. As the substituents on the 4-alkyl group were varied in a manner which stabilized carbonium ions, the yield of carbon dioxide and alkyl pyridines was negligible. The reactions of 4-isopropylpyridine 1-oxide (**12,** R = CH_3), 4-(1-phenylethyl)pyridine 1-oxide (**12,** R = C_6H_5), and 4-diphenylmethylpyridine 1-oxide (**1,** $R_1 = R_2 = C_6H_5$) with acetic anhydride produced 1.66, 0.76, and 0.69% of carbon dioxide, respectively. These observations are consistent with the fragmentation of the anhydro base **4** into ion pair intermediates **11.**

The reaction of pivalic anhydride (**2,** $R_3 = (CH_3)_3C$) (which favors radical products) and 4-diphenylmethylpyridine 1-oxide (**1,** $R_1 = R_2 = C_6H_5$) (which favors ionic products) proceeded to give predominantly diphenyl(4-pyridyl)-methyl pivalate (**5,** $R_1 = R_2 = C_6H_5$, $R_3 = (CH_3)_3C$) (68%); however, the amount of radical products (31% CO_2 and 28% 4-diphenylmethylpyridine) greatly increased. Similarily in the reaction of 4-(1-phenylethyl)pyridine 1-oxide (**12,** R = C_6H_5) and pivalic anhydride, the radical products (35% CO_2 and 28% 4-(1-phenylethyl)pyridine) increased, but the ionic products [1-phenyl-1-(4-pyridyl)ethyl pivalate (**13,** R = C_6H_5, $R_3 = (CH_3)_3C$) (18%) and 1-phenyl-1-(4-pyridyl)ethene (**14,** R = C_6H_5) (26%)] still represented the major reaction pathway. In addition, the yield of alkene also exceeded the yield of ester. These results lend further support to ion pair precursors for both ester and alkene formation. The origin of radicals in these reactions may be attributed to the homolytic fission of the N–O bond in the anhydro base intermediate **4.** An increase in radical products simply reflects a greater contribution *via* homolytic fission or a multi bond fission to the fragmentation of the anhydro base. The dual character of the N–O bond cleavage in **4** will be considered in the subsequent paper.[20]

Experimental Section[21]

2-(4-Pyridyl)-2-propanol. Methyllithium (0.04 mol in 20 ml of ether) was added dropwise at room temperature to 4-acetylpyridine (5.0 g, 0.04 mol) in ether (20 ml) under N_2, and the reaction was stirred for 2 hr. After the reaction was quenched with H_2O (50 ml), the resulting solid was filtered, washed (H_2O), and dried. Recrystallization of the solid from ethyl acetate gave 4.6 g (86%) of 2-(4-pyridyl)-2-propanol: mp 134° (lit.[22] mp 135–135.4°); ir (KBr) 3180 cm^{-1} (br s, OH); nmr ($CDCl_3$) δ 8.47 (m, 2, pyr C_2, C_6 H's), 7.43 (m, 2, pyr C_3, C_5 H's), 4.52 (br s, 1, OH), and 1.56 (s, 6, 2 CH_3's).

1-Phenyl-1-(4-pyridyl)ethanol. Employing the above procedure, 4-benzoylpyridine (32.0 g, 0.17 mol) and methyllithium (0.20 mol) in ether (300 ml) produced, after 2 hr, 30.0 g (87%) of 1-phenyl-1-(4-pyridyl)ethanol, mp 146–148° (recrystallized from ethyl acetate) (lit.[23] mp 146–147°, nmr data[24]).

1-(4-Pyridyl)-2,2-dimethyl-1-propanol. A solution of 4-pyridinecarboxaldehyde (10.7 g, 0.10 mol) in ether (50 ml) was added dropwise to a vigorously stirred solution of *tert*-butylmagnesium chloride (1.6 *M*, 100 ml) in tetrahydrofuran. After the reaction mixture was stirred for 15 min and quenched with H_2O (50 ml) at 0°, the organic phase was separated and dried ($MgSO_4$), and the solvent was removed *in vacuo* to give 11.9 g (72%) of crude alcohol. Chromatography of 10 g of crude product on basic alumina (450 g) and elution with benzene–ether (3:1) gave an alcohol, mp 110–112°, which, upon recrystallization from ethyl acetate, provided pure 1-(4-pyridyl)-2,2-dimethyl-1-propanol: mp 115.5–

116.5°; ir (NaCl melt) 3200–3100 (br s, H-bonded OH), 2970 (s), 2900 (s), 1610 (s), 1475 (m), 1460 (m), 1390 (m), 1350 (m), 1305 (m), 1230 (m), 1218 (m), 1095 (m), 1065 (s), 1015 (m), 1005 (s), 825 (m), 735 (m), and 650 cm^{-1} (m); nmr ($CDCl_3$) δ 8.35 (m, 2, pyr C_2, C_6 H's), 7.20 (m, 2, pyr C_3, C_5 H's), 4.34 (s, 1, $CHOH$), 4.12 (s, 1, $CHOH$), 0.88 [s, 9, $-C(CH_3)$]; mass spectrum (70 eV) *m/e* (rel intensity), 165 (3.3), 150 (4.9), 109 (100), 108 (58), 80 (32), 79 (9.8), 57 (57).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.75; H, 9.08. Found: C, 72.91; H, 9.09.

4-Alkylpyridines. 4-(2-Phenylethyl)pyridine [mp 69–70° (lit.[25] mp 70–70.8°), nmr ($CDCl_3$) δ 8.43 (m, 2, pyr C_2, C_6 H's), 7.35–7.05 (m, 5, C_6H_5), 6.96 (m, 2, pyr C_3, C_5 H's), 2.84 (m, 4, $-CH_2CH_2-$)] was prepared by the method of Avramoff.[25]

4-(1-Phenylethyl)pyridine [bp 128–135° (0.1 Torr) (lit.[24] bp 128–135° (0.1 Torr)] was obtained in 82% yield by reduction of 1-phenyl-1-(4-pyridyl)ethanol with Zn and concentrated hydrochloric acid.

4-Neopentylpyridine [bp 82–84° (9 Torr) (lit.[26] bp 134° (101 Torr); bp[13] 87–88° (13 Torr); perchlorate salt, mp 120.5° (lit.[26] mp 120.7–122.2°)] was formed in 19% yield by reaction of *tert*-butyl bromide and 4-picolyllithium.[26]

The picrate of 4-neopentylpyridine was prepared, and recrystallization from methanol gave yellow needles: mp 166.5–167°; nmr (d_6-DMSO) δ 12.5 (br s, 1 N–H), 8.59 (m, 2, pyr C_2, C_6 H's), 8.34 (s, 2, $C_6H_2(NO_2)_3O^-$), 7.63 (m, 2, pyr C_3, C_5 H's), 2.52 (s, 2, $-CH_2-$), 0.67 [s, 9, $C(CH_3)_3$]; mass spectrum (70 eV) *m/e* (rel intensity) 229 (100), 199 (28), 171 (11), 150 (11), 149 (26), 93 (84), 92 (58), 91 (84).

Anal. Calcd for $C_{16}H_{18}N_4O_7$: C, 50.82; H, 4.76; N, 14.82. Found: C, 51.06; H, 4.63; N, 14.92.

Preparation of 4-Alkylpyridine *N*-Oxides. General Procedure. A solution of the 4-alkylpyridine (0.13–0.25 mol) in acetic acid (150 ml) and 30% H_2O_2 (45 ml) was heated for 5 hr at 70–80°. A second quantity of 30% H_2O_2 (total 0.3–0.6 mol) was added and the reaction heated (70–80°) for *ca.* 20 hr. The reaction mixture was concentrated to *ca.* 100 ml under reduced pressure, diluted with H_2O, and concentrated again as far as possible. The residue was made alkaline ($NaHCO_3$, solid), shaken with $CHCl_3$, and filtered. After the filtrate was dried ($MgSO_4$), the solvent was removed and the residue recrystallized from ethyl acetate.

4-(Diphenylmethyl)pyridine 1-oxide [mp 156.3–157.7°; ir (KBr) 3020 (s), 2950 (m), 1595 (m), 1475 (s), 1440 (s), 1240 (s), 1160 (m), 1090 (m), 1030 (m), 830 (s), 743 (s), 695 cm^{-1} (s); nmr ($CDCl_3$) δ 8.27–8.13 (m, 2, pyr C_2, C_6 H's), 7.53–6.98 (m, 12, pyr C_3, C_5 H's and 2 C_6H_5's), 5.50 (s, 1, $-CH(C_6H_5)_2$)] was isolated in 89% yield.

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.72; H, 5.78; N, 5.36. Found: C, 82.98; H, 5.72; N, 5.16.

4-(1-Phenylethyl)pyridine 1-oxide [bp 175–176° (0.1 Torr), mp 48–49°; ir (KBr), 3040 (w), 1580 (m), 1478 (s), 1245 (s), 1170 (m), 845 (m), 700 cm^{-1} (m); nmr ($CDCl_3$) δ 8.13–8.00 (m, 2, pyr C_2, C_6 H's), 7.50–6.90 (m, 7, pyr C_3, C_5 H's, and C_6H_5), 4.08 (q, 1, J = 7 Hz, $-CH(CH_3)C_6H_5$), 1.55 (d, 3, J = 7 Hz, $-CH_3$)] was prepared in 90% yield.

The *picrate* was prepared in the usual manner and after recrystallization from methanol had mp 93.5–94.5°.

Anal. Calcd for $C_{19}H_{16}N_4O_8$: C, 53.27; H, 3.76; N, 13.08. Found: C, 53.54; H, 3.76; N, 12.97.

4-Isopropylpyridine 1-oxide [mp 78–79°; ir (KBr) 3040 (w), 2980 (m), 1485 (m), 1390 (w), 1255 (s), 1175 (m), 850 (s), 700 cm^{-1} (m); nmr ($CDCl_3$) δ 8.32–8.20 (m, 2, pyr C_2, C_6 H's), 7.37–7.21 (m, 2, pyr C_3, C_5 H's), 2.92 [m, 1, J = 7 Hz, $-CH(CH_3)_3$], 1.25 (d, 6, J = 7 Hz, $-CH(CH_3)_2$)] was formed in 63% yield.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08. Found: C, 69.84; H, 8.04.

4-(2-Phenylethyl)pyridine 1-oxide [mp 120–122°; ir (KBr) 3020 (w), 2920 (w), 2860 (w), 1595 (m), 1465 (s), 1445 (s), 1232 (s), 1170 (s), 820 (s), 750 (s), 700 cm^{-1} (s); nmr ($CDCl_3$), δ 8.20–8.08 (m, 2, pyr C_2, C_6 H's), 7.40–6.96 (m, 7, pyr C_3, C_5 H's and C_6H_5), 2.90 (s, 4, $-CH_2CH_2C_6H_5$)] was obtained in near quantitative yield.

Anal. Calcd for $C_{13}H_{12}NO$: C, 78.36; H, 6.57; N, 7.03. Found: C, 78.49; H, 6.57; N, 6.90.

4-Neopentylpyridine 1-oxide [mp 84–85° (lit.[26] bp 169° (6 Torr), sublimed 97–98°); ir (capillary film) 3140 (w), 3120 (w), 3060–3020 (m), 2960 (s), 2870 (s), 1475 (s), 1362 (m), 1245–1220 (s), 1175 (m), 1040 (m), 875 (m), 850 (m), 820 (m), 790 (m), 748 cm^{-1} (m); nmr ($CDCl_3$) δ 8.20–8.06 (m, 2, pyr, C_2, C_6 H's), 7.09–6.97 (m, 2, pyr C_3, C_5 H's), 2.52 (s, 2, $-CH_2-$), 0.93 (s, 9, $-C(CH_3)_3$); mass spectrum (70 eV) *m/e* (rel intensity) 165 (100), 150 (54), 149 (27), 134 (45), 109 (93), 108 (91), 93 (64), 92 (65), 57 (42)] was prepared in 76% yield from 4-neopentylpyridine (6.0 g, 0.040 mol), 40% peracetic acid (30 ml), and acetic acid (10 ml) using the above general procedure.

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.75; H, 9.08. Found: C, 72.53; H, 8.87.

An alternate method for the preparation of 4-neopentylpyridine 1-oxide, mp 83–84° (67%), entailed the oxidation of 4-neopentylpyridine (12.0 g, 0.08 mol) with *m*-chloroperbenzoic acid (15.0 g, 0.085 mol) in $CHCl_3$ (100 ml) at reflux for 3 hr followed by 12 hr at room temperature. Work-up was according to the above general procedure.

A picrate was obtained in the usual manner: mp 130–132° (recrystallization from CH_3OH); nmr (d_6-DMSO) δ 8.49 (s, 2, picrate anion), 8.14–8.28 (m, 2, pyr C_2, C_6 H's), 7.33–7.05 (m, 2, pyr C_3, C_5 H's), 2.56 (s, 2, $-CH_2-$), 1.00 [s, 9, $C(CH_3)_3$]; mass spectrum (70 eV) *m/e* (rel intensity) 229 (89), 199 (47), 171 (19), 166 (53), 165 (100), 150 (37), 109 (75), 93 (18), 92 (55), 91 (83), 57 (78).

Anal. Calcd for $C_{16}H_{16}N_4O_8$: C, 48.76; H, 4.57; N, 14.22. Found: C, 48.73; H, 4.49; N, 14.09.

1-Phenyl-1-(4-pyridyl)ethyl Acetate. A solution of 1-phenyl-1-(4-pyridyl)ethanol (2.0 g, 0.01 mol) and acetic anhydride (11.0 g, 0.09 mol) was refluxed for 2 hr, and distillation of the reaction mixture gave 1.5 g (71%) of 1-phenyl-1-(4-pyridyl)ethyl acetate: bp 138–139° (0.125 Torr); ir (neat) 1740 cm^{-1} (ester, C=O); nmr ($CDCl_3$) δ 8.40–8.33 (m, 2, pyr C_2, C_6 H's), 7.3–6.9 (m, 7, pyr C_3, C_5 H's, and C_6H_5), 2.11 (s, 3, $-O_2CCH_3$), 2.04 [s, 3, $-C(C_6H_5)(OAc)CH_3$].

Anal. Calcd for $C_{15}H_{16}NO_2$: C, 74.66; H, 6.26; N, 5.80. Found: C, 74.41; H, 6.15; N, 5.83

2-(4-Pyridyl)-2-propyl Acetate. A mixture of 2-(4-pyridyl)-2-propanol (1.0 g, 0.007 mol) and acetic anhydride (7 ml) was refluxed for 3 hr. The reaction mixture was neutralized (aqueous $NaHCO_3$) and was extracted with $CHCl_3$. After the solvent was removed, distillation of the residue gave 1.1 g (80%) of 2-(4-pyridyl)-2-propyl acetate: bp 94° (0.09 Torr); ir (neat) 1730 cm^{-1} (ester, C=O); nmr ($CDCl_3$) δ 8.61–8.50 (m, 2, pyr C_2, C_6 H's), 7.30–7.20 (m, 2, pyr C_3, C_5 H's), 2.55 (s, 3, $-O_2CCH_3$), 1.70 [s, 6, $>C(CH_3)_2$].

1-(4-Pyridyl)-2,2-dimethyl-1-propyl Acetate. A mixture of 1-(4-pyridyl)-2,2-dimethyl-1-propanol (500 mg, 3 mmol) and acetic anhydride (20 ml) was refluxed for 8 hr, cooled, and diluted with H_2O (30 ml). The solution was made basic with $NaHCO_3$ (solid) and extracted with $CHCl_3$. After the extract was dried ($MgSO_4$), the solvent was removed and gave 0.62 g (100%) of 1-(4-pyridyl)-2,2-dimethyl-1-propyl acetate. A sample purified by gas chromatography [⅛ in. × 6 ft copper column packed with 20% Carbowax 20M on Chromosorb WAW HMDS (80–100 mesh), 190°, He flow rate 28.5 cc/min] had the following spectral characteristics: ir (NaCl film) 1738 cm^{-1} (s, C=O); nmr ($CDCl_3$) δ 8.65–8.54 (m, 2, pyr C_2, C_6 H's), 7.25–7.14 (m, 2, pyr C_3, C_5 H's), 5.44 [s, 1, $-CH(O_2CCH_3)-$], 2.12 (s, 3, $-O_2CCH_3$), 0.93 [s, 9, $-C(CH_3)_3$]; mass spectrum (70 eV) *m/e* (rel intensity) 207 (0.9), 165 (2.7), 151 (25), 109 (100), 108 (55), 80 (12), 57 (51).

Diphenyl(4-pyridyl)methyl Pivalate. A mixture of diphenyl(4-pyridyl)methanol (4.0 g, 0.015 mol) and pivalic anhydride (17 g, 0.09 mol) was refluxed for 2 days. After most of the pivalic acid and pivalic anhydride was removed under vacuum, the residue was neutralized (aqueous $NaHCO_3$) and extracted with $CHCl_3$. The solvent was removed and the dark brown residue was chromatographed on alumina. Elution with benzene gave 1.6 g (30%) of diphenyl(4-pyridyl)methyl pivalate: mp 95–96.2° (after sublimation); ir (neat) 1735 cm^{-1} (ester, C=O); nmr ($CDCl_3$) δ 8.62–8.20 (m, 2, pyr C_2, C_6 H's), 7.5–70 (m, 12, pyr C_3, C_5 H's and 2 C_6H_5's), 1.23 [s, 9, $-C(CH_3)_3$].

Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.96; H, 6.71; N, 4.07. Found: C, 79.71; H, 6.49; N, 3.92.

1-Phenyl-1-(4-pyridyl)ethene. The procedure of Villani, King, and Papa[23] was employed to convert 1-phenyl-1-(4-pyridyl)etha-

nol (7.3 g, 0.036 mol) to 3.7 g (56%) of 1-phenyl-1-(4-pyridyl)ethene: bp 103–108° (0.2 Torr) (lit.[23] bp 113–114° (1 Torr); ir (neat) 1593 cm^{-1} (>C=CH_2); nmr ($CDCl_3$) δ 8.63–8.49 (m, 2, pyr C_2, C_6 H's), 7.40–7.08 (m, 7, pyr C_3, C_5 H's and C_6H_5), 5.52 (s, 2, =CH_2).

2-Phenyl-1-(4-pyridyl)ethene. A solution of 4-methylpyridine (50 g, 0.53 mol), benzaldehyde (57 g, 0.54 mol), and acetic anhydride (200 g) was refluxed 10 hr. After the reaction mixture was steam distilled, the residual liquid was cooled and poured into ice-water. The solid precipitate was washed (H_2O), dried, and gave 55 g (57%) of crude product which was recrystallized from methanol–ether to give pure 2-phenyl-1-(4-pyridyl)ethene, mp 129–132° (lit.[27] mp 131°); ir (KBr) 1585 cm^{-1} (-CH=CH-).

Reaction of 4-Alkylpyridine *N*-Oxides with Acid Anhydrides. General Procedure. The apparatus used for these reactions was described previously.[13] The 4-alkylpyridine *N*-oxide, dissolved in the acid anhydride (Table I, entries 2 and 5) or a mixture of acid anhydride and the corresponding acid (Table I, entries 1 and 6), was added to the refluxing anhydride over a period of 10 to 15 min, and the reaction mixture was heated for an additional 2.5 to 3.0 hr. In entries 3, 4, and 7 of Table I, the acid anhydride was added to a refluxing solution of the 4-alkylpyridine *N*-oxides dissolved in the corresponding acid, and the mixture was heated 2.75 hr. The reaction mixture was cooled to room temperature, and the amount of CO_2 collected in the barium hydroxide traps was determined by the volumetric procedure of Nieuwenberg and Hegge.[28] The reaction mixture was distilled under reduced pressure (except entries 6 and 7, Table I, which were steam distilled or entry 5 which was neutralized directly), and the residue was neutralized ($NaHCO_3$) and extracted with $CHCl_3$ (except entry 1 which was chromatographed on alumina without neutralization). The solvent was removed and the residue subjected to analysis by nmr (entry 5), chromatographed on alumina (entries 4, 6 and 7), or distilled *in vacuo* (entries 2, 3, and 8). The distillate was analyzed by nmr or glc and the products were isolated by column chromatography or a second fractional distillation. Identification of the products is described below, and Table I provides a summary of these results.

Identification of Products. 4-(Diphenylmethyl)pyridine *N*-Oxide with Acetic Anhydride. Chromatography of the residue gave, upon elution with ether–benzene (1:2), diphenyl(4-pyridyl)methyl acetate: mp 109–110° (sublimed); ir (KBr) 1740 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 8.35–8.25 (m, 2, pyr C_2, C_6 H's), 7.3–7.0 (m, 12, pyr C_3, C_5 H's, and 2 C_6H_5's), 2.02 (s, 3, CH_3).

Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65; N, 4.64. Found: C, 79.13; H, 5.44; N, 4.48.

Elution with ether–benzene (1:1) provided diphenyl(4-pyridyl)methanol, mp 239.5–241.5° (lit.[27] mp 237–238°). The ir and nmr spectra of the alcohol were identical with those of an authentic sample.

4-(1-Phenylethyl)pyridine *N*-Oxide with Acetic Anhydride. The yield of products was calculated from the nmr spectrum of the distillate, bp 96–120° (0.1 Torr), using the peaks at δ 5.52 (C=CH_2) and 2.11 (CH_3CO_2-). Chromatography provided a pure sample of 1-phenyl-1-(4-pyridyl)ethyl acetate which had ir and nmr spectra identical with those of an authentic sample. 1-Phenyl-1-(4-pyridyl)ethene was not isolated in the pure state but was identified by comparison of the ir and nmr spectra of the distillate with those of the authentic sample. Also the picrate of 1-phenyl-1-(4-pyridyl)ethene, mp 200–202° (authentic sample mp 198–200°), was prepared.

4-Isopropylpyridine *N*-Oxide with Acetic Anhydride. The distillate, bp 50–90° (0.3 Torr), was analyzed by glc[29] and was found to contain 4-isopropylpyridine (retention time 5.5 min), 2-(4-pyridyl)propene (retention time 7.5 min), and 2-(4-pyridyl)-2-propyl acetate (retention time 2.5 min). Peak enhancement without distortion was observed when the distillate was enriched individually with authentic samples of the components. The yield of products was determined from the nmr spectrum of the distillate using the peaks at δ 1.70 [>$C(CH_3)_2$ of the ester] and δ 5.55 and 5.23 (C=CH_2 of the olefin). Fractional distillation of the above distillate gave I, bp 59–66° (0.6 Torr); ir showed mainly 2-(4-pyridyl)propene and II, bp 85–88° (0.3 mm); ir and glc showed mainly 2-(4-pyridyl)-2-propyl acetate.

4-(2-Phenylethyl)pyridine *N*-Oxide with Acetic Anhydride. Chromatography of the residue on alumina gave on elution with benzene 2-phenyl-1-(4-pyridyl)ethyl acetate: bp 142° (0.18 Torr); ir (neat) 1740 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 8.82–8.57 (m, 2, pyr C_2, C_6 H's), 7.5–6.9 (m, 7, pyr C_3, C_5 H's, and C_6H_5), 5.88 [t, 1, J = 7 Hz, -C*H*(OAc)-], 3.06 (d, 2, J = 7 Hz, -CH(OAc)C*H*$_2$-), 2.02 (s, 3, CH_3CO_2-). Elution with benzene–ether (1:1) provided 2-phenyl-1-(4-pyridyl)ethene, mp 128–130° (from ethanol) (authentic sample mp 129–132°); the ir and nmr spectra were identical with those of an authentic sample. Elution with $CHCl_3$ gave 2-phenyl-1-(4-pyridyl)ethanol: mp 144°; ir (KBr) 3150 cm^{-1} (-OH); nmr ($CDCl_3$) δ 8.48–8.32 (m, 2, pyr C_2, C_6 H's), 7.46–7.13 (m, 7, pyr C_3, C_5 H's, and C_6H_5), 4.85 (t, 1, J = 6.5 Hz, -C*H*(OH)CH_2-), 3.60 (s, 1, OH), 2.97 (d, 2, J = 6.5 Hz, -CH(OH)C*H*$_2$-). The picrate of the alcohol was prepared, mp 161–162.5° (lit.[30] mp 162–163°).

4-Neopentylpyridine *N*-Oxide with Acetic Anhydride. After the reaction was processed as described above, the solid which precipitated from the residue was filtered and washed with cold pentane. The crude material (125 mg, mp 150–160°) was recrystallized from ethyl acetate and gave 4-neopentyl-2(1*H*)-pyridone, as a white solid: mp 183–184.5°; ir (KBr) 3105 (w), 2960 (s), 1660 (s), 1525 (m), 1448 (s), 1360 (m), 1245–1238 (m), 997 (s), 930 (m), 910 (m), 866 (m), 810 (s), 780 (m), 748 cm^{-1} (m); nmr ($CDCl_3$) δ 7.30 (d, 1, J = 3.5 Hz, pyr C_6-H), 6.34 (s, 1, pyr C_3-H), 6.11 (d, 1, J = 3.5 Hz, pyr C_5-H), 2.38 (s, 2, -CH_2-), 0.96 [s, 9, $C(CH_3)_3$]; mass spectrum (70 eV) *m/e* (rel intensity) 165 (31), 150 (100), 122 (34), 110 (85), 109 (58), 108 (40) 94 (27), 93 (25), 91 (96), 80 (88).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.74; H, 9.08; N, 8.47. Found: C, 72.76; H, 9.16; N, 8.25.

The pentane was removed from the above filtrate and the residue upon analysis by temperature-programmed glc[31] contained 4-neopentylpyridine (A, R_f = 7.3 min, 4%), 2-(4-pyridyl)-3-methyl-2-butene (B, R_f 7.7 min, 54%), 1-(4-pyridyl)-2,2-dimethyl-1-propyl acetate (C, R_f 11.3 min, 21.5%), 1-(4-pyridyl)-2,2-dimethyl-1-propanol (D, R_f 12.4 min, 9.5%), and an unidentified substance (E, R_f 13.4 min, 3–5%).[32] Compounds A and D were identified as 4-neopentylpyridine and 1-(4-pyridyl)-2,2-dimethyl-1-propanol,[33] respectively, by addition of authentic samples to the product mixture which gave peak enhancement without distortion in glc. In addition, the presence of 4-neopentylpyridine was confirmed by nmr and tlc. Preparative glc gave fraction I (mixture of A and B, predominately B) and fraction II (C contaminated with some B + D). In fraction I, the ratio of A to B was 2:98. The major component was 2-(4-pyridyl)-3-methyl-2-butene: ir (NaCl film) 3070 (m), 3015 (m), 2990 (m), 2920 (s), 2865 (m), 1599 (s), 1539 (m), 1445 (m), 1411 (s), 1375 (m), 1215 (m), 1130 (m), 1060 (m), 990 (m), 820 (s), 750 (m), 690 cm^{-1} (m); nmr ($CDCl_3$) δ 8.83–8.0 (broad s, 2, pyr C_2, C_6 H's), 7.1–6.9 (broad s, 2, pyr C_3, C_5 H's), 1.94 (s, 3, CH_3C=$C(CH_3)$-CH_3), 1.80 (s, 3, CH_3C=$C(CH_3)$-CH_3), 1.60 (s, 3, CH_3C=$C(CH_3)CH_3$).

The picrate of 2-(4-pyridyl)-3-methyl-2-butene was prepared from fraction I, and fractional crystallization from methanol gave fine yellow needles: mp 165.5–166.5°; nmr (d_6-DMSO) δ 12.45–11.80 (broad s, 1, $\equiv N^+H$), 8.95–8.74 (m, 2, pyr C_2, C_6 H's), 8.59 [s, 2, $C_6H_2(NO_2)_3O^-$], 7.90–7.80 (m, 2, pyr C_3, C_5 H's), 2.04–1.98 (m, 3, -CH_3C=$C(CH_3)CH_3$), 1.87 (s, 3, -$(CH_3)C$=$C(CH_3)CH_3$), 1.70–1.65 (m, 3, -$(CH_3)C$=$C(CH_3)CH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 229 (97), 199 (16), 171 (6), 148 (18), 147 (100), 146 (29), 132 (59), 105 (58), 91 (53), 78 (26), 77 (37), 62 (49).

Anal. Calcd for $C_{16}H_{16}N_4O_7$: C, 51.09; H, 4.25. Found: C, 51.11; H, 4.09.

Sublimation [*ca.* 60° (0.05 Torr)] of fraction II gave 1-(4-pyridyl)-2,2-dimethyl-1-propyl acetate, mp 80–81.5°, which had ir, nmr, and mass spectra identical with those of an authentic sample.

4-(Diphenylmethyl)pyridine *N*-Oxide with Pivalic Anhydride. The residue was chromatographed, and elution with petroleum ether (30–60°)–benzene (1:6) gave 4-(diphenylmethyl)pyridine which had ir and nmr spectra identical with those of an authentic sample. The second fraction eluted with benzene–ether (8:1) was diphenyl-4-pyridylmethyl pivalate which had ir and nmr spectra identical with those of an authentic sample. Further elution with benzene–ether (1:1) gave diphenyl-4-pyridylmethanol, mp 233–238°.

4-(1-Phenylethyl)pyridine *N*-Oxide with Pivalic Anhydride. The initial distillate, bp 100–135° (0.25 Torr), was used to determine the yields of products from the nmr spectrum by employing δ 4.13

(quartet) [-C*H*(CH_3)C_6H_5], 5.61 (s) [-(C_6H_5)C=C*H*$_2$], 2.15 (s) [-C(C*H*$_3$)(C_6H_5)-O-C(=O)C(CH_3)$_3$]. A second distillation gave fraction I, bp 100–126° (0.3 Torr), which contained a mixture of 4-(1-phenylethyl)pyridine and 1-phenyl-1-(4-pyridyl)ethene (identified by comparison of ir and nmr spectra and tlc with those of an authentic sample) and fraction II, bp 126–142° (0.3 Torr), which was mainly 1-phenyl-1-(4-pyridyl)ethyl pivalate: ir (neat) 3040 (m), 2970 (s), 1735 (s) (>C=O), 1595 (s), 1480 (m), 1410 (m), 1365 (m), 1280 (m), 1150 (s), 1110 (m), 1055 (m), 820, 805 (m), 760 (m), 700 cm^{-1} (s); nmr ($CDCl_3$) δ 8.73–8.50 (m, 2, pyr C_2, C_6 H's), 7.45–7.28 (m, 7, pyr C_3, C_5 H's, and C_6H_5), 2.18 [s, 3, -C(C*H*$_3$)(C_6H_5)OC(=O)C(CH_3)$_3$], 1.29 [s, 9, -C(CH_3)(C_6H_5)OC(=O)C(C*H*$_3$)$_3$].

Hydrolysis of Esters Obtained from the Reaction of 4-Alkylpyridine *N*-Oxides with Acid Anhydrides. General Procedure. A mixture of the ester, obtained from the reaction of 4-alkylpyridine *N*-oxide with acid anhydride, and sodium hydroxide in methanol was kept at room temperature for 3 hr. The resulting solid was filtered, washed (H_2O), and dried. Identification involved comparison of the ir and/or nmr spectra of the alcohols with those of authentic samples.

Diphenyl-4-pyridylmethyl acetate was saponified to diphenyl(4-pyridyl)methanol, mp 239.5–241.5° (lit.[22] mp 237–238°), in near quantitative yield.

1-Phenyl-1-(4-pyridyl)ethyl acetate produced 35% of 1-phenyl-1-(4-pyridyl)ethanol, mp 141–144° (lit.[23] mp 146–147°), on hydrolysis.

2-(4-Pyridyl)-2-propyl acetate gave upon hydrolysis 80% of 2-(4-pyridyl)-2-propanol, mp 130–137° (lit.[22] mp 135–135.4°).

2-Phenyl-1-(4-pyridyl)ethyl acetate was saponified in 30% yield to 2-phenyl-1-(4-pyridyl)ethanol, mp 146–147.5° (from ethyl acetate).

Anal. Calcd for $C_{12}H_{13}NO$: C, 78.36; H, 6.59; N, 7.03. Found: C, 78.51; H, 6.38; N, 6.94.

The picrate of 2-phenyl-1-(4-pyridyl)ethanol was prepared and recrystallized from methanol to give mp 161–162.5° (lit.[30] mp 162–163°).

Diphenyl(4-pyridyl)methyl pivalate and sodium hydroxide in methanol were refluxed 3 hr. The reaction mixture was cooled, and the solid that precipitated was filtered, washed (H_2O), and dried. Recrystallization from benzene gave diphenyl(4-pyridyl)methanol, mp 232–235°.

1-Phenyl-1-(4-pyridyl)ethyl pivalate and sodium hydroxide in methanol were refluxed overnight and upon work-up gave 85% yield of 1-phenyl-1-(4-pyridyl)ethanol, mp 135–140°.

Control Experiments. In the reaction where both ester and olefins were formed, each product was individually subjected to the reaction conditions. A mixture containing the ester or olefin (0.2–0.24 g), acetic anhydride (2.5–5 ml), and acetic acid (2.5–5 ml) was refluxed for 2.5 hr. For each experiment with 1-phenyl-1-(4-pyridyl)ethyl acetate and 1-phenyl-1-(4-pyridyl)ethene, the ir and nmr spectra of the refluxed solution were identical with those taken before reflux. In the experiments with 2-(4-pyridyl)-2-propyl acetate and 2-(4-pyridyl)propene, the refluxed solutions were analyzed by glc and showed only a simple peak corresponding to the starting ester or olefin, respectively.

After the solution of 2-phenyl-1-(4-pyridyl)ethyl acetate (1.6 g), acetic anhydride (6 ml), and acetic acid (4 ml) was refluxed 3 hr, the nmr spectrum of the solution was unchanged from that before reflux, and unchanged ester was recovered in 81% yield.

A mixture of 1-(4-pyridyl)-2,2-dimethyl-1-propyl acetate (43 mg) and acetic anhydride (5 ml) was refluxed for 4.5 hr, and analysis by glc showed only acetic anhydride and the starting ester. Work-up of the reaction mixture led to 42 mg (96%) of unchanged starting ester.

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(3) Grateful acknowledgment is made to the National Science Foundation for a research grant (NSF GP-3858) in partial support of this work.
(4) Abstracted from a portion of the Ph.D. Dissertation submitted by K.Y. in Aug 1969 and by J.P.K. in May 1972 at West Virginia University.
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(29) The glc analysis was performed with a Perkin-Elmer Model 154 chromatograph on a 0.25 in. × 6 ft copper column packed with 2.5% NaOH, 25% Carbowax on Chromsorb (45–60) at 222°, and a He flow rate of 30 cc/min.
(30) T. Suzuki, *Pharm. Bull.*, **4**, 211 (1956).
(31) The glc analysis was performed with a Victoreen Model 400 gas chromatograph on a ⅜ in. × 10 ft copper column packed with 4% KOH, 15% Apiezon L on Chromosorb W (45–60 mesh) with oven temperature programmed from 120 to 210° at a rate of 12°/min, and a He flow rate of *ca.* 30 cc/min.
(32) Yields were based on relative integration areas for the various peaks assuming a linear detector response and response ratios approximating unity for this series of 4-substituted pyridines.
(33) The alcohol could not be detected in the reaction mixture by both nmr and tlc analysis. An independent experiment confirmed that the alcohol was formed during glc analysis of the ester under the same column conditions.