3,5-Di-*t*-butyl-3′,5′-dimethyl-4,4′-dihydroxydiphenylmethane (IX). 2,6-Di-*t*-butylphenol (16.5 g) and 2,6-dimethyl-4-hydroxymethylphenol (12.2 g) were dissolved under an atmosphere of nitrogen in 120 ml of methanol containing 9.4 g of KOH. After refluxing under nitrogen for 4 hr, the mixture was cooled and neutralized with dilute HCl. The solution was filtered to remove solid KCl, and the methanol was distilled off under reduced pressure. The oily residue was taken up in ethyl ether, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the ether left 27.7 g of a brownish oil, which was distilled *in vacuo* (0.4 mm). The fraction distilling between 168 and 178° was obtained as a yellow glassy solid; yield 8.0 g. The product was purified by fractional crystallization from ligroin (bp 66–75°). A small amount of the symmetrical diphenylmethane derivative XI crystallized in the first fractions and was filtered off. Continued cooling of the ligroin caused crystallization of the desired product. After several recrystallizations from ligroin, 3.0 g of a white, crystalline solid was obtained which melted at 103° (*Anal.* Calcd for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47. Found: C, 80.70; H, 9.40); ir: hydroxyl bands were found at 3660 (hindered OH) and 3635 cm^{-1}; nmr: τ values ($CDCl_3$): 2.93 (singlet, 2 aromatic H), 3.12 (singlet, 2 aromatic H), 4.92 (singlet, 1 hydroxyl H), 5.46 (singlet, 1 hydroxyl H), 6.2 (singlet, 2 methylene H), 7.78 (singlet, 6 methyl H), and 8.55 (singlet, 18 *t*-butyl H).

3,3′-Di-*t*-butyl-5,5′-dimethyl-4,4′-dihydroxydiphenylmethane (X) was prepared according to the procedure used by Kharasch and Joshi[3] to prepare the diphenylmethane precursor of galvinoxyl. It was identical with the compound prepared previously by Besev, *et al.*[5]

3,3′,5,5′-Tetramethyl-4,4′-dihydroxydiphenylmethane (XI). 2,6-Dimethylphenol (122.1 g) was dissolved in aqueous NaOH (50 g of NaOH and 1000 ml of water) and a 37% formaldehyde solution (178.4 g) added with stirring. After allowing the solution to stand 3 days, it was neutralized with dilute acetic acid and cooled in an ice bath. The crystalline material which separated was filtered and washed with cold water. The product was recrystallized from aqueous ethanol solution (30% ethanol) to yield 44.7 g of a white solid, which on further recrystallization from benzene gave 34.5 g of white needles, melting at 174–176°; ir: the hydroxyl band was found at 3510 cm^{-1} in acetonitrile solution; nmr: τ values ($CDCl_3$): 3.12 (singlet, 4 aromatic H), 5.48 (singlet, 2 hydroxyl H), 6.22 (singlet, 2 methylene H), and 7.72 (singlet, 12 methyl H).

The 30% ethanol solution from the above was extracted with ethyl ether, washed with water, and dried over anhydrous sodium sulfate. Removal of the ether left 77.6 g of a reddish solid, which melted at 97–101°. Recrystallization from benzene gave 66 g of white crystalline needles, with melting point 102.5–104°. The compound was identified as 2,6-dimethyl-4-hydroxymethylphenol.

Active PbO_2.[25] Lead tetraacetate (25 g) was stirred with 200 ml of distilled water until all was converted to brown PbO_2 (about 1 hr). The mixture was centrifuged and washed with 230-ml portions of distilled water each time, until the PbO_2 suspension was neutral to litmus. The precipitate was suspended in 25 ml of water and 13 ml of acetone added; the mixture was centrifuged. Finally, the solid was stirred four times with ethyl ether and the ether decanted. Solvent was removed in a vacuum desiccator and the PbO_2 kept overnight in the desiccator. It was finally ground in an agate mortar; yield 13.2 g.

Acknowledgments. We are indebted to Professor N. Bhacca for some of the nmr measurements. This work was supported in part by a grant from the U. S. Forest Service to C. S.

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The Thermal Rearrangements of 2-Alkenyloxypyridine 1-Oxides[1a]

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Abstract: The thermal rearrangement of 2-alkenyloxypyridine 1-oxides has been shown to give two distinct products. At lower temperatures the product is the 1-alkenyloxy-2-pyridone which forms without a 1,3-allylic bond shift. At higher temperatures an *ortho*-Claisen rearrangement occurs to give the 3-alkenyl-1-hydroxy-2-pyridone as the major product.

Dinan and Tieckelmann showed the thermal rearrangement of 2-alkoxypyridine 1-oxides was facile and gave the 1-alkoxy-2-pyridone in essentially quantitative yield.[2] Allyl and benzyl ethers rearranged at lower temperatures than did the methyl or ethyl compounds. Since added *p*-benzoquinone did not affect the rate of rearrangement, the reactions were assumed to occur *via* an inter- or intramolecular displacement or through ion pairs.

The ease with which the 2-allyloxy- and 2-benzyloxypyridine 1-oxides rearrange parallels the behavior noted by Meisenheimer[3] and subsequent investigators[4] in the rearrangement of tertiary amine oxides. Because the rearrangment of N-crotyl-N-methylaniline 1-oxide in dilute base gave N-methyl-N-α-methylallyloxyaniline, the reactions were assumed to proceed *via* an intramolecular five-membered transition state similar to that of the Claisen rearrangement.[4]

The 2-alkenyloxypyridine 1-oxide system has different geometrical requirements from the nonaromatic tertiary amine oxides studied by Meisenheimer.[3] In order for a 1,3-allylic bond shift to occur, the rearrangement would have to involve a seven-membered transition state. A recent review[5] suggests such a mechanism. This rationalization cannot be invoked as it was implied simply on the grounds that 2-allyloxypyridine 1-oxide rearranged readily at ambient temperatures. In fact, Dinan and Tieckelmann[2] did not propose this mechanism or that the rearrangement was similar to the *ortho*-Claisen rearrangement. In order to elucidate the reaction, we have extended the investigation to other 2-alkenyloxypyridine 1-oxides.

(1) (a) This investigation was supported by Public Health Service Research Grant No. CA-02857 from the National Cancer Institute. (b) Allied Chemical Corporation Fellow, 1966–1967.

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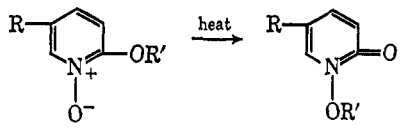
Table I. Products of Rearrangement



1-Oxide R = H	1-Oxide R′	Temp, °C	Solvent	2-Pyridone R = H	2-Pyridone R′	% (vpc)
I	$CH_2CH{=}CH_2$	83–84	Diglyme	X	$CH_2CH{=}CH_2$	100
II	$CH_2CH{=}CHCH_3$	83–84	Diglyme	XI	$CH_2CH{=}CHCH_3$	98
				XII	$CHCH{=}CH_2$ | CH_3	2
III[a]	$CHCH{=}CH_2$ | CH_3	Room	Neat	XII	$CHCH{=}CH_2$ | CH_3	80
				XI	$CH_2CH{=}CHCH_3$	10
IV	$CHCH{=}CHCH_3$ | D	83–84	Diglyme	XIII	$CHCH{=}CHCH_3$ | D	100
V	CH_2–◁	126–127	Diglyme	XIV	CH_2–◁	96
				XV	◁□	4[b]
VI	$CHCH{=}CHCH_3$ | CH_3	83–84	Diglyme	XVI	$CHCH{=}CHCH_3$ | CH_3	100
R = CH_3	**R′**			**R = CH_3**	**R′**	
VII	$CH_2CH{=}CH_2$	83–84	Diglyme	XVII	$CH_2CH{=}CH_2$	100
VIII	$CH_2CH{=}CHCH_3$	83–84	Diglyme	XVIII	$CH_2CH{=}CHCH_3$	100
IX	$CHCH{=}CH_2$ | CH_3	Room	Neat	XIX	$CHCH{=}CH_2$ | CH_3	92[b]
		83–84	Diglyme	XIX	$CHCH{=}CH_2$ | CH_3	30

[a] Approximately 90% pure compound. [b] Based on nmr integration.

Results and Discussion

The pyridine 1-oxides were prepared from the appropriate sodium alcoholates and 2-chloro- or 2-chloro-5-methylpyridine 1-oxide.[6] All exhibit the typical 1-oxide absorbances at 249–250 mμ in the ultraviolet,[6,7] and between 7.6 and 8.2 μ in the infrared.[8] They are hygroscopic solids or liquids and rearrange slowly at room temperatures to the 1-alkenyloxy-2-pyridones.

The nmr data (Experimental Section) indicate that the crotyl and α-methylallyl 1-oxides are readily distinguished by the position of the doublet due to the methyl groups and by the coupling constants. The γ-methyl resonance appears near 1.7 ppm (J = 4.5 cps) and the α-methyl signal is near 1.60 ppm (J = 6.2 cps). Similar behavior has been noted for thiolcarbonates[9] and for 1- or 3-substituted pyridones.[10] On this basis the two methyl signals in the pentenyl ether VI at 1.69 (J = 5.5 cps) and 1.58 ppm (J = 6.0 cps) may be assigned to the γ- and α-methyl groups, respectively. The signal farthest downfield was assigned to the proton in the 6 position because it is adjacent to the strongly deshielding 1-oxide group.[11] In general the methylene signals were sharp doublets with little fine splitting.

The compounds were rearranged in diglyme solutions of approximately 0.2 M concentration. The sealed tubes were heated in stirred oil baths, and the reactions were judged complete when the 1-oxide absorbance near 250 mμ had disappeared.[6,7] The products were isolated by vapor phase chromatography (vpc) and identified by infrared, ultraviolet, and nmr spectroscopy. The 1-alkenyloxy-2-pyridones and the 1-alkenyloxy-5-methyl-2-pyridones exhibit strong carbonyl absorption near 6 μ in the infrared[2] and maxima near 225 and 300 mμ in the ultraviolet region.[7,12] The rearrangements are summarized in Table I.

Because the products of rearrangement are structural isomers, their identification is based upon nmr (Experimental Section). The data again clearly distinguish between the γ-methylallyl and α-methylallyl compounds. The coupling constant and the position of the resonance signal due to the γ-methyl group remain essentially constant in the reactant and product, *i.e.*, 4.5 cps and near 1.7 ppm.

Partially resolved 3-penten-2-ol ($[\alpha]^{25}D$ −7.3°) was used to prepare optically active 2-α,γ-dimethylallyloxypyridine 1-oxide (VI, $[\alpha]^{28}_{340}$ +35.0°).[13] Rearrangement at 83–84° in refluxing carbon tetrachloride gave the pyridone XVI which was optically active, $[\alpha]^{28}_{340}$

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(13) We thank Mr. Charles Suchma for supplying the optically active alcohol and for the optical measurements.

−169°. The stereochemistry of this rearrangement has not yet been elucidated. No change in mechanism occurs in this solvent since the deuterated compound IV rearranged in carbon tetrachloride to the same pyridone XIII as was formed in the diglyme rearrangement.

2-Crotoxypyridine 1-oxide (II) gave 1-crotoxy-2-pyridone (XII) as the major product (Table I); similarly 2-α-methylallyloxypyridine 1-oxide (III) gave 1-α-methylallyloxy-2-pyridone (XI) as the major product. Furthermore, 2-(crotoxy-1-*d*)pyridine 1-oxide (IV) gave only 1-(crotoxy-1-*d*)-2-pyridone indicating that the carbon attached to oxygen was the same in both the starting material and the product. This demonstrates that the reaction proceeds without a 1,3-allylic bond shift. Therefore, a cyclic seven-membered transition state is not involved as has been suggested recently.[5]

Since the rearrangement of 2-crotoxypyridine 1-oxide (II) gave only a small amount of 1-α-methylallyloxy-2-pyridone (XII) and 2-α-methylallyloxypyridine 1-oxide (III) gave only a small amount of 1-crotoxy-2-pyridone (XI), these two rearrangements do not proceed through a common intermediate. The presence of these products does suggest, however, that there is some ionic character in the transition state. This rationalization is supported by the observation that 20% crossover product, 1-allyloxy-2-pyridone (X), is formed in the diglyme rearrangement of a mixture of II and VII at 83°. Rearrangement of 2-cyclopropylcarbinyloxypyridine 1-oxide (V) gave about 4% 1-cyclobutyloxy-2-pyridone (XV).

It has been shown[14] that cyclobutyl compounds are characteristic products from carbonium ions but not from carbanions[15] or radicals.[16] In addition, both 2-α-methylallyloxypyridine 1-oxide (III) and 2-α-methylallyloxy-5-methylpyridine 1-oxide (IX) exhibit a large rate enhancement in comparison to the other 2-alkenyloxypyridine 1-oxides. In fact, III could not be purified because it rearranged rapidly at room temperature. This increased reactivity is consistent with an ion-pair process. The rearrangement of VI to optically active XVI shows that the two ionic moieties are not well separated in the transition state.

The observation that only 30% of the product in the rearrangement of 2-α-methylallyloxy-5-methylpyridine 1-oxide (IX) was the expected 1-α-methylallyloxy-5-methyl-2-pyridone (XIX) led us to suspect the occurrence of another reaction. Further investigation of the rearrangement showed 60% was *cis*- and *trans*-3-crotyl-5-methyl-1-hydroxy-2-pyridones (XX) arising from rearrangement to the ring carbon.

Since rearrangement to carbon had not been observed in any other reactions at 83° the generality of this reaction was investigated by using higher rearrangement temperatures. Heating 2-allyloxypyridine 1-oxide (I) in diglyme at 125° produced 50% 3-allyl-1-hydroxy-2-pyridone (XXI) and 43% 1-allyloxy-2-pyridone (X); at 137° the respective amounts were 55 and 39%. In addition, 40% 3-α-methylallyl-1-hydroxy-2-pyridone (XXII) was detected in a cursory nmr investigation of the diglyme rearrangement of 2-crotoxypyridine 1-oxide (II) at 137°.

Compounds XX and XXI are solids with ultraviolet maxima near 200, 230, and 300 mμ. Absorbance at these maxima corresponds with that reported for other 1-hydroxy-2-pyridones.[12] In the infrared they exhibit broad CH and OH bands between 3.0 and 4.0 μ; the carbonyl absorbs near 6.1 μ. The molecular weights of XX and XXI were determined by mass spectroscopy.[17] Molecular ion peaks corresponding to loss of O or OH were also noted, indicating some tautomerization between the 1-hydroxy-2-pyridone and 2-hydroxypyridine 1-oxide systems under the conditions of analysis. In addition, elemental analysis has confirmed the assignment of XX as 3-crotyl-5-methyl-1-hydroxy-2-pyridone.

To establish the origin of the 3-alkenyl-1-hydroxy-2-pyridone, pure 1-α-methylallyloxy-5-methyl-2-pyridone (XIX) was dissolved in diglyme and heated in a sealed tube for 20 hr at 83–84°. Examination of this material by vpc and infrared and nmr spectroscopy showed that decomposition but no rearrangement had occurred. Similar treatment of a neat sample of 1-allyloxy-2-pyridone (X) at 120–130° led only to decomposition; the addition of a small amount of trifluoroacetic acid did not promote a reaction. In order to test the possibility that further rearrangement of the 1-alkenyloxy-2-pyridones might occur under reaction conditions, a mixture of equal amounts of 2-α-methylallyloxy-5-methylpyridine 1-oxide (VIII) and 1-α-methylallyloxy-2-pyridone (XII) was heated in diglyme at 134–135° for 4 hr. Comparison of the nmr of the initial and final mixtures showed no decrease of the signal at 1.43 ppm for the pyridone XII and no increase above that expected in the amount of product from the rearrangement to the 3 position for the γ-methyl at 1.65 ppm. It was concluded that the 3-alkenyl-1-hydroxy-2-pyridones are formed directly from the 1-oxides.

The strong temperature dependence of the reaction was shown by the experiments given in Table II. The energy of activation for the formation of XIX and XX was determined from the product composition by assuming both processes were first order. They are 14.2 and 17.8 kcal/mol, respectively. The entropies of activation were calculated to be −41.4 and −30.0 eu, respectively. The rearrangement to the ring carbon to yield XX is a more energy-demanding but less ordered process; therefore, it can compete favorably with the other rearrangement at high temperature.

Not only is it noteworthy that a Claisen rearrangement occurs in the presence of the 1-oxide function, but also it is significant that the rearrangement occurs at relatively low temperatures (83–137°). In order for the parent pyridyl ethers to undergo a Claisen rearrangement in dimethylaniline, it is necessary to heat them at 245–255°.[10]

Holton[18] found that when two dissimilar *ortho* positions exist in allyl phenyl ethers, rearrangement to the position of highest electron density will occur. Work in this laboratory on the Claisen rearrangement in pyridines,[10] pyrimidines,[19] and isoquinolines[20] in-

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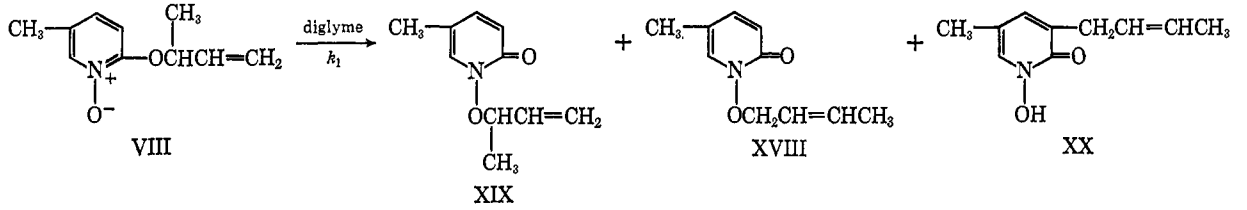
(16) E. Renk, P. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *ibid*, 83, 1987 (1961).
(17) Mass spectral analyses were performed by the Morgan Schaffer Corp., Montreal, Canada.
(18) P. G. Holton, *J. Org. Chem.*, 27, 357 (1962).

Table II. Rates of Reaction and Product Variation with Temperature



VIII XIX XVIII XX

Temp, °C	10^4k_1, sec^{-1}	% XIX	% XVIII	% XX
83	1.2	32	8	59
108	6.8	22	6	71
137	25	20	5	75

dicates that the rearrangement terminus in the heterocyclic ring system is not necessarily the atom which has the higher electron density. Although the 3 position in the pyridine ring is the least affected by the presence of the 1-oxide function,[11,21] here it is the terminus in a relatively facile rearrangement.

Experimental Section

2-Chloropyridine 1-Oxide (XXIII). Material of high purity was obtained without recrystallization by a combination of literature methods.[7b,22] The yield of white needles was 60–70%, mp 69–71° (evacuated capillary) (lit.[7b] 67.0–68.5°).

2-Chloro-5-methylpyridine (XXIV) was recently prepared in 28% yield.[23] We have prepared it by a simplified procedure in better yields.[24]

To a solution of 18.0 g (0.166 mol) of 2-amino-5-methylpyridine in 325 ml of concentrated hydrochloric acid, 18.0 g (0.270 mol) of solid sodium nitrite was added slowly with stirring. The temperature was maintained at 0–10° during the addition. The stirred solution was allowed to come to room temperature and stirring was continued for 1.5 hr before it was recooled and made strongly basic with 40% sodium hydroxide. The resultant water and oil were multiply extracted with a total of 400 ml of chloroform. After drying, the filtered solution was evaporated and vacuum distilled to give a clear oil plus 0.58 g of unreacted starting material. The yield (cor) was 11.4 g (0.089 mol), bp 48–49° (1.9–2.0 mm). Consistent yields of 50–55% were obtained by this method; uv_{max} (C_2H_5OH) 214 (8300), sh 264 (3100), 271 (3500), and sh 278 mμ (ε 3000).

Anal. Calcd for C_6H_6ClN: C, 56.47; H, 4.74; Cl, 27.82. Found: C, 56.39; H, 4.69; Cl, 27.85.

2-Chloro-5-methylpyridine 1-Oxide (XXV). The hydrochloride has been reported.[25] The free 1-oxide was prepared by the procedure used for XXIII in 50–88% yield, mp 70–72° (evacuated capillary); uv_{max} (H_2O) 218 (ε 38,600), 257 (10,200), and sh 287 mμ; ir (Nujol mull) strong 1-oxide bands[8] at 7.81–7.91 μ; nmr[26] singlet at 2.32 (relative area 3.0), multiplet at 7.08 (0.98), 7.43 (0.98), and 8.20 ppm (0.96).

Anal. Calcd for C_6H_6ClNO: C, 50.18; H, 4.21; Cl, 24.69. Found: C, 50.24, 50.22; H, 4.12, 4.31; Cl, 24.48, 24.73.

2-Crotoxypyridine 1-Oxide (II). 2-Chloropyridine 1-oxide (XXIII, 9.05 g, 0.070 mol) in 30 ml of crotyl alcohol was added dropwise to a stirred mixture of 1.72 g (0.075 g-atom) of sodium in 45 ml of crotyl alcohol at a bath temperature of 41–45°. The reaction was complete after 1 hr at 45°. Excess crotyl alcohol was removed by vacuum distillation (bp 29–30° (6.7 mm)). The residue was mixed with chloroform and filtered. The chloroform was flash evaporated at a temperature which did not exceed 30°. The yield of crude orange residue was 11.19 g (96.9%), mp 82.0–84.5° (evacuated capillary). It was stored in a freezer and crystallized as needed from dry ethyl acetate and hexane (2.7:1 by volume) at a temperature not exceeding 65°; uv_{max} (H_2O) 216 (27,600), 249 (8400), and 294 mμ (ε 4700); ir ($CHCl_3$, 1.30% by weight) strong 1-oxide bands[8] at 7.9–8.4 and double bond at 10.3 μ;[27] nmr γ-CH_3 1.74, doublet, J = 4.5 cps (relative area 3.0); CH_2 4.82, doublet, J = 4.5 cps (2.0); CH=CH 5.88 multiplet (1.94); $H_{3,4,5}$ 7.09, multiplet (3.35); H_6 8.28 ppm (1.1).

Anal.[28] Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.38, 65.20; H, 6.84, 6.62; N, 8.30, 8.55.

2-α-Methylallyloxypyridine 1-oxide (III) was prepared by the procedure used for II. The product was highly hygroscopic and in an impure state rearranged readily at room temperature. It could not be purified by recrystallization, column chromatography, or thin layer chromatography. Relatively pure samples, based on nmr and ir analyses were allowed to rearrange at room temperature and the products isolated and identified; nmr α-CH_3 1.60, doublet, J = 6.2 cps (relative area 3.0); CH 6.00, multiplet (1.0); CH=CH_2 5.28, multiplet (3.1); $H_{3,4,5}$ 7.08 (3.4); H_6 8.28 ppm (1.0).

2-α-Methylallyloxy-5-methylpyridine 1-Oxide (IX). Sodium hydride (1.42 g, 0.059 mol) was covered with 20 ml of tetrahydrofuran and the mixture heated to 40°. A solution of 4.23 g (0.059 mol) of 3-buten-2-ol in 20 ml of tetrahydrofuran was added dropwise and the reaction refluxed until all of the sodium hydride had reacted. The solution was cooled to 40°, and 7.56 g (0.053 mol) of 2-chloro-5-methylpyridine 1-oxide (XXV) in 20 ml of tetrahydrofuran was added slowly to maintain the 40° external temperature. The addition was completed in 10 min and the reaction kept at 40° for 2 hr. The reaction was cooled in ice and extracted with 200 ml of tetrahydrofuran. The filtrate was flash evaporated and the residue extracted with anhydrous ether. After filtering, the ether was flashed off to give the crude product as a brown oil containing some solid. An infrared spectrum showed it to be essentially all 1-oxide. The yield, 4.80 g, was 50% of the theoretical.

Chloroform was used to dissolve 2.3 g of the crude product, and 10 g of neutral Woelm alumina was coated by flash evaporation of the solvent. The "column" was then eluted with chloroform. Evaporation of the solvent gave 1.73 g of a pale yellow oil containing some solid. This was shown by nmr, ir, and uv spectroscopy to be free of unreacted starting material and polymer; uv_{max} (H_2O) 217 (22,800), 250 (6300), and 300 mμ (ε 3800); ir (neat) strong 1-oxide[8] at 7.76–7.95 and vinyl bands[29] at 10.75–11.1 μ; nmr 5-CH_3 2.23, singlet (relative area 3.0); α-CH_3 1.52, doublet, J = 6.2 cps (3.0); CH 5.99, multiplet (0.97); CH=CH_2 5.30, multiplet (3.0); $H_{3,4}$ 7.05, multiplet (2.1); H_6 8.09 ppm, broad multiplet (1.0).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 65.02; H, 7.31; N, 7.82. Found: C, 66.63, 66.40; H, 7.45, 7.35; N, 7.98, 7.75.

The following 1-oxides were similarly prepared.

(19) F. J. Dinan, H. J. Minnemeyer, and H. Tieckelmann, *J. Org. Chem.*, **28**, 1015 (1963); H. J. Minnemeyer, P. B. Clarke, and H. Tieckelmann, *ibid.*, **31**, 406 (1966).

(20) H. Win and H. Tieckelmann, *ibid.*, **32**, 59 (1967).

(21) G. Illuminati, *Advan. Heterocyclic Chem.*, **3**, 324 (1964).

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(23) C. L. Bell, R. S. Egan, and L. Bauer, *J. Heterocycl. Chem.*, 2, 420 (1965).

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(25) E. V. Brown, *J. Amer. Chem. Soc.*, **79**, 3565 (1957).

(26) The spectra were obtained on a Varian A-60 instrument except for compounds XIII, XX, and XXI where an HA-60 instrument was used. Unless noted deuteriochloroform was the solvent and tetramethylsilane was the internal standard.

(27) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 45.

(28) All of the allylic 1-oxides were difficult to analyze because they rearrange and decompose during shipment. All were freshly purified and put into sealed tubes under nitrogen, packed in Dry Ice, and flown to Galbraith Laboratories, Knoxville, Tenn., for immediate analysis.

(29) Reference 28, p 49.

2-α,γ-Dimethylallyloxypyridine 1-Oxide (VI). Recrystallization from ethyl acetate and heptane gave VI in 21.5% yield, mp 49.5–51.5° (evacuated capillary); uv_{max} (H_2O) 223 (6500) and 298 mμ (ε 4800); ir (Nujol mull) strong 1-oxide[8] at 7.6–8.1 and double bond[27] at 10.1 μ; nmr α-CH_3 1.58, doublet J = 6.0 cps (relative area 3.0); γ-CH_3 1.69, doublet, J = 5.5 cps (3.0); CH 5.23, multiplet (1.0); CH=CH 5.73, multiplet (2.0); $H_{3,4,5}$ 7.15, multiplet (3.1); H_6 8.25 ppm, multiplet (1.0).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.68, 66.77; H, 7.25, 7.28; N, 7.70, 7.96.

2-Crotoxy-5-methylpyridine 1-Oxide (VIII). Recrystallization from ethyl acetate and heptane gave VIII in 34% yield, mp 89–92° (evacuated capillary); uv_{max} (H_2O) 216 (29,900), 249 (7900), and 300 mμ (ε 4700); ir (Nujol mull) strong 1-oxide[8] at 7.6–8.0 and double bond[27] at 10.1 μ; nmr 5-CH_3 2.25, singlet (relative area 3.0); γ-CH_3 1.73, doublet, J = 4.5 cps (2.8); CH_2 4.80, doublet, J = 4.5 cps (1.9); CH=CH 5.86, multiplet (1.8); $H_{3,4}$ 7.02, multiplet (2.1); H_6 8.10 ppm, broad multiplet (1.2).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.25, 66.98; H, 7.32, 7.38; N, 7.90, 7.66.

2-Allyloxypyridine 1-Oxide (I). Preparation by the above method gave the pale yellow oil in 77% yield (lit.[2] 46%); nmr CH_2 4.80, doublet, J = 5.0 cps (relative area 1.9); CH= 5.97, multiplet (1.0); CH_2= 5.30 (2.0); $H_{3,4,5}$ 7.20, multiplet (3.0); H_6 8.10 ppm, multiplet (1.0).

2-Allyloxy-5-methylpyridine 1-Oxide (VII). Chromatography performed as for IX gave 31% of the pure liquid; uv_{max} (H_2O) 217 (27,300), 249 (7600), and 300 mμ (ε 4300); ir (neat) strong 1-oxide[8] at 7.6–8.0 and a vinyl band[29] at 10.4–10.9 μ; nmr 5-CH_3 2.25, singlet (relative area 3.0); CH_2 4.88, doublet, J = 5.0 cps (2.0); CH= 6.10, multiplet (0.93); CH_2= 5.40, multiplet (2.0); $H_{3,4}$ 7.01, multiplet (2.1); H_6 8.08 ppm, broad multiplet (1.0).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 64.27, 64.50; H, 7.15, 7.30; N, 8.11, 8.15.

Crotyl Alcohol-1-*d* (XXVI). This was prepared according to the literature[30] from crotonaldehyde and lithium aluminum deuteride. The index of refraction was $n^{25.5}D$ 1.4241, bp 119–122°; nmr (neat, TMS) γ-CH_3 1.62, quartet, J = 4.5 cps (relative area 3.0); CHD 3.93, broad multiplet (1.0); CH=CH 5.62, multiplet (2.0); OH 4.92 ppm, singlet (1.0); ir (neat) double bond[27] at 10.35 and hydroxyl[31] at 3.0 μ.

2-(Crotoxy-1-*d*)pyridine 1-Oxide (IV). Recrystallization from ethyl acetate gave IV in 47% yield, mp 82–85° (evacuated capillary). The nmr confirmed this structure; uv_{max} (H_2O) 216 (32,700), 249 (7800), and 295 mμ (ε 4400); ir (Nujol mull) strong 1-oxide[8] at 7.7–8.1 and double bond[27] at 10.1–10.3 μ; nmr γ-CH_3 1.73, doublet, J = 4.5 cps (relative area, 3.0); CHD 4.82, broad doublet (0.94); CH=CH 5.88, multiplet (2.0); $H_{3,4,5}$ 7.07, multiplet (3.1); H_6 8.30 ppm, multiplet (1.1).

2-Cyclopropylcarbinyloxypyridine 1-Oxide (V). Recrystallization from ethyl acetate and heptane gave V in 30% yield, mp 78–81° (evacuated capillary); uv_{max} (H_2O) 215 (27,600), 249 (7600), and 295 mμ (ε 4300); ir (Nujol mull) strong 1-oxide[8] at 7.6–8.1 and cyclopropyl[32] 9.76 μ; nmr CH_2 4.20 doublet J = 7.0 cps (relative area, 2.0); CH 1.38, multiplet (1.0); CH_2CH_2 0.54, multiplet (4.0); $H_{3,4,5}$ 7.12, multiplet (3.1); H_6 8.25 ppm, multiplet (1.0).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.05, 64.94; H, 6.71, 6.80; N, 8.28, 8.35.

1-Alkenyloxy-2-pyridones. The rearrangements were carried out in sealed tubes which were suspended in stirred oil baths at the appropriate temperatures. The diglyme solvent was purified prior to use by distillation from calcium hydride or lithium aluminum hydride. All of the products were obtained from an F & M Model 500 gas chromatograph with a 20% DC 200 silicon oil column on Chromosorb W. Yields are in Table I. The nmr data are below. Pertinent ir and uv data appear in Table III.

Nmr Identification[26] of the 1-Alkenyloxy-2-pyridones. 1-Allyloxy-2-pyridone (X): CH_2 4.67, doublet, J = 6.0 cps (relative area, 2.1); CH_2= 5.23, multiplet (1.9); CH=, H_5 5.92, multiplet (2.0); H_3 6.47, quartet (1.0); $H_{4,6}$ 7.29 ppm, multiplet (2.0).

1-Crotoxy-2-pyridone (XI): (CCl_4, TMS) γ-CH_3 1.72, doublet, J = 4.5 cps (3.0); CH_2 4.65, doublet, J = 5.5 cps (1.8); CH=CH, H_5 5.87, multiplet (2.0); H_3 6.47, quartet (1.0); $H_{4,6}$ 7.23 ppm multiplet (3.0).

Table III.[a] Infrared and Ultraviolet Data for 1-(2-Alkenyloxy)-2-pyridones

Pyridone	(C=O)[2] ir strong, μ	Double bond[27,29]	—Uv_{max} (H_2O), mμ (ε)—	
X	6.05	10.1–10.7	226 (5700)	297 (5600)[b,c]
XI[e]	6.01	10.3	225 (6400)	297 (5800)
XII	6.01	10.65, 11.1	226 (5400)	298 (5300)
XIII[e]	6.01	10.35	225	298
XIV[b]	6.04	Cyclopropane[32] 9.74	226 (5500)	298 (5300)
XVI	6.05	10.3, 12.0	224 (5900)	299 (5100)
XVII	6.01	10.0–10.7, 11.3	227 (6900)	305 (5500)
XVIII	6.0	10.3	227 (7200)	305 (5700)
XIX	6.0	10.7, 11.39	228 (6800)	306 (5500)

[a] Compounds X, XI, XII, and XV[b] have been prepared from 2-ethoxypyridine 1-oxide and the alkyl chloride or bromide. Little comparative data were available.[c,d] [b] Compound XIV contained about 4% of the cyclobutyl compound XV. [c] L. A. Paquette, U. S. Patent No. 3,213,100; *Chem. Abstr.*, **64**, 2069 (1966); U. S. Patent No. 3,213,101; *Chem. Abstr.*, **64**, 2063 (1966). [d] L. A. Paquette, *Tetrahedron*, **22**, 25 (1966). [e] Molecular weight by mass spectral determination was 165 (XI) and 166 (XIII). We thank Mr. Gary Hermann for this determination.

1-α-Methylallyloxy-2-pyridone (XII): (CCl_4, TMS) α-CH_3 1.43, doublet, J = 6.2 cps (3.0); CH=CH_2 5.13, multiplet (3.0); CH, H_5 5.83, multiplet (2.1); H_3 6.48, quartet (1.0); $H_{4,6}$ 7.23 ppm, multiplet (2.2).

1-(Crotoxy-1-*d*)-2-pyridone (XIII): γ-CH_3 1.63 doublet, J = 4.5 cps (3.0); CHD 4.60, broad multiplet (1.1); CH=CH, H_5 5.88, multiplet (3.0); H_3 6.58, quartet (1.3); $H_{4,6}$ 7.30 ppm, multiplet (2.2).

1-Cyclopropylcarbinyloxy-2-pyridone (XIV): CH_2 4.19, doublet, J = 7.5 cps (2.0); CH_2CH_2 0.50, multiplet (4.0); CH 1.21, multiplet (1.0); H_5 6.21, multiplet (1.0); H_3 6.73, quartet (1.0); $H_{4,6}$ 7.55 ppm multiplet (2.0). This contained about 4% 1-cyclobutyloxy-2-pyridone (XV); center 2.12 ppm. The integration is corrected.

1-α,γ-Dimethylallyloxy-2-pyridone (XVI): α-CH_3 1.43, doublet, J = 6.5 cps (3.0); γ-CH_3 1.66, doublet J = 4.5 cps (3.0); CH=CH 5.62, multiplet (2.0); CH 5.06, multiplet (1.0); H_5 6.12, multiplet (1.1); H_3 6.70, multiplet (1.1); $H_{4,6}$ 7.35 ppm, multiplet (2.1).

1-Allyloxy-5-methyl-2-pyridone (XVII): 5-CH_3 2.08, singlet (3.0); CH_2 4.80, doublet, J = 6.2 cps (1.8); CH_2= 5.41, multiplet (1.8); CH= 6.04, multiplet (1.0); H_3 6.65, multiplet (1.0); $H_{4,6}$ 7.23 ppm, multiplet (2.1).

1-Crotoxy-5-methyl-2-pyridone (XVIII): 5-CH_3 2.04, singlet (3.1); γ-CH_3 1.73, doublet, J = 4.2 cps (3.0); CH_2 4.80, multiplet (1.9); CH=CH 5.80, multiplet (2.0); H_3 6.62, multiplet (1.1); $H_{4,6}$ 7.20 ppm, multiplet (2.3).

1-α-Methylallyloxy-5-methyl-2-pyridone (XIX): 5-CH_3, 2.05, singlet (3.0); α-CH_3 1.44, doublet J = 6.2 cps (3.0); CH=CH_2 5.08, multiplet (2.8); CH 5.90, multiplet (1.0); H_3 6.59, multiplet (1.0); $H_{4,6}$ 7.18 ppm, multiplet (2.0).

The small upfield shift of the α-methyl resonance to 1.43 ppm probably reflects the change in the deshielding effects in going from the ether linkage which is strongly affected by the neighboring 1-oxide function[11] to the pyridone system where the carbonyl group is the adjacent function. The 5-methyl group is on the position β to the 1-oxide function in the starting material; therefore, it should be relatively unaffected by the 1-oxide group.[21] Thus, it seems probable that the upfield shift in the pyridone is due to the change in the ring properties. Elvidge and Jackman[33] have found that the 2-pyridone system has about 35% of the aromatic character of benzene.

Assignment of the ring protons may be confirmed from a comparison of the pyridones: the H_5 proton, the farthest upfield is absent in XVII, XVIII, and XIX. The H_3 quartet present in X, XI, XII, XIII, and XIV becomes a broad multiplet when the methyl substituent is introduced due to coupling.[23] A comparison of the resonance positions of the ring protons in the 1-oxide *vs.* the pyridones reveals an upfield shift. The upfield shift of the H_6 signal from about 8.1 ppm to about 7.4 ppm in the pyridone is striking.

(30) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 1197 (1947).
(31) Reference 28, p 99.
(32) Reference 28, p 29.
(33) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

The shift reflects the change in aromatic character of the ring[33] and also the loss of the inductive and resonance effects of the 1-oxide function.[11]

3-Alkenyl-1-hydroxy-2-pyridones. The starting 1-oxides were dissolved in diglyme and rearranged in sealed tubes at 137°. The products were isolated and identified spectrally as before. The physical properties are given.

Nmr Analysis[26] of 3-Alkenyl-1-hydroxy-2-pyridones. ***cis*- and *trans*-3-Crotyl-5-methyl-1-hydroxy-2-pyridones (XX):** (CCl_4, TMS) 5-CH_3 2.09, singlet (relative area, 3.0); γ-CH_3 1.65, quartet (3.0); OH 12.4, broad singlet (1.1); CH_2 3.10, broad multiplet (2.0); CH=CH 5.43, broad multiplet (2.0); H_4 6.92, broad multiplet (1.0); H_6 7.33 ppm, broad multiplet (1.0).

3-Allyl-1-hydroxy-2-pyridone (XXI): (CCl_4, TMS) CH_2 3.23, doublet J = 6.7 cps (2.0); OH 13.5, broad singlet (0.8); CH_2= 5.05, multiplet (1.8); CH=, H_5 6.14, multiplet (2.0); $H_{4,6}$ 7.18 ppm, multiplet (1.9).

The position of the OH resonance was concentration dependent. Similar behavior has been noted for oximes.[34]

Note that the resonance due to the methylene group is upfield at 3.10 ppm for XX and at 3.23 ppm for XXI. It appears between 4.2 and 4.8 ppm in both the 1-oxides and the 1-alkenyloxy-2-pyridones. As can be seen, substitution of the methyl group in the 5 position results in the loss of the signal farthest upfield. Furthermore, the ring substituent has smeared the methylene signal in the alkene moiety.[23] Therefore, the allylic group is on the 3 position of the ring.

***cis*- and *trans*-3-Crotyl-5-methyl-1-hydroxy-2-pyridones (XX).** The solution of the 2-α-methylallyloxy-5-methylpyridine 1-oxide (IX, 0.1 g) was heated for 1 hr. After removal of the solvent and cooling, the product was isolated by suction filtration. Sublimation at 70° (0.01 mm) gave XX in 65% yield, mp 111–112° (softens 105°). Mass spectral analysis[17] using a direct inlet source showed the parent peak (22%) at *m/e* 179; ir (Nujol mull) broad OH and CH at 3.0–4.0 and carbonyl at 6.05 μ; uv_{max} (C_2H_5OH) 207, 234, and 303 mμ.

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.05, 66.94; H, 7.43, 7.50; N, 7.77, 7.69.

3-Allyl-1-hydroxy-2-pyridone (XXI). The solvent was removed after heating a 0.2-g sample of 2-allyloxypyridine 1-oxide (I) for 3.5 hr. Partial separation to give 0.03 g (XXI) was achieved by column chromatography on silica gel using ethyl acetate as the eluent. Two sublimations at 60° (0.1 mm) gave the pure sample, mp 92–94°. Mass spectral analysis[17] using a direct inlet source showed the parent peak (10%) at *m/e* 151; ir (Nujol mull) broad OH and CH at 3.0–4.0 μ and carbonyl at 6.13 μ; uv_{max} (C_2H_5OH) 206, 231, and 304 mμ.

Crossover Experiment. Equimolar quantities (4×10^{-4} M) of 2-crotoxypyridine 1-oxide (II) and 2-allyloxy-5-methylpyridine 1-oxide (VII) were dissolved in 2 ml of diglyme and heated in a sealed tube at 83° for 24 hr when the reaction was complete. After concentration of the solution the components were partially resolved by using a 5-ft 20% DC 200 silicon oil column on Chromosorb W. Infrared analysis showed pure 1-allyloxy-2-pyridone (X) was present (20% by vpc).

Rate Determinations. Samples of 2-α-methylallyloxy-5-methylpyridine 1-oxide (VIII) were dissolved in diglyme and placed in sealed nmr tubes. The initial spectrum was taken on a Varian A-60 instrument before the tube was heated in a stirred oil bath at the appropriate temperature. The increase in the signal at 1.7 ppm due to the γ-methyl group was followed to infinite time by removing the tube at intervals and quenching the reaction by cooling in Dry Ice. The rate of 1-oxide disappearance was obtained by plotting log (integral$_\infty$ − integral$_t$) *vs.* time. Excellent straight lines were obtained in this manner. This method assumes that the ratio of the individual rate constants remains constant throughout the reaction.[35] The composition was corrected for any signal due to the 1-crotoxy-5-methyl-2-pyridone (XVIII) by obtaining the ratio of it to 1-α-methylallyloxy-5-methyl-2-pyridone (XIX) using vpc analysis. The integral was then corrected and the percentages of XVIII, XIX, and XX obtained from the nmr integrations.

(34) G. C. Kleinspehn, J. A. Jung, and S. A. Studniarz, *J. Org. Chem.*, 32, 460 (1967).

(35) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 3; F. Daniels and R. A. Alberty, "Physical Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 12.

Factors Governing Orientation in Metalation Reactions. IV. The Role of Alkoxide in Metalation Reactions Involving Organosodium Compounds

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Abstract: The metalation of *t*-butylbenzene with *n*-amylsodium, both in the presence and absence of sodium *t*-butoxide, was studied. The yield of the alkoxide metalation was much higher than the yield without alkoxide. A variable which affects isomer distribution, both in the presence or absence of alkoxide, is the amount of dimetalation which occurs, since the latter takes place principally at the expense of the *meta* isomer. In the presence of alkoxide, the *meta* isomer, which initially forms rapidly (presumably because of favorable statistics, *i.e.*, two *meta*, one *para* position), equilibrates with excess *t*-butylbenzene *via* a transmetalation and ultimately is converted to the more thermodynamically favored *para* isomer. Pure *m*-*t*-butylphenylsodium in the presence of sodium *t*-butoxide and excess *t*-butylbenzene was isomerized 70–80% to the *para* isomer. Under comparable conditions, pure *p*-*t*-butylphenylsodium was isomerized only about 2% to the *meta* isomer. A study of the supernatant layers which arise from centrifuging *n*-amylsodium and *n*-amylsodium–sodium alkoxide combinations in nonane was carried out. Evidence was obtained that the sodium *t*-butoxide tends to disperse or peptize the *n*-amylsodium aggregates.

In his pioneering work on organosodium chemistry, Professor A. A. Morton and his collaborators demonstrated that metal alkoxides[1] exert a profound effect on certain reactions involving organosodium compounds. Thus, the rate of Wurtz coupling reactions between organosodium compounds and alkyl halides is accelerated by a variety of alkoxides,[2] and the catalytic activity of

(1) A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *J. Org. Chem.*, 20, 428 (1955).

(2) A. A. Morton and A. E. Brachman, *J. Am. Chem. Soc.*, 73, 4363 (1951).