4. *Free-radical Substitution of Pyridine* 1-*Oxide.*

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Pyridine 1-oxide has been phenylated with diazoaminobenzene, and the reactivities of the nuclear positions to free-radical substitution are found to be in the order 2 > 4 > 3. Infrared spectra of pyridine 1-oxides in the 870—710 cm.$^{-1}$ region are discussed.

THE reactivities of the three nuclear positions in pyridine 1-oxides to free-radical attack have not previously been fully determined. Colonna and Quilico [1] treated it with phenyl- and *p*-chlorophenyl-diazonium salts and isolated the 2-arylpyridine 1-oxides, but they did not mention the 3- and 4-aryl derivatives which would also be expected from a free-radical substitution.

We have treated pyridine 1-oxide with benzoyl peroxide at 100° but the yield of phenyl-pyridine oxides was too low to be useful: the product was largely the 2-phenyl isomer. Much better yields of phenylated product were obtained by reaction with diazoamino-benzene at 131° or 181°; the reactivities of the 2-, 4-, and 3-position being in the ratio 9·9 : 3·9 : 1. This order, 2 > 4 > 3, follows the predictions of Barnes,[2] whose molecular-orbital calculations found the radical localisation energies, A_r, to be 2·42, 2·47, and 2·53β for the 2-, 4-, and 3-position respectively. Barnes estimated (by analogy with Brown's calculations [3] on pyridine) that a difference of 0·03β between the A_r values of two positions would correspond to a two-fold difference in rate of substitution, and the experimental values of relative reactivities agree with this estimate.

EXPERIMENTAL

M. p.s are corrected. Analyses are by the C.S.I.R.O. and University of Melbourne Micro-analytical Laboratory. Light petroleum was a fraction of b. p. 55—60°.

Reagents.—Pyridine 1-oxide was prepared by oxidation of pyridine with peracetic acid.[4] The crude product was fractionated, through a 40 cm. column packed with glass helices, to remove traces of pyridine. The fraction of b. p. 110°/1 mm. was collected (Found: C, 63·5; H, 5·25; N, 15·0. Calc. for C$_5$H$_5$NO: C, 63·2; H, 5·3; N, 14·8%). Benzoyl peroxide (B.D.H.) was twice crystallised from chloroform–methanol at 0° and was dried *in vacuo* (Found: equiv., by iodometric titration, 122. Calc.: equiv., 121). Diazoaminobenzene (B.D.H.) crystallised from light petroleum (b. p. 80—100°) as golden needles, m. p. 98° (lit., 99°).

2-Phenylpyridine 1-oxide was isolated after reaction of diazoaminobenzene with pyridine 1-oxide at 181°. The crude product was isolated by chromatography in benzene on alumina. A sample was retained for infrared analysis (see run 1, Table 3); the remainder crystallised from benzene as colourless prisms, m. p. 157—158° (lit., 157°). The infrared frequencies (1600—675

[1] Colonna and Quilico, *Atti Accad. naz. Lincei, Rend. Classe. Sci. fiz. mat. nat.*, 1959, **26**, 39.
[2] Barnes, *J. Amer. Chem. Soc.*, 1959, **81**, 1935.
[3] Brown, *J.*, 1956, 272.
[4] Ochiai, *J. Org. Chem.*, 1953, **18**, 534.

cm.$^{-1}$) and intensities in acetonitrile solution were unaltered after the sample had been further chromatographed in benzene on silica. The picrate (bright yellow needles from ethanol or toluene) had m. p. 150—151° (lit.,[5] 150—151°). 3- and 4-Phenylpyridine 1-oxide were prepared by oxidation of the appropriate phenylpyridine with peracetic acid,[6] and had m. p.s 119·5—120° (lit.,119°) and 152—153° (lit., 152·5°) respectively. The picrates had the recorded m. p.s. 4-Nitropyridine 1-oxide, m. p. 162—163° (lit., 163°), was obtained by nitration of pyridine 1-oxide,[7] and 4-ethoxypyridine 1-oxide, m. p. 32—33° (lit., 30—33°), prepared by refluxing 4-nitropyridine 1-oxide with ethanolic sodium ethoxide for 3 hr.

Infrared Spectra.—Spectra were recorded with a Perkin–Elmer Model 112 single-beam, double-pass spectrometer, with a sodium chloride prism, scanning speed 8, and 1 mm. cell thickness. Fractionated acetonitrile was used as solvent since it combines good solvent power

TABLE 1. *Infrared spectra of pyridine* 1-*oxides in solution.*

Subst.	—	2-Ph	3-Ph	3-Ph	4-Ph	4-NO$_2$	4-OEt
Solvent	MeCN	MeCN	MeCN	CHCl$_3$	MeCN	MeCN	MeCN
Concn. (mole l.$^{-1}$)	0·416	0·153	0·141	0·090	0·119	0·059	0·070
		1590 *	1608 (115)	1602 (175)	1588 * (20)	1608 (320)	1633 (100)
			1565 * (95)	1583 (55)		1591 (180)	
		1480 * (265)	1477 * (155)	⌈1562 (100)	1478 * (445)		
		1340 (80)		⎨1482 (150)			
				⎩1461 † (75)			
				1422 (180)	⌈1312 *† (35)	1344 (520)	
					1305 * (45)		
					⎩1290 * (50)		
	⌈1327 † (10)	1284 (30)					1289 (230)
	⎨1256 (285)	1244 (395)	1310 (225)	1314 (235)	⌈1254 (355)	⌈1296 (690)	⌈1234 (310)
	⎩1246 † (230)		1275 * (20)		⎩1245 †	⎩1287 (840)	⎩1223 (545)
						1227 (110)	
	⌈1195 † (40)	1185 (35)	⌈1248 *† (15)		⌈1193 † (100)	⌈1186 † (75)	1170 (100)
			⎨1213 (315)	1198 * (160)			
			⎩1205 †				
	⎩1174 (145)	1158 (40)	1165 (130)	1165 (165)	⎩1177 (295)	⎩1171 (155)	1151 (75)
		1111 (60)	1093 *	1093 * (20)	1134 (30)	⌈1120 (540)	1131 (120)
					1107 * (15)	⎩1113 † (250)	
	1072 (25)	1076 * (45)	1080 *	1080 * (20)		1092 (160)	1095 (50)
			1062 * (50)				
	⌈1020 (130)	1016 * (85)	1016 (190)	1018 (205)			
	⎩1008 *† (20)	998 * (50)	1001 * (55)	1002 (40)	1000 * (20)		
	969 * (5)	948 * (30)	952 * (20)				
	907 * (15)		903 (220)	904 (250)			
	⌈ 841 (165)	847 (200)	873 (45)	875 (75)	851 (250)	871 (310)	856 (70)
	⎩ 827 † (25)		802 (83)			857 (220)	844 (140)
	774 (190)	770 ‡ (350)	766 (375)		770 (340)	753 (170)	774 (245)
		⌈733 †	732 (125)		727 (85)		
		⎨726 (165)			716 (82)		
		⎩699 (220)	702 (205)		699 (150)		
	679 (145)		682 (95)			677 (100)	

* Poorly defined, being either broad and weak or obscured by solvent absorptions.   † Shoulder.
‡ Asymmetry on the high-frequency side, but no shoulder.

TABLE 2. *Major peaks in the infrared spectra of pyridine* 1-*oxides in Nujol mulls at* 880—750 *cm.*$^{-1}$.

Subst.	—	2-Ph	3-Ph	4-Ph	4-NO$_2$ [15]	4-OEt
Frequencies and intensities	836s 771s	844s ⌈772w ⎩760s	797w 759m	855w 770m	867s 749m	858s 772s

for pyridine oxides with fairly good transparency in the 1350—670 cm.$^{-1}$ region. Frequencies above 1350 cm.$^{-1}$ are only approximate. The spectrum of 3-phenylpyridine 1-oxide in chloroform solution is also reported. Apparent molar extinction coefficients, ε_A, were measured from the recorder traces, and appear accurate to ±5%. The spectral slit widths used were 3·0 cm.$^{-1}$ at 1250 cm.$^{-1}$ and 2·5 cm.$^{-1}$ at 850 cm.$^{-1}$. The spectra are tabulated in Table 1. Table 2

[5] Edward and Gilman, *Canad. J. Chem.*, 1953, **31**, 457.
[6] Hands and Katritzky, *J.*, 1958, 1754.
[7] den Hertog and Ovenhoff, *Rec. Trav. chim.*, 1950, **69**, 468.

reports features of the spectra of pyridine 1-oxide and some of its derivatives in Nujol mulls, recorded in the region 850—680 cm.⁻¹.

Phenylation with Benzoyl Peroxide.—Benzoyl peroxide (20·00 g.) was added to molten pyridine 1-oxide (149 g.) which had been saturated with carbon dioxide. The solution was heated at 100° for 3 hr., by which time evolution of carbon dioxide (0·112 mol., measured volumetrically) was complete. Crude pyridine 1-oxide (b. p. 95—105°/0·2 mm.) was recovered by distillation. This fraction was redistilled at reduced pressure from sodium carbonate, and acidification of the distillation residue yielded benzoic acid (9·45 g., 0·94 mol.), m. p. and mixed m. p. 122—123°. The first distillation residue (22·35 g.) was extracted with hot benzene. Extraction with sodium carbonate solution did not remove benzoic acid from this benzene extract. The benzene extract (16·35 g.) was refluxed for 9 hr. with potassium hydroxide (5 g.) in ethanol (150 ml.) and water (20 ml.). The solvents were distilled off, and extraction of the residue with hot benzene afforded a tar (0·73 g.). The residue was acidified, to yield benzoic acid (6·50 g., 0·64 mol.), m. p. and mixed m. p. 121—122°. The tar from the benzene extract was chromatographed in benzene on alumina, affording 63 mg. of crude material (m. p. 153—155°) whose infrared spectrum resembled that of 2-phenylpyridine 1-oxide (mixed m. p. 148—153°).

Phenylation with Diazoaminobenzene at 181°.—Diazoaminobenzene (16·50 g.) was added to molten pyridine 1-oxide (114 g.) in a vapour-jacketed vessel which was flushed out three times with dry, oxygen-free nitrogen before being heated in phenol vapour (181°). After 24 min., evolution of nitrogen started (too violently to permit collection). Gas evolution subsided after 4 min., but continued very slowly for 4 hr. Excess of pyridine 1-oxide, and aniline, were recovered from the mixture by distillation (b. p. 80—95°/0·01 mm.). The residue was further distilled, giving an orange sticky solid (6·180 g.), b. p. 131—156°/0·02 mm. The tarry residue (3·43 g.) did not distil at 240° (bath)/0·02 mm. The orange solid was chromatographed in benzene on alumina. Elution with benzene yielded a pale orange solid (4·728 g.; fraction 1), and addition of ethanol to the eluate gave a sticky yellow solid (1·277 g.; fraction 2). Crystallisation of fraction 1 from benzene–light petroleum removed highly soluble orange oils and yielded colourless needles (3·426 g.), m. p. 156—157° (Found: C, 77·5; H, 5·3. Calc. for $C_{11}H_9NO$: C, 77·3; H, 5·25%). Fraction 2 similarly crystallised to yield a colourless solid (0·548 g.) (Found: C, 77·5; H, 5·35%). The isomeric composition of each of these crystallised fractions was determined by infrared spectroscopy; the isomer ratio in the total phenylated fraction is reported in Table 3. The mother-liquors from both crystallisations were red oils from which no pure products were isolated. One or more of the strong bands in the infrared spectrum of each phenylpyridine oxide was absent from the spectra of these oils. No significant amounts of phenylpyridine oxide have therefore been lost in the crystallisations.

Phenylation with Diazoaminobenzene at 131°.—When runs were carried out as above, nitrogen evolution commenced immediately when the mixture was heated in chlorobenzene vapour (131°). The rate of nitrogen evolution was very variable. In run 2 it was steady for 3 hr. and very slow for a further 10 hr.; in run 3 it was violent for 6 min. and very slow for 5 hr.; in run 4 it was fast for 20 min. and very slow for 4 hr. The working-up procedure is described for run 4. Distillation yielded a sticky solid, b. p. 95—100°/0·2 mm., followed by orange crystals (3·229 g.), b. p. 108—148°/0·1 mm. The black amorphous residue weighed 4·56 g. The first fraction was dissolved in water (120 ml.), and extracted with benzene (3 × 120 ml.). The aqueous layer was then continuously extracted with chloroform, and the extract was distilled for recovery of pyridine 1-oxide, b. p. 102°/0·3 mm. (Found: C, 63·6; H, 5·4; N, 14·6%). The benzene extract, after drying (Na_2SO_4), yielded a pale red oil (4·19 g.), which was refluxed for 30 min. with acetic anhydride (5 ml.) and acetic acid (5 ml.). Acetanilide (2·646 g.), m. p. and mixed m. p. 114—115°, was isolated by crystallisation and sublimation. The remainder of the red oil was also examined (see next paragraph). The second distillation fraction was taken up in hot benzene (100 ml.). An insoluble red oil (0·18 g.) was separated (see next paragraph). The soluble material (3·045 g.) was chromatographed on a silica column. Benzene eluted first a red oil (1·362 g.; fraction 1), followed by a sticky solid (1·029 g.; fraction 2). Progressive addition of ethanol (up to 2% v/v) to the benzene led to elution of the remainder of the phenylated material (0·392 g.; fraction 3). Addition of 5% v/v ethanol gave pyridine 1-oxide (26 mg.) which was identified from its infrared spectrum and as picrate (m. p. and mixed m. p. 181°). From benzene–light petroleum fraction 2 gave crystals (0·850 g.) (Found: C, 77·3; H, 5·55%), whose mother-liquor was combined with fraction 1. Fraction 3 (Found:

C, 77·7; H, 5·3%) was not crystallised. Fraction 3 and the crystalline material from fraction 2 were subjected to infrared spectroscopy; the isomer ratio in the total phenylated fraction is reported in Table 3. Fraction 1 is considered below.

TABLE 3. *Products of reactions of diazoaminobenzene with pyridine* 1-*oxide.*

Run no.	Temp.	Diazo-amino-benzene (g.)	Reactant ratio *	N$_2$	Acet-anilide	Phenyl-ated	Oils †‡ (g.)	Wt. distn. residue †	2-Ph (%)	3-Ph (%)	4-Ph (%)
1	181°	16·5	14·5	—	—	0·28	0·13	0·21	79·0	7·7	13·3
2	131	16·5	18·6	0·73	0·42	0·48	0·10	0·33	76·4	8·3	15·3
3	131	11·7	18·6	—	0·32	0·07	0·24	0·41	80·9	5·6	13·5
4	131	9·1	18·5	0·78	0·43	0·16	0·20	0·50	71·3	9·6	19·2

* Moles of pyridine 1-oxide per mole of diazoaminobenzene.   † G. per g. of diazoaminobenzene.
‡ These oils are those distilling in the phenylpyridine 1-oxide fraction and then isolated by chromato-graphy.

By-products from Diazoaminobenzene Reactions.—(1) *Benzene-insoluble oils from phenylated distillation fraction.* This material was found in runs 2 (0·54 g.), 3 (0·70 g.), and 4 (0·18 g.). The oil (0·40 g.) formed a picrate (0·29 g.), m. p. 155°, from ethanol. Recrystallisation from warm ethanol yielded needles (0·19 g.), m. p. and mixed m. p. 188° with 4-phenylpyridine picrate (Found: C, 53·4; H, 3·5; N, 14·6. Calc. for C$_{17}$H$_{12}$N$_4$O$_7$; C, 53·2; H, 3·15; N, 14·6%).

(2) *Oils from acetylation.* Attempted sublimation at 100°/0·2 mm. of the red oil (2·38 g.) remaining after the isolation of acetanilide in run 4 resulted in distillation of an oil. This oil (0·65 g.) formed a picrate (0·63 g.), crystallising from ethanol and benzene as prisms, m. p. 164—165° (Found: C, 53·2; H, 3·2; N, 14·5%). The free base (80 mg.) was liberated from the picrate (200 mg.) by chromatography in ethanol on alumina [Found: *M* (Rast), 166. Calc. for C$_{11}$H$_9$N: *M*, 155]. The infrared spectrum (3500—680 cm.$^{-1}$) of a liquid film closely resembled that of 2-phenylpyridine, with a shoulder at 1540 cm.$^{-1}$ indicating the presence of a small proportion of 4-phenylpyridine.[8] The absence of a band at 810 cm.$^{-1}$ indicated that very little, if any, 3-phenylpyridine was present.[9]

(3) *Oils from chromatography.* The leading fraction from the chromatography of the phenyl-ated fraction from each run was rechromatographed in benzene on silica. Successive elution with benzene, 1% v/v ethanol–benzene, 3% v/v ethanol–benzene, and ethanol produced four sticky orange solids in each case. The first fraction (1·10 g.) of these from run 3 yielded a crystalline picrate (0·64 g.), m. p. 162·5—164° and mixed m. p. 164° with the previous picrate of m. p. 164—165°. The infrared spectrum of a film of the oily free base confirmed the identity of this product as largely 2-phenylpyridine, with a small proportion of 4-phenylpyridine and no detect-able 3-phenylpyridine. The third oily fraction (0·25 g.) afforded 4-phenylpyridine picrate (49 mg.), m. p. and mixed m. p. 188°. The second and the fourth fraction (0·08 g. and 0·10 g. respectively) could not be characterised. In all three runs at 131°, the infrared spectra of the four fractions all showed the strong 696—698 and 765—767 cm.$^{-1}$ bands of the phenyl group,[10] but important features of the spectra of all the phenylpyridine 1-oxides were absent. None of the four fractions from run 2 showed bands in the N–H stretching region (3600—3100 cm^{-1}). The oils did not contain azo-compounds since no N–H stretching bands were detected after reduction with stannous chloride in ethanolic hydrochloric acid for 5 min. at 100°.

(4) *Distillation residues.* Attempts to isolate pure products by solvent extraction, chromato-graphy on silica and alumina, and crystallisation were unsuccessful. None of the fractions obtained formed a picrate or sublimed at 220° (bath)/0·03 mm.

Origin of Tars.—(1) *Stability of phenylpyridine* 1-*oxides to distillation.* A mixture of the three phenylpyridine 1-oxides (1·075 g.) was distilled (b. p. 120—140°/0·1 mm.; bath 160°), and only 28 mg. of tar remained. The isomer ratio was unchanged.

(2) *Reaction between aniline and pyridine* 1-*oxide.* Pyridine 1-oxide (4·32 g.) was refluxed for 6 hr. with aniline (10 ml.). Distillation afforded an oil (6·06 g.), b. p. 72—82°/2 cm. The oil was treated with acetic anhydride and acetic acid, and, after dilution with 2N-hydro-chloric acid, the mixture was extracted with chloroform to remove acetanilide. The aqueous

[8] Hands and Katritzky, *J.*, 1958, 2202.
[9] Hands, Jones, and Katritzky, *J.*, 1958, 3165; Hey, Stirling, and Williams, *J.*, 1955, 3963.
[10] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., p. 65.

layer was treated with excess of sodium hydrogen carbonate, and was then extracted with chloroform. Pyridine was isolated from the extract as its picrate (4 mg.). The distillation residue was shaken with benzene and water. The benzene layer yielded a black tar (0·94 g.).

A similar reaction between aniline and 2-phenylpyridine 1-oxide at 131° led neither to reduction nor to tar formation.

Infrared Determination of Isomer Ratios.—The peaks used were at 802 cm.$^{-1}$ (3-phenyl-pyridine 1-oxide) and 716 cm.$^{-1}$ (4-phenyl isomer); Beer's law was obeyed for each isomer. There was no suitable peak for the 2-phenyl isomer, which was determined by difference. Three synthetic isomeric mixtures, of differing compositions, were analysed. The calculated concentrations of the 3-, 4-, and 2-phenyl isomers differed from the known concentrations by averages of 4·5, 3·4, and 8·1% respectively. Corrections for overlap (which did not exceed 10% of the total absorption at either peak) were applied. Isomeric mixtures from the phenylation runs were analysed by dissolving the total sample in acetonitrile, diluting it to the required concentration, and analysing two samples. The infrared spectrum of each mixture was scanned, and the frequencies and intensities of the bands were examined to ensure that only phenylpyridine 1-oxides were present.

Complex Formation between Pyridine 1-Oxide and Diazoaminobenzene.—The infrared spectrum (calcium fluoride prism) of pyridine 1-oxide in chloroform solution (0·165M) showed the following peaks: 1606 (ε_A 95), 1487 sh (50), 1463 (840), 1410 (20), 1274 sh, and 1253 cm.$^{-1}$ (405). A 0·165M-solution of diazoaminobenzene showed peaks at 3322 (ε_A 75), 1619 (100), 1603, (585), 1516 sh (285), 1506 (400), 1481 (300), 1469 (360), 1430 (370), 1419 (145), 1310 (115), 1298 (45), 1290 (50), and 1242 cm.$^{-1}$ (555). The spectrum of a chloroform solution, 0·165M in pyridine 1-oxide and 0·164M in diazoaminobenzene, was compared with the sum of the two separate spectra: despite overlapping, the 1463 cm.$^{-1}$ peak in the pyridine 1-oxide spectrum was less intense and the 1253 cm.$^{-1}$ peak more intense. The bands at 1516, 1506, 1481, 1469, 1430, 1298, and 1290 cm.$^{-1}$ in the spectrum of diazoaminobenzene were all weaker by about 20% in the mixture. The most striking changes in the spectrum of diazoaminobenzene were at 3322 cm.$^{-1}$ (νN$-$H), where ε_A decreased from 75 to 45, and at 1619 cm.$^{-1}$ (δN$-$H), where ε_A increased from 100 to 150. The bonded N$-$H stretching band of diazoaminobenzene,[11] expected in the region of 3200 cm.$^{-1}$, was not sufficiently well-defined for measurement in either spectrum.

DISCUSSION

Benzoyl Peroxide Reaction.—Extensive substitution of pyridine 1-oxide by benzoyloxy-radicals is evident from the high yield of benzoic acid (0·64 mol.) liberated on alkaline hydrolysis, and indicates [12] that pyridine 1-oxide is reactive to free-radical attack. The hydroxypyridine 1-oxides produced on hydrolysis were largely lost in aqueous extracts. Because of the unknown nature of the very extensive tar-producing side reactions, the low yield of carbon dioxide (0·11 mol.) does not necessarily support this evidence of high reactivity.

Diazoaminobenzene Reactions.—A feature of these reactions is the wide variation in yields (Table 3). The lower yields of phenylpyridine 1-oxides were accompanied by the highest yields of distillation residue and of only partly identified oils. This variability may be connected with the widely varying rates of reaction. The isomer ratio was nevertheless constant.

The yield of nitrogen (0·73—0·78 mole per mole of diazoaminobenzene) was surprisingly low, and indicates either attack by Ph·N$_2$· radicals on pyridine 1-oxide or a non-homolytic side-reaction. Attempts to detect azo-compounds in the tractable products by nitrogen analysis or reduction to amines were not successful, but the tars were not examined.

Although the phenylpyridine 1-oxides were shown to resist thermal deoxygenation under the conditions used, appreciable amounts of phenylpyridines (6% from run 3) were isolated. Aniline has been stated [13] to reduce heterocyclic *N*-oxides, although it effected

[11] Dyall, *Austral. J. Chem.*, 1960, **13**, 230.
[12] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 165.
[13] Katritzky, *J.*, 1956, 2404; Kloetzel and Pachter, *J. Amer. Chem. Soc.*, 1952, **74**, 971.

very little reduction of pyridine 1-oxide or of 2-phenylpyridine 1-oxide (the former reaction produced tars and may explain both the large production of tars and the low recovery of aniline; cf. recoveries of 0·56—0·64 mol. of aniline by Hardie and Thomson [14]). The isolation of 4-phenylpyridine picrate from a benzene-insoluble oil is particularly interesting: the solubility precludes presence of 4-phenylpyridine before treatment with picric acid.
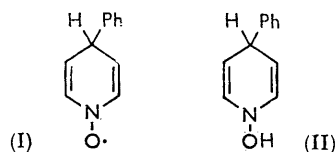
It is suggested that the radical-adduct (I) disproportionates to 4-phenylpyridine 1-oxide and the hydroxy-compound (II). The latter may be benzene-insoluble and might undergo acid-catalysed dehydration in the presence of picric acid.

The relative amounts of the phenylpyridines produced were $2 > 4 > 3$. Deoxygenation of some of the oxides is not likely to cause serious error in the relative reactivities calculated from the isomer composition (also $2 > 4 > 3$) of the phenylpyridine 1-oxides.

The infrared spectrum of a 1 : 1 mixture of diazoaminobenzene and pyridine 1-oxide in chloroform showed fairly marked modifications in the aromatic skeletal vibrations of both components. The two compounds thus appear to form a charge-transfer complex, which is further stabilised by hydrogen bonding and, if it were stable up to the temperatures of phenylation, could lead to an isomer distribution dependent on the geometry of the complex as well as on the relative reactivities of the nuclear positions. The stability of such a complex should be temperature-dependent, and the isomer ratios at 131° and 181° would then be different if the complex survived to these temperatures. Fortunately the isomer ratio was not temperature-dependent, and it can be assumed that complex formation does not affect the reaction.

Infrared Spectra.—The position of the $^+N^-O^-$ deformational band has not yet been established. Shindo [15] favours a band of strong or medium intensity at 840—870 cm.$^{-1}$ in the solid spectra of 23 of the 28 compounds he studied. Katritzky and Gardner [16] considered the 842—860 cm.$^{-1}$ band in the chloroform solution spectra of 4-substituted pyridine 1-oxides to be due to an unidentified $^+N^-O^-$ vibrational mode, but Hands and Katritzky [17] assigned this band to out-of-plane C$^-$H vibrations in the 2-substituted compounds. The 870—705 cm.$^{-1}$ region shows at least two strong bands in 27 of Shindo's compounds, and in many instances there is no reliable basis for assignment. The spectra of fifteen 4-substituted pyridine 1-oxides have been examined by Shindo [15] and the authors in the solid state, and fourteen showed strong bands at 829—705 cm.$^{-1}$ (average 770). Thirteen 3-substituted pyridine 1-oxides absorbed at 770—721 cm.$^{-1}$ (average 749), and four 2-substituted pyridine 1-oxides at 767—739 cm.$^{-1}$ (average 755). Assignment of this band to the $^+N^-O^-$ deformational mode appears equally as satisfactory as the 870—840 cm.$^{-1}$ assignment. Unfortunately, bands in neither region display shifts related to the electrical effects of substituents. Both bands show a wide scatter in frequencies when the spectra of Nujol mulls are examined, and the present work (Tables 1 and 2) indicates that this scatter also occurs when the spectra are examined in solution.

The bands near 730 and 700 cm.$^{-1}$ in the spectra of the phenylpyridine 1-oxides are attributed to the phenyl group.

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[14] Hardie and Thomson, *J.*, 1958, 1286.
[15] Shindo, *Chem. and Pharm. Bull.* (*Japan*), 1958, **6**, 117.
[16] Gardner and Katritzky, *J.*, 1958, 2192.
[17] Hands and Katritzky, *J.*, 1958, 2195.