Periselectivity between the [1,4] and [3,3] Thermal Sigmatropic Rearrangements of 2-Allyloxypyridine *N*-Oxides

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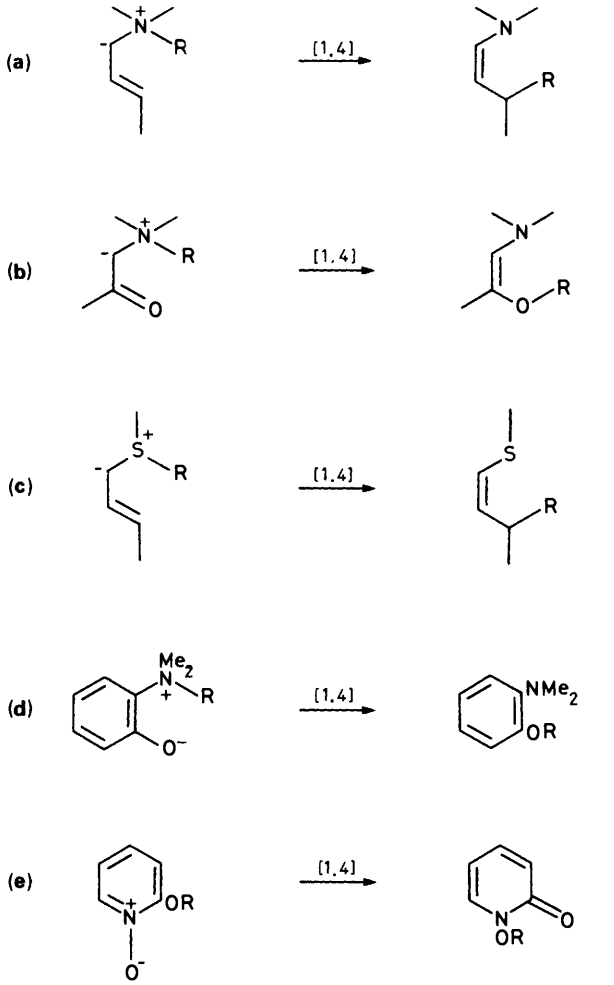
Thermal rearrangement of 2-allyloxypyridine *N*-oxides (**4a–c**) yields *N*-allyloxy-2-pyridones (**5a–c**) and 3-allyl-*N*-hydroxy-2-pyridones (**6a–c**). These transformations are shown to be regiospecific and on this basis it is proposed that the reactions involve concerted [1,4] and [3,3] sigmatropic rearrangements. Supporting evidence based on solvent effects, temperature effects, and substituent effects is given.

Survey of [1,4] *Sigmatropic Rearrangements.*—Thermal [1,4] sigmatropic rearrangements[1] may be categorised into three classes depending upon the intermediate, which may be cationic, anionic, or dipolar (ylide or betaine). Cationic [1,4] sigmatropic rearrangements are 4-electron processes and normally proceed in the [1_s,4_s] mode which is associated with inversion of configuration at the terminus of the migrating group. In contrast, anionic and dipolar [1,4] sigmatropic rearrangements involve 6-electron [1_s,4_s] processes associated with retention of configuration at the terminus of the migrating group.

The inversion of configuration of cationic [1,4] sigmatropic shifts constrained to proceed suprafacially has been convincingly demonstrated in the rapid equilibration of protonated bicyclohexenones[2] and the degenerate migration of the cyclopropane ring around the periphery of the 5-membered allylic cation during the [1,4] sigmatropic rearrangement of hexamethylbicyclo[3.1.0]hexenyl cations.[3] Formal [1,4] migrations of crotyl and benzyl groups have been observed[4] in the acid catalysed reaction between 1,1-disubstituted β-naphthalenones and acetic anhydride–sulphuric acid. In a detailed investigation of the acid-catalysed rearrangement of various 4-allylcyclohex-2-en-ols, Schmid has demonstrated that [3,4] sigmatropic rearrangements involving cyclohexadienyl cations do occur, whereas [1,4] sigmatropic rearrangements occur relatively infrequently.[5]

Anionic sigmatropic rearrangements are exemplified by the Wittig rearrangement of ethers and the corresponding base-catalysed rearrangements of thioethers. With allyl ethers, competition between the [1,2] and [1,4] sigmatropic rearrangements is possible and this aspect has been examined by several groups.[6–9] Felkin and Frajerman[7] have shown that the [1,2] and [1,4] rearrangements of *S*-allyl 1-phenylethyl ether both proceed with predominant retention of configuration and approximately the same extent of racemisation (*ca.* 30%). They conclude[7,8] that the [1,2] and [1,4] rearrangements both proceed by a non-concerted radical + radical anion cleavage–recombination mechanism. The possible role of a 'radical concerted' process in the Wittig [1,2] rearrangement has been carefully explored by Garst and Smith.[10] The simultaneous occurrence of [1,2] and [1,4] shifts has been observed in the Wittig rearrangement of allyl vinylcyclopropylmethyl ethers and again it was suggested that these products were formed by radical coupling.[11] The 5,6-dihydro-2*H*-pyran-2-ide→cyclopropyl enolate rearrangement can be regarded as proceeding exclusively by a [1,4] sigmatropic rearrangement. However, on the basis of the experimental evidence available, it is not possible to distinguish between concerted or stepwise processes.[9] The analogous [1,4] rearrangement of an allylic thioether occurs when 6,6-diphenylthiacyclohex-3-ene is treated with butyl-lithium.[12] An attempt to promote a [1,4] rearrangement involving carbon→carbon migration was not achieved.[13]



Scheme 1. [1,4] Sigmatropic rearrangements involving dipolar intermediates.

A classification of [1,4] sigmatropic rearrangements involving dipolar intermediates is given in Scheme 1. The base-catalysed rearrangement (a) of *N*-allylammonium cations is believed to involve ylide intermediates which can participate in

either [1,2] or [1,4] rearrangements.[14–22] The competition between [1,2] and [1,4] sigmatropic rearrangements has been investigated[14–22] and both reactions were shown to proceed with predominant retention of configuration at the terminus of the migrating group (R = 1-phenylethyl).[14] Jenny and Druey[14] have proposed that [1,2] and [1,4] rearrangements both involve a tight ion-pair intermediate. More recently the proposal that the [1,2] sigmatropic rearrangement of ammonium ylides involves radical pair intermediates has been favoured.[23] The extension of this view to include a radical pair intermediate as the precursor of the [1,4] product is also possible. However, definitive experimental evidence on this possibility is not yet available. Radical pair intermediates have also been proposed for the [1,4] rearrangements (**b**)[24] and (**c**).[25]

The rearrangements (**d**) and (**e**) were explicitly recognised by Tenud, Farooq, Seibl, and Eschenmoser[26] as belonging to a special class of endocyclic intramolecular nucleophilic substitutions which could proceed in a concerted fashion. They also emphasised that concerted endocyclic reactions would involve retention of configuration at the terminus of the migrating group. However, our investigations[27–30] of the mechanism of the thermal transformation (**d**) of 2-oxyanilinium ylides has established that this [1,4] rearrangement does not proceed solely by a concerted pathway.[29] Support for the view that a non-concerted dissociation–recombination process could be involved was provided by the observation of a CIDNP effect and scrambling results obtained using specifically deuterium labelled *N*-allyl precursors.[29] These studies also demonstrated, using suitably substituted 2-oxyanilinium ylides, that the [1,4] sigmatropic rearrangement (**d**) could compete with [3,2][27,28] and [5,4][30] sigmatropic rearrangements.

The thermal rearrangement (**e**) of 2-alkoxypyridine *N*-oxides is a [1,4] rearrangement which has been the subject of mechanistic enquiry.[31–36] The isomerisation was discovered in 1964 by Dinan and Tieckelmann[31] who considered that the reaction proceeded either by intra- or inter-molecular nucleophilic attack by the exocyclic anionoid oxygen atom upon the O–R group. Homolytic processes were not considered to be involved in the rearrangement.[31] Subsequently, Litster and Tieckelmann[32] investigated the thermal rearrangement of 2-alkenyloxypyridine *N*-oxides and discovered that these compounds could participate either in [1,4] or in [3,3] sigmatropic processes.

Schöllkopf and Hoppe[33,34] have described their careful investigation of the thermal rearrangement of 2-alkoxypyridine *N*-oxides. With chiral O–R substituents it was shown that the rearrangement occurred with retention of configuration at the terminus of the migrating group. The reaction was shown to be first order with a small enthalpy of activation but a large negative entropy of activation. On the basis of these results, it was proposed that the [1,4] sigmatropic rearrangement of 2-alkoxypyridine *N*-oxides normally proceeds by a concerted process. However, in some cases, for example R = Ph_2CH, where the migrating group could form a stable free radical, the opinion was expressed that radical pair intermediates could be involved. This opinion was supported by observable CIDNP effects.[33,34]

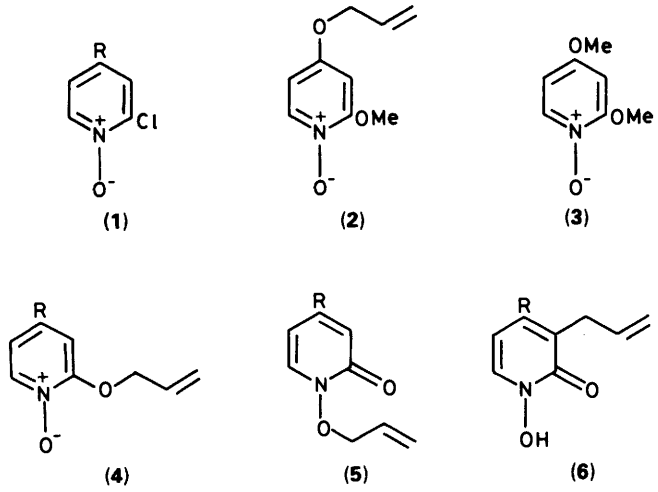
In an attempt to make a quantitative distinction between concerted and non-concerted pathways in [1,4] sigmatropic rearrangements, Gerhart and Wilde[35] have examined, in a carefully designed experiment, the thermal rearrangement of the *threo*- and *erythro*-isomers of 2-(1′,2′-diphenyl-2′-methylbutoxy)quinoline *N*-oxide. From the determination of product ratios and CIDNP intensity ratios, it was concluded that the minimum extent of rearrangement by radical pair pathways is for the *erythro*-isomer (75%) and for the *threo*-isomer (20%). However, it was emphasised that these figures are minimum values which are experimentally detectable. It is not possible, by these experimental methods, to distinguish between concerted pathways and pathways which involve closely interacting radical pair intermediates which do not give rise to observable CIDNP effects and do recombine stereospecifically with retention of configuration.

Le Noble and Daka[36a] have studied the effect of pressure on the rates of rearrangement of 2-benzyloxypyridine *N*-oxide and 2-benzhydryloxypyridine *N*-oxide. On the assumption that a concerted process would have a smaller transition state than an intermediate radical pair,[36b] then it was concluded that the [1,4] rearrangement of 2-benzyloxypyridine *N*-oxide was concerted, whereas that of 2-benzhydryloxypyridine *N*-oxide proceeded *via* radical pairs. This belief that there is a dependence of mechanism upon the nature of the migrating group imposes limitations upon the methods which can be usefully adopted for the experimental scrutiny of the rearrangement of 2-alkoxypyridine *N*-oxides. However, in view of the quantitative distinction[29] between concerted and non-concerted processes which was made possible using specifically labelled allyl substituents, it was decided to use allyl substituents as mechanistic probes of the [1,4] rearrangement (**e**) of 2-alkoxypyridine *N*-oxides. It is interesting to note that the thermal rearrangement of 2-allyloxypyridine *N*-oxides is obviously encouraged thermodynamically by the formation of conjugated pyridones. In contrast, [1,4] sigmatropic rearrangements are not observed[37] in the base-catalysed transformations of catechol mono-allyl ethers.

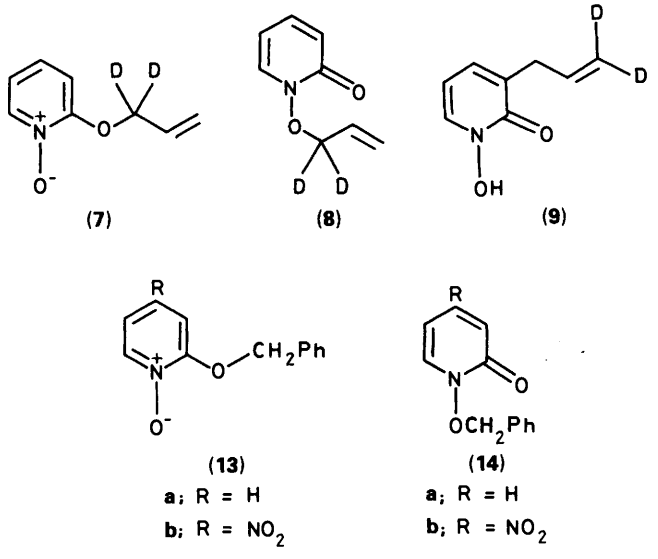
This survey of [1,4] sigmatropic rearrangements is concluded by reference to several others transformations which formally involve [1,4] shifts. However, their mechanisms have not yet been established and in some cases it is possible that a sequence of, for example, [1,2] shifts could be involved. Examples include (i) the acid-catalysed rearrangement of 10,10-dibenzyl-9-anthranols giving 9,10-dibenzylanthracenes,[38a] (ii) the promotion of the transannular rearrangement of 9,9-dibenzyl-9,10-dihydroanthracene to 9,10-dibenzylanthracene by triphenylmethyl tetrafluoroborate,[38b] (iii) a rearrangement of selenonium ylides which formally involves a [1,4] benzyl migration from selenium to oxygen,[38c] and (iv) the base-promoted rearrangement of 10-aryl-10-thiaanthracenes to the corresponding 9-substituted thioxanthenes.[38d] The last reaction (iv) involves a formal [1,4] aryl shift. In a particularly challenging but frustrating investigation, it was eventually established that this reaction (iv) is the first example of an asymmetric induction in the transfer of chirality from sulphur to carbon accompanying an intramolecular [1,4] rearrangement.[38e] Considerable interest has been shown in the mechanism of [1,4] alkyl migrations which are observed in some Fischer indole cyclisations.[39] These considerations necessarily involve some of the uncertainty which still exists regarding the details of the bond-forming and bond-breaking processes associated with the benzidine rearrangement, the Fischer indole synthesis and mechanistically related reactions.[39a] However, the experimental evidence currently available[39b,39c] suggests that the [1,4] alkyl migrations which do occur in some Fischer indole cyclisations could well involve either three [1,2] shifts or one [1,5] shift followed by a [1,2] shift. Clearly [1,4] sigmatropic rearrangements provide an area of mechanistic investigation which still demands careful experimental enquiry.

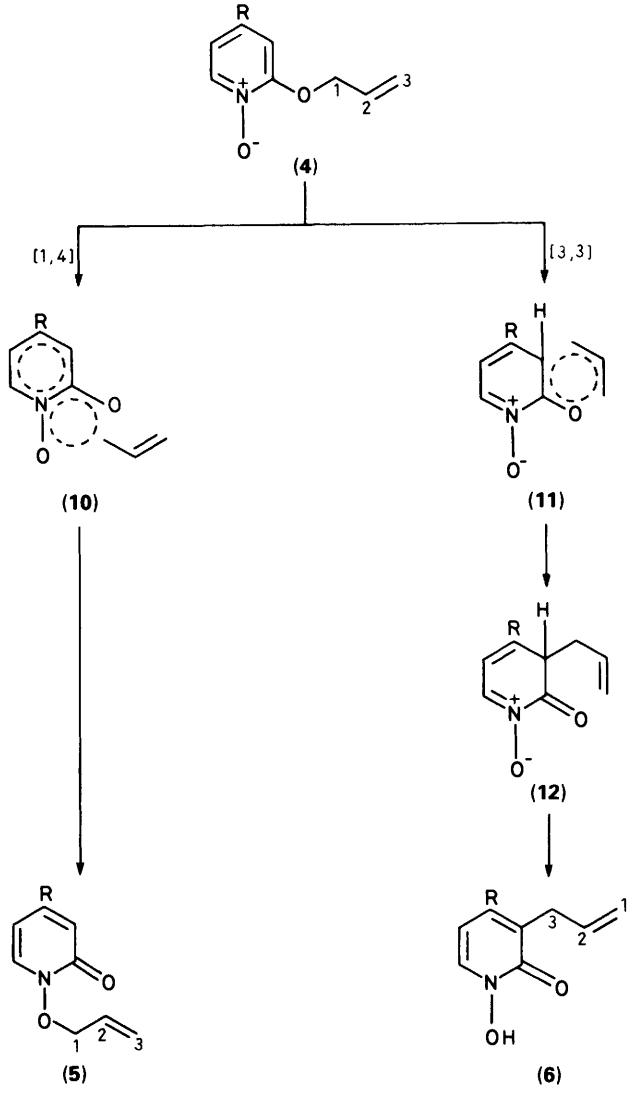
Results and Discussion

The decision to examine the thermal rearrangements of 2-allyloxy-4-substituted pyridine *N*-oxides required the synthesis of 2-chloro-4-substituted pyridine *N*-oxides (**1a–c**). Nucleophilic substitution of 2-chloropyridine *N*-oxide[40,41] (**1a**) and 2-chloro-4-nitropyridine *N*-oxide (**1b**) proceeded normally with sodium allyl oxide in tetrahydrofuran yielding 2-allyloxypyridine *N*-



In formulae (1), (4), (5), and (6): **a**, R = H; **b**, R = NO_2; **c**, R = OMe.





Scheme 2. Regiospecific [1,4] and [3,3] sigmatropic rearrangements of 2-allyloxypyridine *N*-oxide (**4**).

oxide[31,32] (**4a**) and 2-allyloxy-4-nitropyridine *N*-oxide (**4b**).[42,43] However, a similar reaction between 2-chloro-4-methoxypyridine *N*-oxide[44,45] (**1c**) and sodium allyloxide yielded an unexpected result: the product was a mixture of the expected 2-allyloxy-4-methoxypyridine *N*-oxide (**4c**) and the unexpected 4-allyloxy-2-methoxypyridine *N*-oxide (**2**). The formation of the latter isomer by a nucleophilic displacement of the 4-methoxy group by the allyloxide anion was supported by the reaction between 2,4-dimethoxypyridine *N*-oxide (**3**)[44] and sodium allyl oxide. This also yielded a mixture of 2-allyloxy-4-methoxypyridines *N*-oxide (**4c**) and 4-allyloxy-2-methoxypyridine *N*-oxide (**2**). The availability of the 2-allyloxypyridine *N*-oxides (**4a–c**) permitted the examination of solvent and substituent effects upon the thermal rearrangement of pyridine *N*-oxides.

2-Allyloxypyridine *N*-oxide (**4a**) in boiling dimethylformamide was smoothly transformed during 2.5 h at 154 °C into *N*-allyloxy-2-pyridone (**5a**) (yield 12%) and 3-allyl-*N*-hydroxy-2-pyridone (**6a**) (yield 88%). In dramatic contrast, when 2-allyloxypyridine *N*-oxide was heated at 160 °C during 2 h in the absence of solvent, then the relative yields of the thermal isomers (**5a**) (yield 95%) and (**6a**) (yield 5%) were strikingly different. Furthermore, it was established that the thermal isomers (**5a**) and (**6a**) did not interconvert and were stable under thermal conditions that were more vigorous than those which were associated with the transformation (**4a**) ⟶ (**5a**) + (**6a**).

These results raised interesting questions regarding the mechanism of the thermal isomerisation of 2-allyloxypyridine *N*-oxide (**4a**). In principle, the thermal isomers (**5a**) and (**6a**) could have been produced, either by concerted [1,4] and [3,3] sigmatropic rearrangement, or the precursor (**4a**) could have been transformed into an intermediate radical pair which could then recombine giving *N*-allyloxy-2-pyridone (**5a**) and 3-allyl-*N*-hydroxy-2-pyridone (**6a**). An experimental distinction between these two pathways was based upon the premise that the concerted reactions would be regiospecific in relation to the allyl group, whereas scrambling of the allyl group might be a consequence of its participation as an allyl radical in a radical pair. In the event, specifically labelled 2-(1,1-dideuterioallyloxy)-pyridine *N*-oxide (**7**) was synthesised from 1,1-dideuterioallyl alcohol.[46] Its thermal transformation in dimethylformamide (100 °C; 25 h) yielded the [1,4] product (**8**) and the [3,3] product (**9**) regiospecifically. This result directly supports the view summarised in Scheme 2 that the thermal transformation (**4**) ⟶ (**5**) + (**6**) involves concerted [1,4] and [3,3] sigmatropic rearrangements associated with the transition states (**10**) and (**11**). Transition state (**11**) leads to the intermediate dienone (**12**) which is a tautomer of the [3,3] product (**6**).

It is inconceivable that the regiospecificity associated with the [1,4] and [3,3] sigmatropic rearrangements of 2-allyloxy-

pyridine *N*-oxide (Scheme 2; R = H) could be satisfactorily interpreted in terms of *two* independent dissociation–recombination processes involving *two* topologically different but tight radical pairs. However, it must be emphasised that this result applies to one compound and it does not follow that thermal rearrangements of all 2-alkoxypyridine *N*-oxides proceed only by concerted reactions.

Periselectivity between the [1,4] and [3,3] sigmatropic rearrangements of 2-allyloxypyridine *N*-oxide (**4a**) is clearly influenced by reaction temperature and solvent (Table 1). Analogous results for the thermal rearrangements of 2-(1,1-dideuterioallyloxy)pyridine *N*-oxide (**7**) are given in Table 2.

The results (Tables 1 and 2) show informative solvent and temperature effects. Solvents of low polarity favour the [1,4] sigmatropic rearrangement, whereas solvents of high polarity favour the [3,3] sigmatropic rearrangement. These observations are in accord with the views summarised in Scheme 2. Thus, the [1,4] sigmatropic rearrangement proceeds from the dipolar precursor (**4**), *via* the transition state (**10**), to the product (**5**). The development of the transition state (**10**) is associated with charge dissipation so that the sequence (**4**) ⟶ (**10**) ⟶ (**5**) could operate satisfactorily in a low polarity solvent. In contrast, a concerted [3,3] sigmatropic rearrangement involves the sequence (**4**) ⟶ (**11**) ⟶ (**12**) ⟶ (**6**) in which there is a maintenance of charge separation in the transition state (**11**). The [3,3] sigmatropic rearrangement would therefore be encouraged in solvents of high polarity. The [1,4] sigmatropic rearrangement is obviously preferred when 2-alloxypyridine *N*-oxide is kept in a molten state in the absence of solvent.

Temperature effects (Tables 1 and 2) show the trend that higher temperatures favour the [3,3] sigmatropic rearrangement with respect to the [1,4] rearrangement. This indicates that the activation energy, E_a, for the [3,3] sigmatropic rearrangement is larger than the activation energy for the [1,4] sigmatropic rearrangement.

Possible influence by substituent effects upon the [1,4] and [3,3] sigmatropic rearrangements (Scheme 2; R = NO_2 or OMe) have been examined using 2-allyloxy-4-nitropyridine *N*-oxide (**4b**) (Table 3) and 2-allyloxy-4-methoxypyridine *N*-oxide (**4c**) (Table 4). Mechanistically informative substituent effects are not observed, but clearly the rates of the [1,4] and [3,3] sigmatropic rearrangements are both increased by the 4-nitro substituent. A most remarkable result was obtained when 2-allyloxy-4-nitropyridine *N*-oxide was stored in the refrigerator. During 13 months at −15 °C it was transformed quantitatively in the solid state into the [1,4] product (**5b**). 2-Allyloxypyridine *N*-oxide was stable under these conditions.

In view of the accelerating effect of the nitro group upon the rate of the rearrangement (**4b**) ⟶ (**5b**) + (**6b**) a comparative study has been made of the influence of a 4-nitro substituent upon the [1,4] rearrangement of 2-benzyloxypyridine *N*-oxides (**13a**)[31] and (**13b**). At 100 °C in the absence of solvent the rearrangement (**13a**)⟶(**14a**) requires 12 h, whereas under the same conditions the rearrangement (**13b**)⟶(**14b**) requires 1 h.

Experimental

Unless otherwise stated, IR spectra were measured in chloroform and 220 MHz ^{1}H NMR spectra in deuteriochloroform (tetramethylsilane as internal reference). Only significant bands from these spectra are quoted. Mass spectra were determined using AEI MS-9 and MS-12 high resolution mass spectrometers. M.p.s were determined using a Kofler hot stage apparatus and are uncorrected. Extracts were dried with either anhydrous magnesium sulphate or anhydrous sodium sulphate. Evaporation refers to evaporation under diminished pressure.

Separations by column chromatography were carried out using silica gel (Whatman, CT SO TLC) and aluminium oxide (Whatman, Basic CT APPO). Merck Kieselgel G was used for preparative thick layer and thin layer chromatography. Products were located by examination under UV illumination or by exposure to iodine vapour. When necessary, Hyflo Supercel (Hopkin and Williams) was used to assist filtration.

Deuterium labelled alcohols were prepared using lithium aluminium deuteride (Fluka; >99 atom % pure). Sodium hydride (Koch-Light) was supplied as a 50% dispersion in mineral oil. Before use, the mineral oil was removed by washing with anhydrous pentane and the residual solvent was evaporated. Light petroleum refers to the fraction (b.p. 40–60 °C).

When substances are stated to be identical, their identity has been established by comparison of m.p. and mixed m.p. and, where appropriate, comparison of IR, NMR, and mass spectra and their behaviour on thin layer chromatography.

2-*Chloropyridine* N-*Oxide* (**1a**).—Aqueous hydrogen peroxide (27.5% w/v; 136 ml) was added to a solution of 2-chloropyridine (57 g) in glacial acetic acid (380 ml) and the mixture was heated (80 °C) for 12 h. Concentration (to 150 ml) under diminished pressure, chloroform extraction, and recrystallisation from ethanol–ether gave 2-chloropyridine *N*-oxide (48.6 g, 75%) as colourless rhombs, m.p. 66–68 °C (lit.,[40] 67–68.5 °C; lit.,[41] 69–69.5 °C); ν_{max} 2 990, 1 470, 1 420, 1 270, 1 140, and 1 080 cm^{-1}; δ 7.19–7.48 (m, 3-H and 5-H), 7.48–7.70 (m, 4-H), and 8.30–8.50 (m, 6-H).

2-*Chloro*-4-*nitropyridine* N-*Oxide* (**1b**).—Nitration of 2-chloropyridine *N*-oxide[40,41] gave 2-chloro-4-nitropyridine *N*-oxide (93%) as yellow plates, m.p. 156–157 °C from acetone (lit.,[42] 140–143 °C; lit.,[43] 152–153 °C); ν_{max} 1 580, 1 510, 1 460, 1 410, 1 345, 1 300, 1 150, and 895 cm^{-1}; δ 8.40 (d, *J* 3 Hz, 3-H), 8.08 (dd, *J* 7 and 3 Hz, 5-H), and 8.44 (d, *J* 7 Hz, 6-H).

2-*Chloro*-4-*methoxypyridine* N-*Oxide* (**1c**).—An ice-cold solution of sodium hydride (96 mg) in methanol (40 ml) was added to a solution of 2-chloro-4-nitropyridine *N*-oxide (700 mg) in methanol (10 ml) at 0 °C. After 30 min at 0 °C [monitored by TLC (chloroform–methanol, 80:20)] the reaction was complete. Evaporation of methanol, addition of water (150 ml), extraction with chloroform, short-path column chromatography (silica gel; chloroform–methanol, 80:20), and evaporation yielded 2-chloro-4-methoxypyridine *N*-oxide (447 mg, 70%) as colourless rhombs, m.p. 79–81 °C (decomp.) (lit.,[44] 82 °C; lit.,[45] 82 °C) (Found: $M^{+\bullet}$, 159. Calc. for $C_6H_6ClNO_2$: *M*, 159); ν_{max} 2 980, 1 620, 1 540, 1 480, 1 425, 1 300, 1 070, and 1 025 cm^{-1}; δ 7.09 (d, *J* 3.5 Hz, 3-H), 6.87 (dd, *J* 7.5 and 3.5 Hz, 5-H), 8.28 (d, *J* 7.5 Hz, 6-H), and 3.90 (s, OCH_3). This compound is unstable[45] and must be stored at −20 °C.

2-*Allyloxypyridine* N-*Oxide* (**4a**).—Redistilled allyl alcohol (1.16 g) in tetrahydrofuran (15 ml) was added dropwise to a stirred suspension of sodium hydride (430 mg) in tetrahydrofuran (25 ml). After 15 min, 2-chloropyridine *N*-oxide (1.29 g) in tetrahydrofuran (10 ml) was added and the mixture was stirred at room temperature. After 4 h [monitored by TLC (chloroform–methanol, 94:6)], the reaction was complete. Filtration (Hyflo Supercel), evaporation, short-path column chromatography (silica gel; chloroform–methanol, 94:6), and recrystallisation from ethyl acetate–light petroleum gave 2-allyloxypyridine *N*-oxide (1.09 g, 73%) as colourless, hygroscopic rhombs, m.p. 48–55 °C (lit.,[31,32] oil); ν_{max} 2 980, 1 610, 1 570, 1 500, 1 440, 1 315, 1 275, 1 119, and 990 cm^{-1}; δ 6.85–7.05 (m, 3-H and 5-H), 7.29 (dt, *J* 7 and 2 Hz, 4-H), 8.28 (dd, *J* 7 and 2 Hz, 6-H), $ABCX_2$ system, δ_A 5.46, δ_B 5.37, δ_C 6.07, δ_X 4.88 [J_{AB} 1, J_{AC} 18, J_{BC} 10, J_{CX} 6 Hz; $OC(H_X)_2CH_C{=}CH_AH_B$].

Table 1. Thermal rearrangement of 2-allyloxypyridine *N*-oxide (**4a**) in various solvents under various conditions. The last three entries refer to product ratios on heating the molten *N*-oxide alone.

Solvent	Temp. (°C)	Time (h)	Product composition (%)		
			N-Oxide (**4a**)	[1,4] Rearrangement product (**5a**)	[3,3] Rearrangement product (**6a**)
Tetrachloroethylene	100	24	61	34	5
Toluene	100	24	60	30	10
Dioxane	100	24	51	26	23
Diethyl ketone	100	24	47	21	32
Aniline	100	24	41	15	44
Dimethyl sulphoxide	100	24	0	43	57
	140	6	0	17	83
	180	1.5	0	12	88
Dimethylformamide	80	48	83	5	12
	100	3	89	2	8
	100	24	28	9	63
	120	12	7	7	86
	154	2.5	0	12	88
Formamide	100	24	0	9	91
	160	3.5	0	2	98
Water	100	10	0	8	92
No solvent	100	3.5	4	87	9
	100	20	0	91	9
	160	2	0	95	5

Table 2. Thermal rearrangement of 2-(1,1-dideuterioallyloxy)pyridine *N*-oxide (**7**) in [$^2H_6$]dimethyl sulphoxide and [$^2H_7$]dimethylformamide at 100 °C. The last entry refers to the product ratio on heating the molten *N*-oxide alone at 100 °C.

Solvent	Time (h)	Product composition (%)		
		N-Oxide (**7**)	[1,4] Rearrangement product (**8**)	[3,3] Rearrangement product (**9**)
[$^2H_6$]Dimethyl sulphoxide	1	80	9	11
	2	67	13	20
	4	49	23	28
	8	33	30	37
	12	30	32	38
	20	13	42	44
	24	6	44	50
	28	0	46	54
[$^2H_7$]Dimethylformamide	1	98	0	2
	2	84	0	16
	4	78	4	18
	8	67	8	25
	14	51	10	39
	26	24	17	59
	36	15	20	65
	40	11	22	67
	46	0	24	76
No solvent	2.5	20	75	5

2-(1,1-*Dideuterioallyloxy)pyridine* N-*Oxide* (**7**).—2-Chloropyridine *N*-oxide and 1,1-dideuterioallyl alcohol[46] gave, using the procedure described in the preceding experiment, 2-(1,1-*dideuterioallyloxy)pyridine* N-*oxide* as colourless, hygroscopic rhombs, m.p. 43–45 °C (Found: $M^{+\cdot}$, 153. $C_8H_7D_2NO_2$ requires *M*, 153). The NMR spectrum corresponded with that of the preceding compound except that no signal was observed at δ_X 4.88 and the multiplicity of the signal assigned to H_C of the allyl group was simplified to a double doublet (J_{AC} 18, J_{BC} 10 Hz).

2-*Allyloxy*-4-*nitropyridine* N-*Oxide* (**4b**).—As in the preceding experiment, redistilled allyl alcohol (1.74 g) in tetrahydrofuran (20 ml) was added at 0 °C with stirring to a suspension of sodium hydride (720 mg) in tetrahydrofuran (20 ml). After 25 min, a solution of 2-chloro-4-nitropyridine *N*-oxide (1.74 g) in tetrahydrofuran (15 ml) was added and the mixture stirred at room temperature. After 50 min [monitored by TLC (chloroform–methanol, 92:8)] the reaction was complete. Isolation as in the preceding experiment yielded 2-*allyloxy*-4-*nitropyridine* N-*oxide* (870 mg, 44%) as yellow rhombs, m.p. 73–75 °C, from ethyl acetate–pentane (Found: C, 49.0; H, 4.2; N, 14.4%; $M^{+\cdot}$, 196.0483. $C_8H_8N_2O_4$ requires C, 49.0; H, 4.1; N, 14.3%; *M*, 196.0484); ν_{max} 3 000, 1 610, 1 530, 1 500, 1 350, 1 300, 1 100, 1 000, and 945 cm^{-1}; δ([$^2H_6$]acetone) 8.22 (s, 3-H), 8.19 (d, *J* 5.5 Hz, 5-H), 8.70 (d, *J* 5.5 Hz, 6-H), $ABCX_2$ system, δ_A 5.85, δ_B 5.65, δ_C 6.43, δ_X 5.31 [J_{AC} 18, J_{BC} 10, J_{CX} 5.5 Hz; $OC(H_X)_2CH_C{=}CH_AH_B$].

Table 3. Thermal rearrangement of 2-allyloxy-4-nitropyridine *N*-oxide (**4b**) in various solvents under various conditions. The last two entries refer to (i) heating the molten *N*-oxide alone and (ii) keeping the crystalline *N*-oxide in a refrigerator.

			Product composition (%)		
Solvent	Temp. (°C)	Time (h)	*N*-Oxide (**4b**)	[1,4] Rearrangement product (**5b**)	[3,3] Rearrangement product (**6b**)
Tetrachloroethylene	100	1	27	60	13
Toluene	100	1	21	56	23
Diethyl ketone	100	1	12	51	37
Dioxane	100	1	11	49	40
Aniline	100	1	9	41	50
Dimethyl sulphoxide	100	1	6	40	54
Dimethylformamide	100	1	4	38	58
Water	100	1	0	24	76
Tetrahydrofuran	60	9	0	53	47
Benzene	80	6	0	68	32
No solvent	100	1.5	0	47	53
No solvent	−15	13 months	0	100	0

Table 4. Thermal rearrangement of 2-allyloxy-4-methoxypyridine *N*-oxide (**4c**) in various solvents under various conditions.

			Product composition (%)		
Solvent	Temp. (°C)	Time (h)	*N*-Oxide (**4c**)	[1,4] Rearrangement product (**5c**)	[3,3] Rearrangement product (**6c**)
Tetrachloroethylene	100	2	83	17	0
Dimethylformamide	100	2	66	21	13
	154	2	0	40	60
Water	100	3	30	14	56

2-Allyloxy-4-methoxypyridine N-*Oxide* (**4c**) *and* 4-*Allyloxy-2-methoxypyridine* N-*Oxide* (**2**).—As in the preceding experiment, redistilled allyl alcohol (580 mg) in tetrahydrofuran (10 ml) was added at 0 °C with stirring to a suspension of sodium hydride (240 mg) in tetrahydrofuran (20 ml). After 15 min, a solution of 2-chloro-4-methoxypyridine *N*-oxide (790 mg) in tetrahydrofuran (10 ml) was added and the mixture was kept at room temperature for 30 min. Filtration (Hyflo Supercel) and evaporation gave a product which was shown to be a mixture of two compounds by TLC (alumina; methanol–dichloromethane, 5:95). Fractionation by column chromatography (alumina; dichloromethane followed by methanol–dichloromethane, 12:88) gave two products. 4-*Allyloxy-2-methoxypyridine* N-*oxide* (90 mg, 10%) was obtained as a colourless oil (Found: C, 59.4; H, 6.1; N, 7.6%; $M^{+\bullet}$, 181. $C_9H_{11}NO_3$ requires C, 59.6; H, 6.1; N, 7.7%; *M*, 181); ν_{max} 2 930, 1 600, 1 570, 1 480, 1 410, 1 330, 1 200, 1 160, and 1 040 cm^{-1}; δ 6.20 (d, *J* 3 Hz, 3-H), 6.43 (dd, *J* 7.5 and 3 Hz, 5-H), 7.90 (d, *J* 7.5 Hz, 6-H), $ABCX_2$ system, δ_A 5.35, δ_B 5.20, δ_C 6.06, δ_C 6.06, δ_X 4.81 [J_{AC} 16, J_{BC} 10, J_{CX} 5.5 Hz; $OC(H_X)_2CH_C{=}CH_AH_B$], and δ 3.74 (s, OCH_3).

2-Allyloxy-4-methoxypyridine N-*oxide* (460 mg, 52%) crystallised from ethyl acetate–hexane as colourless rhombs, m.p. 79–81 °C (Found: C, 59.4; H, 6.2; N, 7.9%; $M^{+\bullet}$, 181. $C_9H_{11}NO_3$ requires C, 59.6; H, 6.1; N, 7.7%; *M*, 181); ν_{max} 2 950, 1 625, 1 560, 1 495, 1 430, 1 320, 1 185, and 1 165 cm^{-1}; δ 6.25 (m, 3-H), 6.25 (m, 5-H), 8.15 (d, *J* 7 Hz, 6-H), $ABCX_2$ system, δ_A 5.46, δ_B 5.34, δ_C 6.08, δ_X 4.86 [J_{AC} 18, J_{BC} 11, J_{CX} 5.5 Hz; $OC(H_X)_2CH_C{=}CH_AH_B$], and δ 3.86 (s, OCH_3).

2,4-Dimethoxypyridine N-*Oxide* (**3**).—2-Chloro-4-nitropyridine *N*-oxide (1.0 g) was added to a solution of sodium (430 mg) in anhydrous methanol (40 ml). The mixture was heated under reflux (1 h), concentrated, diluted with water, and extracted with chloroform. Evaporation and crystallisation from ethyl acetate–hexane yielded 2,4-dimethoxypyridine *N*-oxide (620 mg, 70%) as colourless rhombs, m.p. 85–86 °C (lit.,[44] 85 °C); ν_{max} 2 960, 1 630, 1 570, 1 505, 1 485, 1 435, 1 190, 1 025, and 905 cm^{-1}; δ 6.45 (d, *J* 3 Hz, 3-H), 6.50 (dd, *J* 7 and 3 Hz, 5-H), 8.15 (d, *J* 7 Hz, 6-H), 4.06 (s, OCH_3), and 3.87 (s, OCH_3).

Reaction of 2,4-*Dimethoxypyridine* N-*Oxide* (**3**) *with Sodium Allyl Oxide: Formation of* 4-*Allyloxy-2-methoxypyridine* N-*Oxide* (**2**) *and* 2-*Allyloxy-4-methoxypyridine* N-*Oxide* (**4c**).—Redistilled allyl alcohol (580 mg) in tetrahydrofuran (15 ml) was added dropwise to a stirred suspension of sodium hydride (240 mg) in tetrahydrofuran. After 20 min a solution of 2,4-dimethoxypyridine *N*-oxide (770 mg) in tetrahydrofuran (20 ml) was added and the mixture was kept at room temperature for 1.5 h. Work-up as in the above experiment yielded 4-allyloxy-2-methoxypyridine *N*-oxide (370 mg, 41%) and 2-allyloxy-4-methoxypyridine *N*-oxide (390 mg, 44%), identical with authentic samples.

Thermal Transformation of 2-*Allyloxypyridine* N-*Oxide* (**4a**).—(i) *Formation of* N-*allyloxy-2-pyridone* (**5a**) *and* 3-*allyl*-N-*hydroxy-2-pyridone* (**6a**). A solution of 2-allyloxypyridine *N*-oxide (120 mg) in dimethylformamide (25 ml) was heated at 100 °C for 12 h. Evaporation gave a residue which was partitioned between aqueous sodium hydroxide (0.5M; 30 ml) and chloroform.

The residue obtained by evaporation of the chloroform extract was fractionated by short-path column chromatography (silica gel; chloroform–methanol, 97:3) giving *N*-allyloxy-2-pyridone (43 mg, 36%) and unchanged 2-allyloxypyridine *N*-oxide (12 mg, 10%). The aqueous alkaline extract was acidified and extracted with chloroform. These extracts yielded 3-allyl-*N*-hydroxy-2-pyridone (58 mg, 48%). *N*-Allyloxy-2-pyridone was obtained as an oil (lit.,[31] oil); $\nu_{max}(CCl_4)$ 1 680, 1 600, 1 532, 1 275, 1 140, 1 100, and 940 cm^{-1}; δ 6.66 (dd, *J* 8 and 2 Hz, 3-H), 7.30 (dt, *J* 8 and 2 Hz, 4-H), 5.95–6.18 (m, 5-H), and

7.48 (dd, J 7 and 2 Hz, 6-H), $ABCX_2$ system, δ_A 5.26–5.45, δ_B 5.26–5.45, δ_C 5.95–6.18, δ_X 4.78 [J_{CX} 7 Hz; other coupling constants could not be determined by first order analysis due to overlap of signals; $OC(H_X)_2CH_C{=}CH_AH_B$].

3-Allyl-*N*-hydroxy-2-pyridone was obtained as colourless rhombs, m.p. 93–95 °C, from carbon tetrachloride (lit.,[32] 92–94 °C) (Found: $M^{+\bullet}$, 151.0633. Calc. for $C_8H_9NO_2$: M, 151.0633); ν_{max} 3 000, 1 640, 1 555, 1 430, and 1 360 cm^{-1}; δ 7.23 (d, J 7 Hz, 4-H), 6.28 (t, J 7 Hz, 5-H), 7.68 (d, J 7 Hz, 6-H), $ABCX_2$ system, δ_A 5.05–5.19, δ_B 5.05–5.19, δ_C 5.94, δ_X 3.35 [J_{AC} 17, J_{BC} 10, J_{CX} 7 Hz; $C(H_X)_2CH_C{=}CH_AH_B$], and δ 8.9–9.6 (br s, OH).

(ii) *Solvent effects upon the thermal transformation of* 2-*allyloxypyridine* N-*oxide* (**4a**). Samples of 2-allyloxypyridine *N*-oxide (20 mg) were heated in a sealed NMR tube in various solvents (10 ml) for the indicated times and temperatures (Table 1). The relative proportions of starting material and the two thermal rearrangement products were determined from the integrated intensities of the signals (δ 8.28, 4.78, and 3.35). These signals correspond to 2-allyloxypyridine *N*-oxide (δ 8.28; 6-H), *N*-allyloxy-2-pyridone (δ 4.78; H_X), and 3-allyl-*N*-hydroxy-2-pyridone (δ 3.35; H_X).

(iii) *Thermal stability of* N-*allyloxy-2-pyridone* (**5a**) *and* 3-*allyl*-N-*hydroxy-2-pyridone* (**6a**). Solutions of the thermal isomers (15 mg) in [$^2H_6$]dimethyl sulphoxide (15 ml) were heated in sealed NMR tubes for 36 h at 100 ± 1 °C and then for a further 12 h at 185 ± 1 °C. No change was observed in the NMR spectra which were determined after these periods.

Thermal Transformation of 2-(1,1-*Dideuterioallyloxy*)*pyridine* N-*Oxide* (**7**).—(i) *Formation of* N-(1,1-*dideuterioallyloxy*)-2-*pyridone* (**8**) *and* 3-(3,3-*dideuterioallyl*)-N-*hydroxy*-2-*pyridone* (**9**). A solution of 2-(1,1-dideuterioallyloxy)pyridine *N*-oxide (50 mg) in dimethylformamide (10 ml) was heated (100 ± 1 °C) for 25 h. Work-up as described in experiment (i) of the preceding section gave N-(1,1-*dideuterioallyloxy*)-2-*pyridone* (20 mg, 40%) and 3-(3,3-*dideuterioallyl*)-N-*hydroxy*-2-*pyridone* (25 mg, 50%).

N-(1,1-Dideuterioallyloxy)-2-pyridone was obtained as a colourless oil (Found: $M^{+\bullet}$, 153. $C_8H_7D_2NO_2$ requires M, 153). The NMR spectrum corresponded exactly with that of authentic *N*-allyloxy-2-pyridone (see above) except that no signal was observed at δ_X 4.78 and the multiplicity of the signal assigned to H_C of the allyl group was simplified to a double doublet (δ_C 5.95–6.12).

3-(3,3-Dideuterioallyl)-*N*-hydroxy-2-pyridone was obtained as colourless crystals, m.p. 88–89 °C, from ethyl acetate (Found: $M^{+\bullet}$, 153. $C_8H_7D_2NO_2$ requires M, 153). The NMR spectrum corresponded exactly with that of authentic 3-allyl-*N*-hydroxy-2-pyridone (see above) except that no signal was observed at δ_A and δ_B 5.05–5.19 and the multiplicity of the signal assigned to H_C of the allyl group was simplified to a triplet (δ_C 5.94, J_{CX} 7 Hz).

(ii) *Thermal transformation of* 2-(1,1-*dideuterioallyloxy*)*pyridine* N-*oxide* (**7**) *in* [$^2H_6$]*dimethyl sulphoxide and* [$^2H_7$]*dimethylformamide for various times.* These experiments were carried out essentially following the procedures described in experiment (ii) of the preceding section. The results are recorded in Table 2.

Thermal Transformation of 2-*Allyloxy*-4-*nitropyridine* N-*Oxide* (**4b**).—(i) *Formation of* N-*allyloxy*-4-*nitro*-2-*pyridone* (**5b**) *and* 3-*allyl*-N-*hydroxy*-4-*nitro*-2-*pyridone* (**6b**). The *N*-oxide (50 mg) was heated (100 ± 1 °C) in a sealed, evacuated tube for 2 h. Work-up as in experiment (i) of the preceding section gave N-*allyloxy*-4-*nitro*-2-*pyridone* (23 mg, 46%) and 3-*allyl*-N-*hydroxy*-4-*nitro*-2-*pyridone* (25 mg, 50%).

N-Allyloxy-4-nitro-2-pyridone crystallised from ethyl acetate–pentane as yellow rhombs, m.p. 103–106 °C (Found: C, 49.1; H, 4.0; N, 14.1%; $M^{+\bullet}$, 196.0485. $C_8H_8N_2O_4$ requires C, 49.0; H, 4.1; N, 14.3%; M, 196.0484); ν_{max} 3 120, 1 640, 1 600, 1 550, 1 430, and 1 360 cm^{-1}; δ 7.78 (s, 3-H), 7.83 (dd, J 7 and 2 Hz, 5-H), 8.37 (d, J 7 Hz, 6-H), and $ABCX_2$ system, δ_A 5.56, δ_B 5.48, δ_C 6.11, δ_X 4.96 [J_{AC} 18, J_{BC} 10, J_{CX} 5 Hz; $OC(H_X)_2$-$CH_C{=}CH_AH_B$].

3-Allyl-*N*-hydroxy-4-nitro-2-pyridone was obtained as a colourless oil (Found: C, 48.7; H, 4.0; N, 14.1%; $M^{+\bullet}$, 196.0483. $C_8H_8N_2O_4$ requires C, 49.0; H, 4.1; N, 14.3%; M, 196.0484); ν_{max} 2 940, 1 680, 1 610, 1 530, 1 350, 1 300, 1 100, and 1 000 cm^{-1}; δ 6.73 (d, J 6 Hz, 5-H), 7.88 (d, J 6 Hz, 6-H), and $ABCX_2$ system, δ_A 5.19, δ_B 5.11, δ_C 5.89, δ_X 3.59 [J_{AC} 18, J_{BC} 10, J_{CX} 5 Hz; $C(H_X)_2CH_C{=}CH_AH_B$].

(ii) *Solvent effects upon the thermal transformation of* 2-*allyloxy*-4-*nitropyridine* N-*oxide* (**4b**). Investigation as in the corresponding study of 2-allyloxypyridine *N*-oxide (**4a**) [experiment (ii)] gave the results summarised in Table 3. The relative proportions of starting material (**4b**) and the two rearrangement products (**5b**) and (**6b**) were determined from the integrated intensities of the signals (δ 5.31, 4.96, and 3.59). These signals correspond to 2-allyloxy-4-nitropyridine *N*-oxide (δ 5.31; H_X), *N*-allyloxy-4-nitro-2-pyridone (δ 4.96; H_X), and 3-allyl-*N*-hydroxy-4-nitro-2-pyridone (δ 3.59; H_X).

Thermal isomerisation of the *N*-oxide (**4b**) in the absence of solvent either on heating (100 °C; 1.5 h) or refrigeration (−15 °C; 13 months) is also recorded in Table 3.

(iii) *Thermal stability of* N-*allyloxy*-4-*nitro*-2-*pyridone* (**5b**) *and* 3-*allyl*-N-*hydroxy*-4-*nitro*-2-*pyridone* (**6b**). This was established as for the thermal isomers (**5a**) and (**6a**) [experiment (iii)].

Thermal Transformation of 2-*allyloxy*-4-*methoxypyridine* N-*Oxide* (**4c**).—(i) *Formation of* N-*allyloxy*-4-*methoxy*-2-*pyridone* (**5c**) *and* 3-*allyl*-N-*hydroxy*-4-*methoxy*-2-*pyridone* (**6c**). As in previous experiments (i), 2-allyloxy-4-methoxypyridine *N*-oxide (100 mg) in dimethylformamide (20 ml) was heated under reflux for 2 h to yield N-*allyloxy*-4-*methoxy*-2-*pyridone* (32 mg, 32%) and 3-*allyl*-N-*hydroxy*-4-*methoxy*-2-*pyridone* (48 mg, 48%).

N-Allyloxy-4-methoxy-2-pyridone crystallised from ethyl acetate–pentane as colourless rhombs, m.p. 98–100 °C (Found: C, 59.4; H, 6.1; N, 7.5%; $M^{+\bullet}$, 181. $C_9H_{11}NO_3$ requires C, 59.6; H, 6.1; N, 7.7%; M, 181); ν_{max} 2 990, 1 665, 1 605, 1 545, 1 480, and 1 345 cm^{-1}; δ 5.95 (d, J 3 Hz, 3-H), 5.78 (dd, J 7.5 and 3 Hz, 5-H), 7.31 (d, J 7.5 Hz, 6-H), $ABCX_2$ system, δ_A 5.25–5.43, δ_B 5.25–5.43, δ_C 6.05, δ_X 4.74 [J_{AC} 16, J_{BC} 10, J_{CX} 7 Hz; $OC(H_X)_2CH_C{=}CH_AH_B$], and δ 3.73 (s, OCH_3).

3-Allyl-*N*-hydroxy-4-methoxy-2-pyridone crystallised from ethyl acetate–hexane as colourless rhombs, m.p. 119–120 °C (Found: C, 59.6; H, 5.9; N, 7.8%; $M^{+\bullet}$, 181. $C_9H_{11}NO_3$ requires C, 59.6; H, 6.1; N, 7.7%; M, 181); ν_{max} 2 990, 1 635, 1 550, 1 460, 1 430, and 1 260 cm^{-1}; δ 6.10 (d, J 8 Hz, 5-H), 7.67 (d, J 8 Hz, 6-H), $ABCX_2$ system, δ_A 4.85–5.05 δ_B 4.85–5.05, δ_C 5.78–5.97, δ_X 3.29 [J_{CX} 5.5 Hz; other coupling constants could not be determined by first order analysis due to overlap of signals; $C(H_X)_2CH_C{=}CH_AH_B$], δ 10.3–11.1 (br s, OH), and 3.82 (s, OCH_3).

(ii) *Solvent effects upon the thermal transformation of* 2-*allyloxy*-4-*methoxypyridine* N-*oxide* (**4c**). Investigations as in the corresponding study of 2-allyloxypyridine *N*-oxide (**4a**) [experiment (ii)] gave the results summarised in Table 4. The relative proportions of starting material (**4c**) and the two rearrangement products (**5c**) and (**6c**) were determined from the integrated intensities of the signals (δ 8.15, 7.31, and 7.67). These signals correspond to 2-allyloxy-4-methoxypyridine *N*-oxide (δ 8.15; 6-H), *N*-allyloxy-4-methoxy-2-pyridone (δ 7.31; 6-H, and 3-allyl-*N*-hydroxy-4-methoxy-2-pyridone (δ 7.67; 6-H).

(iii) *Thermal stability of* N-*allyloxy*-4-*methoxy*-2-*pyridone* (**5c**) *and* 3-*allyl*-N-*hydroxy*-4-*methoxy*-2-*pyridone* (**6c**). This was

established as for the thermal isomers (**5a**) and (**6a**) [experiment (iii)].

2-Benzyloxy-4-nitropyridine N-*Oxide* (**13b**).—As in the preceding experiments, redistilled benzyl alcohol (760 mg) in tetrahydrofuran (20 ml) was added at 0 °C with stirring to a suspension of sodium hydride (220 mg) in tetrahydrofuran. After 30 min a solution of 2-chloro-4-nitropyridine-*N*-oxide (870 mg) in tetrahydrofuran (15 ml) was added and the mixture was stirred at room temperature. After 20 min [monitored by TLC (chloroform–methanol, 92:8)] the reaction was complete. Filtration (Hyflo Supercel), addition of water (300 ml), extraction with dichloromethane, short-path column chromatography (chloroform–methanol, 90:10), and recrystallisation from ethyl acetate yielded *2-benzyloxy-4-nitropyridine* N-*oxide* (970 mg, 79%) as yellow plates, m.p. 126–128 °C (Found: C, 58.4; H, 3.9; N, 11.4%; $M^{+\cdot}$, 246. $C_{12}H_{10}N_2O_4$ requires C, 58.5; H, 4.1; N, 11.4%; *M*, 246); ν_{max} 2 990, 1 610, 1 520–1 480, 1 340, 1 300, 1 095, and 995 cm^{-1}; δ 7.72 (d, *J* 3 Hz, 3-H), 7.77 (dd, *J* 7 and 3 Hz, 5-H), 8.33 (d, *J* 7 Hz, 6-H), 7.30–7.55 (m, C_6H_5), and 5.46 (s, CH_2).

Thermal Transformation of 2-Benzyloxy-4-nitropyridine N-*Oxide* (**13b**): *Formation of* N-*Benzyloxy-4-nitro-2-pyridone* (**14b**).—A solution of 2-benzyloxy-4-nitropyridine *N*-oxide (50 mg) in dimethylformamide (25 ml) was heated under reflux for 1.5 h. Evaporation and crystallisation from ethyl acetate–light petroleum gave N-*benzyloxy-4-nitro-2-pyridone* (43 mg, 86%) as yellow plates, m.p. 132–135 °C (Found: C, 58.8; H, 4.4; N, 11.4%; $M^{+\cdot}$, 246. $C_{12}H_{10}N_2O_4$ requires C, 58.5; H, 4.1; N, 11.4%; *M*, 246); ν_{max} 1 680, 1 610, 1 530, 1 350, and 1 105 cm^{-1}; δ 7.46 (d, *J* 3 Hz, 3-H), 5.59 (dd, *J* 8 and 3 Hz, 5-H), 7.25 (d, *J* 8 Hz, 6-H), 7.38 (s, C_6H_5), and 5.31 (s, CH_2).

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