# Regiospecific Thermal Rearrangements of 2-Allyloxypyridine *N*-Oxides

**David Alker, Sivapathasuntharam Mageswaran, W. David Ollis,* and Hooshang Shahriari-Zavareh**
*Department of Chemistry, The University, Sheffield S3 7HF*

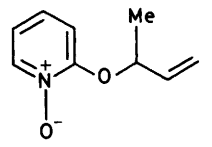
The results reported of an earlier investigation of the thermal rearrangement of derivatives of 2-allyloxypyridine *N*-oxide have been shown to be incorrect. Only [1,4] and [3,3] sigmatropic rearrangements are observed and this regiospecificity supports the view that these [1,4] and [3,3] rearrangements proceed by concerted symmetry-allowed pathways.

Our recent investigations[1] have demonstrated that the thermal rearrangements of 2-allyloxypyridine *N*-oxides only yield products which are attributable to competing [1,4] or [3,3] sigmatropic rearrangements. Both reactions exhibit the precise regiospecificity which would be obligatory for participation by an allyl group in a concerted [1,4] or [3,3] sigmatropic rearrangement. Our results[1] were totally incompatible with the results of a previous investigation.[2] It was therefore hoped that these inconsistencies might be resolved by a careful re-examination of the reactions reported earlier.[2] Our enquiry was, of course, considerably assisted using modern methods of isolation as well as structural aids: these techniques were apparently not used extensively during the previous study.[2] We now report the results of our re-examination and show that the original claims are not acceptable. The correct results are in satisfactory agreement with our recent mechanistic proposals.[1]

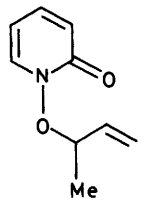
Litster and Tieckelmann[2] have reported that 2-(1-methylallyloxy)pyridine *N*-oxide (**1**) could not be obtained as a crystalline solid or purified easily. According to their report,[2] 2-(1-methylallyloxy)pyridine *N*-oxide (**1**) *rearranged at room temperature* in the absence of solvent yielding a mixture of the isomeric pyridones (**2**) (80% yield) and (**3**) (10% yield) which could be regarded as [1,4] and [3,4] sigmatropic rearrangement products, respectively. In contrast, we obtained 2-(1-methylallyloxy)pyridine *N*-oxide (**1**) as a crystalline solid, and it was *stable at room temperature*. On heating (100 °C; 20 h) in tetrachloroethylene, 2-(1-methylallyloxy)pyridine *N*-oxide (**1**) was smoothly and exclusively transformed into the [3,3] sigmatropic rearrangement product (**4**) (90% yield). No trace of the previously claimed thermal isomerisation products (**2**) or (**3**) could be detected. The rearrangement (**1**) ⟶ (**4**) was shown to be completely regiospecific in a variety of solvents. Furthermore, the influence of solvent polarity upon the relative rates of reaction (Table 1) showed that the thermal transformation (**1**) ⟶ (**4**) is encouraged by polar solvents in accord with the view that it is a concerted [3,3] sigmatropic rearrangement associated with the maintenance of charge separation in the transition state. 3-[(2*E*)-3-Methylallyl]-*N*-hydroxy-2-pyridone (**4**) was shown to be thermally stable under the conditions associated with its formation. Our results are identical with the transformation (**1**) ⟶ (**4**) already mentioned by Schöllkopf and Hoppe,[3] but so far as we are aware their experimental details for this transformation have not been reported. It should be emphasised that, with this exception, the only type of thermal rearrangement of pyridine *N*-oxides encountered by Schöllkopf and Hoppe[3] in their careful and extensive survey was the [1,4] sigmatropic rearrangement.

Litster and Tieckelmann have reported[2] that 2-[(2*E*)-3-methylallyloxy]pyridine *N*-oxide (**5**) when heated (83–84 °C) in diglyme was transformed into the [1,4] product (**3**) (98% yield) and the [3,4] product (**2**) (2% yield). Our results are different. When 2-[(2*E*)-3-methylallyloxy]pyridine *N*-oxide (**5**) was heated in dimethylformamide (100 °C; 12 h) the minor product was identified as the [1,4] product (**3**) (31% yield) and the major product was the previously unknown [3,3] sigmatropic rearrangement product (**6**) (62% yield). In contrast with the result reported by Litster and Tieckelmann,[2] when 2-[(2*E*)-3-methylallyloxy]pyridine *N*-oxide (**5**) was heated in diglyme (83 ± 2 °C; 20 h) then we obtained only the [1,4] product (**3**) (51% yield) and the [3,3] product (**6**) (32% yield). The dramatic influence of solvent polarity upon product ratio and rates of isomerisation are indicated in Table 2.

We cannot explain the results reported by Litster and Tieckelmann.[2] We should also mention that there are some inconsistencies in their paper which we do not understand. However, our re-investigation has established that the thermal transformations exhibited by the pyridine *N*-oxides (**1**) and (**5**) are entirely regiospecific and apparently proceed as concerted [1,4] and [3,3] sigmatropic rearrangements. This is in accord




(1)

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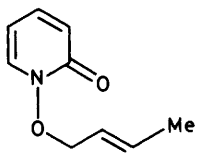


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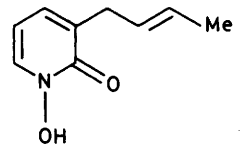


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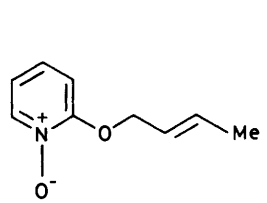
**Table 1.** Thermal rearrangement of 2-(1-methylallyloxy)pyridine *N*-oxide (**1**) in various solvents.

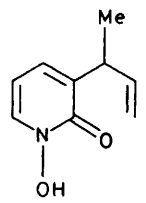
| Solvent | Temp. (°C) | Time (h) | Product composition (%) *N*-Oxide (**1**) | [3,3] Rearrangement product (**4**) |
|---|---|---|---|---|
| Tetrachloroethylene | 100 | 2 | 55 | 45 |
| | 100 | 20 | 0 | 100 |
| Diglyme | 83 | 20 | 12 | 88 |
| Dimethylformamide | 100 | 0.5 | 61 | 39 |
| | 100 | 2 | 0 | 100 |
| Water | 100 | 2 | 0 | 100 |

**Table 2.** Thermal rearrangement of 2-[(2*E*)-3-methylallyloxy]pyridine *N*-oxide (**5**) in various solvents.

| Solvent | Temp. (°C) | Time (h) | Product composition (%) *N*-Oxide (**5**) | [1,4] Rearrangement product (**3**) | [3,3] Rearrangement product (**6**) |
|---|---|---|---|---|---|
| Tetrachloroethylene | 100 | 2 | 71 | 29 | 0 |
| Diglyme | 83 ± 2 | 20 | 17 | 51 | 32 |
| Dimethylformamide | 100 | 2 | 47 | 34 | 19 |
| Water | 100 | 2 | 0 | 24 | 76 |



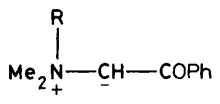
(**5**)



(**6**)

with our previous observations[1] and expectations. The observation of the [1,4] sigmatropic rearrangement (**5**) ⟶ (**3**) and the failure to observe the corresponding transformation (**1**) ⟶ (**2**) is presumably due to a steric effect. In the latter case (**1**) ⟶ (**2**), it is proposed that there is a steric inhibition in the transition state of the [1,4] rearrangement by the methyl group bonded to the carbon atom at the terminus of the migrating group so that the competing [3,3] sigmatropic rearrangement predominates.

During our earlier studies of [3,2] and [1,4] thermal sigmatropic rearrangements of ylides, instructive results were obtained by comparing the rearrangement of isomeric ylides containing *cis*-cinnamyl and *trans*-cinnamyl substituents. These endeavours were motivated by the hope that comparison of the behaviour of such diastereoisomeric precursors might shed light on two matters, (i) the favoured geometry of the transition states involved in concerted [3,2] pericyclic reactions[4,5] and (ii) the possibility of providing an experimental distinction between concerted rearrangements and equivalent but non-concerted processes involving radical-pair intermediates.[6]



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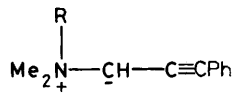

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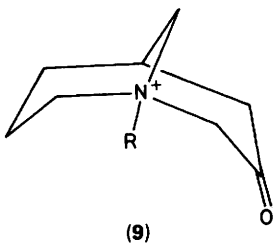

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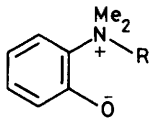
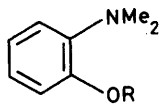


(**10**)



(**11**)

In formulae (**7**)–(**11**): a, R = (*Z*)PhCH=CHCH$_2$; b, R = (*E*)PhCH=CHCH$_2$.

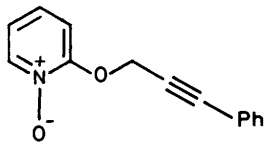
Base-catalysed rearrangements of the *cis*-and *trans*-cinnamyl quaternary ammonium bromides corresponding to the ylides (**7a**) and (**7b**) each gave mixtures of two diastereoisomers **A** and **B** which were [3,2] sigmatropic rearrangement products. The product ratios were (**7a**) ⟶ **A:B** (2:1) and (**7b**) ⟶ **A:B** (5:1).[7] Similarly, the ylides (**8a**) and (**8b**) gave corresponding [3,2] rearrangement products: the product ratios were (**8a**) ⟶ **A:B** (10:90) and (**8b**) ⟶ **A:B** (86:14).[4] Under the same conditions (120 °C; 5 min), the thermal rearrangement of the *cis*-cinnamyl ylide (**9a**) did not proceed as cleanly as the rearrangement of the *trans*-cinnamyl ylide (**9b**).[8] Thus, the *cis*-cinnamyl ylide (**9a**) gave the [3,2] rearrangement product (total yield, 45%) as a mixture of two diastereoisomers (**A:B** = 1:2), whereas the *trans*-cinnamyl ylide (**9b**) rearranged much more smoothly and gave only one diastereoisomer **A** in high yield (85%). The [1,4] rearrangement of 2-oxidoanilinium ylides can proceed either by a concerted pathway or by a route involving radical-pair intermediates.[9] The co-existence of these two types of reaction pathway has also been explored using the *cis*- and *trans*-cinnamyl oxidoanilinium ylides (**10a**) and (**10b**), but the results were not conclusive. The *cis*-cinnamyl ylide (**10a**) in boiling ether gave a moderate yield (45%) of the [1,4] rearrangement product which was a mixture (3:1) of the *cis*- and *trans*-cinnamyl ethers (**11a**) and (**11b**). In contrast, the *trans*-cinnamyl ylide (**10b**) rearranged smoothly at 80 °C giving the *trans*-cinnamyl ether (**11b**) in good yield (79%): a second product, 2-hydroxy-5-(1-phenylallyl)-*N*,*N*-dimethylaniline, was also isolated, but its mechanistic origin was not clear.[9]

The extension of this approach to a comparison of the thermal rearrangement of the *cis*- and *trans*-cinnamyl ethers of 2-hydroxypyridine *N*-oxides (**14**) and (**16**) has yielded results which are remarkably clear-cut. The [1,4] rearrangement (**12**) ⟶ (**13**) occurred in excellent yield (91%) on heating (78 °C; 30 h). Similarly, the *cis*-cinnamyl ether pyridine *N*-oxide (**14**) was *exclusively* transformed into the *cis*-cinnamyl ether pyridone (**15**) (yield 80%) on heating (53 °C; 60 h). Under these conditions, the transformation (**14**) ⟶ (**15**) was stereospecific and no trace of the *trans*-cinnamyl isomer (**17**) was detectable in the product. The transformation of the *trans*-cinnamyl ether pyridine *N*-oxide (**16**) was also stereospecific and perispecific (**16**) ⟶ (**17**) when the reactant (**16**) was heated (78 °C; 18 h) in the absence of solvent. However, in various solvents (Table 3), competition between the [1,4] sigmatropic rearrangement (**16**) ⟶ (**17**) and the [3,3] sigmatropic rearrangement (**16**) ⟶ (**18**) was observed. The influence of solvent polarity and reaction temperature recorded in Table 3 shows the same trends as those indicated in Table 2. These results are in accord with the rationalisations already presented[1] to account for the influence of solvent polarity and reaction temperature upon the periselectivity observed between the [1,4] and [3,3] thermal sigmatropic rearrangements of 2-allyloxypyridine *N*-oxides.

The absence of an experimentally detectable stereomutation in the [1,4] rearrangements of pyridine *N*-oxides (**14**) ⟶ (**15**) and (**16**) ⟶ (**17**) is in striking contrast to the result observed in the [1,4] rearrangements of 2-oxidoanilinium ylides (**10a**) ⟶ (**11a**) + (**11b**) and (**10b**) ⟶ (**11b**). This application of *cis*- and *trans*-cinnamyl groups as mechanistic probes is best appreciated on the basis of current knowledge regarding the configurational stability of allylic radicals. It is widely believed that allylic radicals are configurationally stable,[10,11] but this view may well have to be modified on the basis of experimental

**Table 3.** Thermal rearrangement of 2-[(2*E*)-cinnamyloxy]pyridine *N*-oxide (**16**) in various solvents.

| Solvent | Temp. (°C) | Time (h) | Product composition (%) [1,4] Rearrangement product (**17**) | [3,3] Rearrangement product (**18**) |
|---|---|---|---|---|
| Tetrachloroethylene | 100 | 3 | ~98 | ~2 |
| Dimethylformamide | 100 | 3 | 91 | 9 |
| Formamide | 100 | 3 | 81 | 19 |
| Dimethylformamide | 154 | 0.5 | 82 | 18 |
| None | 78 | 18 | 100 | 0 |



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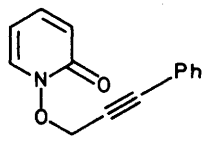

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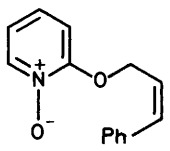

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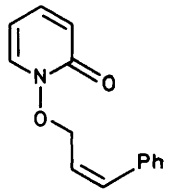

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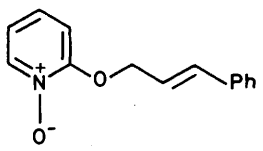

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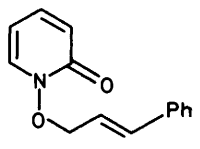

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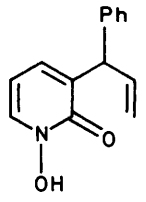

(18)

evidence recently published on the influence of substituents on the rates of stereomutation of allylic radicals. The important study of Kochi and Krusic[12] showed that *syn*- and *anti*-1-methylallyl radicals could be stereospecifically generated from (2*Z*)-and (2*E*)-but-2-enes. The *syn*- and *anti*-1-methylallyl radicals showed characteristic ESR spectra and there was no evidence of stereomutation of these radicals over the temperature range −130 to 0 °C.[13] Examination of the kinetics of geometrical isomerisation of the 1-methylallyl radicals gave a value of $\Delta G^{\ddagger} \leqslant 14.3$ kcal mol$^{-1}$.[14] Subsequently, the opinion was expressed that $\Delta G^{\ddagger}$ for internal rotation of an allyl radical was greater than 17 kcal mol$^{-1}$.[15] Interesting kinetic results on the effect of substituents on the rates of internal rotation of allylic radicals have been reported.[15,16] A striking increase in the rate of stereomutation is observed with halogen substituted allylic radicals.[15] The identification of the *syn*- and *anti*-forms of the 1-cyanoallyl radical has been achieved by ESR spectroscopy and a kinetic analysis gave an Arrhenius activation energy, $E_A = 9.9 \pm 2$ kcal mol$^{-1}$, for their interconversion.[15]

The relation between these experimental values for the activation energies for internal bond rotation in allyl radicals and the values predicted using theoretical methods is of interest. The allyl radical is the simplest radical in which delocalisation is possible, but although there has been general agreement about its preferred planar conformation, considerable controversy has existed over the value of the allylic resonance energy. Values quoted have extended over the range 10–25 kcal mol$^{-1}$, but ultimately an apparently reliable thermochemical estimate of 9.6 ± 3 kcal mol$^{-1}$ was proposed.[17] Recently *ab initio* generalised valence bond and configuration interaction calculations have led to a theoretical value of 11.4 kcal mol$^{-1}$.[18] The allylic radical has recently been examined by photoelectron spectroscopy and this has indicated that the unpaired electron in the allyl radical is mainly non-bonding.[19] *Ab initio* molecular orbital calculations have indicated that there is a slight thermodynamic preference (0.2 kcal mol$^{-1}$) in favour of the *anti*-1-methylallyl radical with respect to its *syn*-conformer.[20] The energy barrier of 4.3 kcal mol$^{-1}$ calculated by the MINDO-3 version[21] of the semi-empirical SCF-MO method is not in good agreement with experimental observations.[15]

The formation of dimeric products, by the coupling of allylic radical pairs as intermediates, has been reported for a number of reaction types. The thermolysis of (*E*,*E*)- and (*Z*,*Z*)-4,4′-azobut-2-ene yielded mixtures containing various proportions of six dimethylhexa-1,5-dienes.[22] The mechanism[23] and the synthetic utility[24,25] of the thermolysis of azoalkanes, including those generating allylic radicals as intermediates, has been examined. Stereomutation of allylic radicals has been neatly demonstrated during Kolbe electrolytic coupling reactions of *cis*- and *trans*-βγ-ethylenic acids.[26] Careful analysis established that the products consisted of mixtures of six dienes resulting from the three possible modes of dimerisation of *syn*- and *anti*-mesomeric allylic radicals derived from the βγ-ethylenic acids. When the double bonds in the dimeric products occupy positions corresponding with that of the precursor then, although some stereomutation is detected, predominant retention of stereochemistry is observed.

An extremely interesting result has been described by Griller, Ingold, and Walton.[27] Pentadienyl has been generated in the (*E*,*E*)- and (*E*,*Z*)-conformations. These two conformations have been identified by ESR spectroscopy and the spectrum of the (*E*,*E*)-conformer is unchanged over the temperature range −130 to +180 °C. The relative thermodynamic stabilities of the (*E*,*E*)- and (*E*,*Z*)-conformations of pentadienyl could not be determined, but the fact that their interconversion is not observed over the temperature range studied places a lower limit and a high value upon the energy barrier for their stereomutation.

There is no quantitative information on the rate of interconversion between *syn*- and *anti*-cinnamyl radicals. However, a highly significant result has been reported by Boche and Schneider.[28] They have established that the (*Z*,*E*)-1,3-diphenylallyl radical undergoes stereomutation to the (*E*,*E*)-1,3-diphenylallyl radical at a rate which competes with the rate of radical coupling even at −82 °C in tetrahydrofuran. The total yield of the products of radical dimerisation is excellent (97%): the proportions of the three constitutionally different products have been firmly established. Estimated activation parameters at −67 °C ($k < 5 \times 10^8$ s$^{-1}$; $\Delta G^{\ddagger} > 3.7$ kcal mol$^{-1}$) show

that the stereomutation of the (*Z*,*E*)-1,3-diphenylallyl radical yielding the (*Z*,*Z*)-1,3-diphenylallyl radical is a fast process. This result provided a good model for the belief that stereomutation of *syn*-cinnamyl to *anti*-cinnamyl radicals would also be a fast process. Thus, if stereomutation of a *cis*-cinnamyl substituent is observed during its migration in [1,4] sigmatropic rearrangements then we conclude that a radical pair intermediate is probably involved. If stereomutation is not observed, then a radical pair intermediate is not involved and this is strong evidence in favour of a concerted process. On this basis we conclude that the [1,4] sigmatropic rearrangement (**10a**) ⟶ (**11a**) of oxidoanilinium ylides can proceed either by a concerted process or by a radical pair process.[9] In contrast, the [1,4] sigmatropic rearrangement (**14**) ⟶ (**15**) is concerted.

## Experimental

The general methods are those recorded in reference 1.

(*Z*)-*Cinnamyl Alcohol*.—A solution of 3-phenylprop-2-yn-1-ol (10.00 g) in methanol (60 ml) was stirred in the presence of 5% palladium on barium sulphate (0.50 g) under hydrogen (1 atm) at room temperature. After the uptake of 1 mol equiv. of hydrogen, the mixture was filtered and evaporated and the residue distilled to give (*Z*)-cinnamyl alcohol (8.80 g, 87%) as a colourless oil, b.p. 88–90 °C/0.8 Torr (lit.,[29] 115 °C/5 Torr); $\nu_{max}$(neat) 3 300, 1 485, 1 010, 775, and 700 $cm^{-1}$; $ABX_2$ system, $\delta_A$ 6.46, $\delta_B$ 5.80, $\delta_X$ 4.35 ($J_{AB}$ 12, $J_{AX}$ 2, $J_{BX}$ 6 Hz; $OC(H_X)_2CH_B{=}CH_AC_6H_5$), δ 7.27–7.44 (m, $C_6H_5$), and 6.81 (br s, OH).

*Preparation of Pyridine* N-*Oxides*.—The following general procedure was used. A solution of the appropriate alcohol in tetrahydrofuran was added to a stirred suspension of sodium hydride in tetrahydrofuran. After 30 min, a solution of 2-chloropyridine *N*-oxide in tetrahydrofuran was added and the mixture stirred (2.5–18 h) at room temperature. The reaction was monitored by TLC and, when all the starting *N*-oxide had been consumed, the mixture was filtered through Hyflo Supercel, evaporated, and purified by short-path column chromatography (silica gel; chloroform–methanol).

2-(1-*Methylallyloxy*)*pyridine* N-*oxide* (**1**) (69%) was obtained using 1-methylallyl alcohol (860 mg), sodium hydride (330 mg), and 2-chloropyridine *N*-oxide (1.29 g) as colourless, hygroscopic rhombs, m.p. 44–46 °C, from ethyl acetate–light petroleum (Found: C, 65.15; H, 6.7; N, 8.6%; $M^{+\bullet}$, 165. $C_9H_{11}NO_2$ requires C, 65.4; H, 6.7; N, 8.5%; *M*, 165); $\nu_{max}$ 2 970, 1 610, 1 495, 1 485, 1 305, 1 115, and 1 045 $cm^{-1}$; δ 6.87–6.98 (m, 3-H), 7.20 (dt, *J* 8 and 2 Hz, 4-H), 6.87–6.98 (m, 5-H), 8.25 (d, *J* 6 Hz, 6-H), ABCX system, $\delta_A$ 5.20–5.36, $\delta_B$ 5.50–5.36, $\delta_C$ 5.95, $\delta_X$ 5.20–5.36 [$J_{AC}$ 18, $J_{BC}$ 11, $J_{CX}$ 7 Hz; $OCH_XMeCH_C{=}CH_AH_B$], and δ 1.60 (d, *J* 7 Hz, $CH_3$).

2-[(2E)-3-*Methylallyloxy*]*pyridine* N-*oxide* (**5**) (63%) was obtained using (2*E*)-3-methylallyl alcohol (1.15 g), sodium hydride (360 mg), and 2-chloropyridine *N*-oxide (1.55 g) as colourless rhombs, m.p. 82–83 °C (lit.,[2] 82–84.5 °C), from ethyl acetate–light petroleum (Found: C, 65.1; H, 6.7; N, 8.5%; $M^{+\bullet}$, 165. Calc. for $C_9H_{11}NO_2$: C, 65.4; H, 6.7; N, 8.5%; *M*, 165); $\nu_{max}$ 2 900, 1 610, 1 500, 1 440, 1 315, and 1 120 $cm^{-1}$; δ 6.83–6.98 (m, 3-H), 7.17–7.31 (m, 4-H), 6.83–6.98 (m, 5-H), 8.24 (dd, *J* 6 and 1.5 Hz, 6-H), $ABX_2$ system, $\delta_A$ 5.63–6.02, $\delta_B$ 5.63–6.02, $\delta_X$ 4.78 [$J_{BX}$ 7 Hz; other coupling constants could not be determined by first-order analysis due to overlap of signals; $OC(H_X)_2CH_B{=}CH_AMe$], and δ 1.74 (d, *J* 8 Hz, $CH_3$).

2-(3-*Phenylpropynyloxy*)*pyridine* N-*oxide* (**12**) (38%) was obtained using 3-phenylpropynyl alcohol (6.50 g), sodium hydride (1.20 g), and 2-chloropyridine *N*-oxide (6.0 g) as a colourless solid, m.p. 130 °C (Found: C, 74.3; H, 5.1; N, 6.1%; $M^{+\bullet}$, 225. $C_{14}H_{11}NO_2$ requires C, 74.7; H, 4.9; N, 6.2%; *M*, 225); $\nu_{max}$ 2 920, 2 220, 1 600, 1 485, 1 290, 1 270, 1 110, 1 005, and 990 $cm^{-1}$; δ 6.88–7.41 (m, 3-H), 6.88–7.41 (m, 4-H), 6.88–7.41 (m, 5-H), 8.27 (dd, *J* 6 and 2 Hz, 6-H), 4.72 (s, $CH_2$), and 6.88–7.41 (m, $C_6H_5$).

2-[(2Z)-*Cinnamyloxy*]*pyridine* N-*oxide* (**14**) (44%) was obtained using (*Z*)-cinnamyl alcohol (6.70 g), sodium hydride (1.20 g), and 2-chloropyridine *N*-oxide (6.50 g) as colourless plates, m.p. 83–84 °C (Found: C, 73.6; H, 6.2; N, 6.1%; $M^{+\bullet}$, 227. $C_{14}H_{13}NO_2$ requires C, 74.0; H, 5.8; N, 6.2%; *M*, 227); $\nu_{max}$ 2 950, 1 600, 1 495, 1 300, 1 265, 1 115, 1 000, and 850 $cm^{-1}$; δ 6.67 (dd, *J* 7 and 2 Hz, 3-H), 7.05–7.38 (m, 4-H), 6.85 (dt, *J* 6.5 and 2 Hz, 5-H), 8.21 (dd, *J* 6 and 1.5 Hz, 6-H), $ABX_2$ system, $\delta_A$ 6.76, $\delta_B$ 5.95, $\delta_X$ 5.10 [$J_{AB}$ 12, $J_{BX}$ 6.5, $J_{AX}$ 1.5 Hz; $OC(H_X)_2CH_B{=}CH_AC_6H_5$], and δ 7.05–7.38 (m, $C_6H_5$).

2-[(2E)-*Cinnamyloxy*]*pyridine* N-*oxide* (**16**) (61%) was obtained using (*E*)-cinnamyl alcohol (6.70 g), sodium hydride (1.20 g), and 2-chloropyridine *N*-oxide (6.50 g) as a pale yellow solid, m.p. 107–109 °C, from ethyl acetate (Found: C, 74.0; H, 6.0; N, 6.0%; $M^{+\bullet}$, 227. $C_{14}H_{13}NO_2$ requires C, 74.0; H, 5.8; N, 6.2%; *M*, 227); $\nu_{max}$ 2 920, 1 600, 1 495, 1 305, 1 125, and 980 $cm^{-1}$; δ 6.88–7.06 (m, 3-H), 7.20–7.47 (m, 4-H), 6.88–7.06 (m, 5-H), 8.25 (d, *J* 8 Hz, 6-H), $ABX_2$ system, $\delta_A$ 6.72, $\delta_B$ 6.39, $\delta_X$ 5.01 [$J_{AB}$ 16, $J_{BX}$ 6.5 Hz; $OC(H_X)_2CH_B{=}CH_AC_6H_5$], and 7.20–7.47 (m, $C_6H_5$).

### *Thermal Rearrangement of Pyridine* N-*Oxides*

The pyridine *N*-oxides were heated either neat or in solution and the products isolated and characterised as described below.

3-[(2E)-3-*Methylallyl*]-N-*hydroxy*-2-*pyridone* (**4**).—2-(1-Methylallyloxy)pyridine *N*-oxide (50 mg) was heated (100 °C; 20 h) in tetrachloroethylene. Evaporation and crystallisation of the residue from ethyl acetate–hexane gave 3-[(2E)-3-*methylallyl*]-N-*hydroxy*-2-*pyridone* (45 mg, 90%) as colourless rhombs, m.p. 97–99 °C (Found: C, 65.2; H, 6.6; N, 8.3%; $M^{+\bullet}$, 165. $C_9H_{11}NO_2$ requires C, 65.4; H, 6.7; N, 8.5%; *M*, 165); $\nu_{max}$ 2 900, 1 635, 1 555, 1 510, and 1 430 $cm^{-1}$; δ 7.20 (d, *J* 7 Hz, 4-H), 6.23 (t, *J* 7 Hz, 5-H), 7.64 (d, *J* 7 Hz, 6-H), $ABX_2$ system, $\delta_A$ 5.50–5.58, $\delta_B$ 5.50–5.58, $\delta_X$ 3.25 [coupling constants could not be determined by first order analysis due to overlap of signals; $OC(H_X)_2CH_B{=}CH_ACH_3$], δ 1.67 (d, *J* 4 Hz, $CH_3$), and 8.20–8.45 (br s, OH).

N-[(2E)-3-*Methylallyloxy*]-2-*pyridone* (**3**) *and* 3-(1-*Methylallyl*)-N-*hydroxy*-2-*pyridone* (**6**).—2-[(2*E*)-3-Methylallyloxy]-pyridine *N*-oxide (100 mg) was heated (100 °C; 12 h) in dimethylformamide and evaporated. The residue was partitioned between 0.5M aqueous sodium hydroxide and chloroform. The combined chloroform extracts yielded N-[(2E)-3-*methylallyloxy*]-2-*pyridone* (31 mg, 31%) which was obtained as a colourless oil after short-path column chromatography (silica gel; chloroform–methanol, 90:10) (Found: C, 65.2; H, 6.6; N, 8.5%; $M^{+\bullet}$, 165. $C_9H_{11}NO_2$ requires C, 65.4; H, 6.7; N, 8.5%; *M*, 165); $\nu_{max}$ 2 940, 1 660, 1 590, 1 530, 1 450, 1 275, 1 100, and 970 $cm^{-1}$; δ 6.14 (dd, *J* 9 and 2 Hz, 3-H), 7.30 (dt, *J* 8 and 2 Hz, 4-H), 6.10 (dt, *J* 8 and 2 Hz, 5-H), 7.46 (dd, *J* 7 and 2 Hz, 6-H), $ABX_2$ system, $\delta_A$ 5.63–5.95, $\delta_B$ 5.63–5.95, $\delta_X$ 4.20 [$J_{BX}$ 7 Hz; other coupling constants could not be determined by first order analysis due to overlap of signals; $OC(H_X)_2CH_B{=}CH_ACH_3$], and δ 1.20 (d, *J* 6 Hz, $CH_3$).

The combined alkaline extracts were acidified and extracted with chloroform. These extracts yielded 3-(1-*methylallyl*)-N-*hydroxy*-2-*pyridone* (62 mg, 62%) as colourless rhombs, m.p. 89–90 °C, from ethyl acetate–hexane (Found: C, 65.5; H, 6.9; N, 8.5%; $M^{+\bullet}$, 165. $C_9H_{11}NO_2$ requires C, 65.4; H, 6.7; N, 8.5%; *M*, 165); $\nu_{max}$ 2 960–2 920, 1 635, 1 545, 1 425, and 1 365 $cm^{-1}$; δ 7.11 (d, *J* 7 Hz, 4-H), 6.17 (t, *J* 7 Hz, 5-H), 7.10 (d, *J* 7 Hz, 6-H),

ABCX system, $\delta_A$ 4.95–5.20, $\delta_B$ 4.95–5.20, $\delta_C$ 5.85–6.06, $\delta_X$ 3.82 [coupling constants could not be determined by first order analysis due to overlap of signals; $OCH_XMeCH_C{=}CH_AH_B$], and δ 1.22 (d, *J* 8 Hz, $CH_3$).

N-(3-*Phenylpropynyloxy*)-2-*pyridone* (**13**).—2-(3-Phenylpropynyloxy)pyridine *N*-oxide (930 mg) was heated (78 °C; 30 h) under nitrogen and the product purified by preparative TLC (silica gel; chloroform) to give N-(3-*phenylpropynyloxy*)-2-*pyridone* (850 mg, 91%) as a colourless gum (Found: $M^{+\cdot}$, 225. $C_{14}H_{11}NO_2$ requires *M*, 225); $\nu_{max}$ 2 220, 1 650, and 1 590 $cm^{-1}$; δ 6.68 (dd, *J* 9.5 and 2 Hz, 3-H), 7.35–7.49 (m, 4-H), 6.10 (dt, *J* 7 and 2 Hz, 5-H), 7.65 (dd, *J* 7 and 2 Hz, 6-H), 5.18 (s, $CH_2$), and 7.35–7.49 (m, $C_6H_5$).

N-[(2Z)-*Cinnamyloxy*]-2-*pyridone* (**15**).—2-[(2*Z*)-Cinnamyloxy]pyridine *N*-oxide (500 mg) was heated (53 °C; 60 h) under nitrogen and the product purified by preparative TLC (silica gel; chloroform) to give N-[(2Z)-*cinnamyloxy*]-2-*pyridone* (400 mg, 80%) as a colourless gum (Found: C, 73.8; H, 5.9; N, 5.95%; $M^{+\cdot}$, 227. $C_{14}H_{13}NO_2$ requires C, 74.0; H, 5.8; N, 6.2%; *M*, 227); $\nu_{max}$ 1 650 $cm^{-1}$; δ 6.56 (dd, *J* 9 and 1.5 Hz, 3-H), 7.08–7.37 (m, 4-H), 6.01 (dt, *J* 7 and 1.5 Hz, 5-H), 7.46 (dd, *J* 7.5 and 2.5 Hz, 6-H), $ABX_2$ system, $\delta_A$ 6.72, $\delta_B$ 5.91, $\delta_X$ 4.99 [$J_{AB}$ 12, $J_{BX}$ 7.5, $J_{AX}$ 1 Hz; $OC(H_X)_2CH_B{=}CH_AC_6H_5$], and δ 7.08–7.37 (m, $C_6H_5$).

N-[(2E)-*Cinnamyloxy*]-2-*pyridone* (**17**) *and* 3-(1-*Phenylallyl*)-N-*hydroxy*-2-*pyridone* (**18**).—2-[(2E)-Cinnamyloxy]pyridine *N*-oxide (360 mg) was heated (100 °C; 3 h) in formamide and the solution poured into 0.5M aqueous sodium hydroxide and extracted into chloroform. The combined chloroform extracts were washed with 0.5M aqueous sodium hydroxide, dried ($K_2CO_3$), and evaporated. The residue was purified by preparative TLC (silica gel; chloroform) and recrystallised from light petroleum to give N-[(2E)-*cinnamyloxy*]-2-*pyridone* (290 mg, 81%) as colourless needles, m.p. 99–100 °C (Found: C, 74.2; H, 6.0; N, 6.0%; $M^{+\cdot}$, 227. $C_{14}H_{13}NO_2$ requires C, 74.0; H, 5.8; N, 6.2%; *M*, 227); $\nu_{max}$ 1 655, 1 590, and 970 $cm^{-1}$; δ 6.66 (dd, *J* 7 and 1.5 Hz, 3-H), 7.16–7.38 (m, 4-H), 6.02 (dt, *J* 7 and 1.5 Hz, 5-H), 7.43 (dd, *J* 7 and 1.5 Hz, 6-H), $ABX_2$ system, $\delta_A$ 6.64, $\delta_B$ 6.33, $\delta_X$ 4.90 [$J_{AB}$ 16, $J_{BX}$ 7 Hz; $OC(H_X)_2CH_B{=}CH_AC_6H_5$], and δ 7.16–7.38 (m, $C_6H_5$).

The combined alkaline extracts were acidified and extracted with chloroform. These extracts yielded 3-(1-*phenylallyl*)-N-*hydroxy*-2-*pyridone* (41 mg, 11%) as a colourless, crystalline solid, m.p. 115–117 °C, from ethanol (Found: $M^{+\cdot}$, 227.0947. $C_{14}H_{13}NO_2$ requires *M*, 227.0947); $\nu_{max}$ 1 640 and 1 557 $cm^{-1}$; δ 7.07–7.38 (m, 3-H), 7.07–7.38 (m, 4-H), 6.06–6.32 (m, 5-H), 7.54–6.54 (m, 6-H), ABMX system, $\delta_A$ 4.90, $\delta_B$ 5.17, $\delta_M$ 6.06–6.32, $\delta_X$ 5.05 ($J_{AM}$ 17.5, $J_{BM}$ 10.5, $J_{MX}$ 6 Hz; $OCH_XPhCH_M{=}CH_AH_B$), δ 9.3–10.0 (br s, OH), and 7.07–7.38 (m, $C_6H_5$).

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