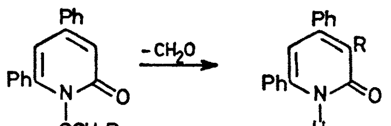
Novel Thermal and Photochemical Rearrangements of *N*-Substituted 2-Pyridones

By Alan R. Katritzky,* Andrew V. Chapman, Michael J. Cook,* and George H. Millet
(*School of Chemical Sciences, University of East Anglia, Norwich* NR4 7TJ)

Summary Examples of four novel rearrangements of 1-substituted 4,6-diphenyl-2-pyridones are reported: (a) 1-phenethoxy and 1-but-3-enoxy give 3-benzyl and 3-prop-2-enyl derivatives, respectively, with elimination of CH_2O; (b) 1-octyloxy gives 3-octyloxy; (c) 1-α-(*p*-tolylimino)benzyloxy gives 3- and 5-*N*-benzoyl-*p*-toluidino; (d) 1-*p*-toluoyloxy gives 3- and 5-*p*-toluoyloxy-derivatives.

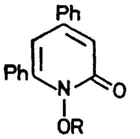
We report novel rearrangements which increase significantly the range of those known for heteroaromatic *N*-oxides.[1] Our studies[2] on the thermolysis of 1-alkoxy-4,6-diphenyl-2-pyridones to give aldehydes showed that, whereas benzaldehydes are formed without appreciable amounts of side products, the aliphatic aldehydes obtained from this route are accompanied not only by alcohols but also by by-products derived from rearrangements. We have now elucidated the structures of these by-products and the courses of these and related rearrangements.



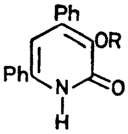
(1) R = CH_2Ph
(2) R = $CH_2CH{:}CH_2$
(3) R = CH_2Ph
(4) R = $CH_2CH{:}CH_2$

Thermolysis of the phenethoxypyridone (1) at 220 °C yields [in addition to phenylacetaldehyde (49%) and 4,6-diphenyl-2-pyridone[2]] 26% of 3-benzyl-4,6-diphenyl-2-pyridone (3);† spectral properties indicated that the structure was (3) or the isomeric 5-benzyl-4,6-diphenyl-2-pyridone and the former was proved by conversion into 5-benzyl-2,4-diphenylpyridine identified as such by comparison of spectra (especially proton coupling constants) with those of 2,4-diphenylpyridine. Similarly, the butenoxy derivative (2) on thermolysis at 230 °C gives [in addition to crotonaldehyde (50%)[2]] 3-allyl-4,6-diphenyl-2-pyridone (4) (33%). The conversion (1) → (3) was also effected photochemically, although in lower yield (14%).

We also found earlier[3] that the photolysis or thermolysis of the 1-octyloxy derivative (5) gives octaldehyde with some octanol: we have now found that a minor by-product in these reactions ($\leqslant 5\%$) is the 3-octyloxy-compound (8). However, in a similar photolysis of the 5-nitro-2-pyridyloxy-derivative (6) the 3-substituted compound (9) is the major (50%) product.



(5) R = $[CH_2]_7Me$
(6) R = 5-nitro-2-pyridyl
(7) R = $CO{\cdot}C_6H_4Me$-*p*



(8) R = $[CH_2]_7Me$
(9) R = 5-nitro-2-pyridyl
(10) R = $CO{\cdot}C_6H_4Me$-*p*
(11) R = H

Photolysis (at λ 350 nm in MeCN) of the imidate derivative (12) gives *two* rearrangement products (13, 15) in approximately equal quantities (*ca.* 20%) together with benzo-*p*-toluidide (19%) and 4,6-diphenyl-2-pyridone (22%).‡ The structures of products (13, 15) follow from

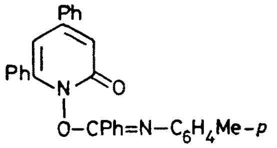
---

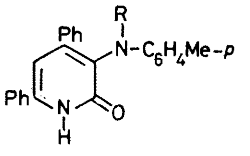
† Satisfactory elemental analyses were obtained for all new compounds reported.

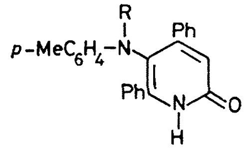
‡ Further examples of rearrangements of these general types will be given in the full paper.

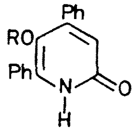
their n.m.r. and i.r. spectra and the products of their hydrolysis in 70% aq. H_2SO_4, *viz.* benzoic acid and compounds assigned the arylamino-2-pyridone structures (**14**, **16**) on spectral evidence.

Similar photolysis of the *N*-aroyloxy-derivative (**7**) also gives two rearrangement products (**10**, **17**) in approximately equal amounts (*ca.* 10%) as well as *p*-toluic acid (12%) and 4,6-diphenyl-2-pyridone (36%).‡ Here, structural assignment was based on spectral evidence and on products of basic hydrolysis in 20% aq. NaOH *viz.* toluic acid and (**11**) and (**18**). Thus rearrangements of (**12**) and (**7**) proceed non-regiospecifically.

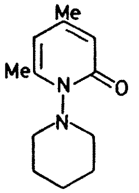

(12)

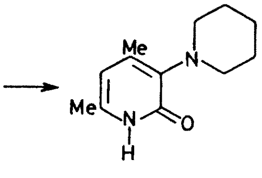

(13) R = COPh
(14) R = H

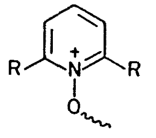

(15) R = COPh
(16) R = H

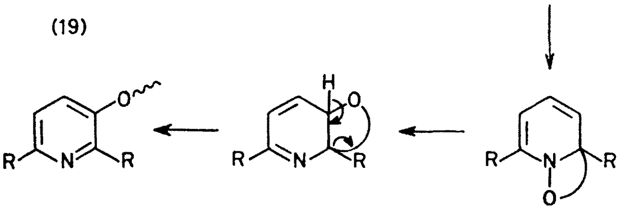

(17) $R = COC_6H_4Me\text{-}p$
(18) R = H

There appear to be few close analogies for the present set of rearrangements in pyridine *N*-oxide chemistry. Furrer[4] studied the photolysis of 1-alkoxy-4,6-dimethyl-2-pyridones but found no rearrangement products: however the photochemical cleavage of the N–N bond in the *N*-piperidino-derivative (**19**) gave the 3-substituted derivative (**20**) (10%). Various pyridine *N*-oxide derivatives, blocked at the 2- and 6-positions, are known to undergo rearrangement leading to substitution at the 3-position and these can often be rationalised in terms of the pathway (**21**) → (**22**).[1b] Of the present conversions (**12**) → (**13**), with formation of a N–C-3 bond rather than an O–C-3 bond, provides the clearest contrast with this scheme.§ Without isotopic labelling experiments we do not know which oxygen became attached to the ring carbon in (**10**) and (**17**), but the reaction appears to be analogous to (**12**) → (**13**). The formation of (**3**), (**4**), and (**8**) also clearly does not fall into the previous pattern (**21**) → (**22**): production of (**3**) and (**4**) by loss of formaldehyde evidently requires the $O{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}C$ group in the starting material.


(19)


(20)


(21)


(22)

We thank the S.R.C. for financial support (to A.V.C.).

(*Received, 12th December* 1978; *Com.* 1322.)

---

§ In particular contrast are results reported by R. A. Abramovitch, R. B. Rogers, and G. M. Singer, *J. Org. Chem.*, 1979, **40**, 41.

[1] For reviews see A. R. Katritzky and J. M. Lagowski, 'Chemistry of the Heterocyclic *N*-Oxides,' Academic Press, London, 1971, *e.g.* p. 288, 296: R. A. Abramovitch and I. Shinkai, *Accounts Chem. Res.*, 1976, **9**, 192.
[2] M. J. Cook, A. R. Katritzky, and G. H. Millet, *Heterocycles*, 1977, **7**, 227.
[3] A. R. Katritzky, M. J. Cook, S. B. Brown, R. Cruz, and G. H. Millet with A. Anani, *J.C.S. Perkin I*, in the press.
[4] H. Furrer, *Tetrahedron Letters*, 1974, 2953.