Benzisoxazolo[2,3-*a*]pyridinium Tetrafluoroborates. Possible Generation of an Aryloxenium Ion

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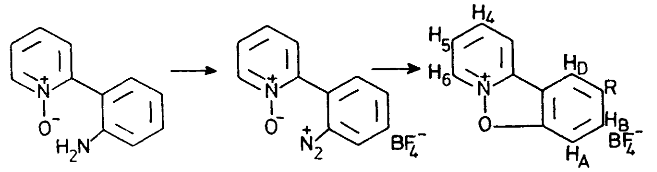
Summary Thermolysis and photolysis of the title compounds (**1**) give aryloxenium ions which undergo intermolecular reactions when R = H but intramolecular cyclisation when R = NO_2.

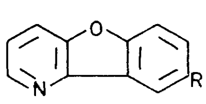
THE generation of aryloxenium ions has been proposed in the thermolysis of *N*-aryloxypypridinium salts,[1] by the decomposition of aryloxydiazonium salts,[2] and from *NN*-diacylphenoxyamines on heating with acid.[2] They undergo intermolecular aromatic substitution of activated aromatic substrates.[1,2] We now report the preparation of the novel benzisoxazolo[2,3-*a*]pyridinium ring system (**1**) and some of its reactions. It was hoped that generation of the aryloxenium ion from this internal aryloxypyridinium salt would lead to intramolecular substitution of the pyridine ring. Though the latter is strongly deactivated towards electrophilic attack it was expected that the intramolecularity of the reaction would facilitate electrophilic attack.

The ring system (**1**) was unknown, though the aza-analogue, pyrido[1,2-*b*]indazole, has been studied.[3] The preparation of 5-bromo-4-hydroxyisoxazolo[2,3-*a*]pyridinium bromide has also been reported.[4] The parent (**1a**)‡ can be synthesised readily (80% yield) from 2-(*o*-aminophenyl)pyridine 1-oxide (**2**)[3b] *via* the diazonium tetrafluoroborate (**3**).§ Thus, although intermolecular phenylation of pyridine 1-oxide was unsuccessful[5] the intramolecular phenylation takes place readily. Nitration of (**1a**) gave (**1b**) (88%), m.p. 148·5—150 °C.

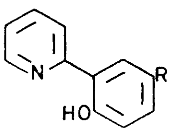


(2) (3) (1) a: R = H_C
b: R = NO_2

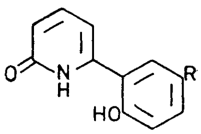
Thermolysis of (**1a**) in mesitylene at 190 °C for 16 h gave no benzofuro[3,2-*b*]pyridine (**4a**). The only product isolated, in addition to intractable tarry material, was 2-(5-fluoro-2-hydroxyphenyl)pyridine (**5**) (18%), m.p. 56—57 °C, identical with a sample obtained by the Schiemann reaction with diazotized 2-(5-amino-2-hydroxyphenyl)pyridine (**6**).



(4) a: R = H
b: R = NO_2

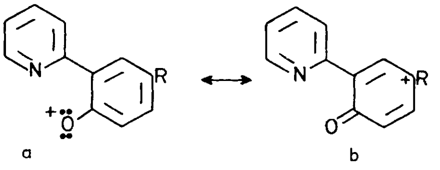


(5) R = F
(6) R = NH_2
(7) R = NHCOPh
(8) R = NHCOMe
(9) R = NO_2



(10) R = H
(11) R = NO_2

Only starting material was recovered when (**1a**) was heated in benzene at 190 °C for 2 days.¶ Thermolysis of (**1a**) in benzonitrile at 200 °C for 2 days gave 2-(5-benzamido-2-hydroxyphenyl)pyridine (**7**)** (17%), m.p. 189—190 °C, together with tars. Similarly, photolysis (3000 Å, MeCN, N_2) of (**1a**) gave the acetamide (**8**) (59%), m.p. 182—183 °C.** When (**1a**) was heated in hexamethylphosphoric triamide (HMPA) at 120—125 °C, 6-(2-hydroxyphenyl)-2-pyridone (**10**) (65·5%), m.p. 260—261 °C, was obtained, identical with the product formed from (**1a**) and 1% aq. sodium hydroxide. This provides a useful route to such 6-aryl-2-pyridones.



(12)

In none of the above cases was any (**4a**) detected. It was reasoned that this could be due to (i) the proposed oxenium ion intermediate (**12**) not being electrophilic enough to attack a pyridine β-position and/or (ii) contributions from (**12b**) being more important than (**12a**). Introduction of a nitro group *para* to the oxygen should remedy both of these problems. Indeed, when (**1b**) was heated (190 °C, 24 h) in benzene, 7-nitrobenzofuro[3,2-*b*]pyridine (**4b**) (20%), m.p. 220—222 °C, identical with an authentic sample,[6] was obtained, together with 2-(2-hydroxy-5-nitrophenyl)-pyridine (**11**) (16%), identical with an authentic sample

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‡ M.p. 187—188 °C; i.r. (KBr) 1100 cm^{-1}; n.m.r. [$(CD_3)_2SO$] δ 10·14 (1H, d, $J_{5,6}$ 6·8 Hz, 6-H), 9·14 (1H, d, J_{CD} 8 Hz, H_D), 8·95—8·50 (2H, m, 4-H and H_C), 8·43—7·70 (4H, m, 3- and 5-H, and H_A and H_B); *m/e* 257 (M^+).

§ All new compounds gave satisfactory elemental and spectroscopic data.

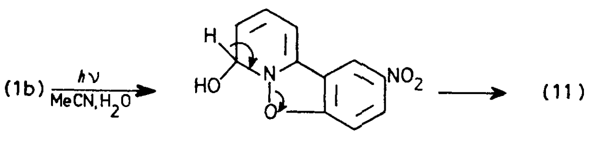
¶ (**1a**) is insoluble in hot benzene.

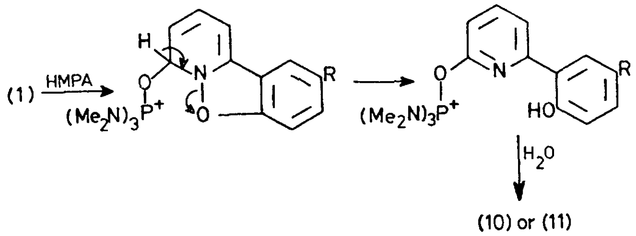
** Identical with an authentic sample prepared from (**6**).

obtained by a base-catalysed rearrangement of *N*-(*p*-nitrophenoxy)pyridinium tetrafluoroborate.[5]

On the other hand, photolysis (3000 Å) of (**1b**) in acetonitrile gave (**11**) (52%) and (**9**) (15%). Compound (**1b**) was stable in aqueous acetonitrile in the absence of u.v. light. The pyridone (**11**), m.p. > 300 °C, was also obtained (65%) by heating (**1b**) in HMPA at 120—125 °C.

These results may be explained in terms of the thermal heterolytic fission of the N–O bond in (**1**) to form an aryloxenium ion (**12**). A concerted mechanism is eliminated by the data given in ref. 2. When R = H, (**12**) and BF_4^- in mesitylene give the Schiemann product (**5**), while in benzonitrile the Ritter reaction product (**7**) is formed. Photolysis of (**1a**) similarly leads to singlet (**12**) which, in acetonitrile, yields the Ritter product. When R = NO_2 in (**12**) it destabilises the resonance structure (**12b**) and the now more electrophilic (**12a**) can undergo intramolecular aromatic substitution to yield (**4b**). The phenol (**9**) may be formed by intersystem crossing of (**12a**; R = NO_2) to the triplet followed by hydrogen abstraction. Photolysis of (**1b**) seems to involve two competing processes: (i) heterolytic fission of photoexcited (**1b**) to an excited singlet (**12**) followed by intersystem crossing and hydrogen abstraction, or intersystem crossing of photoexcited (**1b**) to the triplet followed by heterolytic cleavage to give to triplet (**12**) directly; and (ii) reaction of photoexcited (**1b**) with small amounts of water in the solvent to give (**11**). There is some precedent for such a light catalysed hydration in the photolysis of phenazine.[7] Nucleophilic attack at C-6 in compounds (**1**) by HMPA would account for their oxidation to (**10**) and (**11**). It is interesting that in this case, as well as in the treatment of (**1**) with hydroxide ion opening of the pyridine ring[8] does not occur.





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