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# THE FIRST ISOLATION OF ISOMERIC α- AND β-PHENYLAZOXYPYRIDINE-N-OXIDES

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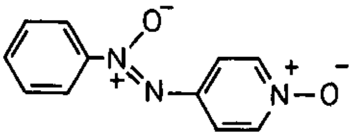
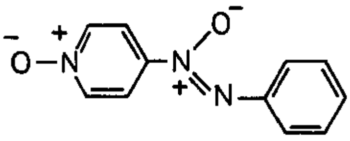
Abstract — The oxidation of 4-phenylazopyridine gives rise to the isomeric α- and β-4-phenylazoxypyridine-N-oxides, contrary to a previous literature report. 3-Phenylazopyridine similarly affords the respective α- and β-azoxy compounds but 2-phenylazopyridine yields only the α-azoxy product.

The oxidation of unsymmetrical azobenzene derivatives generally gives rise to a mixture of the isomeric α- and β-azoxybenzenes whose ratio is often close to 1:1.[1,2] Exceptions to this are known, however, such as when the azobenzene carries a bulky ortho substituent on one ring in which case oxidation gives predominantly the isomer in which oxygen becomes bonded to the remote nitrogen.[3]

A different situation has been reported in the oxidation of azo compounds containing a pyridine nucleus. Thus from the oxidation of 4-phenylazopyridine with peracetic acid the sole product reported was 4-(phenyl-α-azoxy)pyridine-N-oxide (1), none of the isomeric β product (2) being obtained.[4a] Similarly, in the peracetic acid oxidation of 2-phenylazopyridine, only the 2-(phenyl-α-azoxy)pyridine-N-oxide was found.[4a,b] Interestingly, 3-(phenyl-α-azoxy)pyridine (as well as 3-phenylazopyridine) was reported as formed from the condensation of 3-aminopyridine with nitrosobenzene under certain reaction conditions.[4c] Thus none of the isomeric phenyl-β-azoxypyridine derivatives have been prepared so far.



(1)



(2)

As an extension of our studies of the Wallach rearrangement of azoxyarenes,[5] we have begun investigation of the phenylazoxypyridine series. However, we have found that oxidation of 4- and 3-phenylazopyridine with peracetic acid under prescribed conditions[4] gives rise to the α- as well as the β-azoxypyridine-N-oxides, in an approximate ratio of 2:1, which is contrary to the earlier reports.[4a-c] 2-Phenylazopyridine yielded on oxidation only the 2-(phenyl-α-azoxy)pyridine-N-oxide, in accord with previous observations.[4a,b] Separation of the above α- and β-azoxy derivatives was effected by high performance liquid chromatography (HPLC) using a solvent mixture of toluene/ethyl acetate/methanol (4:2:1). The mp and UV characteristics of the products are recorded in Table 1. While the $^1$H NMR spectra of the α- and β-phenylazoxypyridine-N-oxides are complex, the deoxygenated α- and β-phenylazoxypyridines (obtained from the N-oxides by reaction with $PCl_3$) exhibit well resolved spectra which are readily interpretable in accord with these structural assignments.

Table 1. Characteristics of α- and β-phenylazoxypyridine-N-oxides[a]

| | m.p. | $\lambda_{max}$ (nm) | log ε |
|---|---|---|---|
| 4-(phenyl-α-azoxy)pyridine-N-oxide (1) | 144-145° | 367 | 4.38 |
| | | 289 | 3.91 |
| 4-(phenyl-β-azoxy)pyridine-N-oxide (2) | 146-147° | 349 | 4.38 |
| | | 232 | 4.12 |
| 3-(phenyl-α-azoxy)pyridine-N-oxide | 124-126° | 308 | 4.20 |
| | | 278 | 4.34 |
| 3-(phenyl-β-azoxy)pyridine-N-oxide | 134-135° | 331 | 4.17 |
| | | 278 | 4.34 |
| 2-(phenyl-α-azoxy)pyridine-N-oxide | 136-137° | 330 | 3.89 |
| | | 268 | 4.29 |

[a] Satisfactory analytical data were obtained for the compounds reported in this table.

Independent confirmation of structure was obtained by X-ray crystallography for two representative compounds in this series, namely 4-(phenyl-β-azoxy)pyridine-N-oxide and 4-(phenyl-α-azoxy)pyridine which itself was formed by deoxygenation of 4-(phenyl-α-azoxy)pyridine-N-oxide. Full details of the crystal structure studies will be published in due course.[5c]

The exclusive obtention of one isomer in the oxidation of phenylazopyridines in the previous work was thought to be the result of differential electron density at the two nitrogen centres.[4c,d] The present results for the 3- and 4-phenylazopyridines suggest that this factor does not control orientation in these systems. The fact that 2-phenylazopyridine does give rise to only the β-azoxy compound is then explicable in terms of a field and/or steric effect with respect to the approaching electrophile. Future work on related systems will be directed towards clarification of the origins of these effects.

The obtention of the isomeric α- and β-phenylazoxypyridine derivatives in the present work could be significant regarding the potential usefulness of azoxy compounds as liquid crystal materials.[6] Of special interest to us, however, is an unexpectedly large and to our knowledge unprecendented difference in the reactivities of the α- and β-phenylazoxypyridines that we have observed under Wallach rearrangement[7] conditions in strong sulfuric acid media. These results will be reported on in a subsequent communication.[5d]

## ACKNOWLEDGEMENT

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