An Improved Method for Aromatic Hydroxylation with Heteroaromatic Oxides

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Summary Photolysis of the boron trifluoride complex of pyridine-*N*-oxide in benzene gives a higher yield of phenol than photolysis of pyridine-*N*-oxide alone; with some intramolecular models, intramolecular hydroxylation can be achieved.

OF the available methods which mimic biological hydroxylation of aromatic rings,[1] the photolysis of heteroaromatic *N*-oxides in inert solvents containing the aromatic substrate best satisfies the mechanistic criteria, *viz.* a polar mechanism in which NIH shifts of labels are observed.[2] Unfortunately, the chemical yields of such hydroxylation

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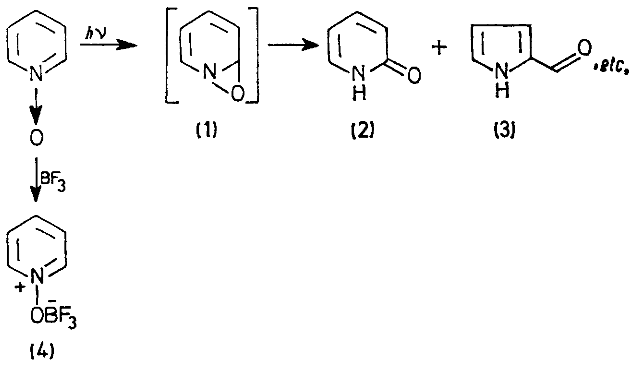
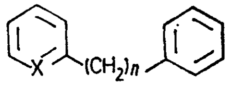
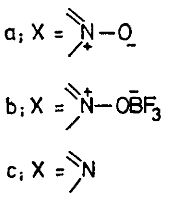
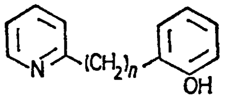
processes are generally low since intramolecular oxygen migration competes with the intermolecular transfer of oxygen. For example, pyridine-*N*-oxide produces products such as (**2**) and (**3**) upon irradiation and these are currently postulated to arise from a labile intermediate of the type (**1**).



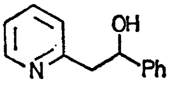


(**5**), *n* = 1
(**6**), *n* = 2





(**7**); *n* = 1
(**8**); *n* = 2



(**9**)

It has now been found that internal oxygen rearrangements can be blocked by protecting the oxide function with a Lewis acid, in particular, boron trifluoride. For example, irradiation of 0·1M pyridine *N*-oxide in 1:1 benzene–dichloromethane using a medium pressure mercury lamp and a Pyrex filter gave an isolatable yield of less than 1% phenol, together with the rearrangement products (**2**) and (**3**), but a similar reaction involving the complex (**4**) (0·04M) gave phenol (7%), with none of the side products (**2**) and (**3**).

Phenol formation was also enhanced using the model compounds (**5**) and (**6**), where intramolecular hydroxylation occurred. Thus, for the boron trifluoride complex of the oxide (**5b**), photoreaction in dichloromethane produced the phenol (**7**) in 43% yield; a small amount of the deoxygenated product (**5c**) also formed. Photolysis of the free *N*-oxide (**5a**) only gave the phenol in 3% yield, as well as side products corresponding to the rearrangement products (**2**) and (**3**). In neither case was oxidation of the benzylic, *meta*-, or *para*-positions noted. This result indicates either an intramolecular process or transient formation of a very reactive species which is essentially reacting in a solvent cage. At present we cannot discriminate between these paths; further work on the mechanism of the hydroxylation is in progress.

With the homologous oxide, as its boron trifluoride complex (**6b**), irradiation afforded both the phenol (**8**) (8%) and the alcohol (**9**) (10%) as well as the deoxygenated compound (**6c**) (7%).

All new compounds have been characterised by microanalytical and spectral methods.

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[3] E. C. Taylor and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231.