

γ -Ray Induced Reactions of Heteroaromatic *N*-Oxides

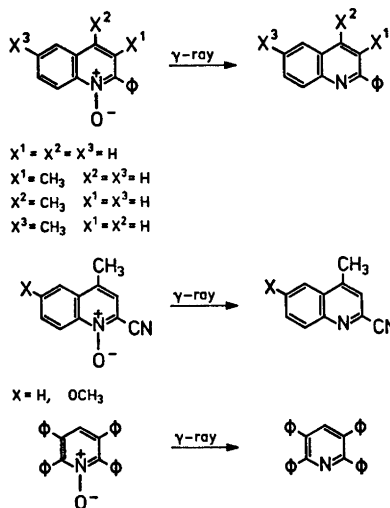
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The light-induced reactions of aromatic amine *N*-oxides are complex, resulting in a variety of products. The product distribution is highly dependent on solvent, and the isolable products vary considerably with the substituents.¹

We wish to report the γ -ray-induced reactions of 2-phenyl and 2-cyano substituted quinoline *N*-oxides and 2,3,5,6-tetra-phenylpyridine *N*-oxide in acetone solution. These lead to the parent amine as the main products.

The reactions can be summarized as follows:



Occasionally, traces of the corresponding 1,3-oxazepines could be detected in the reaction mixture (TLC). The chemical yield for the formation of the parent amine was as high as 30%, but no attempt was made to optimize this yield. The remaining material was mainly unchanged starting

material accompanied by small amounts of unidentified materials.

It is interesting to compare these results with those of the light-induced reactions. Although in most cases it was found that deoxygenation to the parent amines takes place in the light-induced reactions for the specific *N*-oxides tested, the amines were only minor photochemical products. This difference in the behavior in light- and γ -ray-induced reactions indicates that deoxygenation of the amine *N*-oxides takes place from one excited state, and isomerization to oxazepines *via* another; specifically, the triplet state in the former process and the singlet state in the latter. The data from the light-induced reactions seem to support this hypothesis.² Since in the γ -irradiated systems the triplet excited molecules are formed to a higher degree than might be anticipated by analogy with photochemistry,³ the reactions in which the triplet state is the excited precursor predominate.

Experimental. The γ -ray-induced reactions were performed in glass tubes which were placed into the ⁶⁰Co γ -source Gammacell 220 (Atomic Energy of Canada Ltd., Ottawa), the dose rate being 7.5×10^{17} eV ml⁻¹ min⁻¹. The solutions were flushed with oxygen-free nitrogen for 15 min before irradiation. The products formed were isolated by chromatography on silica gel. Care was taken to prevent exposure of the reaction mixture to light before and after irradiation. The *N*-oxides were all previously described, and prepared by the reported methods.⁴

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