Photolysis of 4-Methylcinnoline 1- and 2-*N*-Oxides

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Summary 4-Methylcinnoline 1- and 2-*N*-oxides are photolabile; in the case of the 2-*N*-oxide, products are formed by formal loss of N_2, CO, and NO.

THE photochemical reactions of the *N*-oxides of the benzodiazines, phthalazine, quinazoline, and quinoxaline are well-documented.[1] However, the closely related cinnoline *N*-oxides were reported to be photochemically inert.[2] We report here that both the 1- and 2-*N*-oxides of 4-methylcinnoline are photochemically reactive provided extended irradiation is employed.

4-Methylcinnoline 2-*N*-oxide[3] (**1**) (0·5 g)† on irradiation‡ in methanol or benzene for 84 h gives 4-methylcinnoline (**7**) (58%),§¶ 3-methylindazole (**4**) (25%), 3-methylindole (**6**) (8%), and 3-methylbenzofuran (**3**) (*ca.* 1%). The yields of all the products except (**7**) were the same with or without nitrogen purging. The yield of (**7**) was lower when the nitrogen purge was omitted, clearly demonstrating the influence of oxygen (air) on the deoxygenation reaction. The oxygen quenching of 4-methylcinnoline formation indicates deoxygenation occurs *via* a triplet state while the other products are formed *via* a singlet state.

Several reactions, loss of N_2, NO, and CO, appear to take place at the same time. The last of these processes would formally give product (**4**). A likely precursor to this is the amide[5] (**8**) but independent photolysis of this material failed to yield the indazole. An alternative route might involve isomerisation to the 3*H*-indazole (**2**). Though these species are known to lose nitrogen on photolysis,[6] loss of the 3-formyl group may also occur, possibly by a photochemical or thermal[6c] 1,3-rearrangement, followed by decarbonylation of the resulting 1-formylindazole.

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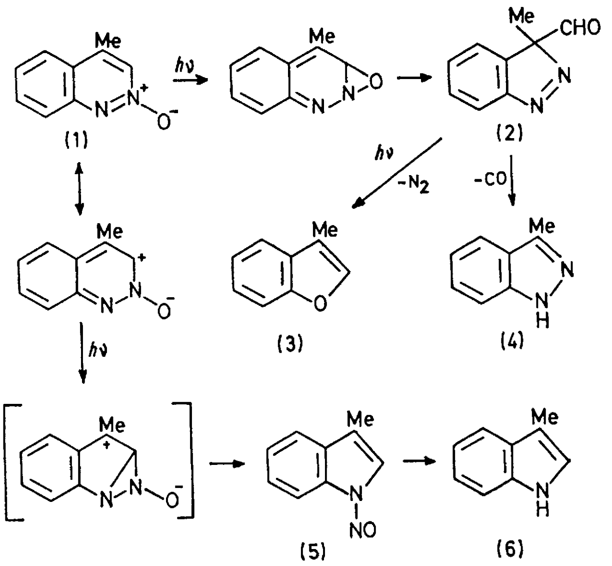
† The structures of the 1-*N*-oxide and 2-*N*-oxide were assigned by ^{1}H n.m.r. spectroscopy[3] and later verified by mass spectrometry.[4] $Eu(dpm)_3$ shift studies are in full agreement with these assignments.

‡ 450 W medium-pressure mercury arc lamp. All irradiations were performed in Pyrex vessels. The solutions (100 ml) were deoxygenated by a nitrogen purge prior to and during photolysis.

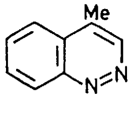
§ Products were identified either by identical physical and spectral characteristics with authentic samples, or by identical g.l.c. retention times with authentic samples on two different columns, at different temperatures, and identical by co-injection on these columns.

¶ Yields quoted are those for the photolysis in methanol.

The path to 3-methylindole (**6**) is less obvious. However, a possible route might be isomerisation to the nitrosoindole (**5**) followed by a thermally induced solvolytic loss of NO^+. The feasibility of such a path is demonstrated by the ready loss of NO from the independently synthesised nitrosoindole[7] (**5**) in methanol. The isomerisation of the cinnoline *N*-oxide (**1**) to the nitroso-indole is an unusual process but a similar rearrangement has been suggested[8] to account for products in the photolysis of 4-phenylbenzo-1,2,3-triazine 3-*N*-oxide.



Scheme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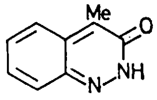
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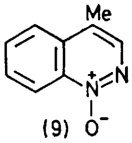
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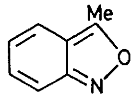
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4-Methylcinnoline 1-*N*-oxide[3] (**9**) is also photo-reactive in methanol. The main product, *via* deoxygenation, is 4-methylcinnoline (42%) but 3-methylanthranil (**10**) (11%) and 2-aminoacetophenone (4%) are also formed. 3-Methylanthranil could be formed by loss of HCN. Such fragmentation has not previously been reported in *N*-oxide photochemistry but the mass spectrum[4] of the 1-*N*-oxide also shows loss of HCN.

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