PREPARATION AND SOME REACTIONS OF o-NITROSOANILINE

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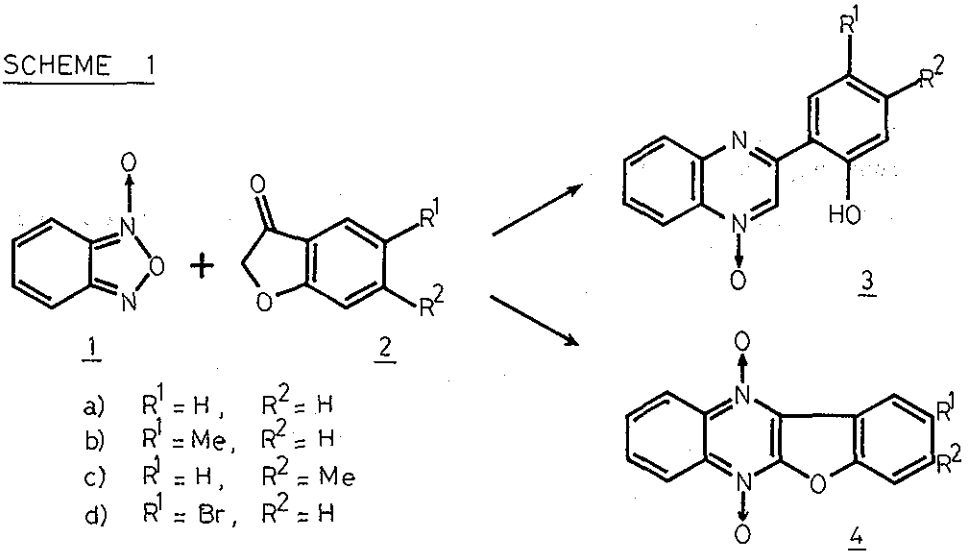
Treatment of o-nitrosoaniline with benzofuran-3(2H)-ones in base gives the corresponding 3-(o-hydroxyphenyl)-quinoxaline 1-oxides in good yield. The reaction of o-nitrosoaniline with benzoin gives a mixture of the mono- and di-N-oxides of 2,3-diphenyl-quinoxaline. o-Nitroso-aniline reacts readily with benzaldehyde to give 1-hydroxy-2-phenylbenzimidazole.

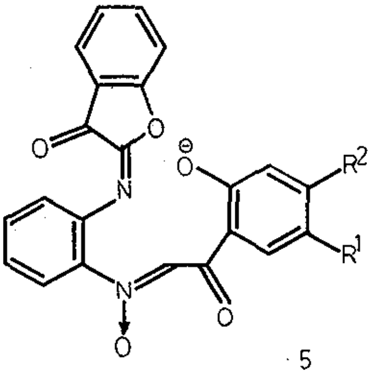
In a previous paper[1] we reported that benzofurazan 1-oxide (1) reacts with benzofuran-3(2H)-ones (2) to give products (3) which are two oxidation levels lower than expected (4, Scheme 1).

SCHEME 1



a) $R^1 = H$, $R^2 = H$
b) $R^1 = Me$, $R^2 = H$
c) $R^1 = H$, $R^2 = Me$
d) $R^1 = Br$, $R^2 = H$

Since the iminonitrone 5, postulated[1] as an intermediate for this reaction, is at the same oxidation level as the aminonitrone 7 expected from a base-catalyzed reaction between



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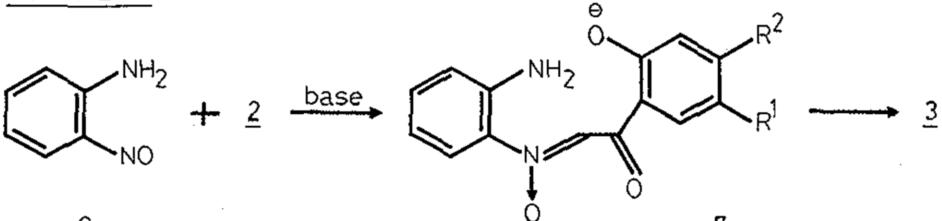
o-nitrosoaniline (6, two oxidation levels below 1) and 2, it seems reasonable to expect that the latter reaction would also lead to 3-(o-hydroxyphenyl)quinoxalin-1-oxides (3, Scheme 2).

SCHEME 2



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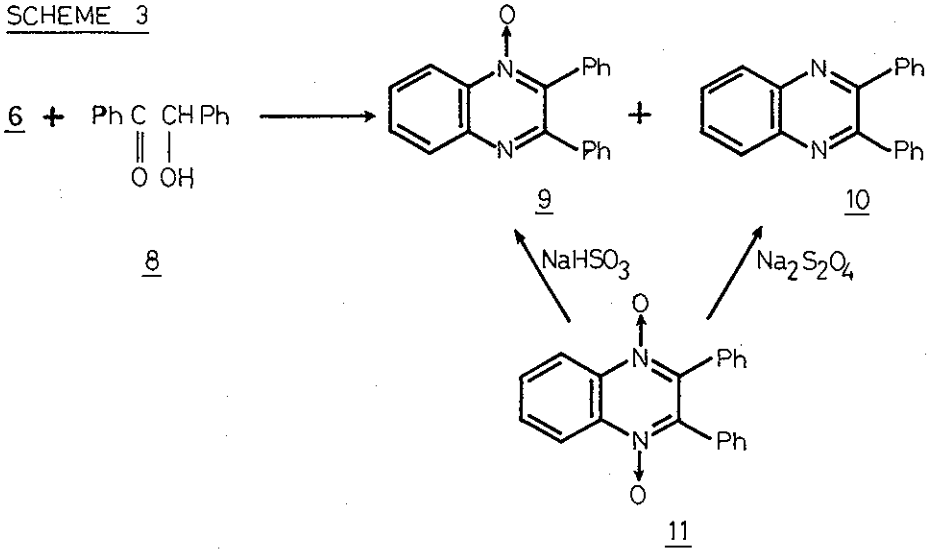
Unfortunately, o-nitrosoaniline is a rare compound whose preparation in small (unspecified) amounts was reported for the first time in 1969 by the reduction of 1 with triphenylphosphine[2]. Having no practical route to 6 at our disposal, we were hitherto unable to verify this expectation.

The recent isolation in our laboratory of 6, in small but reproducible yield, has enabled us to establish the generality of Scheme 2 as a route to the monoxides 3. The elusive o-nitrosoaniline was obtained as follows[3]: o-quinonedioxime (5.0 grams) was refluxed in diethylamine (150 ml) for 15 hours, and the resulting solution was allowed to stand at room temperature in an evaporating dish until the diethylamine evaporated completely. The residue (a two-phase system comprising a solid and a liquid) was mixed intimately with silica gel (8 g) and transferred to the top of a wet (petroleum ether 60-70°) silica gel column (2.5 cm diameter, 28 g silica gel). The chromatogram was monitored by the characteristic dark brown-red band of o-nitrosoaniline on the silica gel column, and by the green stain that appears on the cotton plug at the end of the column. Elution was carried out first with petroleum ether (300 ml), then with petroleum ether:benzene (1:1) until the cotton plug turned green (usually about 300 ml), and finally with benzene. The green eluant was evaporated to dryness and the residue was recrystallized from petroleum ether. Yield: 100-125 mg of dark green needles melting at 78°; IR (KBr, cm^{-1}): 3350-3000, 1620, 1580, 1485, 1395, 1365, 1265, 1200, 1160, 1110, 750.

A vigorous reaction ensued when a solution of 2 and 6 (1:1 molar ratio) in methanol was treated with 5% methanolic potassium hydroxide. The mixture was allowed to stand at room temperature for four hours and then acidified with acetic acid. The precipitated products (3a to 3d) were identical with authentic samples prepared in comparable yields[1] from the reaction of 1 with 2 (1:2 molar ratio, Scheme 1).

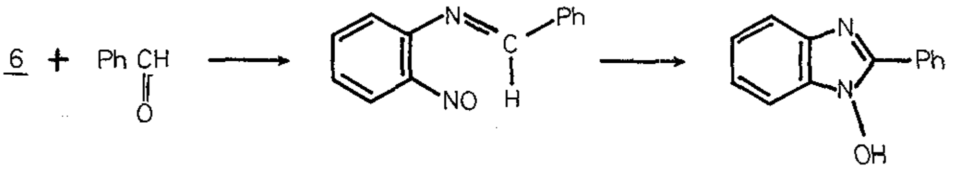
In an attempt to extend the scope of this reaction we treated 6 with alpha hydroxy-ketones such as benzoin (8) in base (Scheme 3). The product was a mixture (separable by chromatography on a silica gel column) comprising not only the sought-after monoxide 9 but also the quinoxaline 10. Identification was based on comparison with authentic samples prepared from 2,3-diphenylquinoxaline-1,4-dioxide[4] (11, Scheme 3). Of particular interest is the selective reduction of 11 (1.8 g in 60% refluxing ethanol) to 9 by dropwise addition over a period of 20 minutes of aqueous sodium bisulfite (7.0 g) followed by a further reflux period of 4 hours. The monoxide (9, isolated by dilution with cold water and extraction with ether) was obtained in 73% yield (analysis for $C_{20}H_{14}N_2O$; m.p. 193-195° (lit.[5] 196°); IR (KBr, cm^{-1}): 1568, 1475, 1345, 945, 768, 758, 695).

SCHEME 3



When a solution of o-nitrosoaniline (6, 50 mg) in benzaldehyde (85 mg) was treated with two drops of acetic acid, an exothermic reaction occurred. After a few minutes the mixture was diluted with water and the precipitated product recrystallized from EtOH-H_2O (m.p. 224° dec., 52% yield). This product was identical with an authentic sample of 1-hydroxy-2-phenylbenzimidazole (12, lit.[6] m.p. 222°) prepared by refluxing o-nitroaniline and benzaldehyde in dry toluene for 3 days[6]. The reaction with o-nitrosoaniline probably goes by cyclization and prototropic shift of an intermediate nitrosoimine (Scheme 4).

SCHEME 4



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