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# ON THE REACTION OF β-NAPHTHOL WITH N,N-DIMETHYLHYDRAZINE - A NEW RADICAL AMINATION PROCESS

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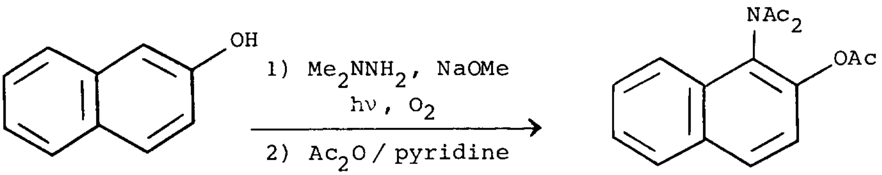
Reaction of β-naphthol with N,N-dimethyl-hydrazine under carefully defined conditions leads via a radical process to the formation of 1-amino-2-naphthol in high yield.

The reaction of β-naphthol with hydrazine[1] and with phenylhydrazine[2] was first described at the turn of the century and shown to lead to a smooth replacement of the phenolic hydroxyl group by the corresponding hydrazine moiety. We now report that the reaction of β-naphthol with N,N-dimethylhydrazine follows an entirely different course.

In the first instance, attempted reaction under a variety of conditions led in an irreproducible fashion to a relatively complex mixture of products. It was of interest, however, to note the formation of 1-amino-2-naphthol, albeit in low and variable yield (15-30%). The isolation and identity of this substance was confirmed by the preparation of its crystalline triacetyl derivative[3] and comparison with an authentic sample. Consideration of these facts suggested that a radical reaction was involved. A systematic study of various parameters was undertaken in order to determine optimal reaction conditions.

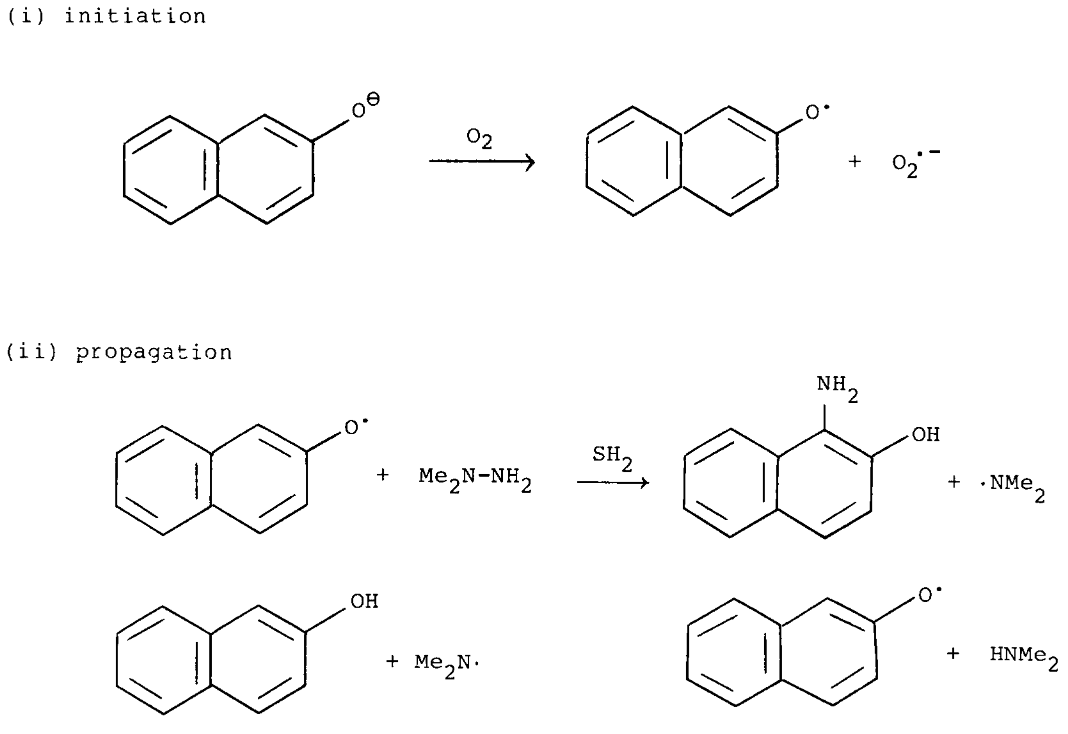
The influence of oxygen, in particular, is of paramount importance for a successful reaction; no aminated product being detected in blank experiments performed under an argon atmosphere. Although reaction does occur in the dark, the overall rate is considerably increased when the reaction is run in the presence of a tungsten lamp. We have also observed that the reaction proceeds most efficiently in the presence of a defined quantity of sodium methoxide (0.15 mmol equiv.), higher or lower concentrations leading to longer reaction times. Under these rigorously defined conditions it is possible to isolate the triacetyl derivative of 1-amino-2-naphthol in 90% yield[4].



In a typical experiment sodium methoxide (4 mg, 0.074 mmol) in methanol (0.8 ml) was added to β-naphthol (73.3 mg, 0.51 mmol) in N,N-dimethylhydrazine (1.5 ml, 20.4 mmol). The reaction mixture was heated to 60°C, irradiated with a tungsten lamp (OSRAM halogen, Bellaphot 300 W) placed at a distance of 50 cm, and a current of oxygen was passed through the solution for 20 minutes. The disappearance of starting material was complete after 30 minutes (by t.l.c.). Solvent was removed *in vacuo* and the residue was treated with acetic anhydride (2 ml) in pyridine (18 h), diluted with water and thoroughly extracted with dichloromethane. The organic extract was successively washed with copper sulphate solution (10%), water, and brine and dried ($Na_2SO_4$). Removal of solvent and recrystallisation from ethanol gave the triacetate of 1-amino-2-naphthol (130 mg, 90%) m.p. 119-20°C (lit.[3] 119.5°C).

Although the influence of light and oxygen provides strong presumptive evidence for the involvment of radical intermediates further support comes from the fact that the addition of radical scavengers, such as 2,2,5-trimethyl $\Delta^5$-pyrroline-*N*-oxide or 2,2,6,6-tetramethylpiperidine-*N*-oxyl leads to a much longer induction period for the reaction. An experiment using ferric chloride as initiator under an argon atmosphere also gave an acceptable yield (60%) of 1-amino-2-naphthol but in a slower reaction.

We have also examined the use of other hydrazines in this reaction. No observable amination occured with hydrazine or *N*,*N*-diphenylhydrazine, although in the latter case it was possible to isolate diphenylamine (55%, based on β-naphthol). *N*,*N*-dimethylhydrazine can however be effectively replaced by *N*,*N*-diethylhydrazine.



Scheme 1

From the mechanistic standpoint it is possible to envisage that the key step in the reaction sequence involves an $SH_2$ displacement reacton on dimethylhydrazine by the phenoxy radical (Scheme 1). Such a step has been postulated in the reaction of alkyl radicals with tetrafluorohydrazine[4], although in this instance the N-N bond strength is much weaker (19 K cal/ mole). In view of the fact that phenoxy radicals can abstract hydrogen atoms from oximes and hydroxylamines[5], an alternative chain mechanism can also be designed involving attack of phenolate anion on a (protonated) dimethylhydrazyl radical and subsequent hydrogen atom abstraction from dimethylhydrazine by the liberated dimethylamino radical.

Efforts to extend this reaction to other phenols (phenol, oestradiol, *p*-cresol, 2,6-dimethylphenol, *p*-nitrophenol) have been unsuccessful.

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