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A new radical way to *N*,*N*-dimethylaniline hydroperoxide (DMAHP) and its application in organic synthesis

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Abstract

N,*N*-Dimethylaniline hydroperoxide was obtained when treating *N*,*N*-dimethylaniline with NHPI/$Co(OAc)_2/O_2$ *via* a radical reaction mechanism. This intermediate has potential application in the synthesis of some important chemical scaffolds.

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Recent studies showed that *N*-hydroxyphthalimide (NHPI) in combination with molecular oxygen and metal salt cocatalysts, such as $Co(OAc)_2$ or $Co(acac)_2$, was a valuable catalytic system for aerobic oxidation of various organic compounds under mild reaction conditions [1–6]. It is believed that the phthalimide *N*-oxyl (PINO) radical generated in situ from the reaction of O_2 and NHPI is able to abstract a hydrogen atom from the organic substrates. The newly formed carbon radical then rapidly reacts with O_2 to give hydroperoxide [7]. Normally, hydroperoxide will further convert into a variety of ultimately oxygenated products [7,8]. In this paper, we wish to report some useful results in the reaction of *N*,*N*-dimethylaniline (DMA) in NHPI/$Co(OAc)_2/O_2$ system.

The reaction was carried out in a two-neck flask equipped with a stopper and an oxygen balloon. DMA (10 mmol) was dissolved in acetonitrile (20 mL) followed by the addition of NHPI (10 mol%) and $Co(OAc)_2\cdot 4H_2O$ (0.5 mol%). After stirring at rt for 30 min, a brown solution formed. TLC showed that DMA had disappeared and a product had formed. Although, this product underwent decomposition (the product on the TLC gradually became dark within 10 min), it could be purified with flash chromatography in 37% yield as a straw yellow semi-solid. From analysis data [9] of the product, we could deduce that the oxygenated products was *N*,*N*-dimethylaniline hydroperoxide (DMAHP). The proposed mechanism was shown in Scheme 1. Aleksandrov reported the formation of DMAHP *via* oxidation of DMA by molecular oxygen (AIBN as initiator). To our knowledge, DMAHP has not yet been fully investigated [10,11], so many experiments should be carried out to confirm its structure and also to demonstrate its application.

A surprising result was observed when an acetonitrile solution of DMAHP was exposed to an aqueous solution of sodium hydrosulfite. The reaction underwent rapidly and a new compound with great polarity was found in aqueous layer. We deduced the reaction occurring according to the equation as shown in Scheme 2. However, we had no direct

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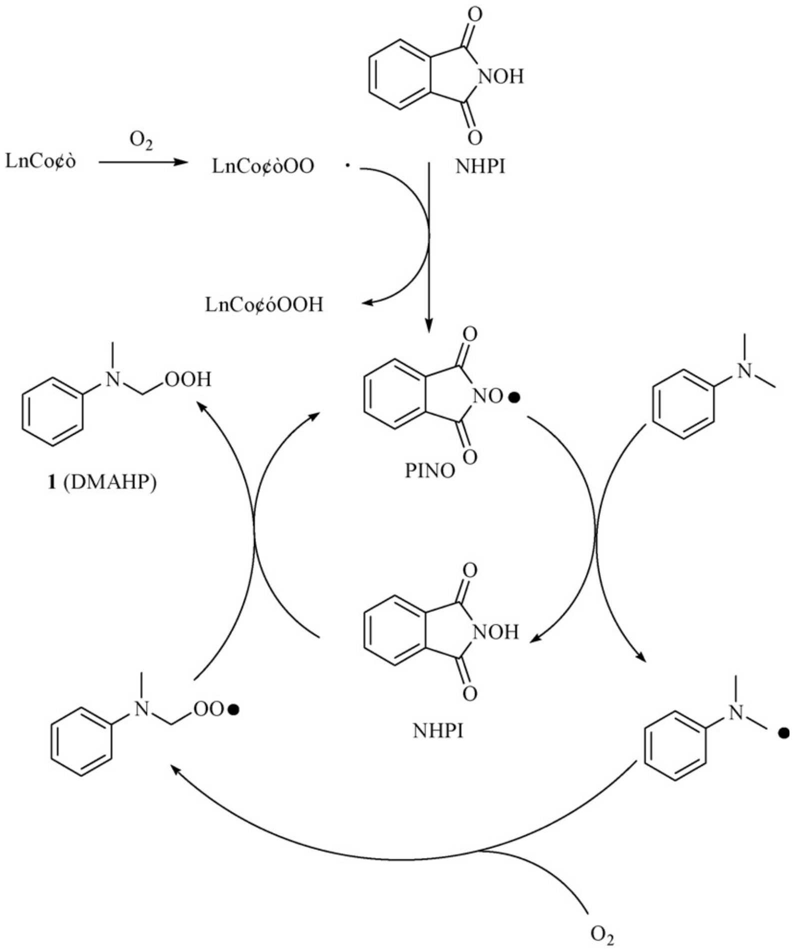
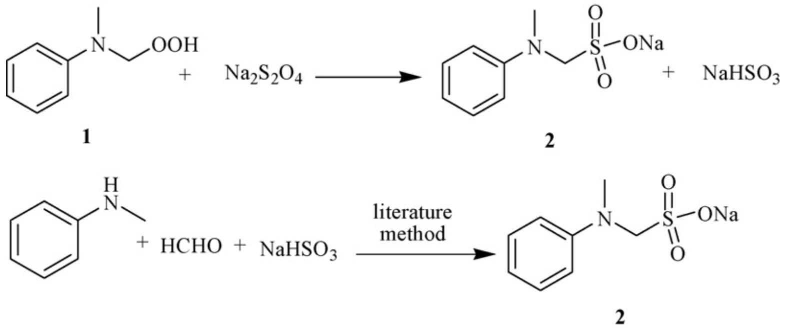


Scheme 1. The proposed mechanism for the synthesis of *N*,*N*-dimethylaniline hydroperoxide (DMAHP).

evidence towards this mechanism yet. So compound **2** was synthesized by a reported procedure [12] to corroborate our result. All the characters of compound **2** matched completely with those of the new compound formed by DMAHP with sodium hydrosulfite [13].

In 1982, Shono and coworkers reported the synthesis of tetrahydroquinolines from *N*-methoxylmethyl-*N*-methylaniline and olefins [14]. We envisioned that DMAHP could serve the same purpose for synthesis of congeners of tetrahydroquinolines. DMAHP was first treated with $BF_3\cdot Et_2O$ (1.5 eq) in CH_2Cl_2 at −70 °C for 10 min, then a methylene chloride solution of alkenylether (1.5 eq) was added. After stirred at −70 °C for 30 min, the resulting



Scheme 2.

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