One-pot oxidative transformation of aniline into 4-phenylazodiphenylamine in the DMSO–KOH system

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Aniline 1 undergoes oxidative trimerization into 4-phenylazodiphenylamine 2 in the DMSO–KOH system at 60 °C.

Oxidation of **1** can lead to azobenzene[1] **3**, azoxybenzene or other products[2] depending on the experimental conditions.

We present here a hitherto unknown example of the one-pot transformation of **1** into **2**,[†] reaction (1):

$$\underset{\mathbf{1}}{\mathrm{PhNH_2}} \xrightarrow[60\ ^\circ\mathrm{C}]{\mathrm{DMSO–KOH,\ O_2}} \underset{\mathbf{2}}{\mathrm{PhNH{-}C_6H_4{-}N{=}N{-}Ph}} \qquad (1)$$

The reaction proceeds smoothly under aerobic conditions to give **2**. A considerable amount of oxygen is transferred into the reaction mixture together with powdered KOH. The result differs from that of reaction of **1** with KO_2/18-crown-6-ether in DMSO solution described by Marletta and co-authors.[3] Only traces of **2** were detected in the reaction mixture and 4-nitrodiphenylamine and **3** were the major products. The authors consider that **1** is readily ionized by superoxide or *tert*-butoxide and then oxidized in the radical recombination and N-oxidation processes involving molecular oxygen.

On the other hand, a new base-promoted route to **2** starting from **1** and **3** by way of nucleophilic aromatic substitution of hydrogen (NASH) has recently been reported by Stern and co-workers.[4] The authors found that hydrazobenzene **4** was formed in the reaction between **1** and **3** under anaerobic conditions. However, we failed to detect **4** in the reaction mixtures and no reaction was observed under anaerobic conditions which is consistent with Marletta.[3]

Our process probably includes both oxidative coupling of **1** to **3** and subsequent NASH in **3** by anilide anions to give final product **2**, reaction (2):

$$\mathbf{1} \xrightarrow[\mathrm{NASH}]{^{-}\mathrm{OH}} 2\mathrm{PhNH^-} \xrightarrow{-2e} \underset{\mathbf{4}}{[\mathrm{PhNHNHPh}]} \xrightarrow{-2\mathrm{H}^\bullet}$$

$$\longrightarrow \underset{\mathbf{3}}{\mathrm{Ph{-}N{=}N{-}Ph}} \longrightarrow \mathbf{2} \qquad (2)$$

A small amount of **3** was obtained from the reaction mixture.

It is important to note that compound **2** was not formed when ethanol, 1,4-dioxane or DMF were used as solvent instead of DMSO. Also, *ortho*- and *para*-toluidines showed no reaction activity, whereas *meta*-toluidine gave corresponding trimeric product 4-(*m*-tolylamino)-*m*-azotoluene **2a**.[‡]

We should say that the preliminary results presented here are not sufficient to make a final conclusion and the mechanism of the process needs to be carefully investigated further.

References

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[†] A typical procedure for the synthesis of 4-phenylazodiphenylaniline **2** starting from aniline **1**. Aniline **1** (5 ml, 54 mmol) was added to a suspension of KOH (12 g, 214 mmol) in 10 ml of DMSO. The reaction mixture was kept at 60 °C for 30 h under an argon atmosphere and then poured into 200 ml of cold water. The water solution was treated with benzene (3×50 ml), the organic layers were separated and joint extracts were steam distilled. Unreacted **1** (2.0 ml) was returned. The resinous residue was chromatographed on Al_2O_3 (benzene–hexane, 1:1) to obtain 1.35 g (46%) of **2** as an orange-yellow crystalline powder, mp 88–89 °C. MS *m*/*z* for **2** (16 eV) 273 (M^+), 196 ($M^+ - Ph$), 182 ($M^+ - PhN$), 168 ($M^+ - PhN_2$). Anaerobic reactions were carried out in sealed 50 ml flasks. Argon was dried and made oxygen-free by passage through a gas purifier. Aniline and DMSO were purged by bubbling with argon both prior to and during the reaction. KOH was powdered in a dry box under an argon atmosphere.

[‡] Characterization data for **2a**: orange oil. ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H, Me), 2.26 (s, 3H, Me$'$), 2.37 (s, 3H, Me$''$), 5.56 (s, 1H, NH). MS, *m*/*z* 315 (M^+).

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