

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

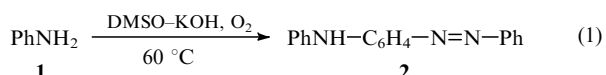
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Aniline **1** undergoes oxidative trimerization into 4-phenylazodiphenylamine **2** in the DMSO–KOH system at 60 °C.

Oxidation of **1** can lead to azobenzene¹ **3**, azoxybenzene or other products² depending on the experimental conditions.

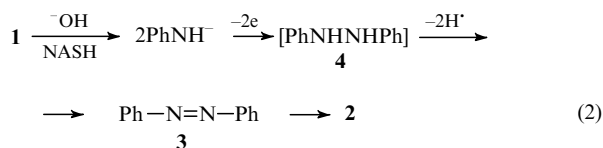
We present here a hitherto unknown example of the one-pot transformation of **1** into **2**,[†] reaction (1):



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 KO₂/18-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):



[†] A typical procedure for the synthesis of 4-phenylazodiphenylamine **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 Al₂O₃ (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⁺–PhN₂). 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. ¹H NMR (CDCl₃) 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⁺).

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

- 1 S. Jeon and D. T. Sawyer, *Inorg. Chem.*, 1990, **29**, 4612.
- 2 M. Hedayatullah, *Bull. Soc. Chim. Fr.*, 1972, 2957.
- 3 D. J. Stuehr and M. A. Marletta, *J. Org. Chem.*, 1985, **50**, 694.
- 4 M. K. Stern, B. K. Cheng, F. D. Hileman and J. M. Allman, *J. Org. Chem.*, 1994, **59**, 5627.

Received: Moscow, 23rd October 1995

Cambridge, 6th December 1995; Com. 5/07153D