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Short communication

A rapid and easy method for the synthesis of azoxy arenes using tetrabutylammonium peroxymonosulfate

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Abstract

A simple and efficient method for the selective oxidation of aromatic amines to azoxy arenes using tetrabutylammonium peroxymonosulfate in high/excellent yield (75–95%) after short reaction times (2–10 min) has been developed.

Keywords: Azoxy arenes; Oxidation; Aromatic amines; Tetrabutylammonium peroxymonosulfate

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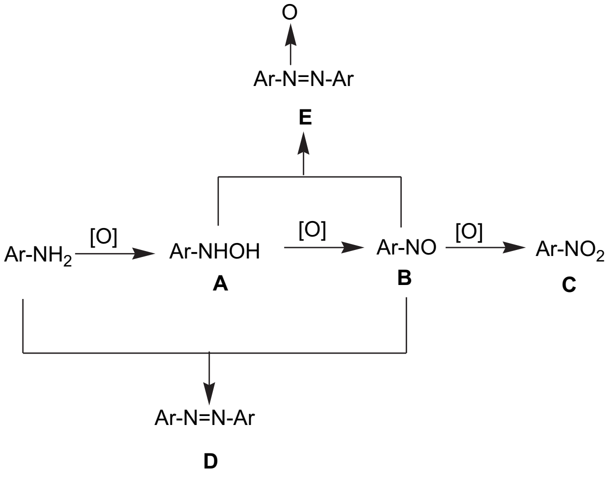
Azoxy arenes are key materials for electronic devices due to their liquid crystalline properties [1]; they have also been utilized as therapeutic medicines, polymer inhibitors, stabilizers, dyes, reducing agents and analytical reagents [2]. Hence, the development of an efficient and selective method for the preparation of these valuable compounds is a worthwhile goal. Although the oxidation of amines is a fundamental reaction in the case of the synthesis of oxygen-containing amines such as azoxy compounds, as outlined in Scheme 1, a variety of oxidation products such as *N*-arylhydroxylamine (A), nitroso; (B), nitro (C) derivatives and also azo arene (D) are frequently observed together with azoxy arene (E) [3]. Thus, selectivity in this reaction is required in order to obtain the desired product.

Relatively few general methods exist for the oxidation of aromatic amines to azoxy arenes. Aqueous peracids oxidize aniline to a mixture of azo- and azoxybenzene and oxidize *ortho*-substituted anilines to nitrobenzene [4]. *t*-BuOOH in



Scheme 1.

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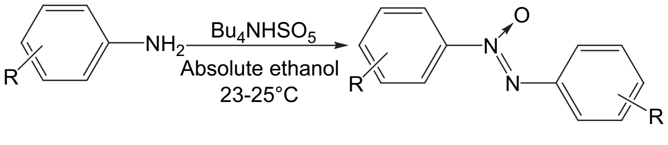
the presence of Mo(VI), V(V) and Ti(IV) has been employed under both homogeneous and heterogeneous conditions in the oxidation of aniline to nitrobenzene as main product along with azoxybenzene in low yield [5]. To improve the efficiency and also the selectivity of the oxidation reaction for the preparation of azoxy arenes, a number of catalytic systems using H_2O_2 in combination with Na_2WO_4 [6], $RuCl_3$ [7], cetylpyridinium heteropolyoxometalates (PCWP) [8], titanosilicate zeolite (TS-1, 2) [9,10], perfluorinated ketone attached to silica [11], ETS-10 molecular sieves [12] as well as Preyssler heteropolyacid [13] have been employed. However, such reactions require expensive or unavailable catalysts, harsh reaction conditions (low or high temperature) and all suffer from very long reaction times. Thus, available methods for the preparation of azoxy arenes hardly satisfy the current demand for rapid chemical transformation in high efficiency and selectivity under mild and metal-free conditions using a simple and practical procedure.

Tetrabutylammonium peroxymonosulfate (Bu_4NHSO_5), which is an organic salt of Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), has been introduced for using in anhydrous conditions without recourse to a buffered, two phase system [14]. The compound has been employed successfully in limited oxidation reactions under both catalytic and non-catalytic conditions [15]; Oxone® has been used for the oxidation of certain anilines to the corresponding nitro- and nitroso derivatives [16]. We have found that Bu_4NHSO_5 in ethanol is an excellent oxidation system for the conversion of arylamines to azoxy arenes in high/excellent yield and offers a good level of selectivity under very mild conditions and short reaction times (Scheme 2).

The oxidation system was initially employed with aniline under solvent-free conditions, but this resulted in a sticky mass and the formation of a complex mixture of oxidation products. A systematic investigation of the oxidation of aniline in various solvents was then performed. Among the solvents tried (ethanol, methanol, acetonitrile, acetone, chloroform and dichloromethane) ethanol was found to be the best, in terms of yield, selectivity and reaction time. It was also observed that the reaction proceeded most rapidly and gives optimal yield and selectivity at 23–25 °C. Under the optimized conditions, azoxybenzene was obtained in 95% yield within 3 min.

To evaluate the scope and limitation of the method, various substituted aromatic amines were subjected to oxidation (Table 1). The results in Table 1 show that the system worked well with different anilines containing electron-donating and electron-withdrawing groups in yields ranging from 77 to 95% after <10 min reaction (entries 1–8). The extent of conversion of different substituted anilines was found to follow the order: *p*-OMe-aniline > aniline > *p*-Me-aniline > *p*-Cl-aniline ∼ *p*-Br-aniline > *o*-Me-aniline > *p*-COMe-aniline > *p*-NO_2-aniline. However, the selectivity towards azoxy arene in the final product was found to be of the order: aniline > *p*-NO_2-aniline > *p*-COMe-aniline > *p*-Cl-aniline > *p*-Br-aniline > *p*-Me-aniline > *p*-OMe-aniline > *o*-Me-aniline. Thus, whilst all substituted anilines were less selective than aniline, it was observed that the presence of electron-withdrawing groups on the phenyl ring of aniline (Table 1, entries 7, 8) increased the selectivity of the azoxy product as well as the reaction time compared to other substituted anilines. When this system was applied to the oxidation of 1-naphthylamine, the related azoxy was secured in 75% yield within 10 min (entry 9).



Scheme 2.

The simplicity of this high yielding, metal-free oxidation method and the use of ethanol and ethyl acetate as environmentally friendly solvents in the reaction and work-up procedures, respectively, highlight the usefulness of this methodology.

In conclusion, a practical and efficient procedure for the rapid and easy preparation of various azoxy arenes using tetrabutylammonium peroxymonosulfate in ethanol in high/excellent yield and good selectivity under very mild and metal-free conditions has been developed. The method offers ready scalability, employs ethanol as a ‘green’ solvent as well as easy and safe work-up.

1. Typical procedure

To a solution of absolute ethanol (125 ml) containing aniline (0.025 mol, 2.33 g) was added freshly prepared tetrabutylammonium peroxymonosulfate (17.5 g) [18]. The mixture was stirred under air at 23–25 °C and the reaction was followed by TLC. The ethanol was evaporated under vacuum and the product extracted by the addition of anhydrous ethyl acetate followed by simple filtration. Evaporation of the solvent gave azoxybenzene (94.5% yield; 2.33 g, 0.012 mol). Further purification was achieved by silica chromatography eluting with *n*-hexane/ethyl acetate (10/3). Yellow solid, m.p. 36 °C (lit. 35 °C) [19]; IR (neat) 1478, 1437, 1296, 1162, 1071, 1024, 917, 762, 683, 521 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.39–7.54 (6H, m), 8.17–8.30 (4H, m); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 123, 125.2, 128.2, 128.4, 128.9, 130.8, 143.3 and 147.6; MS: *m/z* 198 (M^+). [Note: The procedure for purification of other products is similar to azoxybenzene only for entries 7, 8 using the 10/6 ratio of *n*-hexane/ethyl acetate.]

Acknowledgments

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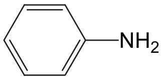
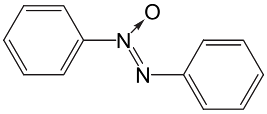
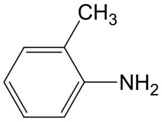
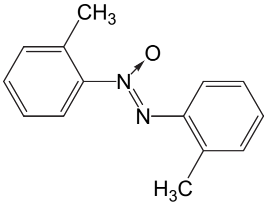
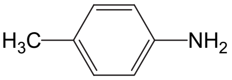
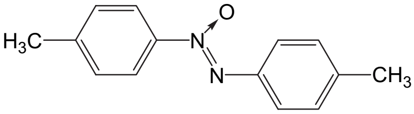
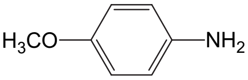
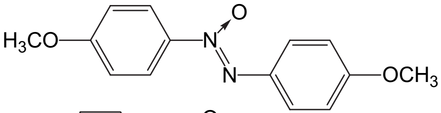
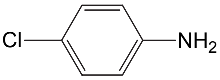
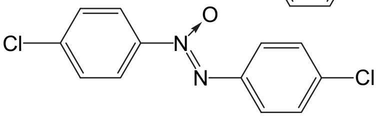
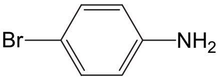
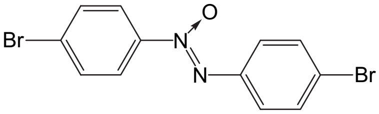
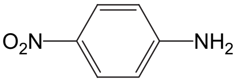
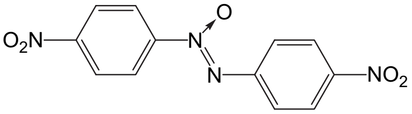
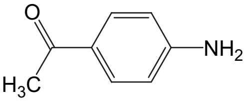
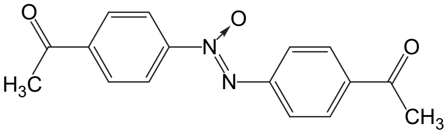
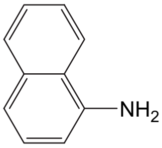
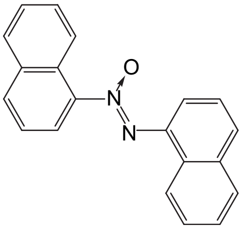
Table 1
Oxidation of arylamines to azoxy arenes using Bu_4NHSO_5 in absolute ethanol[a]

Entry	Amine	Product[b]	Time (min)	Isolated yield (%)[c]	M.p. (°C) (lit.)	Ref.
1			3	95	36 (35)	[19]
2			5	77	59–60 (60)	[19]
3			5	92	69 (68)	[19]
4			2	87	118, 135 (118, 136)	[19]
5			5	83	155 (155–156)	[19]
6			5	80	172 (172)	[19]
7			10	85	191–192 (192)	[19]
8			10	87	192 (191–193)	[19]
9			10	75	125 (123)	[10]

[a] Reactions were run at 23–25 °C using amine (1.0 mmol), Bu_4NHSO_5 (0.7 g) in absolute ethanol (5 ml).

[b] All products were identified by their IR, ^1H NMR, ^{13}C NMR and MS spectral data in comparison with those reported in literature [10,17].

[c] The remainder is essentially unreacted amines and other minor unidentified products.

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(b) Travis BR, Ciaramitaro BP, Borhan B. Eur J Org Chem 2002;3429. It is notable that freshly prepared Bu_4NHSO_5 displayed much stronger oxidizing ability than commercially available samples. **Caution**: this peroxide should be considered as a potential explosive.

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