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In-situ Oxidation and Coupling of Anilines towards Unsymmetric Azobenzenes Using Flow Chemistry

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Molecular switches, especially azobenzenes, are used in numerous applications, such as molecular solar thermal storage (MOST) systems and photopharmacology. The Baeyer-Mills reaction of anilines and nitrosobenzenes has been established as an efficient synthetic method for non-symmetric azobenzenes. However, nitrosobenzenes are not stable, depending on their substitution pattern and pose a health risk. An in-situ oxidation of anilines with Oxone® was optimized under continuous flow conditions avoiding isolation and contact. The in-situ generated nitrosobenzene derivatives were subjected to a telescoped Baeyer-Mills reaction in flow. That way azobenzenes with a broad substituent spectrum were made accessible.

Introduction

In recent years, colored azobenzenes (AB), originally known primarily for their use as dyes even as food additives,[1] have gained great popularity due to their wide range of applications as molecular switch.[2] These applications range from energy and information storage,[3] organocatalysis,[4] photobiology and photopharmacology[5] to host-guest chemistry,[6] molecular mechanics[7] and molecular machines.[8] This surge in popularity is primarily attributed to the remarkable isomerization ability of ABs, which can undergo reversible conversion between the energetically stable (*E*)-configuration and the metastable (*Z*)-isomer upon exposure to either light or thermal stimuli.[9] This isomerization process not only changes the geometry of the molecule from an extended planar (*E*)-AB to a twisted (*Z*)-AB, but also modifies its physical properties, including dipole moment and polarity.[10]

Various methods for the synthesis of ABs have been reported in literature over time,[11,12] making the choice of the most suitable synthetic approach dependent on the required substitution pattern. Traditionally, ABs are synthesized through azo coupling reactions, which involve the electrophilic aromatic substitution of a diazonium compounds with an electron rich aromatic system.[13] Although this method provides fast reaction rates and high yields, its narrow substrate scope and hazardous nature pose significant limitations on its applicability.[13] An effective alternative for the synthesis of symmetrical ABs is represented by the Cu-catalyzed oxidative coupling of aniline derivatives.[14] While this method can be applied to produce wide range of symmetrical ABs, its application to unsymmetric compounds is restricted to specific aniline substrates. Therefore, a more selective approach for the preparation of unsymmetric azobenzenes is based on the well-established Baeyer-Mills reaction, firstly described by Baeyer in 1874 and further investigated by Mills.[15] This reaction involves a nucleophilic attack of anilines on nitrosobenzene derivatives in acidic or basic media and proves particularly efficient when electron-rich anilines react with electron-poor nitrosobenzenes.[16]

Despite the availability of numerous synthetic routes, suitable methods for a modular and large-scale production process, crucial for the practical application of azobenzenes in functional materials, are still limited. Continuous flow synthesis has emerged as a possible solution to this challenge. This technique offers several advantages, including the absence of size limitations for reaction vessels and stirring, as the reagents are continuously pumped through the reactor. In addition, it enables precise control over reaction time and temperature, resulting in higher yields and purity.[17]

Over the past years, continuous flow chemistry has been employed for Cu-catalyzed synthesis of symmetric AB derivatives and azo coupling for non-symmetric ABs (Figure 1).[18] However, these syntheses faced challenges in the efficient preparation of unsymmetrically substituted ABs and encounters limitations in terms of accessible substrates. Therefore, a continuous flow synthesis method for non-symmetric AB compounds *via* the Baeyer-Mills reaction was developed by us.[19] This approach enabled the rapid and efficient preparation of large quantities of AB products from various substrates. Nonetheless, this method was limited to the use of electron-rich anilines, resulting in low or no yields for the corresponding ABs synthesized from electron-deficient anilines. Additionally, the use of nitrosobenzenes raises concerns due to their potential low stability and susceptibility to oxidation during the isolation process. Moreover, nitrosobenzenes pose a health

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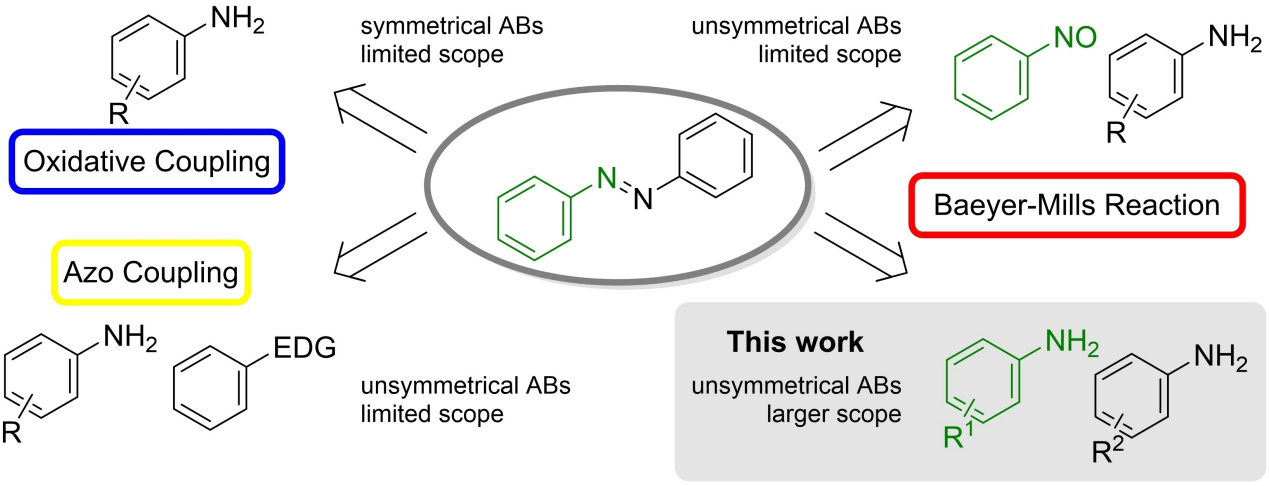


Figure 1. Overview of azobenzene syntheses in continuous flow via oxidative coupling, azo coupling, Baeyer-Mills reaction and this work.[17,18]

hazard as they have been shown to be toxic and can damage DNA strains.[20,21] To circumvent these drawbacks and to increase work safety,[22] an in-situ oxidation of anilines to nitrosobenzenes was developed and is presented herein. This versatile compound class has been applied in a number of other transformations as either electrophile or nucleophile as well as in cycloaddition reactions.[20] As an example of a telescopic reaction of these in situ generated intermediates, the coupling to unsymmetric azobenzenes was demonstrated.

Results

In our initial attempt to broaden the scope of azobenzenes using our previously reported method, we explored substituted nitrosobenzene derivatives within the same flow set-up.[19] Remarkably, this approach successfully led to the formation of the targeted ABs in high yields under the same optimized conditions. However, as anticipated, the freshly prepared nitrosobenzene derivatives displayed limited stability when stored for extended periods at ambient conditions. An in-situ preparation of nitrosobenzenes was targeted to overcome this obstacle and would also eliminate any health risks connected with the direct contact.

The oxidation of anilines towards their corresponding nitrosobenzene derivatives can be achieved through a biphasic reaction involving Oxone® to minimize side reactions.[11,23] This approach aligns perfectly with our methods, as biphasic reactions profit from a continuous flow set-up due to the extended surface area between the phases compared to batch reactions. For this purpose, the aniline derivative was dissolved in dichloromethane (DCM) and Oxone® was dissolved in water. Both solutions were separately pumped and joined in a T-Mixer followed by a tube reactor (10 mL volume). The output of the reactor was fed into an in-line phase separator (Zaiput SEP-10, Figure 2). The organic phase was analysed by an in-line IR spectrometer (Mettler Toledo ReactIR 702L) and collected. This reaction was tested first for a *meta*-nitro-substituted aniline **1 b**.

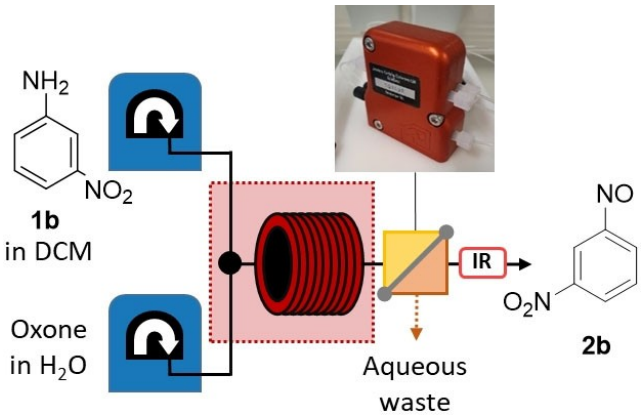


Figure 2. Schematic representation of the continuous flow synthesis of nitrosobenzenes.

The continuous flow reaction showed full conversion after a residence time of 50 min at room temperature and gave reasonable pure nitrosobenzene **2 b** without the need for any further purification (Figure 2).

In the next step, we developed a flow system able to combine the oxidation of anilines to nitrosobenzenes with the subsequent Baeyer-Mills coupling to form ABs (Figure 3). Even though the oxidation was successful at room temperature, the reactor **R1** was placed in an oil bath to ensure the possibility of increasing the temperature for less reactive starting materials. The output of the first reactor (**R1**, formation of the nitrosobenzene) was connected through a back-pressure generator (BPR) to an in-line phase separator. In-line reaction control was realized *via* an IR spectrometer and the output collected in a nitrogen-flushed container at 0 °C, as soon as a steady state was reached with a high conversion. The bright green solution of nitrosobenzene was then pumped into a second reactor to undergo the Baeyer-Mills reaction with a second aniline derivative (Figure 3). Also in this case, the reactor was placed into an oil bath to provide flexibility in temperature control. Additionally, more solvent was added after the second reactor

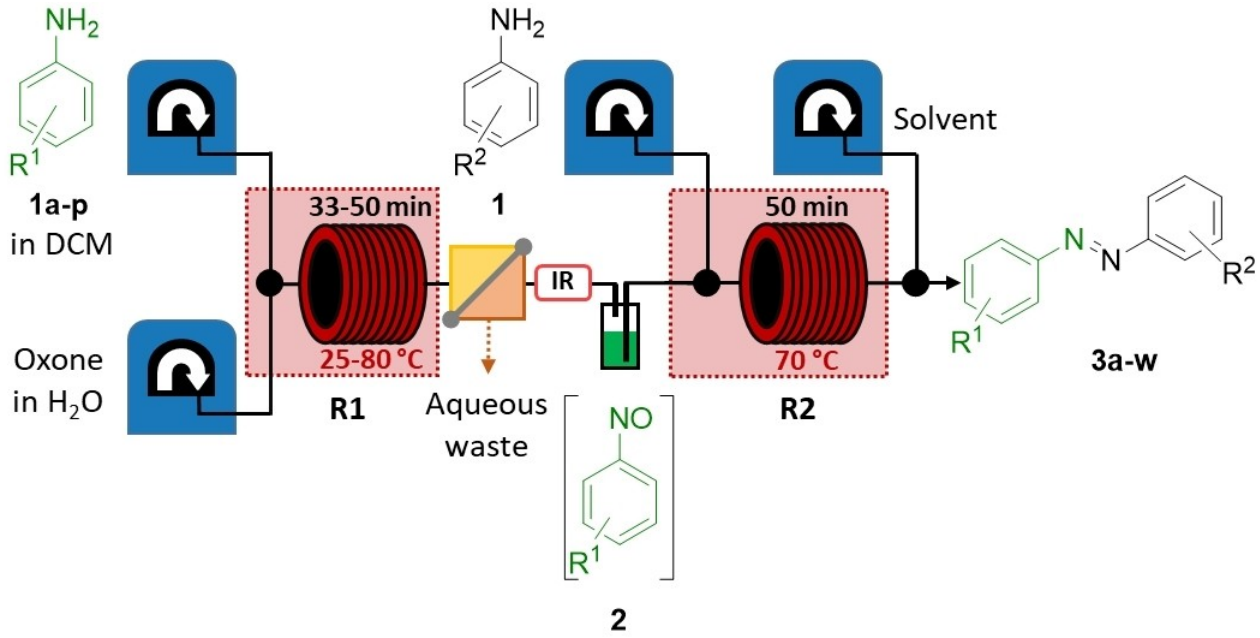


Figure 3. Schematic representation of the continuous flow synthesis of nitrosobenzenes followed by the telescoped Baeyer-Mills reaction.

to dilute the azobenzene solution and facilitates the reaction work up. To realize a reaction temperature of 70 °C, an additional BPR was used prior the collection valve.

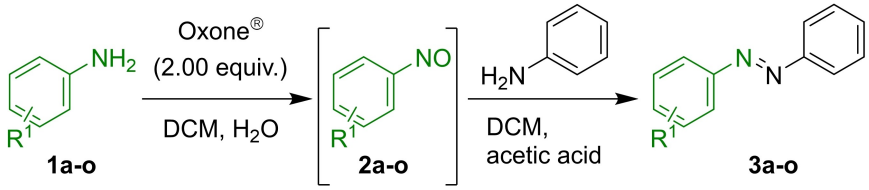
Accordingly, the in-situ synthesis of different nitrosobenzenes was performed using unsubstituted aniline as coupling partner. The procedure proved to be highly effective starting from electron-poor anilines (–NO_2, –CN, Table 1, entries 1–6). For each aniline, the reaction temperature of the first step was screened and the conversion was analysed by in-line IR spectroscopy or thin layer chromatography (Table 1). Despite of the use of dichloromethane as solvent, temperatures up to 80 °C were possible by the use of a BPR (75 psi), which represent an advantage over conventional batch synthesis. For most of the anilines, it was possible to increase the concentration up to 0.32 M. Attempts with a higher concentration of Oxone® resulted in reactor blockages. To keep the stoichiometric ratio, the flow rate was increased from 100 to 200 μL/min and the reaction time ranged from 33 min to 50 min. The telescoped Baeyer-Mills reaction was performed at 70 °C for 50 min, as optimized during the previous studies.[19] The products were extracted with cyclohexane and finally obtained as red compounds after solvent evaporation. To further explore the applicability of this method, additional anilines were tested.

Halide substituted anilines exhibited high yields for bromides and fluorides (Table 1, entries 8 and 9). In contrast, iodoaniline **1g** only gave moderate yields and led to reactor blockages, necessitating the use of less concentrated solutions (Table 1, entry 7). Electron rich substituted anilines (**1j**–**1o**) provided, as expected, only moderate yields and displayed over-oxidation to their nitro-analogues at elevated temperatures (Table 1, entries 10–15). Attempts to use larger alkyl groups, such as *n*-butyl, proved futile as they also resulted in over-oxidation even at low temperatures. Similar outcomes were observed for moieties with a +M-effect, such as –OMe. Nevertheless, these electron-rich anilines exhibited good yields when employed as the coupling partner in the second step of the reaction, due to the electronic requirements of the Baeyer-Mills reaction, particularly with regard to nucleophilic attack.[18] As a limitation, substituents that could undergo oxidations with Oxone® may cause low yields. However, it has been reported that Oxone® has been successfully used for the synthesis of nitrosobenzenes in the presence of a benzylic alcohol or an aldehyde.[24]

To further investigate the applicability of the method, unsymmetric ABs with more complex substitution pattern were synthesized (Figure 4). As mentioned before, electron-poor anilines are particularly suitable for the in-situ formation of nitrosobenzenes. Consequently, nitro- and cyano-substituted anilines were employed in the first reactor, while anilines, such as bromo-substituted (Figure 4, **3p**–**q**) and the electron-rich methoxy-substituted (Figure 4, **3r**), were used as second coupling partner. Those combinations gave excellent yields and depict an efficient and fast way to access the corresponding azobenzenes **3p**–**3v**. The synthesis of unsymmetric alkyl-alkyl-substituted azobenzenes resulted in a broad range of moderate yields, strongly influenced by the substitution pattern (Figure 4, **3s**–**3v**). Although the achieved yields were not excellent, this pathways proved to be a valid alternative for the synthesis of alkyl-alkyl-substituted ABs, reducing consistently the reaction time and work load for their synthesis from days to hours.[25]

Finally, an asymmetric azobenzene containing two different halides was targeted as a modular building block for the synthesis of larger azobenzene-containing systems (Figure 4, **3w**). This specific substitution pattern enables to perform two selective cross-couplings with a minimal loss of selectivity.[26] At first, the synthesis was done with the same conditions reported

Table 1. Optimized condition for the oxidation of different anilines and the yield after the telescoped Baeyer-Mills reaction in continuous flow.



Entry	1st Aniline (R^1 =)		c(Aniline)/M	T (**R1**)/°C	Reaction time **R1**/min	Yield of AB/%	
1	**1a**	*o*-NO_2	0.16	80	50.0	**3a**	51
2	**1b**	*m*-NO_2	0.16	25	50.0	**3b**	76
3	**1c**	*p*-NO_2	0.16	50	50.0	**3c**	79
4	**1d**	*o*-CN	0.32	60	33.3	**3d**	85
5	**1e**	*m*-CN	0.32	50	33.3	**3e**	99
6	**1f**	*p*-CN	0.32	40	33.3	**3f**	71
7	**1g**	*o*-I	0.16	60	50.0	**3g**	59
8	**1h**	*o*-Br	0.32	55	33.3	**3h**	98
9	**1i**	*o*-F	0.32	55	33.3	**3i**	95
10	**1j**	*o*-Me	0.32	40	33.3	**3j**	69
11	**1k**	*p*-Me	0.32	45	33.3	**3k**	66
12	**1l**	*o*-Et	0.32	40	33.3	**3l**	59
13	**1m**	*p*-Et	0.32	50	33.3	**3m**	72
14	**1n**[1]	*p*-^{t}Bu	0.32	42	40.0	**3n**	54
15	**1o**[2]	*3,5*-di ^{t}Bu	0.27	50	50.0	**3o**	50

[1] Aniline **1n** was dissolved in DCM/acetic acid (7/3) and Oxone® was pumped with 150 µL (1.5 equiv.). [2] Oxone® was pumped with a flow rate of 100 µL (1.18 equiv.). See general procedure for further reaction conditions.

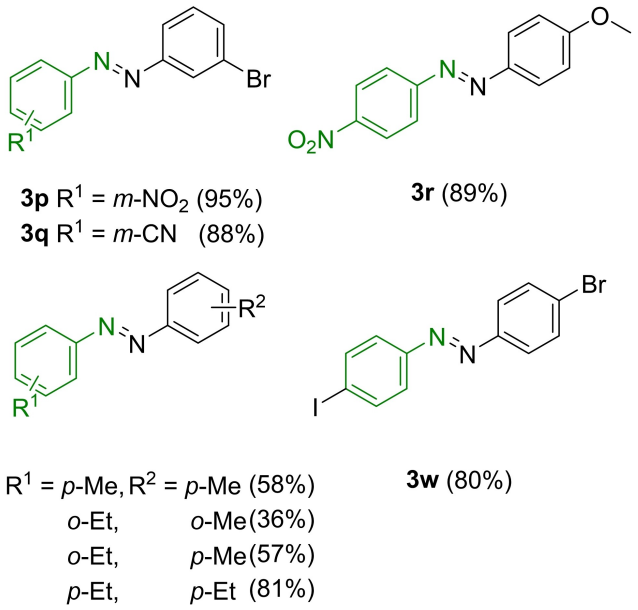


Figure 4. Substituted ABs, which were synthesized from substituted anilines using the same continuous flow set-up.

above. However, the target azobenzene crushed out in the second reactor causing a blockage in the flow set-up. Therefore, the solvent for the second aniline (4-bromoaniline) was changed to a mixture acetic acid and dichloromethane (1:9). This adjustment proved to be successful, resulting in the formation of AB **3w** in a yield of 80%.

Most of the synthesized ABs showed small amounts of substituted nitrobenzenes from over-oxidation or azoxybenzenes as impurity. The crude products were purified or flash column chromatography. However, good results were already obtained by filtration through a pad of silica in some cases.

Conclusions

In conclusion, a continuous flow method for the synthesis of nitrosobenzene compounds through oxidation using Oxone® was developed. The reaction conditions were optimized for a variety of different electron-poor and electron-rich anilines. These reactive intermediates were further used in a telescoped Baeyer-Mills reaction to obtain different ABs in moderate to high yields. This method represents a safer access to substituted nitrosobenzenes, which finds application in a variety of other transformations. The application of flow chemistry does not only allow accessing larger amounts of material, the in-situ generation of the hazardous and instable nitrosobenzene intermediate minimizes the health risk. Moreover, it provides an alternative modular and timesaving way to synthesize azobenzene derivatives as the choice of anilines for the nitroso

synthesis can be conveniently altered depending on its reactivity for the desired substrate.

Experimental Section

1-Nitro-3-nitrosobenzene 2 b

A solution of 3-nitroaniline (**1 b**) in dichloromethane (0.32 M) and a solution of Oxone® in water (0.16 M) were pumped individual with a flow rate of 100 μL/min for the aniline solution (1.00 equiv.) and 200 μL/min for the Oxone® solution (2.00 equiv.). The streams were joined in a T-mixer, followed by a tube reactor (10 mL, 33.3 min residence time). The biphasic reactor output was separated by an in-line phase separator (SEP-10, hydrophobic OB-900 membrane). After equilibration, the green organic phase was collected for 30 min and the solvent was removed using a stream of nitrogen. An off-white solid was obtained (117 mg, 0.769 mmol, 79%).

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.65–8.55 (m, 2H), 8.38–8.30 (m, 1H), 7.95–7.83 (m, 1H).

Due to the low stability only ^{1}H NMR data were recorded. Analytical data correspond to the literature.[27]

General procedure for the synthesis of AB derivatives 3 a–3 w

Aniline was dissolved in dichloromethane (0.16 M or 0.32 M, see Table 1). Oxone® was dissolved in water (0.32 M). Both solutions were pumped individual with a flow rate of 100 μL/min for the aniline solution (1.00 equiv.) and 200 μL/min for the Oxone® solution (1.18–2.00 equiv., see Table 1). The streams were joined in a T-mixer, followed by a tube reactor (10 mL, 33.3 min–50.0 min residence time). A BPR (75 psi) was used after the reactor. The biphasic reactor output was separated by an in-line phase separator (SEP-10, hydrophobic OB-900 membrane). After equilibration, the green organic phase was collected in a container (cooled to 0 °C). A second aniline was dissolved in acetic acid (0.16 M or 0.32 M) and pumped with a flow rate of 100 μL/min (1.00 equiv.). Both, the nitrosobenzene solution (flow rate of 100 μL/min) and the second aniline solution were pumped through a second mixer followed by a tube reactor at 70 °C (10 mL, 50.0 min residence time). After this reactor, cyclohexane was added in a third mixer with a flow rate of 1.00 mL/min. A BPR (75 psi) was used after the third mixer. The output was collected in a separatory funnel. The organic phase was extracted with dichloromethane and dried over sodium sulfate. The solvent was removed under reduced pressure. Crude products were purified by column chromatography [SiO_2, cyclohexane/toluene (*v*/*v* = 2/1 or 1/1)]. Yields are given in Table 1 or Figure 4. Further experimental details, spectra and analytical data are reported in the supporting information.

The authors have cited additional publications as a reference for analytical data in the supporting information.[28]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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