Oxidation of Anilines with Hydrogen Peroxide and Selenium Dioxide as Catalyst

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Abstract: A variety of substituted anilines are selectively oxidized to afford high yields of azoxyarenes by using 30% hydrogen peroxide and selenium dioxide as catalyst in methanol at room temperature. The oxidation of 4-alkoxyanilines under the same reaction conditions furnishes the corresponding 4-alkoxy-*N*-(4-nitrophenyl)anilines in reasonable yields, alongside other oxidation by-products. The structure of 4-methoxy-*N*-(4-nitrophenyl)aniline is elucidated by X-ray crystal structure analysis. From these results, some general aspects of the reaction pathways of aniline oxidation are discussed.

Key words: azoxyarenes, oxidation, anilines, hydrogen peroxide, selenium dioxide

The oxidation of anilines, affording N-oxygenated products, strongly depends on the reagents, the reaction conditions and the substitution pattern of the substrates.[1,2] Methods for the preparation of nitroso compounds from anilines,[3] and for the formation of symmetrically substituted azo and azoxy derivatives,[4,5] have been the subject of increasing interest over the years. Nitroso compounds are valuable starting materials for organic synthesis and asymmetric catalysis.[6] Azoarenes are interesting building blocks for material science and life science due to their photochromism,[7] whereas azoxyarenes have attracted interest as dyes, stabilizers, and for biological applications.[8] Both classes of compounds are interesting building blocks for electronic devices in the field of optical data storage,[9,10] nonlinear optics and as liquid crystals.[11,12]

Products from the oxidation reactions of anilines are summarized in Scheme 1. Besides oxidants used in stoichiometric amounts, a variety of catalytic methods using hydrogen peroxide have been reported.[13] However, general, simple and efficient protocols for the synthesis of either class of oxidation products in high yields and on a large scale are still rare. The oxidized products **2**, **3** and **4** are formed by *N*-oxygen transfer. The condensation of nitrosoarenes **3** with the hydroxylamine intermediates **2** yields azoxyarenes **6** (Scheme 1, pathway a),[14] and azoarenes **5** are obtained by condensation from the parent anilines **1** and nitrosoarenes **3** (Scheme 1, pathway b). The formation of azoarenes **5** and azoxyarenes **6** may also proceed by oxidative coupling reactions (pathway c) followed by N-oxygenation (pathway d).[15–17] Oxidative coupling may also yield oligo- and polymerization products.

Recently, we reported the efficient preparation of nitrosoarenes for the synthesis of unsymmetrically substituted azobenzenes by the application of Oxone® in a biphasic system.[18] In the course of the study we also investigated catalytic oxidations with hydrogen peroxide for the preparation of nitrosoarenes, especially focusing on the transformation of methyl 4-aminobenzoate (**1c**). When using selenium dioxide, a well-established catalyst for the formation of nitrones from secondary amines,[19] a strong solvent dependence of the product ratio was observed at room temperature. In a homogeneous methanol solution, solely the azoxyarene **6c** was isolated after precipitation from the reaction mixture (Table 1, entry 1).

Under the same reaction conditions, in a homogeneous dichloromethane solution, a nitrosoarene content of 80% was obtained (Table 1, entry 7). Catalytic oxidations with SeO_2/H_2O_2 can be rationalized by the formation of selenious acid (H_2SeO_3) from water and the acidic oxide, and the conversion of the acid into the catalytically active species peroxyselenious acid (H_2SeO_4). Recently, a variety of organoselenium-catalyzed oxidation procedures with hydrogen peroxide were reported,[20] e.g. the in situ generation of nitrosoarenes from anilines and their subsequent one-pot use in hetero-Diels–Alder reactions.[21] In oxidative amine chemistry, the stoichiometric use of benzeneseleninic anhydride for the conversion of hydroxylamines into nitrosoarenes was also published.[22] We now wish to report a comprehensive survey of the oxidation of substituted anilines with SeO_2/H_2O_2. At first we extended the study with aniline **1c** as a test compound and focused on the effect of additional solvents and pH (Table 1) as well as the concentration of the reaction mixtures (Table 2, entry 3); parameters that were previously found to be of importance for optimization of the product ratios.[18]

By using *n*-heptane and heterogeneous reaction conditions, the nitrosoarene content could be further increased to 95% (Table 1, entry 8). All reactions were carried out in approximately 0.13 M solutions until consumption of the aniline was complete (TLC monitoring). In a 1:1 mixture of ethanol and chloroform, an azoxyarene content of 93% was obtained; similar results were obtained in the presence of 100 mol% H_3PO_4 (Table 1, entries 2 and 3). During scale-up of the oxidation of aniline **1c** in methanol, a strong concentration dependence of the reaction time became obvious. For 0.3 M solutions a three-fold decrease

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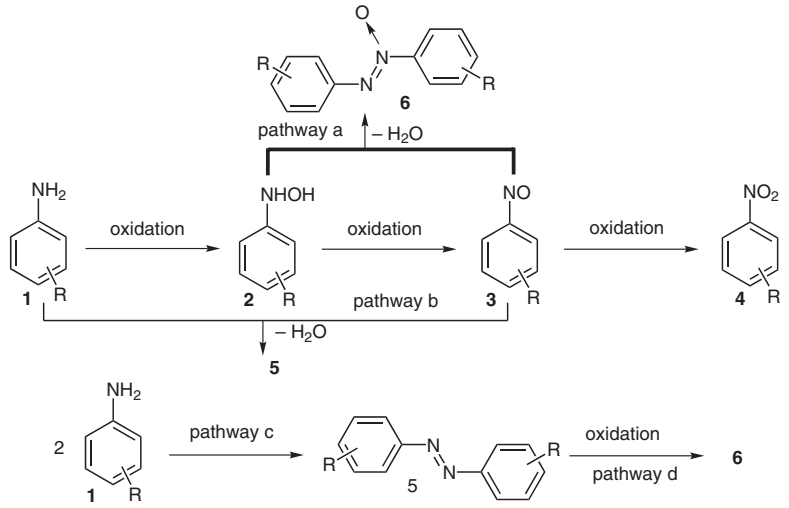
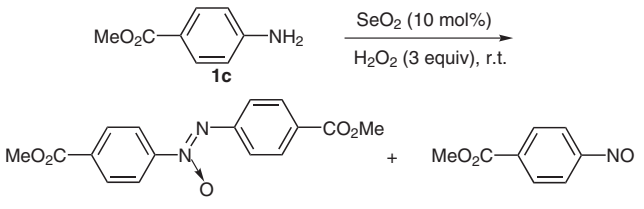


Scheme 1 Products from the oxidation of anilines

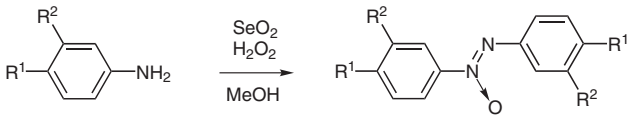
Table 1 Solvent Dependence of the Oxidation of **1c** with SeO_2/H_2O_2[a]



Entry	Solvent (5 mL)	Time (h)	**6c** (%)	**3c** (%)
1	MeOH	72	100	0
2	EtOH/$CHCl_3$	24	93	7
3	EtOH/$CHCl_3$/H_3PO_4	19	96	4
4	Et_2O	23	90	10
5	EtOAc	20	70	30
6	toluene	22	68	32
7	CH_2Cl_2	22	20	80[19]
8	heptane	20	5	95

[a] All reactions were performed on a 662 mol scale in 0.13 M solution. Product ratios were determined by ^{1}H NMR (200 MHz).

Table 2 Oxidation of Anilines with SeO_2/H_2O_2[a]



Entry	**1/6**	R^1	R^2	Time (h)	Temp	Yield (%)[b]
1	**a**	H	CN	24	r.t.	91
2	**b**	H	CO_2Me	11	r.t.	88[c,d]
3	**c**	CO_2Me	H	23	r.t.	83[c,d]
4	**d**	Br	H	9	r.t.	83
5	**e**	Cl	H	11	r.t.	82[c,d]
6	**f**	CN	H	65	r.t.	(95)[e]
7	**f**	CN	H	48	reflux	84
8	**g**	NO_2	H	8 d	r.t.	(80)[e]
9	**g**	NO_2	H	35	reflux	76
10	**h**	C_2H_5	H	20	r.t.	67

[a] All reactions were performed on a 3 mmol scale with SeO_2 (10 mol%) and H_2O_2 (3 equiv) in MeOH (10 mL, 0.3 M) unless otherwise indicated.
[b] Isolated yields.
[c] 30 mmol scale in MeOH (60 mL, 0.5 M): **6b** (1 h, 82%); **6c** (1 h, 83%); **6e** (6.5 h, 91%).
[d] 30 mmol scale in MeOH/CH_2Cl_2 (3:1): **6b** (0.75 M, 1 h, 86%); **6c** (0.75 M, 4 h, 85%); **6e** (0.6 M, 8 h, 83%).
[e] Conversion was determined by ^{1}H NMR (200 MHz).

(Table 2, entry 3, 3 mmol scale), and for 0.5 M solutions a 72-fold decrease (Table 2, footnote c, 30 mmol scale) in the reaction times were observed. Similar dependencies were observed for anilines **1b** and **1e** in methanol (Table 2, entries 2 and 5) and also for anilines **1b**, **1c** and **1e** in methanol/dichloromethane (3:1, 0.6–0.75 M solutions, see Table 2, footnote d).

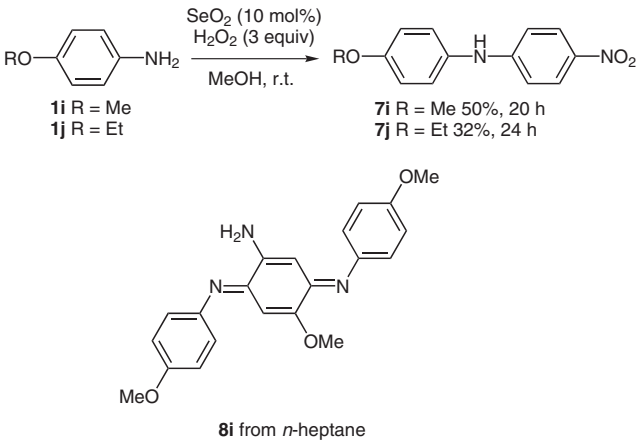
The synthetic perspectives for the SeO_2/H_2O_2 oxidation of anilines with an electron-withdrawing group or an alkyl substituent in the *meta*- or *para*-position are summarized in Table 2. All reactions were carried out at room temperature, employing SeO_2 (10 mol%) and H_2O_2 (3 equiv) in methanol or methanol/dichloromethane mixtures. As by-products, the nitro compounds **4a** and **4f** (<3%), as well as the azoarenes **5b–f** (<3%) and **5g** (9%) were isolated by chromatography and characterized by ^{1}H NMR and HRMS in comparison with literature data. In all cases, except for azoxyarene **6h**, partial precipitation of the prod-

ucts from the reaction solutions was observed. Reactions carried out with the less reactive anilines **1f** (R^1 = CN, R^2 = H, entries 6 and 7) and **1g** (R^1 = NO_2, R^2 = H, entries 8 and 9) were heated to reflux to reduce the reaction time required for complete conversion, without effecting by-product formation and composition. Furthermore, oxidation to the nitro compounds was not observed. As shown in Scheme 1 (pathway d), at elevated temperatures the formation of azoxyarenes from the corresponding azoarenes becomes feasible.[5] Therefore, the azoarenes **5b** and **5g** were subjected to the oxidation process of the parent anilines **1b** and **1g** (Table 2, entries 2 and 9), but even after prolonged reaction times of 11 hours and 35 hours, respectively, formation of the corresponding azoxyarenes **6b** and **6g** could not be detected.

The oxidation of aniline **1h** gave azoxyarene **6h** after chromatography, in 67% isolated yield (Table 2, entry 10), and a brown by-product which could not be further characterized. Generally, the oxidation chemistry of anilines with an electron-donating group is commonly accompanied by the formation of brown and black polymeric by-products due to oxidative coupling reactions.[23,24] In oxidations with lead dioxide/acetic acid and potassium ferricyanide/sodium carbonate, similar trends towards a preference for one-electron oxidation and subsequent coupling steps, followed by *N*-oxygenation, have been reported for electron-rich anilines.[25] This bottle-neck of selectivity was also seen in transition-metal-catalyzed hydrogen peroxide mediated oxidations, and remains a challenge.

Nevertheless, the oxidation of the more reactive 4-methoxyaniline (**1i**) and 4-ethoxyaniline (**1j**) with SeO_2/H_2O_2, under standard conditions in methanol, surprisingly led to completely different products and product ratios. The reaction of aniline **1i** furnished diarylamine **7i** in 50% isolated yield from a homogeneous reaction solution after 20 hours reaction time (Scheme 2); a black by-product and traces of azoarene **5i** (<3%) and nitro compound **4i** (<3%) were also formed.

The structure of 4-methoxy-*N*-(4-nitrophenyl)aniline (**7i**) was elucidated by X-ray crystal structure analysis



Scheme 2 Formation of diarylamines **7i** and **7j**, and trimer **8i**

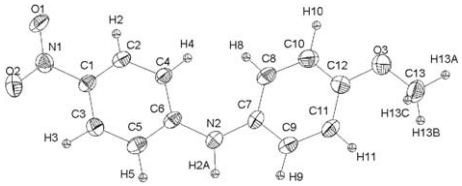
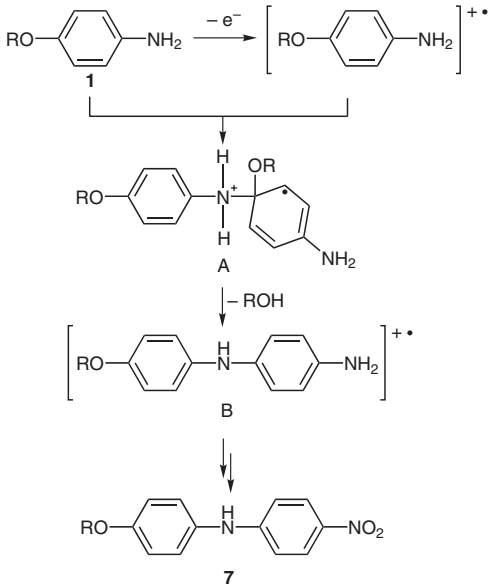


Figure 1 Molecular structure of 4-methoxy-*N*-(4-nitrophenyl)aniline **7i**

(Figure 1). Diarylamine **7j** was isolated in 32% yield starting from aniline **1j** (24 h, homogeneous reaction mixture), besides the azoarene **5j** (8%) and traces of the nitro compound **4j** (<3%).

In addition, aniline **1i** was treated on a small scale (812 μmol) under heterogeneous conditions in *n*-heptane solution (0.16 M) with SeO_2 (10 mol%)/H_2O_2 (3 equiv) to give, after chromatography, diarylamine **7i** (12%) and azoarene **5i** (12%); the nitrosoarene **3i** (22%) and the trimer **8i** (10%, 90% purity) were also formed along with a black by-product. Thus, for the reaction of aniline **1i** in *n*-heptane, a preference for the formation of the nitrosoarene can also be concluded. Trimer **8i**[26] (Scheme 2) is a typical coupling product for the oxidation of alkoxy-substituted anilines under anodic oxidation or in the presence of oxidants involving mechanisms based on one-electron oxidation or proton-coupled two-electron transfer.[16,17,25]

In Scheme 3, plausible intermediates of a possible electron-transfer reaction sequence furnishing compounds **7** are summarized. One-electron oxidation of alkoxy-substituted anilines **1** and head-to-tail-coupling to the parent aniline is expected to give intermediate A.[25–27] From the latter intermediate, ROH may be released, furnishing B, followed by N-oxygenation of the amino functionality to the nitro group. Nitroso precursors of **7i** and **7j** could be neither detected nor isolated, and the formation of the



Scheme 3 Plausible intermediates of an electron-transfer reaction sequence furnishing compounds **7**

nitro-substituted compounds **7** from the parent nitroso precursors **3** and the aniline **1** by nucleophilic aromatic substitution seems to be a less reasonable mechanism under the strong oxidizing reaction conditions employed.[28] The formation of **8** is expected to proceed by a reaction sequence involving an initial oxidative head-to-*ortho* coupling step.[25,27]

In summary, we have shown that the oxidation of anilines **1** with 30% H_2O_2, catalyzed by selenium dioxide in methanol at room temperature, provides a simple and efficient method for the preparation of a variety of azoxyarenes **6**. The oxidation of 4-alkoxy-substituted anilines under the same conditions yields 4-alkoxy-*N*-(4-nitrophenyl)anilines **7**. We are currently investigating transition-metal-catalyzed oxidations of anilines in the presence of hydrogen peroxide in order to improve the selectivities towards N-oxygenation for electron-rich compounds.

Solvents used for the reactions were obtained from the following sources: MeOH, EtOH, $CHCl_3$: Fisher Scientific (HPLC grade); EtO_2: Acros (pure); toluene: Acros (extra dry); CH_2Cl_2: Acros (p.a. grade); heptane: Alfa Aesar (99%); EtOAc: (dried over K_2CO_3). Solvents for chromatography were dried according to standard procedures and distilled prior to use.[29] Anilines **1a** and **1f** were purified prior to use by column chromatography (silica gel, CH_2Cl_2), **1e** and **1i** by sublimation in vacuo (1×10^{-2} mbar), and **1h** and **1j** by distillation in vacuo (2.5×10^{-2} mbar). Anilines **1b**, **1c**, **1d** and **1g** were used as received. All reactions were performed under nitrogen. IR spectra were recorded on a Perkin-Elmer 881 spectrometer. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100.6 MHz on a Bruker AM 400. Residual solvent protons were used as internal standards. All chemical shifts are given in ppm relative to TMS and coupling constants are in Hz. HRMS were obtained on a Varian MAT 711 spectrometer using an ionization potential of 70 eV. Melting points were determined using open capillaries by Dr. Tottoli (Büchi) with exception of the melting points for **4i**, **5i** and **4j**, which were determined using a microscopy pad of glass on a Leica Galen III 'heating-microscopic-board' with a control unit (Wagner–Munz), all values are uncorrected. TLC was carried out on silica gel 60 F_{254} (Merck) and was visualized under UV light, or using Seebach or ninhydrin stain. Column chromatography was performed on silica gel (ICN Biomedicals GmbH silica; 32–63 μm, 60 Å).

X-ray crystallographic data for **7i**: Empirical formula $C_{13}H_{12}N_2O_3$; Crystal system = monoclinic; Space group $P2_1$; Unit cell dimensions $a = 9.9620(15)$ Å, $b = 23.540(5)$ Å, $c = 10.285(3)$ Å, $b = 105.541(18)°$; $V = 2323.8(9)$ Å^3; D (calcd) = 1.396 g cm^{-3}; $Z = 8$; Crystal size $0.19 \times 0.21 \times 0.27$ mm^3; $m = 0.101$ mm^{-1}; Reflections collected 15545; Independent reflections 7656; Number of independent reflection with $I > 2s(I)$ is 842. The final *R* factors were $R1 = 0.0202$, $wR2 = 0.0674$ (all reflections) and $R1 = 0.0320$, $wR2 = 0.0643$ (842 independent reflections); Goodnes-of-fit = 0.900.

X-ray diffraction data were collected on an Oxford Diffraction; Xcalibur S diffractometer. The diffractometer was equipped with a Sapphire CCD detector and an enhanced monochromated MoKα source on a four-circle kappa platform. The diffraction frames were integrated by using the CrysAlisRed program, the sets of data were corrected for empirical absorption with SCALE3 ABSPACK.[30] The structure was solved by direct methods and refined using the program SHELX97.[31] Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre (CCDC) under the deposition number CCDC 668626.

Bis(3-cyanophenyl)diazene Oxide (6a);[32] Typical Procedure

H_2O_2 (30%, 0.92 mL, 9.00 mmol) was added to a solution of aniline **1a** (354 mg, 3.00 mmol) and SeO_2 (33.3 mg, 0.30 mmol) in MeOH (10 mL). The mixture was stirred at r.t. until complete consumption of the starting material was observed by TLC (24 h). After removal of the solvent in vacuo, the residue was partitioned between CH_2Cl_2 (20 mL) and H_2O (20 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 1:2) to give **6a**.

Yield: 340 mg (91%); yellow solid; mp 131 °C; $R_f = 0.34$ (CH_2Cl_2–pentane, 1:1).

IR (ATR): 3082, 2233, 1489, 1459, 800, 675 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (t, *J* = 7.9 Hz, 1 H), 7.65–7.72 (m, 2 H), 7.89 (ddd, *J* = 7.7, 1.3, 1.3 Hz, 1 H), 8.30 (ddd, *J* = 8.2, 2.0, 1.2 Hz, 1 H), 8.55–8.58 (m, 2 H), 8.61–8.62 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.0, 113.4, 117.1, 117.9, 126.1, 126.5, 128.6, 129.8, 130.1, 130.2, 133.1, 135.3, 143.5, 147.9.

HRMS: *m*/*z* [M]$^+$ calcd for $C_{14}H_8N_4O$: 248.0698; found: 248.0693.

Dimethyl 3,3′-Diazene Oxide 1,2-Diyldibenzoate (6b)[33]

After complete consumption of the starting material, H_2O was added and the precipitate was separated, washed with H_2O and dried in a desiccator over Sicacide®. The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 1:3) to give **6b**.

Yield: 414 mg (88%); yellow solid.

Typical Procedure for Scale-Up

H_2O_2 (30%, 9.18 mL, 90 mmol) was added to a solution of aniline **1b** (4.53 g, 30.0 mmol) and SeO_2 (333 mg, 3.00 mmol) in MeOH (60 mL). The mixture was stirred at r.t. until complete consumption of the starting material was observed by TLC (1 h). After removal of the solvent in vacuo, the residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (20 mL). After the separation of the layers, the aqueous phase was saturated by addition of solid NaCl and extracted with CH_2Cl_2 (2×30 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH_2Cl_2–hexane, 1:3) to give **6b**.

Yield: 3.85 g (82%); mp 135 °C; $R_f = 0.46$ (CH_2Cl_2).

IR (ATR): 3080, 3019, 2965, 2847, 1727, 1466, 1301, 1293, 1267, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3 H), 3.99 (s, 3 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.62 (t, *J* = 8.0 Hz, 1 H), 8.08 (ddd, *J* = 7.8, 1.4, 1.4 Hz, 1 H), 8.25 (ddd, *J* = 7.8, 1.3, 1.3 Hz, 1 H), 8.42 (ddd, *J* = 8.1, 2.0, 1.2 Hz, 1 H), 8.53 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1 H), 8.77 (t, *J* = 1.7 Hz, 1 H), 8.97 (t, *J* = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.3, 52.6, 123.6, 126.5, 127.1, 128.9, 129.1, 129.4, 130.7, 130.9, 131.3, 132.7, 143.8, 148.2, 165.7, 166.4.

HRMS: *m*/*z* [M]$^+$ calcd for $C_{16}H_{14}N_2O_5$: 314.0902; found: 314.0902.

Dimethyl 4,4′-Diazene Oxide 1,2-Diyldibenzoate (6c)[34]

After complete consumption of the starting material, H_2O was added and the precipitate was separated, washed with H_2O and dried in a desiccator over Sicacide®. The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 2:3) to give **6c**.

Yield: 392 mg (83%); yellow solid.

For the scaled-up reaction, the crude product was purified by column chromatography on silica gel (CH_2Cl_2–hexane, 1:3).

Yield: 3.92 g (83%); mp 200 °C; R_f = 0.39 (CH_2Cl_2).

IR (ATR): 3107, 3005, 2957, 2852, 1709, 1464, 1276, 1111, 857, 771, 688 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3 H), 3.97 (s, 3 H), 8.14–8.21 (m, 6 H), 8.37–8.40 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.3, 52.6, 122.5, 125.3, 130.2, 130.4, 130.7, 133.3, 146.9, 150.9, 165.7, 166.2.

HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{14}N_2O_5$: 314.0902; found: 314.0902.

Bis(4-bromophenyl)diazene Oxide (6d)[35]

After complete consumption of the starting material, H_2O was added and the precipitate was separated, washed with H_2O and dried in a desiccator over Sicacide®. The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 1:6) to give **6d**.

Yield: 440 mg (83%); yellow glittering flakes; mp 171 °C; R_f = 0.39 (CH_2Cl_2–pentane, 1:6).

IR (ATR): 3097, 3057, 3028, 1478, 1461, 1073, 1009, 826 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.65 (m, 4 H), 8.05–8.09 (m, 2 H), 8.15–8.18 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.6, 123.9, 126.5, 127.2, 131.98, 132.04, 142.6, 147.0.

HRMS: *m/z* $[M]^+$ calcd for $C_{12}H_8N_2OBr_2$: 355.8977; found: 355.8983.

Bis(4-chlorophenyl)diazene Oxide (6e)[35]

The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 1:6).

Yield: 328 mg (82%); yellow solid.

For the scaled-up reaction, the crude product was purified by column chromatography on silica gel (CH_2Cl_2–hexane, 1:6).

Yield: 3.66 g (91%); mp 153 °C; R_f = 0.47 (CH_2Cl_2–pentane, 1:6).

IR (ATR): 3062, 1482, 1464, 829 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.50 (m, 4 H), 8.14–8.18 (m, 2 H), 8.23–8.27 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.7, 127.1, 128.97, 129.03, 135.2, 138.1, 142.2, 146.5.

HRMS: *m/z* $[M]^+$ calcd for $C_{12}H_8N_2OCl_2$: 266.0014; found: 266.0017.

Bis(4-cyanophenyl)diazene Oxide (6f)[36]

The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 1:1).

Yield: 312 mg (84%); yellow solid; mp 221 °C; R_f = 0.60 (CH_2Cl_2).

IR (ATR): 3075, 3044, 2234, 2224, 1491, 1461, 843 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.81 (m, 2 H), 7.85–7.88 (m, 2 H), 8.21–8.24 (m, 2 H), 8.44–8.48 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.1, 116.1, 117.3, 118.2, 123.4, 126.0, 132.8, 133.1, 146.3, 150.2.

HRMS: *m/z* $[M]^+$ calcd for $C_{14}H_8N_4O$: 248.0698; found: 248.0698.

Bis(4-nitrophenyl)diazene Oxide (6g)[37]

After complete consumption of the starting material (TLC), H_2O was added and the precipitate was separated, washed with H_2O and dried in a desiccator over Sicacide®. The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 2:3).

Yield: 297 mg (76%); orange-yellow needles; mp 191 °C; R_f = 0.32 (CH_2Cl_2–pentane, 2:3).

IR (ATR): 3078, 1531, 1523, 1480, 1468, 1346, 1320, 863, 753, 684 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.28–8.32 (m, 2 H), 8.36–8.39 (m, 2 H), 8.41–8.44 (m, 2 H), 8.52–8.56 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.8, 124.4, 124.5, 126.3, 147.4, 147.8, 149.9, 151.3.

HRMS: *m/z* $[M]^+$ calcd for $C_{12}H_8N_4O_5$: 288.0495; found: 288.0491.

Bis(4-ethylphenyl)diazene Oxide (6h)[38]

The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 1:10).

Yield: 251 mg (67%); yellow oil; R_f = 0.60 (CH_2Cl_2–pentane, 1:7).

IR (ATR): 3076, 3031, 2966, 2932, 2873, 1603, 1499, 1462, 839 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.27–1.35 (m, 6 H), 2.70–2.77 (m, 4 H), 7.29–7.36 (m, 4 H), 8.24–8.29 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.00, 15.04, 28.3, 28.6, 122.0, 125.6, 127.77, 127.80, 141.9, 145.9, 146.1, 147.8.

HRMS: *m/z* $[M]^+$ calcd for $C_{16}H_{18}N_2O$: 254.1419; found: 254.1425.

4-Methoxy-*N*-(4-nitrophenyl)aniline (7i)[39]

The crude product was purified by column chromatography on silica gel (CH_2Cl_2–pentane, 1:1).

Yield: 194 mg (50%); orange-red needles; mp 144 °C; R_f = 0.61 (CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.15 (br s, 1 H), 6.74–6.78 (m, 2 H), 6.91–6.95 (m, 2 H), 7.14–7.18 (m, 2 H), 8.05–8.09 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 112.6, 114.9, 125.5, 126.3, 132.0, 139.1, 151.7, 157.4.

HRMS: *m/z* $[M]^+$ calcd for $C_{13}H_{12}N_2O_3$: 244.0847; found: 244.0848.

4-Ethoxy-*N*-(4-nitrophenyl)aniline (7j)[40]

The crude product was purified by column chromatography on silica gel (CH_2Cl_2–hexane, 1:1).

Yield: 125 mg (32%); orange solid; mp 128 °C; R_f = 0.32 (CH_2Cl_2–hexane, 2:1).

IR (ATR): 3352, 3073, 3042, 2980, 2921, 2851, 2414, 1594, 1508, 1477, 1392, 1322, 1303, 1242, 1183, 1111 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (t, *J* = 7.0 Hz, 3 H), 4.05 (q, *J* = 7.0 Hz, 2 H), 6.14 (br s, 1 H), 6.74–6.78 (m, 2 H), 6.90–6.94 (m, 2 H), 7.12–7.16 (m, 2 H), 8.06–810 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 63.8, 112.6, 115.5, 125.5, 126.3, 131.8, 139.0, 151.7, 156.8.

HRMS: *m/z* $[M]^+$ calcd for $C_{14}H_{14}N_2O_3$: 258.1004; found: 258.1004.

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