Simple Preparation of Nitroso Benzenes and Nitro Benzenes by Oxidation of Anilines with H_2O_2 Catalysed with Molybdenum Salts

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Abstract: Nitroso arenes **2a**–**k** are prepared in 53–80% yield from anilines **1a**–**k** by oxidation with H_2O_2 catalysed with MoO_3/KOH, ammonium molybdate or other molybdenum salts. Further oxidation to nitro arenes **3a**,**d**,**j** in 66–90% is also described.

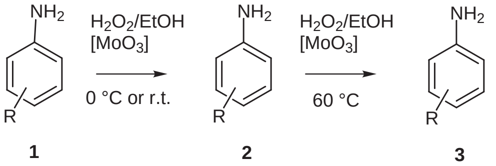
Keys words: nitroso arenes, nitro arenes, oxidation, molybdenum salts

Classic methods for the preparation of aromatic nitroso compounds are oxidation of anilines with peracids,[1] particularly Caro acid,[2] peracetic acid,[1] perbenzoic acid,[3,4] trifluoroperacetic acid[5] or more recently molybdic peroxo-complexes.[6] Catalytic methods using H_2O_2 or *tert*-butyl peroxide as oxidant and sodium tungstate,[7] oxo-molybdate complexes,[8] phosphotungstate,[9–11] phosphomolybdate[10,11] or zirconate salts[12] were published later. Dimeric products such as azo- or azoxy-derivatives[9,13a] as well as over-oxidation to the nitro compounds[7,10,11] were often observed as by-products or sometimes as main products.[6,14] Some methods for the direct oxidation of aromatic amines to nitro derivatives were described with peracids,[15] and more recently with dioxirane,[16] *tert*-butyl peroxide or H_2O_2 as oxidants and metal peroxocomplexes (Mo,[17] W,[6,10,11] V,[17] Zr,[12] Re[18]) or with chromium silicalit[13] as catalyst.

We describe herein a simple oxidation method of anilines, resulting in the corresponding nitroso compounds using 30% H_2O_2 and molybdenum trioxide or other molybdenum salts as catalyst without the formation of azo- or azoxy-derivatives. Further oxidation to nitro compounds was examined in some cases.

Oxidation of Anilines to Nitroso Arenes

Oxidation of anilines **1a**–**k** was carried out in a water–methanol solution in which the anilines were only slightly soluble but the resulting nitroso compounds **2a**–**g**,**j**,**k** were insoluble and could be isolated by filtration (Scheme 1). Side-reactions such as formation of nitro derivatives and dimeric compounds such as azo- or azoxy-derivatives was also minimised. This method appeared to be better than the previous two-phase preparation.[4,8,9,11] A complete oxidation and a sufficient reaction rate required an excess of H_2O_2 (4 equiv) and 0.1 mol of molybdic derivative per 1 mol of aniline, smaller proportions of oxidant or catalyst led to slower or incomplete reactions and favoured the formation of azo- azoxy- or coloured-compounds.



Scheme 1

a) Dependence on the pH–Value

p-Chloroaniline **1a** was used as the model compound and the standard catalyst was 10 mol% MoO_3 in the presence of KOH as the base, which was added in various quantities. Oxidation of *p*-chloroaniline is very dependent on MoO_3/KOH molar ratio. The results are listed in Table 1, and summarised here.

– With MoO_3 only without added base, the oxidation occurred cleanly, but the progress of the reaction was slow (15% reaction after 1 d).

– With MoO_3 and 1–1.8 equiv KOH, the oxidation rate increased with the concentration of base, but coloured impurities were formed when 1.5–1.8 equiv of base (pH value 5–7) were added. The best condition for the oxidation to the nitroso compound was with 1–1.2 equiv KOH, then the oxidation occurred cleanly and gave good yields (86–94%) of the nitroso compounds. Observing the reaction, the solution turned from red at the beginning to yellow after 1 hour and the pH value varied with the consumption of aniline; from pH 6 to pH 5 after 1 hour, pH 4–4.5 after 3 hours and pH 3–4 at the end of the oxidation.

– With Na_2MoO_4 as catalyst, which corresponds to 2 equivalents of base, the pH-value was 6–7, the solution retained its red colour with emission of oxygen and the conversion was incomplete.

It is possible to specify the major molybdenic species in solution from Aubry’s and Griffith’s work.[19–21] The relationship between the structure of monomeric or dimeric peroxomolybdic acids and pH values in aqueous solution

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was already studied: under the optimal conditions for oxidation to nitroso compounds (H_2O_2 concentration ca. 3 M, MoO_3 concentration ca 7×10^{-2} M), the major species was the yellow anion $Mo_2O_3(O_2)_4^{(2-)}$ (pH< 5); while at pH> 5 the unstable red anion $Mo(O_2)_4^{(2-)}$, which easily lost molecular oxygen was present.[19,20] It seems then that $Mo_2O_3(O_2)_4^{(2-)}$ is the main reactive species for this oxidation at pH 3–5. This Mo-peroxide had already been used at this pH range to oxidise alcohols to ketones[20] or to epoxidise[20,21] unsaturated compounds.[22]

b) With other Molybdenum Salts as Catalyst

It was possible to use other molybdenum salts as catalysts and the resulting yields of nitroso compounds were the same so long as the ratio molybdenum/base was near 1 (complex salts were related as their MoO_3 equivalents). The results given in Table 1 and summarized below.

– MoO_3 and 1.0 equivalents of NaOH or KOH (pH 6 to 4–3)

– Na_2MoO_4 and 0.5 equivalents of H_2SO_4 (pH 6 to 4–3)

– 0.143 equivalents of ammonium molybdate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (pH 2)

– 0.083 equivalents of phosphomolybdic acid $Mo_{12}O_{40}PH_3$ and 1.0 equivalents of NaOH (pH 5 to 4–3)

In practice, ammonium molybdate proved to be the most suitable, the reaction rate is faster than with MoO_3/KOH.

c) Generalisation of the Reaction

The oxidation of several *p*-substituted anilines was performed using mainly standard conditions (10% molar MoO_3 and KOH). The results are reported in Table 1. Yields were generally good (80–90%). The reaction time varied from 6 hours to some days according to the aryl-substitution and solubility of the aniline. In most cases, a simple filtration provided pure nitroso compounds. Sometimes partial over-oxidation to nitro derivative was observed and the standard conditions had to be modified:

– aniline **1d** (R = H) and toluidine **1e** (R = Me), the reaction was carried out at 0 °C.

– *p*-methoxy derivatives **1h** (R = OMe), the nitroso compound is a green monomeric species which is soluble in the reaction medium. The reaction was performed at 0 °C in two phases with hexane.

– *p*-nitro derivatives **1j**,**k**, very good results were obtained only with MoO_3 as catalyst without base (pH value 1–1.5). The excellent result validates the long reaction time (almost 1 week).

Table 1 Oxidation of Anilines **1a–k** to Nitroso Compounds **2a–k**

R	Compound	Catalyst (10 mol%)	Conditions	Crude Yield	Pure Yield[a]
p-Cl	**1a**	MoO_3, KOH (1 mmol)	25 °C, 10 h	87–94%	78–84% (EtOH)
	1a	MoO_3, NaOH (1 mmol)	25 °C, 11 h	94%	
	1a	MoO_3, KOH (1.2 mmol)	25 °C, 6 h	89%	
	1a	$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.143 mmol)	25 °C, 3 h	92%	
	1a	MoO_4Na_2, H_2SO_4 (0.5 mmol)	25 °C, 3 h	92%	
	1a	$Mo_{12}O_{40}PH_3$ (0.083 mmol), KOH (1 mmol)	25 °C, 8 h	92%[b]	
4-Cl, 3-Me	**1b**	MoO_3, KOH (1 mmol)	15–20 °C,	81%	77% (MeOH)
p-Br	**1c**	MoO_3, KOH (1 mmol)	25 °C, 43 h	97%	87% (EtOH)
H	**1d**	MoO_3, KOH (1 mmol)	0 °C, 1 d	77–85%	65% (MeOH)
p-Me	**1e**	MoO_3, KOH (1 mmol)	0 °C, 16 h	85%[c]	
p-PhCO	**1f**	MoO_3, KOH (1 mmol)	25 °C, 4 d	98%[d]	78% (EtOH)
p-CO_2Me	**1g**	MoO_3, KOH (1 mmol)	25 °C, 4 d	91–94%	86% (EtOAc)
p-OMe	**1h**	MoO_3, KOH (1 mmol)	0 °C, 16 h	63%	53% (hexane)
p-NO_2	**1j**	MoO_3	25 °C, 10 d	96%	80% (EtOH)
4-NO_2, 3-Me	**1k**	MoO_3	25 °C, 7 d	89%	72% (MeOH)

[a] After recrystallisation.
[b] Darker product, containing ca. 4% impurities.
[c] Containing ca. 5% nitro derivative.
[d] Containing 15% nitro derivative.

Preparation of Nitro Compounds

At a higher temperature (60 °C), nitroso arenes became partially soluble in methanol–H_2O_2 solution and were oxidised to the corresponding nitro derivatives, without decomposition of the oxidant. It is therefore possible to oxidise directly anilines to nitro compounds in two steps, solely by raising the temperature and without isolation of the intermediary nitroso compounds. These oxidations were only studied in the cases R = H and its *p*-chloro and *p*-nitro derivatives.

From Nitroso Compounds

Oxidation of nitroso compounds **2a**,**d**,**j** was performed with ammonium molybdate (10 mol% MoO_3) as catalyst in methanol and 30% H_2O_2 (4 equiv) at 60 °C. In all cases, the corresponding nitro derivatives are obtained in good yields (75–90%; Table 2) after purification by distillation for nitrobenzene **3d** or by sublimation for the *p*-dinitrobenzene **3j**.

Table 2 Oxidation of Nitroso Compounds **2a**,**d**,**j** to Nitro Derivative **3a**,**d**,**j**

R		Catalyst (10 mol%)	Conditions	Yield
p-Cl	**2a**	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.143)	60 °C, 16 h	93%[b]
H	**2d**	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.143)	60 °C, 6 h	77%[a]
p-NO_2	**2j**	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.143)	60 °C, 4 d	76%[c]

[a] After distillation.

[b] The crude product is pure.

[c] After sublimation (5–10 Torr at 125 °C).

From Anilines

Oxidation of aniline and derivatives **1a**,**d**,**j** to their insoluble nitroso compounds was performed in methanol with 6 equivalents of 30% H_2O_2 at room temperature for **1a**,**j** or at 0 °C for **1d** until quasi-consumption of anilines had occured; under these conditions, variable amounts of nitro compounds were already formed (5% of **3a**, *p*-Cl, 7% of **3d**, aniline, 77% of **3j** and 10% azoxy-derivative, *p*-NO_2). The oxidation to nitro compounds **3a**,**d**,**j** was completed at 60 °C and the latter were then isolated in acceptable yields (66–92%; Table 3) after purification as above.

Direct oxidation of anilines **1a**,**d**,**j** at 60 °C provided substantial amounts of azoxy-derivatives which are formed by condensation of the intermediary *N*-hydroxyaniline in the presence of a nitroso derivative.

Table 3 Direct Oxidation of Anilines **1a**,**d**,**j** to Nitro Derivatives **3a**,**d**,**j**

R		Catalyst (10 mol%)	Conditions	Yield
p-Cl	**1a**	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.143)	4.5 h, 20 °C 1 d, 60 °C	92%[a]
H	**1d**	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.143)	24 h, 0 °C 6 h, 60 °C	66%[b]
p-NO_2	**1j**	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.143)	7 d, 25 °C 1 d, 60 °C	68%[c]

[a] Containing 3% nitroso derivative.

[b] Purified by distillation (Eb_6 = 69 °C)

[c] Purification by sublimation (5–10 Torr at 125 °C) containing 5% nitroso derivative.

Conclusion

We have described the oxidation of anilines to nitroso derivatives and further oxidation to nitro derivatives using 30% H_2O_2 and molybdic salts as the catalyst. The resulting yields of pure compounds are good to excellent (53–90%) after purification. Due to their simple work-up procedure, these methods can be used for large-scale synthesis.

Flash chromatography (FC): silica gel (Merck 60, 230–400 mesh). TLC: Al-roll silica gel (Merck 60, F_{254}). Mp: Kofler hot bench, corrected. IR spectra : Perkin-Elmer 157 G. ^{1}H- and ^{13}C NMR spectra: Bruker 400 MHz, TMS and $CDCl_3$ [^{13}C NMR; δ ($CDCl_3$) = 77.0 ppm with respect to TMS] as internal references. Microanalyses were carried out by the Service Central de Microanalyses du CNRS, Vernaison.

H_2O_2 was purchased from Prolabo and was titrated by iodometry as 7.5 M. MoO_3, phosphomolybdic acid were obtained from Fluka purum, ammonium molybdate from Riedel de Haen, anilines **1a**, **1c**, **1h**, **1j**, **1g** from Fluka purum, **1f** from Fluka technicum; **1d** was distilled; **1b** mp 81–84 °C, **1j** mp 146–147 °C, **1e** mp 45 °C were recrystallised from cyclohexane.

Unless otherwise stated IR, ^{13}C, ^{1}H NMR data agreed with the literature values.

Oxidation of Anilines 1a–h to Nitroso Arenes 2a–h; General Procedure

To a stirred solution of aniline **1** (10 mmol) in MeOH (3 mL) were added H_2O_2 (5.5 mL, 40 mmol, 4 equiv) and H_2O (4.5 mL). Aniline **1** precipitated as fine crystals and then MoO_3 (0.144 g, 1 mmol) and aqueous KOH solution (1 mL, 1 mmol) were added and the solution stirred at 25 °C. The solution became brown and then yellow with formation of a precipitate, pH value 3–3.5. The reaction was monitored by ^{1}H NMR in $CDCl_3$. After a given time at 25 °C (see Table 1), H_2O (15 mL) was added and **2** formed as an ochre precipitate, which was filtered, washed with H_2O (2 × 10 mL), cold MeOH (5 mL) and dried. Crude **2** is mainly pure and can be recrystallised to give pure **2**. Crude and recrystallised yields are given in Table 1.

1-Chloro-4-nitrosobenzene (2a)[10,23]

Yellowish crystals; mp 115–118, 130–140 °C (dec.) (EtOH) (lit.[23] 130 °C, lit.[25] 92–3 °C).

^{1}H NMR ($CDCl_3$): δ = 7.86 (dm, H-3, H-5), 7.60 (dm, H-2, H-6, J = 8.6 Hz).

2-Chloro-5-nitrosotoluene (2b)

Yellowish crystals; mp 84–87 °C (MeOH) {lit.[23] 73–74 °C (EtOH)}.

^{1}H NMR ($CDCl_3$): δ = 2.53 (s, Me-1), 7.59 (d, H-3, $J_{3,4}$ = 8.3 Hz), 7.68 (dd, H-4, $J_{4,6}$ = 2.0 Hz), 7.79 (d, H-6).

^{13}C NMR ($CDCl_3$): δ = 20.1 (Me-1), 119.3 (C-4), 123.4 (C-6), 130.0 (C-3), 137.7 (C-1), 141.6 (C-2), 164.1 (C-5).

1-Bromo-4-nitrosobenzene (2c)

Yellowish crystals; mp 98–100 °C (EtOH) (lit.[24] 95 °C).

IR (KBr): 3085, 1575, 1475, 1400, 1283, 1253, 1100, 1063, 1010, 853, 805, 705 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.78 (s, 4 H).

^{13}C NMR ($CDCl_3$): δ = 122.1 (C-3, C-5), 132.7 (C-2, C-6), 131.7 (C-1); 163.8 (C-4).

Nitrosobenzene (2d)[10,26]

Reaction at 0 °C; yellowish crystals; mp 76–80 °C (MeOH) (lit.[24] 67.5–68 °C).

IR,^{1}H NMR and ^{13}C NMR ($CDCl_3$) agreed with the literature.

4-Nitrosotoluene (2e)[10]

Reaction at 0 °C; yellowish crystals; mp 58–60 °C (lit.[24] 48.5 °C, lit.[10] 47–49 °C).

IR (KBr): 3030, 1595, 1500, 1295, 1250, 1160, 1115, 1018, 860, 820, 815, 758 cm^{-1}.

4-Benzoylnitrosobenzene (2f)

Yellowish crystals; mp 120–122 °C (EtOH).

IR (KBr): 3100, 3050, 1645, 1592, 1524, 1403, 1314, 1302, 1276, 1260, 1105, 940, 923, 876, 870, 822, 788, 740, 695, 685 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.53 (tm, 2 H, Ar_m, $J_{o,m}$ = 7.4 Hz), 7.66 (tm, H, Ar_p, $J_{m,p}$ = 7.6 Hz), 7.83 (dm, 2 H, Ar_o), 8.00, 8.02 (2 d, H-2, H-6, H-3, H-5, $J_{2,3}$ = 8.8 Hz).

^{13}C NMR ($CDCl_3$): δ = 120.4 (C-3, C-5), 128.6 (2 C_m), 130.1, 131,0 (2 C_o, C-2,C-6), 133.3 (C_p), 136.5 (C), 142.7 (C-1), 164.0 (C-4), 195.5 (CO).

Anal Calcd for $C_{13}H_9NO_2$ (211.22): C, 73.92; H, 4.30; N, 6.63. Found: C, 73.6; H, 4.1; N, 6.8.

Methyl 4-nitrosobenzoate (2g)[23,27]

After 24 h, MeOH (6 mL) and H_2O (4 mL) were added; yellowish crystals; mp 145–150 °C (EtOAc) (lit.[23] 130 °C, lit.[24] 128.5–129.5 °C)

4-Nitrosoanisole (2h)[23]

Reaction carried out at 0 °C in two phases with addition of hexane (20 mL) for 16 h. The hexane phase was decanted and the aqueous phase extracted with hexane (4 × 20 mL), the combined hexane phases were evaporated at 30 °C and the resulting green resin (0.97 g, 63%) recrystallised from hexane at –30 °C; green crystals; mp 20–21 °C (hexane) (lit.[23] 22 °C, lit.[24] 23 °C).

^{13}C NMR ($CDCl_3$): δ = 55.9 (OMe-1), 113.8 (C-2, C-6), 124.2 (C-3, C-5), 164.0, 165.6 (C-4), C-1).

Nitronitrosobenzenes 2j,k; Typical Procedure

To a stirred suspension of **1j** (1.38 g, 10 mmol) in MeOH (3 mL) at 25 °C were added H_2O_2 (10 mL, 75 mmol, 7.5 equiv) and MoO_3 (0.144 g, 1 mmol). After 2.5–3 d the ochre suspension was diluted with MeOH (3 mL) and H_2O (2 mL); after 10 d the work-up was carried out as above; crude and recrystallised yields are given in Table 1.

1-Nitro-4-nitrosobenzene (2j)[10,23]

Mp 128–130 °C (EtOH) (lit.[23] 128–130 °C; lit.[24] 118.5–119 °C).

2-Nitro-5-nitrosotoluene (2k)

The same procedure as above **1k** (1.52g, 10 mmol), MeOH (3 mL), H_2O_2 (15 mL, 0.11 mol, 11 equiv) and MoO_3 (0.144 g, 1 mmol), 7 d; mp 112–114 °C (EtOH) (lit.[24] 113 °C).

IR (KBr): 3100, 1610, 1575, 1515, 1345, 1308, 1255, 840, 825 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.74 (s, Me-1), 7.74 (dd, H-4, $J_{3,4}$ = 8.5 Hz), 7.98 (d, H-6, $J_{4,6}$ = 2.0 Hz.), 8.13 (d, H-3).

^{13}C NMR ($CDCl_3$): δ = 20.0 (Me-1), 117.7 (C-4), 125.8, 126.0 (C-3,C-6), 135.4 (C-1), 152.3 (C-2), 162.1 (C-5).

Oxidation to Nitro Derivatives 3a,d,j; General Procedure

Oxidation of Nitroso Compounds 2a,d,j

To a stirred suspension at 60 °C of **2a**,**d**,**j** (10 mmol) in MeOH (7.5 mL) were added H_2O_2 (5.5 mL, 41 mmol, 4 equiv) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.178 g, 1 mmol MoO_3). The reaction was monitored by ^{1}H NMR ($CDCl_3$) and after the given time (see Table 2) the suspension was diluted with H_2O (10 mL), chilled and (except for **3d**, see below) filtered, the solid **3** was washed with H_2O and dried over P_2O_5 (for yields see Table 2).

Oxidation of Anilines 1a,d,j

To a stirred solution of anilines **1a**,**d**,**j** (10 mmol) in MeOH (10.5 mL) were added H_2O_2 (8 mL, 60 mmol, 6 equiv) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.178 g, 1 mmol MoO_3). The solution was stirred at 20 °C for **1a**, 0 °C for **1d**, 25 °C for **1f** for the given time, then heated at 60 °C for 6–24 h (see Table 3). Same work-up as above (for yields see Table 3).

4-Chloronitrobenzene (3a)[26]

Pale yellow crystals; mp 81–82 °C (lit.[24] 83–84 °C).

Nitrobenzene (3d)[28]

The dark organic phase was separated, the aqueous phase was diluted with H_2O (10 mL) and extracted with CH_2Cl_2 (3 × 1 mL), organic phases were combined and distilled to give **3d**.

Yellow oil; Eb_6 68 °C (lit.[24] Eb_{10} 85 °C); n_D^{20} 1.5518 (lit.[24] 1.5530).

4-Dinitrobenzene (3j)[13a,26,28]

Crude product isolated as yellow crystals (83–85%) containing 5% of tetranitroazoxybenzene (Method 1) and 11% (Method 2), which was purified by sublimation (130 °C, 4–10 Torr, 2 h, containing 2% azoxyderivative).

Pale yellow crystals; mp 172–174 °C (lit.[24] 173–174 °C).

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