

Catalytic synthesis of C-nitroso compounds by *cis*-Mo(O)₂(acac)₂

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Abstract

The *ortho*, *meta* and *para* mono substituted anilines R–C₆H₄NH₂ (R = 4-Me, 3-Me, 2-Me, 4-Et, 2-Et, 4-Br, 3-Br, 2-Br; 4-Cl, 3-Cl, 2-Cl, 4-F, 4-Prⁱ, 4-Bu^t) were catalytically oxidised by H₂O₂, in the presence of *cis*-Mo(O)₂(acac)₂, (acacH = CH₃C(O)CH₂C(O)CH₃), producing the corresponding C-nitroso derivatives, R–C₆H₄NO. High conversions and selectivities were obtained. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many literature reports deal with stoichiometric and catalytic organometallic synthesis of C-nitroso compounds by oxidation of the corresponding amines [1–11]. The conventional organic approaches are usually unselective [12,13], whereas by using catalytic systems high yields of nitroso compounds can be achieved [8–11]. Another important feature of nitroso syntheses is related to the difficulty of the product-recovering step. The work-up often requires concentration of the reaction media, thus producing a stronger oxidative environment that almost over-oxidises the substrates. The alternative chance offered by chromatographic separation is not a general method as the nitroso compounds

can be degraded by supports. Thus, simple and proper catalytic organometallic reactions are of importance.

2. Experimental

2.1. Materials

The amines, C₆H₅NH₂, 4,CH₃–C₆H₄NH₂, 3,CH₃–C₆H₄NH₂, 2,CH₃–C₆H₄NH₂, 4,C₂H₅–C₆H₄NH₂, 2,C₂H₅–C₆H₄NH₂, 4,Br–C₆H₄NH₂, 3,Br–C₆H₄NH₂, 2,Br–C₆H₄NH₂, 4,Cl–C₆H₄NH₂, 3,Cl–C₆H₄NH₂, 2,Cl–C₆H₄NH₂, 4,F–C₆H₄NH₂, 4,*iso*–C₃H₇–C₆H₄NH₂, 4,*tert*–C₄H₉–C₆H₄NH₂ (Aldrich) were distilled under reduced pressure and stored under N₂. *Cis*-Mo(O)₂(acac)₂ and H₂O₂ (30% in water, *d* = 1.11 g/ml) were from Aldrich and used as received. CH₂Cl₂ and C₆H₁₂ (Fluka) were high purity solvents.

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2.2. Instrumentation

Gas chromatographic analyses were carried out on a Perkin Elmer 8420 capillary gas chromatograph. IR spectra in nujol or KBr wafer were recorded on a BioRad FTS-7CP spectrophotometer. ^1H NMR spectra were recorded on a Bruker VP 80 instrument. Elemental analyses were performed on a Perkin Elmer 2400 CHN Elemental Analyser.

2.3. Catalytic synthesis of nitroso compounds

2.3.1. General procedure

C_6H_{12} (5 ml) and *cis*- $\text{Mo}(\text{O})_2(\text{acac})_2$ (32.6 mg, 0.1 mmol) were mixed under vigorous magnetic stirring in a test tube, at room temperature and in aerobic conditions. The obtained light orange suspension was further stirred for 5 min, then amine (1 mmol) and H_2O_2 (0.5 ml of a 30% w/w aqueous solution, $d = 1.11$ g/ml, 5 mmol) were added, obtaining a two-phase system. The aqueous phase became brownish within 10–15 min. After ca. 1 h, the initial insoluble brick red $\text{Mo}(\text{O})_2(\text{acac})_2$ dissolved, giving a clear organic layer, whose colour is specified in Section 2.3.2. Samples were withdrawn for gas chromatographic analyses, at various intervals. At the end of the reaction, 5 ml of C_6H_{12} and ca. 100 mg of Na_2SO_4 were added. After 20 min, the suspension was filtered and the reaction liquors were worked up in two different ways [(a) and (b)] depending on the nitroso derivative nature.

(a) The liquors of solid nitroso compounds were completely solidified by freezing (-20°C) for ca. 1 h; then the temperature was let to rise. The slowly dissolving masses allowed the precipitation of pure nitroso derivatives. They were filtered off during the dissolving process, dried in vacuo and stored under N_2 .

(b) The liquors of liquid nitroso compounds were dried in vacuo. The oily residues were treated with 40–60 ml of a $\text{C}_6\text{H}_{12}\text{-CH}_2\text{Cl}_2$ mixture (4:6) and hence, flash chromatography on silica gave the pure products.

2.3.2. Nitroso derivatives

A list of the isolated nitroso derivatives is reported below. The IR spectra were recorded in nujol. ^1H NMR spectra were carried out in CDCl_3 [$\delta(\text{ppm})$, $J(\text{Hz})$].

$\text{C}_6\text{H}_5\text{NO}$ (**1a**). Organic solution colour: dark green. Light yellow crystalline solid; m.p. = $64\text{--}7^\circ\text{C}$ (lit. 68°C). $\nu(\text{NO}) = 1499, 1294\text{ cm}^{-1}$. ^1H NMR: 7.28 (multiplet) [Beilstein Reg. No. 605688].

$4\text{-CH}_3\text{-C}_6\text{H}_4\text{NO}$ (**2a**). Organic solution colour: green. Yellow solid; m.p. = $48\text{--}9^\circ\text{C}$ (lit. 48.5°C). $\nu(\text{NO}) = 1507, 1295\text{ cm}^{-1}$. ^1H NMR: 2.45 (3H, s), 7.81 (2H, d), 7.38 (2H, d), $J_{ortho} = 6.2$ [Beilstein Reg. No. 1854613].

$3\text{-CH}_3\text{-C}_6\text{H}_4\text{NO}$ (**3a**). Organic solution colour: dark green. Yellow solid; m.p. = $53\text{--}4^\circ\text{C}$ (lit. 53°C). $\nu(\text{NO}) = 1490\text{ cm}^{-1}$. ^1H NMR: 2.45 (3H, s), 8.0–7.0 (4H, multiplet) [Beilstein Reg. No. 2039233].

$2\text{-CH}_3\text{-C}_6\text{H}_4\text{NO}$ (**4a**). Organic solution colour: dark green. Yellow crystalline solid; m.p. = $72\text{--}5^\circ\text{C}$ (lit. 72°C). $\nu(\text{NO}) = 1265\text{ cm}^{-1}$. ^1H NMR: 3.35 (3H, s), 7.58 (1H, multiplet), 7.17 (2H, multiplet), 6.26 (1H, multiplet) [Beilstein Reg. No. 1927295].

$4\text{-C}_2\text{H}_5\text{-C}_6\text{H}_4\text{NO}$ (**5a**). Organic solution colour: green. Yellow solid; m.p. = $22\text{--}5^\circ\text{C}$ (lit. 22°C). $\nu(\text{NO}) = 1506\text{ cm}^{-1}$. ^1H NMR: 1.30 (3H, t), 2.75 (2H, q), 7.84 (2H, d), 7.42 (2H, d) $J_{ortho} = 8.4$ [Beilstein Reg. No. 1927849].

$2\text{-C}_2\text{H}_5\text{-C}_6\text{H}_4\text{NO}$ (**6a**). Organic solution colour: red-brown. Light yellow crystalline solid; m.p. = $62\text{--}3^\circ\text{C}$ (lit. 61°C). ^1H NMR: 1.65 (3H, t), 4.53 (2H, q), 7.65 (1H, dd, $J^2 = 9.5$ and 7.5 , $J^3 = 1.8$), 7.32 (1H, ddd, $J^2 = 9.5$, $J^3 = 1.8$), 6.82 (1H, ddd, $J^2 = 8.1$ and 7.5 , $J^3 = 0.8$), 6.27 (1H, dd, $J^2 = 8.1$, $J^3 = 1.8$) [Beilstein Reg. No. 2960920].

$4\text{-Br-C}_6\text{H}_4\text{NO}$ (**7a**). Organic solution colour: green. Light yellow solid; m.p. = $94\text{--}5^\circ\text{C}$ (lit. 94°C). $\nu(\text{NO}) = 1499, 1255\text{ cm}^{-1}$. ^1H NMR: 7.48 (4H, multiplet) [Beilstein Reg. No. 2040049].

$3\text{-Br-C}_6\text{H}_4\text{NO}$ (**8a**). Organic solution colour: green. Light yellow solid; m.p. = $78\text{--}9^\circ\text{C}$ (lit.

78°C). $\nu(\text{NO}) = 1463, 1261 \text{ cm}^{-1}$. $^1\text{H NMR}$: 7.80 (4H, multiplet) [Beilstein Reg. No. 2499351].

2,Br-C₆H₄NO (**9a**). Organic solution colour: light yellow. Yellow solid; m.p. = 98–9°C (lit. 97°C). $^1\text{H NMR}$: 7.80 (4H, multiplet) [Beilstein Reg. No. 1858038].

4,Cl-C₆H₄NO (**10a**). Organic solution colour: emerald green. Light yellow solid; m.p. = 89°C (lit. 90°C). $\nu(\text{NO}) = 1490, 1255 \text{ cm}^{-1}$. $^1\text{H NMR}$: 7.91 (2H, d), 7.60 (2H, d), $J_{ortho} = 8.8$ [Beilstein Reg. No. 2040048].

3,Cl-C₆H₄NO (**11a**). Organic solution colour: light green. Light yellow solid; m.p. = 72–7°C (lit. 72°C). $\nu(\text{NO}) = 1534, 1265 \text{ cm}^{-1}$. $^1\text{H NMR}$: 7.90 (4H, multiplet) [Beilstein Reg. No. 2040046].

2,Cl-C₆H₄NO (**12a**). Organic solution colour: yellow. Light yellow solid; m.p. = 58°C (lit. 56°C). $^1\text{H NMR}$: 7.80 (4H, multiplet) [Beilstein Reg. No. 1857717].

4,F-C₆H₄NO (**13a**). Organic solution colour: yellow-green. Yellow crystalline solid; m.p. = 55°C (lit. 51°C). $\nu(\text{NO}) = 1507, 1231 \text{ cm}^{-1}$. $^1\text{H NMR}$: 7.73 (2H, d), 7.38 (2H, d), $J_{ortho} = 8.8$, $J_{FH} = 5.16$ [Beilstein Reg. No. 2040047].

4,*iso*-C₃H₇-C₆H₄NO (**14a**). Organic solution colour: dark green. Emerald green oil. $\nu(\text{NO}) = 1495 \text{ cm}^{-1}$. $^1\text{H NMR}$: 1.3 (6H, d), 3.0 (1H, sept), 7.85 (2H, d), 7.45 (2H, d), $J_{ortho} = 8.6$ [Beilstein Reg. No. 2245250].

4,*tert*-C₄H₉-C₆H₄NO (**15a**). Organic solution colour: light green. Light green oil. $\nu(\text{NO}) = 1504, 1265 \text{ cm}^{-1}$. $^1\text{H NMR}$: 1.38 (9H, s), 7.92 (2H, d), 7.76 (2H, d), $J_{ortho} = 9.3$ [Beilstein Reg. No. 2244849].

2.3.3. Gas chromatographic analyses

Hexamethyl benzene (internal standard) was introduced at the beginning of each catalytic reaction. Response factors were determined for all amines and nitroso derivatives. Conversions (%) were calculated as (mmol of converted amine/mmol of initial amine) × 100. Selectivities (%) were calculated as (mmol of weighted nitroso derivative/mmol of converted amine) ×

100. Turnovers per hour were calculated as (mmol of weighted nitroso derivative/mmol of catalyst × h) × 100.

3. Results and discussion

3.1. Catalytic reactions

In this work, we studied the catalytic oxidation reactions of the following anilines: C₆H₅NH₂ (**1**), 4,CH₃-C₆H₄NH₂ (**2**), 3,CH₃-C₆H₄NH₂ (**3**), 2,CH₃-C₆H₄NH₂ (**4**), 4,C₂H₅-C₆H₄NH₂ (**5**), 2,C₂H₅-C₆H₄NH₂ (**6**), 4,Br-C₆H₄NH₂ (**7**), 3,Br-C₆H₄NH₂ (**8**), 2,Br-C₆H₄NH₂ (**9**), 4,Cl-C₆H₄NH₂ (**10**), 3,Cl-C₆H₄NH₂ (**11**), 2,Cl-C₆H₄NH₂ (**12**), 4,F-C₆H₄NH₂ (**13**), 4,*iso*-C₃H₇-C₆H₄NH₂ (**14**), 4,*tert*-C₄H₉-C₆H₄NH₂ (**15**). All these substrates are soluble in organic solvents with exception of **10**, which is also soluble in water. Cyclohexane was chosen because of its properties (good amine solvent, none polarity, proper nitroso precipitating agent), while the oxidant was a low concentrated aqueous solution of H₂O₂ (30% w/w). Therefore, the reaction medium resulted in a two-phase system. The *cis*-dioxo complex of molybdenum(VI), Mo(O)₂(*acac*)₂ (**16**) (*acac*H = CH₃C(O)CH₂-C(O)CH₃) [14], was adopted as catalyst for the following reasons: (a) it is well known that hydrogen peroxide transforms **16** in a peroxo specie [1] able to transfer an electrophilic oxygen atom to substrates [1,8,9]; (b) the acetylacetonate ligands can be partially or totally replaced by H₂O₂ [1,15–17]; (c) **16** was successfully used in olefin oxidation reactions in the presence of cumyl hydroperoxide [18]; (d) due to its high oxidation state, molybdenum(VI) is a good candidate for the catalytic oxidation of amine substrates [8–11].

At the beginning of the catalytic reaction, the brick red particles of Mo(O)₂(*acac*)₂, completely insoluble in the two-phase system, are physically at the bottom of the flask, in the lower aqueous layer. However, in 1 h, **16**

changes its identity becoming mostly soluble in C₆H₁₂, as established by blank experiments without amine. In fact we determined than an aqueous suspension of **16** reacts with 0.5 ml of hydrogen peroxide expelling acacH ligands after 1 h (ca. 90%, gas chromatographic quantified analyses). In the same conditions, a cyclohexane suspension of **16** loose only small amounts of acacH (ca. 20%).

The components of the studied catalytic system were used in the following molar ratios: catalyst/amine = 0.1; catalyst/oxidant = 0.02; oxidant/amine = 5.

Under these conditions, the amines **1–15** were transformed in the corresponding nitroso derivatives: **1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **7a**, **8a**, **9a**, **10a**, **11a**, **12a**, **13a**, **14a**, and **15a**.

A list of chemical data of the isolated products is reported in Section 2.3.2. Although a part of these values are present in the literature (see Beilstein registry numbers), nevertheless we consider useful for synthetic purposes to have the main characterising parameters of these compounds collected in Section 2. Indeed, the IR data of the *ortho* nitroso derivatives **6a**, **9a** and **12a** are not reported. As the nitroso compounds can exist in monomer as well in dimer form even in the solid state [19–22], we found easier to characterise the *ortho* derivatives in solution by ¹H NMR.

The best catalytic results are illustrated in Table 1. Nitroso compounds **1a–13a** were easily recovered as precipitates (see Section 2) and therefore, the reported yields are based on weighted pure products. Table 1 underlines good conversions (60–100%) and selectivities (70–90%) besides poor turnover per hour (1–5). Nevertheless, substrates as *meta* and *ortho* anilines, usually hard to oxidise, are here transformed in the corresponding nitroso compounds with fair yields (50–90% and 20–86%, respectively, Table 1).

We proved that, after the dissolution of Mo(O)₂(acac)₂, both phases (water and cyclohexane) separately catalysed the oxidation to nitroso, but in any case we observed condensa-

Table 1

Conversions, yields and TOFs of the catalytic system in C₆H₁₂–H₂O

Amine	R	Conversions (%) (1–15)	Yields (%) (1a–15a)	t (h)	TOF (h ⁻¹)
1	H	100	80.2	2	4.0
15	4-Bu ^t	98.7	96.1	2	4.8
14	4-Pr ⁱ	97.6	91.3	2	4.5
5^a	4-Et	100	89.7	4	2.3
2	4-Me	98.2	84.7	2	4.3
7	4-Br	100	90.8	2	4.5
10	4-Cl	97.0	89.4	2	4.3
13	4-F	82.7	94.5	2	4.0
3	3-Me	96.0	90.7	3	2.9
8	3-Br	61.2	51.3	2	1.6
11	3-Cl	74.4	78.0	2	3.0
6	2-Et	54.2	71.3	4	1.0
4	2-Me	95.5	85.8	4	2.1
9	2-Br	26.4	20.2	4	0.13
12	2-Cl	6.3	21.8	2	0.071

^aThe yield of **5a** is lowered by precipitation of **17**.

tion products of amine with nitroso compounds or acetilacetone. Owing to the two phases, it was difficult to find direct correlation between substituted anilines and catalytic activities. However, from a qualitative point of view, only a general trend of TOF (h⁻¹) with the substituting groups can be outlined (Fig. 1).

The *para* anilines [(a) and (b) curves] were better oxidised than *meta* and *ortho* derivatives [(c) and (d) curves]. The electron-donating groups (squares) affect the catalysis more than the withdrawing ones (circles). In particular, the yield of **5a** (Table 1) is lowered by the precipitation of a yellow solid (**17**), which contains **5a** (see Section 3.2).

The catalytic system was also applied by using methylene chloride as solvent but worse results were obtained (Table 2).

3.2. Behaviour of **5**

The catalytic reaction of **5** allowed the precipitation of a light yellow solid, **17** (ca. 10–15 mg, 7.5–11% w/w) after 10–15 min. It was characterised by spectroscopy, elemental analyses and atomic absorption determinations. The quantitative analyses of the components C, H, N

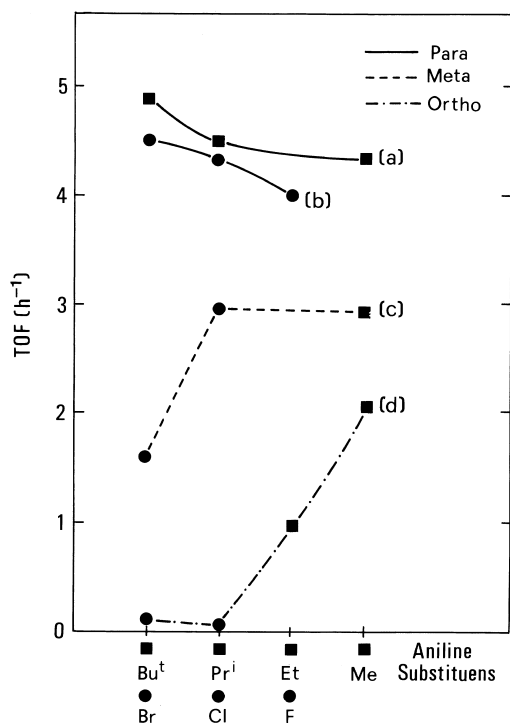


Fig. 1. TOF (h⁻¹) vs. aniline substituents. Squares: electron-donating groups. Circles: electron-withdrawing groups.

and Mo afforded the following percent results: C, 30.9, H 4.0, N 4.5 and Mo 30.5.

The KBr-dispersed infrared spectrum of **17** showed two strong bands at 981.1 and 856.8 cm⁻¹ that awfully differs from the two absorptions of *cis*-Mo(O)₂(*acac*)₂ at 934 and 904 cm⁻¹ [23]. The signal at 981.1 was attributed to the stretching mode of a molybdenum oxo double bond [24–28], while the signal at 856.8 cm⁻¹ was attributed to a single oxygen–oxygen bond of a peroxo ligand [1,10,11,28–31]. A broad band at 3450 cm⁻¹ was attributed to the OH stretching of co-ordinated water molecules [29–31].

In the ¹H NMR spectrum of **17**, the signals due to the nitroso derivative, co-ordinated and free, were detected [8,9] (Fig. 2, CDCl₃, under aerobic conditions). The doublet of doublets centred at 7.30 ppm [7.32 (2H, d), 7.24 (2H, d), *J*_{ortho} = 8.42 Hz] was attributed to the hydrogen atoms of an η²-coordinated nitroso ligand, while

the doublet of doublets centred at 7.69 ppm [7.83 (2H, d), 7.50 (2H, d), *J*_{ortho} = 8.40 Hz] to the hydrogen atoms of the free nitroso derivative **5a** (see Section 2). The doublet of doublets centred at 7.79 ppm [8.12 (2H, d); 7.42 (2H, d); *J*_{ortho} = 8.60 Hz] was assigned to the hydrogen atoms of the nitro derivative, 4-C₂H₅C₆H₄-NO₂, formed in solution by subsequent oxidation of **5a**. Superimposed quartets (centred at 2.67 ppm) and triplets (centred at 1.24 ppm) belong to ethyl groups. The treatment with D₂O (4.5 ppm) reveals the absence of NH₂ groups.

In accordance with these experimental results, we suggest that **17** is the complex (O)Mo(O₂)(η²-NO-C₆H₄-4,C₂H₅)(H₂O)₂, that is a molybdenum(VI) complex co-ordinating an oxo group, a peroxo moiety and an η² nitroso derivative. Two water molecules complete the coordination sphere. The calculated percentages of this compound (C 30.5, H 4.8, N 4.4 and Mo 30.4) fit with the experimental values.

When **17** is dissolved in solvents as acetonitrile, methylene chloride and cyclohexane, it produces the corresponding free nitroso derivative **5a**, as in the cases illustrated by Møller and Jørgensen [8,9]. A UV–visible spectrometric study carried out on a CH₃CN solution of **17**, showed two bands at 743 and 504 nm. The absorbance of this last peak increased from 0.2 to 1.2, as evidenced by recording the spectrum

Table 2
Conversions, yields and TOFs of the catalytic system in CH₂Cl₂

R	Conversions (%)	Yields (%)	t (h)	TOF (h ⁻¹)
H	100	87.0	20	0.43
4-Et	98.0	94.0	20	0.48
4-Me	100	71.2	22	0.32
4-Br	100	92.1	96	0.096
4-Cl	94.0	50.5	45	0.11
3-Me	100	58.5	96	0.061
3-Br	43.1	80.0	48	0.16
3-Cl	69.1	39.2	48	0.081
2-Et	94.2	70.0	43	0.16
2-Me	85.0	95.0	48	0.20
2-Cl	0	0	46	0

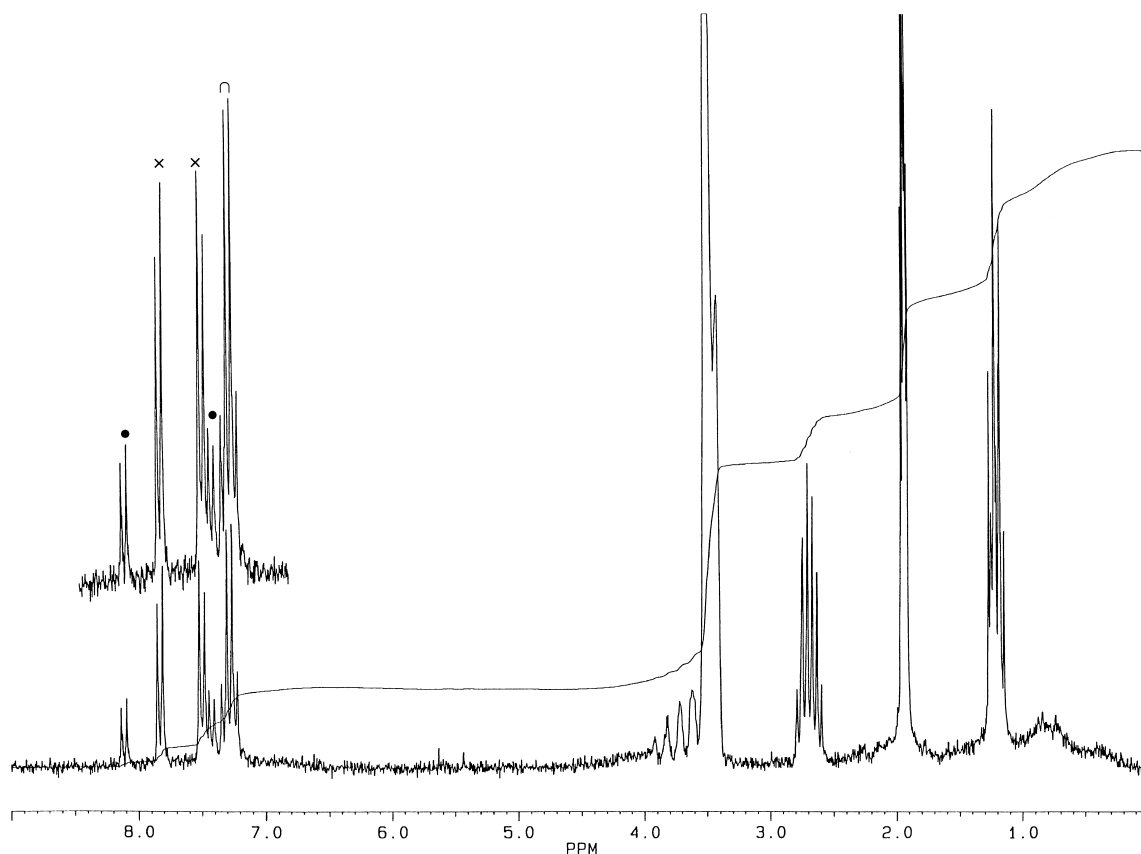


Fig. 2. ^1H NMR of **17** in CDCl_3 . (x) = free $4, \text{C}_2\text{H}_5\text{-C}_6\text{H}_4\text{NO}$; (●) = $4, \text{C}_2\text{H}_5\text{-C}_6\text{H}_4\text{NO}_2$; (o) = co-ordinated $4, \text{C}_2\text{H}_5\text{-C}_6\text{H}_4\text{NO}$.

every 15 min for 5 h. These data, compared with literature values (**5a** in MeOH: $\lambda_{\text{max}} = 745$ nm) [32], indicated free $4, \text{C}_2\text{H}_5\text{-C}_6\text{H}_4\text{NO}$, due to the decomposition of **17**. A blank UV spectrum of **5a** was also carried out as confirm.

4. Conclusions

In this work, a simple catalytic organometallic method to produce (and recover) nitroso derivatives was presented.

In cyclohexane, electronic factors drive the nucleophilic attack of the amine must likely on a peroxo ligand of the molybdenum complex formed in situ by hydrogen peroxide. The two-phase system provides the useful media, as the aqueous phase is the place for generating the

catalyst by H_2O_2 , while the organic phase is the place for oxidising the anilines.

Finally, the freezing of the reaction liquors and their subsequent slow warming represents an alternative way to gently concentrate nitroso solutions, which allows a simple recover of nitroso compounds avoiding decomposition.

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