

Silica Sulphuric Acid as an Efficient Catalyst for the Catalytic and Metal-free Oxidation of Aromatic Amines to their Corresponding Nitro Compounds with Sodium Perborate under Micellar Media

Davood Habibi*, Mohammad A. Zolfigol and Maliheh Safaiee

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran.

Received 6 December 2007, revised 21 April 2008, accepted 10 July 2008.

ABSTRACT

Electron-donating substituted anilines were converted to their corresponding nitro compounds with sodium perborate in the presence of a catalytic amount of silica sulphuric acid under micellar media in moderate to good yields.

KEYWORDS

Sodium perborate, nitro compounds, silica sulphuric acid, oxidation of anilines.

1. Introduction

Production of aromatic nitro compounds is an important industrial process and involves the unsolved problems of regioselectivity, over-nitration and competitive oxidation of substrates.¹ Therefore oxidation of aniline derivatives to their corresponding nitro compounds may be a useful route for the conversion of the NH₂ group into the corresponding nitro group. Several methods for direct oxidation of aromatic amines to nitro derivatives have been reported, such as hypofluorous acid,² peracids, permaleic acid,³ dioxirane,⁴ *tert*-butyl peroxides or H₂O₂ catalysed with transition metal compounds (W,^{5,6} Mo,^{7,8} V⁷ and Re⁹) and titanium and chromium silicates.¹⁰ Some of the procedures described in the literature suffer from harsh reaction conditions, over-oxidation, low yields of the desired products, unavailability of the reagents and formation of azo compounds, etc.¹¹ Selective oxidation of aryl amines is an important reaction in the synthesis of hydroxylamine, and nitroso, oxime, azo, azoxy and other compounds.^{12–17}

The product composition depends on the oxidants, catalysts and reaction conditions employed and the selective oxidation of amines is consequently very rare and valuable. However, for production of the nitro compounds, the best reaction conditions and reagents should be chosen and optimized.

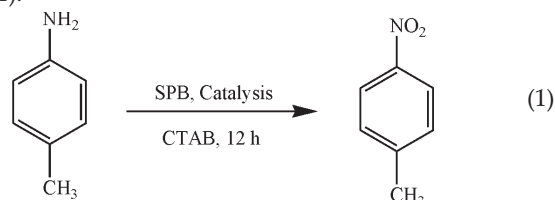
Sodium perborate (SPB, NaBO₃·4H₂O) is an inexpensive, stable, innocuous, easily handled and extensively used ingredient in detergents as a bleaching agent. It generates hydrogen peroxide *in situ* in aqueous solution and is a highly effective oxidizing reagent in glacial acetic acid.¹⁸ It has also been used for functional group oxidation in organic synthesis.^{19–21} In 1987, McKillop reported the use of SPB in acetic acid at 50–55 °C for oxidation of aniline containing electron-withdrawing substituents to the corresponding nitro groups.²² Recently, a tungstophosphoric acid (H₃PW·nH₂O)/SPB system was reported for this purpose under micellar media.²³

In view of the current interest in environmental protection²⁴ and in continuation of our ongoing programme to develop environmentally benign heterogeneous catalysts,^{25–28} we tried to expand the application of silica sulphuric acid (SSA) as a new

versatile heterogeneous inorganic solid acid catalyst^{29–35} for oxidation of anilines. Herein we wish to report the application of SPB in the presence of cetyltrimethylammonium bromide (CTAB) as well as a catalytic amount of SSA in micellar media for the oxidation of different aromatic amines to the corresponding nitro compounds.

2. Results and Discussion

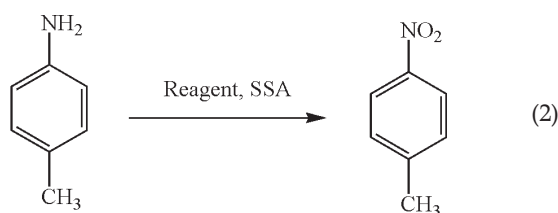
Application of SPB and a catalytic amount of SSA under micellar media oxidized different anilines to the desired nitro compounds without any side products being observed. According to our knowledge, preparation of nitro compounds via nitration of aromatic rings is usually accompanied by the formation of regioisomers, especially when several positions are available for substitution of the nitro group on aromatic rings. Therefore, direct conversion of the amino group into the related nitro functional group is a major advantage of this system so that the nitro group will be created in the exact position and the problem of regioselectivity will be solved. In addition, applying a catalytic amount of silica sulphuric acid is another advantage of this method. For choosing the best catalyst, oxidation of 4-amino toluene was tested with various acidic catalysts (see Equation 1 and Table 1).



CTAB was used as a phase transfer catalyst and for understanding its effect, reactions have also been carried out under the same conditions in the absence of CTAB which showed decreasing yields (see Equation 2 and Table 2).

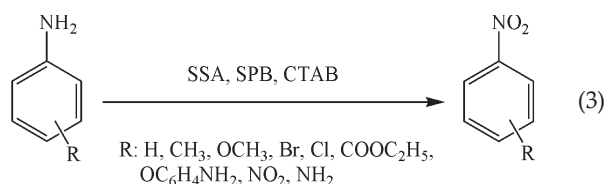
The results obtained indicate that the SPB/SSA/CTAB system is more suitable than the SPB/CTAB system alone. Sodium percarbonate (SPC) and 1,4-diazabicyclo[2.2.2]octane (DABCO)-H₂O₂ were unable to oxidize 4-methyl aniline under the same conditions. When polyvinylpyrrolidone (PVP)-H₂O₂

* To whom correspondence should be addressed. E-mail: davood.habibi@gmail.com



and urea-hydrogen peroxide (UHP) were used for oxidation of 4-amino toluene, sluggish mixtures were formed (see Table 2).

According to Table 3, the SPB/SSA/CTAB system is more suitable for oxidation of the electron-donating substituted anilines (Equation 3) and could not oxidize the anilines with electron-withdrawing groups. Also, mono-oxidation of 1,4-diaminobenzene took place and surprisingly further oxidation to the corresponding dinitro products did not occur.



The major disadvantage of the previously reported procedures for oxidation of anilines is the production of a mixture of products such as diazo-1-oxides,^{9,13} and nitroso and nitro derivatives.⁸ Although some of the reported procedures are practical for this purpose, most of them have used reagents containing transition metals, e.g. Fe, W and Ti within their structures^{14–17,23} and/or unusual reagents,² which are not environmentally friendly methods. Therefore, we believe that the proposed procedure introduces a metal-free reagent system for oxidation of anilines under mild and green conditions without the above mentioned limitations.

3. Conclusion

Silica sulphuric acid (SSA) is a versatile stable protic acid and superior proton source to many reported acidic solid supports and acidic resins.³⁹ This reagent is cheap, safe, easy to handle, environmentally benign and presents fewer disposal problems.⁴⁰ In conclusion, we have reported a new catalytic system for the oxidation of different anilines containing electron-donating groups and we believe that the present methodology is an important procedure which can be added to the existing methodologies.

Table 1 Oxidation of 4-amino toluene to its corresponding nitro compound with NaBO₃·4H₂O (17.7 mmol) and different catalysts at 60 °C in the presence of cetyltrimethylammonium bromide (CTAB).

Entry	Catalyst (1 mmol)	Yield/% ^a
1	H ₂ SO ₄	43
2	H ₃ PO ₄	49
3	HNO ₃	60
4	HCl	25
5	NaHSO ₄	80 (57) ^d
6	KHSO ₄	60
7	Al(HSO ₄) ₃	24
8	Mg(HSO ₄) ₂	89 (47) ^d
9	Fe(HSO ₄) ₃	19
10	SSA ^b	90
11	SSA ^c	60

^a GC yield.

^b 0.05 g SSA.

^c 0.01 g SSA.

^d Reaction carried out in the absence of CTAB.

Some more advantages of the proposed system are: oxidation of different anilines to the desired nitro compounds without observing any side products; direct conversion of the amino group to the related nitro functional group, so that the nitro group will be created in the exact position and the problem of regioselectivity will be solved; application of a catalytic amount of silica sulphuric acid as a low cost solid acid; the system is not able to oxidize anilines with electron-withdrawing groups; introduction of a metal-free reagent system for oxidation of anilines under mild and green conditions rather than application of reagents containing transition metals such as Fe, W and Ti within their structures, which are not environmentally friendly methods; homoselective oxidation⁴¹ of the diamine takes place and further oxidation to the corresponding dinitro products does not occur; application of water as a solvent in view of green chemistry, which is vital and important for the environment.

4. Experimental

Chemicals were purchased from the Merck Chemical Company, Tehran, Iran. The nitro products were characterized by comparison of their spectral and physical data with those of authentic samples.

Table 2 Oxidation of 4-amino toluene (2.5 mmol) with reagents (17.5 mmol) in micellar media under several conditions.

Entry	Reagent	Mass of SSA/g	Temperature/°C	CTAB ^a	Time/h	Yield/% ^b
1	SPB	0.05	55–60	–	24	36
2	SPB	0.05	55–60	–	12	35
3	SPB	0.05	55–60	+	12	90
4	SPB	0.01	55–60	+	12	60
5	SPB	0.01	55–60	–	24	38
6	SPB	0.01	room temp	–	24	16
7	SPB	0.01	room temp	+	24	31
8	SPC ^c	0.05	55–60	+	12	no reaction
9	DABCO/H ₂ O ₂ ^d	0.05	55–60	+	12	no reaction
10	PVP/H ₂ O ₂ ^e	0.05	55–60	+	12	mixture
11	UHP ^f	0.05	55–60	+	12	mixture

^a 2.9 mol L⁻¹.

^b GC yield.

^c Sodium percarbonate.

^d Reference 36.

^e Reference 37.

^f Reference 38.

Table 3 Oxidation of different anilines into their corresponding nitro compounds with sodium perborate tetrahydrate (SPB) in the presence of silica sulphuric acid (SSA) (0.05 g) in micellar media at 60 °C.

Entry	Amine	SPB/substrate	Product	Time/h	Yield/% ^a
1	aniline	7	nitrobenzene	12	50
2	2-methyl aniline	7	2-nitrotoluene	12	42 (93) ^b
3	3-methyl aniline	7	3-nitrotoluene	12	53
4	4-methyl aniline	7	4-nitrotoluene	12	66 (90) ^b
5	4-methoxy aniline	7	4-methoxytoluene	4	57
6	3-bromo aniline	10	1-bromo-3-nitrobenzene	13	13
7	4-bromo aniline	10	1-bromo-4-nitrobenzene	13	50
8	4-chloro aniline	10	1-chloro-4-nitrobenzene	13	15
9	ethyl-4-amino benzoate	10	–	13	–
10	4-(4-aminophenoxy)aniline	10	–	13	–
11	4-nitroaniline	10	–	13	–
12	1,4-diaminobenzene	10	4-nitroaniline	13	30

^a Isolated yield.^b GC yield.

4.1. General Procedure for Oxidation of the Electron-releasing Substituted Anilines (Table 3, entries 1–5)

In a 50 mL round-bottomed flask equipped with a magnetic stirrer were added SSA (0.05 g) and CTAB (5 mL, 2.9 mol L⁻¹). The resulting mixture was stirred at room temperature for 5 min, sodium perborate tetrahydrate (2.69 g, 17.5 mmol) added and the temperature raised to 60 °C. A warm solution of the cleaned anilines (2.5 mmol) in 5 mL of CTAB (2.9 mol L⁻¹) was added slowly three times to the reaction mixture and stirred at 60 °C for the appropriate time. The progress of the reaction was monitored by TLC or GC. The reaction mixture was cooled to room temperature and the organic layer extracted with Et₂O (3 × 25 mL). The ethereal solution was separated, washed with aqueous HCl (6 mol L⁻¹, 2 × 10 mL) and H₂O (2 × 25 mL), and dried over anhydrous Na₂SO₄ (1 g). Evaporation of the solvent gave the almost pure target nitro compounds. Further purification was performed by column chromatography on silica gel using ethyl acetate/light petroleum ether (3:7, b.p. 40–60 °C) as eluent.

4.2. General Procedure for Oxidation of the Electron-deficient Substituted Anilines (Table 3, entries 6–8)

In a 50 mL round-bottomed flask equipped with a magnetic stirrer were added SSA (0.05 g) and CTAB (10 mL, 2.9 mol L⁻¹). The mixture was stirred at room temperature for 5 min, sodium perborate tetrahydrate (3.845 g, 25 mmol) added and the temperature raised to 55–60 °C. The substrate (an electron-deficient aniline, 2.5 mmol) was added to the reaction mixture and stirred at 55–60 °C for the appropriate time. The work-up of the mixture was performed as above.

Acknowledgement

The authors gratefully acknowledge financial support from the Bu-Ali Sina University, Hamedan, Iran.

References

- M.A. Zolfigol, E. Ghaemi, E. Madrakian and A. Ghorbani-Choghmarani, *Mendeleev Commun.*, 2006, 41–42.
- S.M. Dirk, E.T. Mickelson, J.C. Henderson and J.M. Tour, *Org. Lett.*, 2000, 2, 3405–3406.
- R.W. White and W.D. Emmons, *Tetrahedron*, 1962, 17, 31–34.
- R.W. Murray, R. Jeyaraman and L. Mohan, *Tetrahedron Lett.*, 1986, 27, 2335–2336.
- S. Sakaue, T. Tsubakino, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, 1993, 58, 3633–3638.
- E.R. Moller and K.A. Jorgensen, *J. Am. Chem. Soc.*, 1993, 115, 11814–11822.
- G.R. Howe and R.R. Hiatt, *J. Org. Chem.*, 1970, 35, 4007–4012.
- A. Defoin, *Synthesis*, 2004, 706–710.
- R.W. Murray, K. Iyanar, J. Chen and J.T. Wearing, *Tetrahedron Lett.*, 1996, 37, 805–808.
- S. Suresh, R. Joseph, B. Jayachandran, A.V. Pol, M.P. Vinod, A. Sudalai, H.R. Sonawane and T. Rawindranathan, *Tetrahedron*, 1995, 51, 11305–11318.
- C. Karunakaran and P.N. Palanisamy, *J. Mol. Catal. A Chem.*, 2001, 172, 9–17.
- S.B. Waghmode, S.M. Sabne and S. Sivasanker, *Green Chem.*, 2001, 3, 285–288.
- K. Neimann and R. Neumann, *Chem. Commun.*, 2001, 487–488.
- Y.S.S. Wan, K.L. Yeung and A. Gavriilidis, *Appl. Catal. A Chem.*, 2005, 281, 285–293.
- M. Costas, I. Romero, M.A. Martinez, A. Llobet, D.T. Sawyer and J. Caixach, *J. Mol. Catal. A Chem.*, 1999, 148, 49–58.
- N. Jagtap and V. Ramaswamy, *Appl. Clay Sci.*, 2006, 33, 89–98.
- C. Karunakaran, S. Senthilvelan and S. Karuthapandian, *J. Photochem. Photobiol. A*, 2005, 172, 207–213.
- A. McKillop and W.R. Sanderson, *J. Chem. Soc., Perkin Trans.*, 2000, 1, 471–476.
- M. Safaiee, *Synlett.*, 2006, 2513–2514.
- J. Muzart, *Synthesis*, 1995, 1325–1347.
- C. Karunakaran and R. Venkataramanan, *Catal. Commun.*, 2006, 7, 236–239.
- A. McKillop and J.A. Tarbin, *Tetrahedron*, 1987, 43, 1753–1758.
- H. Firouzabadi, N. Iranpoor and K. Amani, *Green Chem.*, 2001, 3, 131–132.
- H. Firouzabadi and A.A. Jafari, *J. Iran. Chem. Soc.*, 2005, 2, 85–114.
- A. Bamoniri, M.A. Zolfigol, I. Mohammadpoor-Baltork and B.F. Mirjalili, *J. Iran. Chem. Soc.*, 2006, 3, 85–88.
- K. Niknam and M.A. Zolfigol, *J. Iran. Chem. Soc.*, 2006, 3, 59–63.
- K. Niknam, M.A. Zolfigol, T. Sadabadi and A. Nejati, *J. Iran. Chem. Soc.*, 2006, 3, 318–322.
- M.A. Zolfigol, M. Bagherzadeh, K. Niknam, F. Shirini, I. Mohammadpoor-Baltork, A. Ghorbani-Choghmarani and M. Baghbazadeh, *J. Iran. Chem. Soc.*, 2006, 3, 73–80.
- M.A. Zolfigol, I. Mohammadpoor-Baltork, B.F. Mirjalili and A. Bamoniri, *Synlett.*, 2003, 1877–1879.
- M.A. Zolfigol and A. Bamoniri, *Synlett.*, 2002, 1621–1624.
- M.A. Zolfigol, *Tetrahedron*, 2001, 57, 9509–9511.
- P. Salehi, M.A. Zolfigol, F. Shirini and M. Baghbazadeh, *Curr. Org. Chem.*, 2006, 10, 2171–2189.
- K. Niknam, M.A. Zolfigol, A. Khorramabadi-Zad, R. Zare and M. Shayegh, *Catal. Commun.*, 2006, 7, 494–498.
- P. Salehi, M. Dabiri, M.A. Zolfigol and M.A. Bodaghi Fard, *Phosphorus, Sulfur, and Silicon and Related Elements*, 2004, 179, 1113–1121.

- 35 P. Salehi, M. Dabiri, M.A. Zolfigol and M.A. Bodaghi Fard, *Tetrahedron Lett.*, 2003, **44**, 2889–2891.
- 36 M.A. Zolfigol, P. Salehi, S.E. Mallakpour and M. Torabi, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 1673–1674.
- 37 M.A. Zolfigol, G. Chehardoli and M. Shiri, *React. Funct. Polym.*, 2007, **67**, 723–727.
- 38 J.A. Damavandi, B. Karami and M.A. Zolfigol, *Synlett.*, 2002, 933–934.
- 39 M.B. Gavande, *Res. J. Chem., Environ.*, 2006, **10**, 93–94.
- 40 A.R. Hajipour, A. Zarei, L. Khazdooz and A.E. Rouho, *Synthesis*, 2006, 1480–1484.
- 41 M.A. Zolfigol, K. Amani, A. Ghorbani-Choghamarani, M. Hajjami, R. Ayazi-Nasrabadi and S. Jafari, *Catal. Commun.*, 2008, **9**, 1739–1744.