



Tungstophosphoric acid catalyzed oxidation of aromatic amines to nitro compounds with sodium perborate in micellar media

H. Firouzabadi,* N. Iranpoor* and K. Amani

Department of Chemistry, Shiraz University, Shiraz 71454, Iran.
E-mail: firouzabadi@chem.susc.ac.ir

Received 29th January 2001

First published as an Advance Article on the web 3rd May 2001

Several primary aromatic amines, substituted with electron-donating groups, were converted to their corresponding nitro compounds in good to excellent yields with sodium perborate tetrahydrate (SPB) in micellar media in the presence of a catalytic amount of tungstophosphoric acid ($\text{H}_3\text{PW}\cdot n\text{H}_2\text{O}$).

Introduction

Oxidation of anilines to their nitro compounds is an important chemical transformation. Oxidation of aromatic primary amines has attracted the attention of chemists in recent years.¹ The nature of the oxidation products formed depends on the type of the oxidant used and the reaction conditions, *i.e.* aqueous or non-aqueous media and the pH employed for the reaction. For this purpose methods are well documented. Various reagents, including metal compounds, organic peroxides and hydrogen peroxide, have been used to form oxygen-containing derivatives of anilines.² Some of the procedures described in the literature suffer from harsh reaction conditions, over-oxidation, low yields of the desired products, and unavailability of the reagents. The non-toxic, inexpensive and easily available peroxygen compound sodium perborate (SPB)($\text{NaBO}_3\cdot n\text{H}_2\text{O}$, $n = 1-4$) is extensively used in the detergent industry as a bleaching and antiseptic agent as well as in organic synthesis. SPB is a good substitute for potentially hazardous concentrated H_2O_2 . SPB has been extensively used for functional group oxidation in organic synthesis and has recently been reviewed.³ McKillop has reported the use of a large excess of sodium perborate (NaBO_3) in acetic acid at 50–55 °C for the oxidation of anilines containing electron-withdrawing groups to the corresponding nitro arenes. In contrast, anilines with electron-donating groups were readily over-oxidized affording the crude nitro arenes⁴ in only low yields and the method was recognized to be unsuitable for this type of oxidation. The use of water as a medium for promoting organic reactions (and also as the solvent in which the vast majority of biochemical processes take place) is very important and in recent years has received much attention.⁵ Micelles, which are dynamic clusters of surfactant molecules which possess both hydrophilic and hydrophobic structures, may associate in aqueous media to form dynamic aggregates.⁶ It is well established that, in many cases, the rates and pathways of many chemical reactions can be altered by performing the reactions in micellar media instead of pure bulk solvents. Micelles can concentrate the reactants within their small volumes; stabilize substrates, intermediates or products and orient substrates so that ionization potential and oxidation–reduction properties, dissociation constants, physical properties and reactivities are changed. Thus they can alter the reaction rate, mechanism, and regio- and stereo-chemistry.⁷ Micellar solubilization has been exploited to speed up and sometimes change the product distribution of several types of reactions.⁸ Tungstophosphoric acid salts have also been used as catalysts

for organic reactions and their properties and uses are extensively studied.⁹

Here we report that a variety of anilines are smoothly and efficiently oxidized to nitro compounds in the presence of a large excess of SPB in aqueous basic media (rather than acidic media in the absence of organic co-solvents). The reaction was conducted in the presence of cetyltrimethylammonium bromide (CTAB) as the micelle source and tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$) as the catalyst.

Results and discussion

The use of sodium perborate (SPB) in water as the reaction medium, cetyltrimethylammonium bromide (10 cmc, 0.02 M) as a surfactant and tungstophosphoric acid ($\text{H}_3\text{PW}\cdot n\text{H}_2\text{O}$) as a catalyst (0.01–0.2 mmol) promote facile oxidation of aniline and anilines substituted with electron-donating groups.

In order to show the important effect of the micellar media upon the reactions in this investigation, oxidation of aniline in water by SPB in the absence of surfactants was studied. Detection by GC showed that even after 24 h at room temperature, nitrobenzene formation only reached 4%. Increasing the temperature to 55–60 °C affected the rate of the reaction

Green Context

The continued innovation in the detergent industries driven by demands for higher levels of cleaning, low temperature efficiency and minimal environmental harm caused by the discharge of enormous volumes of effluent has led to the development of a number of safe and environmentally benign oxidants. Such reagents are becoming increasingly attractive to the environmentally-conscious chemicals manufacturing industries. They are however water-soluble which would normally restrict their value in organic synthesis. Here we see how a micellar environment can be used to overcome the incompatibility of an aqueous oxidant and an aromatic substrate. The synthetically useful transformation of anilines to nitroaromatics can be achieved using an aqueous micellar catalytic system containing the major detergency oxidant, sodium perborate, as the source of oxygen.

JHC

and nitrobenzene formation only reached 60% after 16 h. The effect of several surfactants; cetyltrimethylammonium bromide, CTAB (cationic), sodium dodecyl sulfate, SDS (anionic) and TritonX-100 (neutral) at their critical micellar concentration (cmc) in the presence of SPB in water, upon the rate of oxidation of aniline was also studied. The results show that CTAB at 10 cmc shows the best micellar activity and enhances the chemoselectivity (nitro compound only formed) of the reaction.

In order to avoid higher temperatures which causes generation of by-products, the catalytic effects of sodium tungstate and tungstophosphoric acid were studied. Our investigation showed that in the presence of tungstophosphoric acid the reaction rate almost doubled and the oxidation of aniline reached 97% (GC). Therefore, we applied this reaction condition for the oxidation of substituted anilines. The results showed that in contrast to the previously reported method,⁴ our procedure is suitable for the high yield conversion of aniline and substituted anilines with electron-releasing groups. The results are presented in Table 1.

Table 1 Oxidation of anilines in the presence of CTAB and H₃PW₁₂O₄₀ by NaBO₃·4H₂O at 55–60 °C^a

R = H, Me, OMe, Br, Cl

Entry	Ar	Yield ^b (%)
1	Ph	91
2	2-MeC ₆ H ₄	89
3	3-MeC ₆ H ₄	77
4	4-MeC ₆ H ₄	88
5	2-MeOC ₆ H ₄	81 ^c
6	4-MeOC ₆ H ₄	85 ^c
7	3,4-(MeO) ₂ C ₆ H ₃	68 ^d
8	2-ClC ₆ H ₄	45
9	4-ClC ₆ H ₄	53
10	2-BrC ₆ H ₄	48
11	4-BrC ₆ H ₄	58

^a All reactions performed for 12 h unless otherwise indicated. ^b Yields refer to isolated pure products which were characterized by their physical constants, IR, ¹H NMR and comparison with authentic samples. ^c 10 h. ^d 4 h.

Experimental

Typical procedures

1 Anilines substituted with electron-releasing groups. In a 50 ml round-bottomed flask, equipped with mechanical stirrer, were added tungstophosphoric acid (0.025 mmol) and CTAB [5 ml (10 cmc)]. The mixture was stirred at room temperature for 5 min, sodium perborate tetrahydrate (17.5 mmol) added and the temperature of the mixture raised to 55–60 °C. A warm solution of the cleaned aniline (2.5 mmol) in 5 ml of CTAB (10

cmc) was added slowly (1 h) to the mixture. The reaction mixture was stirred at 55–60 °C for the appropriate time (Table 1). 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). The ethereal solution was separated, and washed with aqueous HCl (6 M, 2 × 10 ml), H₂O (2 × 25 ml), and dried over anhydrous Na₂SO₄. 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 (bp 40–60 °C) (3:7) as eluent.

2 Anilines substituted with electron-deficient groups. In a 50 ml round-bottomed flask, equipped with mechanical stirrer, were added tungstophosphoric acid (0.25 mmol) and CTAB [10 ml (10 cmc)]. The mixture was stirred at room temperature for 5 min and then sodium perborate tetrahydrate (25 mmol) added and the temperature of the mixture raised to 55–60 °C. The aniline (2.5 mmol) added to the mixture. The reaction mixture stirred at 55–60 °C for the appropriate time (Table 1) and the work-up of the mixture was performed as above.

References

- 1 S. M. Dirk, E. T. Mickelson, J. C. Henderson and J. M. Tour, *Org. Lett.*, 2000, **2**, 3405; K. Krohn, J. Kuepke and H. Rieger, *J. Prakt. Chem. /Chem.-Ztg.*, 1997, **339**, 335; E. B. Mel'nikov, G. A. Suboch and E. Y. Belyaev, *Russ. J. Org. Chem.*, 1995, **31**, 1640; S. Suresh, R. Joseph, B. Jayachandran, A. V. Pol and M. P. Vinod, *Tetrahedron*, 1995, **51**, 11305; K. S. Webb and V. Seneviratne, *Tetrahedron Lett.*, 1995, **36**, 2377; S. Tollari, D. Vergani, S. Banfi and F. Porta, *J. Chem. Soc., Chem. Commun.*, 1993, 442; S. Sakaue, T. Tsubakino, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, 1993, **58**, 3633.
- 2 Z. Zhu and J. H. Espenson, *J. Org. Chem.*, 1995, **60**, 1326; S. Sakaue, T. Tsubakino, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, 1993, **58**, 3633; F. Ciminale, M. Camporeale, R. Mello, L. Troisi and R. Curci, *J. Chem. Soc., Perkin Trans. 2*, 1989, 417; L. Ross, C. Barclay, J. M. Dust, S. Brownstein and E. Gabe, *J. Org. Magn. Reson.*, 1981, **17**, 175; K. Kosswig, *Liebigs Ann. Chem.*, 1971, **349**, 206; H. E. Baumgarten, A. Staklis and E. M. Miller, *J. Am. Chem. Soc.*, 1965, **87**, 1203; O. H. Wheeler and D. Gonzalez, *Tetrahedron*, 1964, **20**, 189; K. Nakagawa and T. Tsuji, *Chem. Pharm. Bull.*, 1963, **11**, 296.
- 3 For a review, see: J. Muzart, *Synthesis*, 1995, 1325; G. W. Kabalka and K. Yang, *Synth. Commun.*, 1998, **28**, 3809; A. McKillop and J. A. Tarbin, *Tetrahedron*, 1987, **43**, 1753 and references therein; W. W. Zajac, M. G. Darey, A. P. Subong and J. H. Buzby, *Tetrahedron Lett.*, 1989, **30**, 6495; D. Koyucu, A. McKillop and L. McLaren, *J. Chem. Res. (S)*, 1990, 21; K. L. Reed, J. T. Gupton and T. L. Solarz, *Synth. Commun.*, 1990, **20**, 563; A. McKillop and D. Kemp, *Tetrahedron*, 1989, **45**, 3299.
- 4 P. McKillop and J. A. Tarbin, *Tetrahedron*, 1987, **43**, 1753; P. McKillop and J. A. Tarbin, *Tetrahedron Lett.*, 1983, **24**, 1505.
- 5 P. A. Grieco, *Organic synthesis in water*, Thomson Science, London, 1998.
- 6 T. M. Stein and S. H. Gellman, *J. Am. Chem. Soc.*, 1992, **114**, 3943; D. Myers, *Surfactant Science and Technology*, VCH, Weinheim, 1992; J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley, New York, 1982.
- 7 For a review, see: S. Tascioglu, *Tetrahedron*, 1996, **52**, 11113 and references therein.
- 8 R. P. Bonar-Law, *J. Org. Chem.*, 1996, **61**, 3623 and references therein.
- 9 For a review, see: I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171.