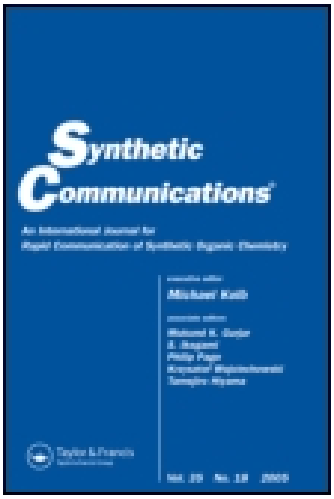


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

The Efficient Palladium-Catalyzed Selective t Synthesis of Benzenesulfonic Acids

Rajenahally V. Jagadeesh [a], Y. Sree Sandhya [a], P. Karthikeyan [a], S. Sudhakar Reddy [a], P. Pradeep Kumar Reddy [a], M. Viniod Kumar [a], K. T. Prabhu Charan [a], R. Narender [a] & P. R. Bhagat [a]

[a] Division of Organic Chemistry, School of Advanced Sciences, VIT University , Vellore , India

Published online: 14 Jun 2011.

To cite this article: Rajenahally V. Jagadeesh , Y. Sree Sandhya , P. Karthikeyan , S. Sudhakar Reddy , P. Pradeep Kumar Reddy , M. Viniod Kumar , K. T. Prabhu Charan , R. Narender & P. R. Bhagat (2011) The Efficient Palladium-Catalyzed Selective t Synthesis of Benzenesulfonic Acids, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:16, 2343-2349, DOI: 10.1080/00397911.2010.502991

To link to this article: http://dx.doi.org/10.1080/00397911.2010.502991

Synthetic Communications®, 41: 2343–2349, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.502991

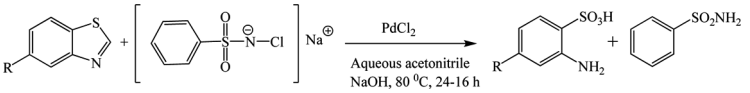
Taylor & Francis
Taylor & Francis Group

THE EFFICIENT PALLADIUM-CATALYZED SELECTIVE t SYNTHESIS OF BENZENESULFONIC ACIDS

Rajenahally V. Jagadeesh, Y. Sree Sandhya, P. Karthikeyan, S. Sudhakar Reddy, P. Pradeep Kumar Reddy, M. Viniod Kumar, K. T. Prabhu Charan, R. Narender, and P. R. Bhagat

Division of Organic Chemistry, School of Advanced Sciences, VIT University, Vellore, India

GRAPHICAL ABSTRACT



Abstract *Palladium-catalyzed synthetic methodology has been developed for the synthesis of 2-aminobenzenesulfonic acids from benzothiazoles in good to excellent yields using chloramine-B in alkaline (pH 12) acetonitrile/water (1:1) at 80 °C.*

Keywords 2-Aminobenzenesulfonic acids; benzothiazoles; chloramine-B; palladium catalyst

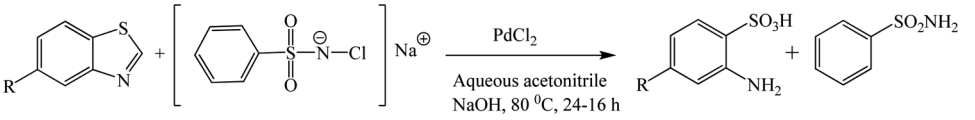
INTRODUCTION

The importance of aminobenzenesulfonic acids resides in their widespread use in the syntheses of various organic dyes[1] and heterocyclic compounds. The amide derivatives of aminobenzenesulfonic acids and certain related substitutes have significant medicinal importance as sulfa drugs. Because of the versatile properties and pharmaceutical applications of aminobenzenesulfonic acids, synthesis of these compounds using convenient and efficient methodologies is an important task.

In synthetic methodology, as the building block of organic synthesis, researchers continuously seek new reagents, better reaction conditions, and more efficient and selective methods. In this regard, a large group of compounds, sodium N-haloarenesulfonamidates (organic haloamines), are widely used in fine organic synthesis.[2–4] Sodium N-haloarenesulfonamidates, because of their versatile properties, have proved to be valuable reagents for a variety of functional group transformations.[2,3] N-Haloamines act as good oxidants and reagents both in alkaline and acidic media and have been widely used for the oxidation and synthesis of a variety

Received February 16, 2010.

Address correspondence to Rajenahally V. Jagadeesh, Division of Organic Chemistry, School of Advanced Sciences, VIT University, Vellore 632014, India. E-mail: rvjdeesh@yahoo.com



Scheme 1. Synthesis of 2-aminobenzenesulfonic acids.

of organic and biomolecules.[3,4] Chloramine-B ($C_6H_5SO_2NClNa \cdot 1.5H_2O$ or $PhSO_2NClNa$ or CAB), the N-chloro derivative of sulfonamide, is gaining importance as oxidant and reagent for the synthesis of a variety of organic molecules. Although the mechanistic aspects of many haloamine reactions have been well documented,[4–9] similar studies on chloramine-B are sparse. In view of this, there is considerable scope for the study with CAB to get better insight into the speciation of CAB reaction models and to understand its redox chemistry in solutions.

Palladium has been extensively used[4,8,10–12] as catalyst for a number of reactions. In recent times, the studies on the use of palladium as catalyst in many redox and synthetic reactions have been increasing. In continuation of our studies with palladium catalysts and the synthetic applications of 2-aminobenzenesulfonic acids, we report herein a new and efficient method for the preparation of 2-aminobenzenesulfonic acids from benzothiazole using chloramine-B and palladium chloride as the catalyst (Scheme 1).

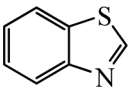
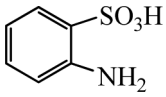
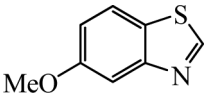
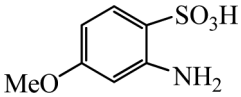
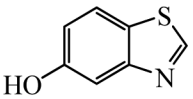
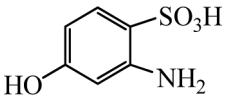
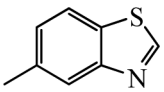
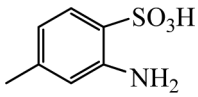
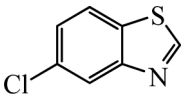
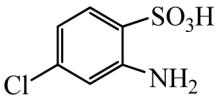
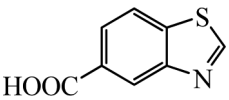
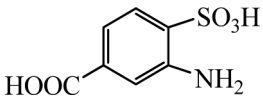
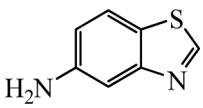
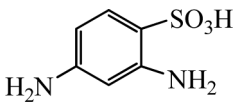
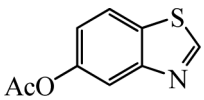
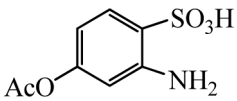
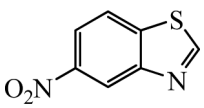
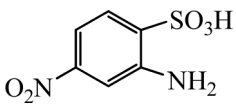
RESULTS AND DISCUSSION

Synthesis of 2-aminobenzenesulfonic acid and substituted 2-aminobenzenesulfonic acids were achieved by using a catalytic amount of palladium chloride in acetonitrile/water (1:1) at 80 °C by chloramine-B with 1:5 substrate/chloramine-B ratio in the presence of alkali. The products and the yields are summarized in Table 1. In general, substrates containing electron-donating moieties were found to be more reactive and required shorter reaction times compared to substrates containing electron-withdrawing groups. The effect of various solvents [acetonitrile, 1,2-dichloromethane, ethanol, and acetonitrile/water (1:1) mixture] was studied using benzothiazole as the model compound. The mixture of acetonitrile/water (1:1) was found to be the best solvent system, perhaps because of the high dielectric constant of water.

The reactions were found to be highly dependent upon the pH of the system. To evaluate the effect of pH, a reaction with benzothiazole was carried out under similar experimental conditions at different pH values. At neutral pH, the synthesis of 2-aminobenzenesulfonic acid from benzothiazole was found to be very slow. Reaction rates increase with increase in pH (addition of NaOH) and reaches a maximum at pH 12. This behavior of the reaction is attributed to the dissociation of chloramine-B in an aqueous medium by furnishing different oxidizing species[13–15] in which $PhSO_2NHCl$ is the predominant species. In presence of alkali, the free acid, $PhSO_2NHCl$, undergoes dissociation[16,17] to furnish the species $PhSO_2NCl^-$ as presented in Eq. (1):

$$PhSO_2NHCl + OH^- \rightleftharpoons PhSO_2NCl^- + H_2O \quad (1)$$

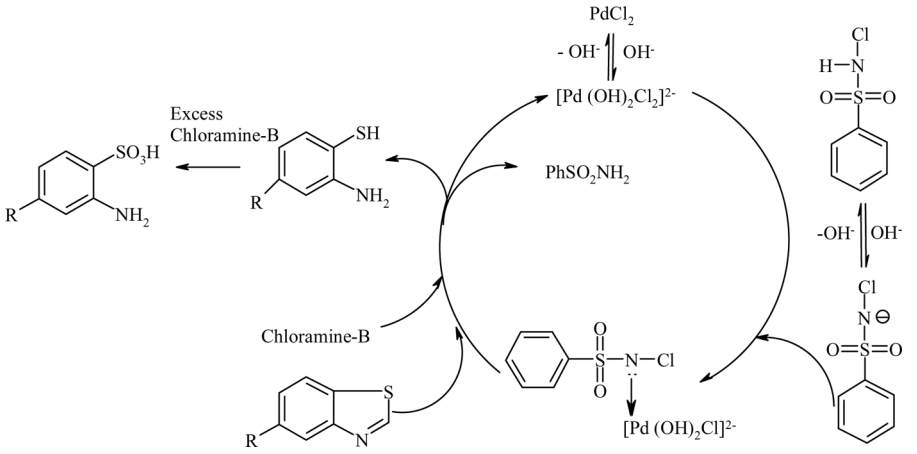
Table 1. Palladium-catalyzed synthesis of aminobenzenesulfonic acids[a]

Entry	Substrate	Product	Yield	Mp (°C)
1			85	298 (300)[b]
2			80	345 (340)
3			85	329 (328)
4			86	278 (273)
5			80	201 (197)
6			80	219 (220)
7			86	241 (239)
8			82	198 (197)
9			81	245 (243)

[a]Substrate: 1 mmol, Chloramine-B = 5 mmol, temperature = 80 °C, time = 24–26 h.
[b]Mps given in parentheses refer to authentic samples.

The species $PhSO_2NCl^-$ furnished by chloramine-B in the presence of alkali enhances the reaction, and thus the reactions proceed with increasing rates.

Palladium(II) chloride catalysis has been observed during various reactions and exists as different complexes in alkaline solutions,[18–20] and the possible Pd(II) complex species are $[Pd(OH)Cl_3]^{2-}$, $[Pd(OH)_2Cl_2]^{2-}$, $[Pd(OH)_3Cl]^{2-}$, and $[Pd(OH)_4]^{2-}$. The species $[Pd(OH)_3Cl]^{2-}$ and $[Pd(OH)_4]^{2-}$ are not commonly found as they are insoluble. Further, the rate increases with increase in $[OH^-]$, and lack of effect of $[Cl^-]$ on the rate of reaction clearly rules out $[Pd(OH)Cl_3]^{2-}$ as the reactive species. Hence, $[Pd(OH)_2Cl_2]^{2-}$ complex ion has been assumed to be the reactive species in the present study.



Scheme 2. Detailed mechanism for the synthesis of 2-aminobenzenesulfonic acids.

The synthesis of 2-aminobenzenesulfonic acid from benzothiazole proceeds with the formation of 2-aminothiophenol as the intermediate. Benzothiazole first utilizes 2 mol of chloramine-B to form 2-aminothiophenol. The formed isatin consumes another 3 mol of chloramine-B to yield the ultimate and desired compound, 2-aminobenzenesulfonic acid. The reaction is shown in Scheme 2.

Ultraviolet–visible (UV-vis) spectroscopic studies indicate that the intermediate complex forms between Pd catalyst and chloramine-B. Absorption maxima in alkaline medium appear at 350 nm for $PdCl_2$, 236 nm for chloramine-B, and 340 nm for a mixture of both. A hypsochromic shift of 10 nm from 350 nm to 340 nm of $PdCl_2$ suggests that the complexation occurs between $PdCl_2$ and chloramine-B. The detailed reactions for the synthesis of 2-aminobenzenesulfonic acids from benzothiazoles are depicted in Scheme 2.

The synthetic reactions were also performed with other N-haloamines, namely chloramine-T and bromamine-B. Reactions with bromamine-B are faster when compared to both chloramine-T and chloramine-B. This is attributable to the difference in electrophilicities of the halo cations Br^+ and Cl^+ involved in the oxidation process and is also related to the ease with which these species are generated in reactions. In these reactions, the electronegativity values of Br^+ and Cl^+ play a vital role. Bromine has an electronegativity of 2.7, while chlorine has a higher value of 3.0. As the electronegativity increases, the electropositive nature decreases, because the halo cations are the reactive species in these oxidation reactions and the electropositive nature is Br > Cl. Hence, it can be generalized that bromamines are stronger oxidants compared to chloramines. Oxidizing power of chloramine-B is more than chloramine-T. This is due the participation of $-CH_3$ group in chloramine-T, which exerts a strong inductive effect in enriching the electron density at the polar N-X (X = Cl or Br) bond, thereby reducing the electrophilicity of the X atom. A similar behavior has been reported[5] in the N-haloamine reactions.

CONCLUSION

Palladium-catalyzed synthesis of 2-aminobenzenesulfonic acids was achieved efficiently using chloramine-B in the presence of alkali. Chloramine-B/palladium chloride system was efficient for the facile conversion of benzothiazoles into 2-aminobenzenesulfonic acids in an alkaline medium in good to excellent yields. The present method developed for the synthesis of 2-aminobenzenesulfonic acids from benzothiazoles offers many advantages including good conversion, short reaction times, and the involvement of nontoxic reagents.

EXPERIMENTAL

Melting points were determined on an X-4 apparatus and are uncorrected. Infrared (IR) spectra were obtained using Shimadzu Fourier transform (FT)–IR-8900 spectrometer. Mass spectral (MS) data were obtained on a 17A Shimadzu gas chromatograph with a QP-5050A Shimadzu mass spectrometer. The mass spectrum was obtained using the electron-impact ionization technique.

Preparation of Chloramine-B

It is prepared by the action of chlorine on benzenesulfonamide in the presence of NaOH. Benzenesulfonamide (1 mol) was added gradually to 4–5 N NaOH solution (2–3 mol) at 298 K with stirring. When the solution became homogeneous, it was filtered, and the filtrate was heated to 338–343 K. Chlorine was bubbled slowly over a period of 1 h. The mass was stirred for 1 h at the same temperature, then heated to 358 K and filtered through a Schott's funnel. A yield of 99% was obtained. The purity of chloramine-B was assayed iodometrically to determine the active halogen content. Chloramine-B was confirmed by IR and MS analysis.

Synthesis of 2-Aminobenzenesulfonic Acids

Catalyst (2 mmol) was added to a stirred solution of benzothiazole (1 mmol) and chloramine-B (5 mmol) in alkaline acetonitrile/water (1:1) mixture (20 mL), and the mixture was stirred at 80 °C for 24–26 h. After completion of the reaction, the reduction product of bromamine-B, benzenesulfonamide ($PhSO_2NH_2$), was extracted with ethyl acetate, identified by thin-layer chromatography (TLC), and confirmed by MS analysis. The aqueous part of the reaction mixture was neutralized with acid, followed by solvent evaporation under reduced pressure. The residue was dissolved in dichloromethane, and the dichloromethane layer was washed twice with water and then dried over sodium sulfate. The solvent was evaporated under reduced pressure, and the residue thus obtained was purified by passing through a short silica-gel column using dichloromethane as eluent. Evaporation of the solvent yields 2-aminobenzenesulfonic acids around 85% yield. The products were identified by TLC and mp by comparison with authentic samples. Further, the compounds were confirmed by IR and MS analysis. The reaction times and yields are given in Table 1. Alternatively, after extracting out benzenesulfonamide, the aqueous layer was neutralized with acid and the 2-aminobenzenesulfonic acids are estimated as their zinc

orthanilates. The procedure for the estimation is as follows:[21] To the reaction mixture, a calculated volume of 1 mol dm^{-3} HCl was added, followed by 10 mL of pH 5.0 buffer and 10 mL of 1% zinc chloride. The precipitate was filtered, dried at 105–110 °C, and weighed, and the recovery of $(C_6H_7SO_3N)_2$ Zn was found be around 85%.

REFERENCES

1. Brewster, R. Q.; McEwen, W. E. *Organic Chemistry*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1961.
2. Kolvari, E.; Choghamarani, A. G.; Salehi, P.; Shirini, F.; Zolfigol, M. A. Application of N-halo reagents in organic synthesis. *J. Iran. Chem. Soc.* **2007**, *4*, 126–174.
3. Campbell, M. M.; Johnson, G. Chloramine-T and related N-halogeno-N-metallo reagents. *Chem. Rev.* **1978**, *78*, 65.
4. Jagadeesh, R. V.; Puttaswamy. Ru(III), Os(VIII), Pd(II), and Pt(IV) catalysed oxidation of glycyl–glycine by sodium N-chloro-p-toluenesulfonamide: Comparative mechanistic aspects and kinetic modeling. *J. Phys. Org. Chem.* **2008**, *21*, 844–858.
5. Puttaswamy; Jagadeesh, R. V. Ruthenium(III)-catalyzed mechanistic investigation of oxidation of an azo dye by sodium N-haloarenesulfonamidates in acid medium: A comparative spectrophotometric kinetic study. *Appl. Catal. A: Gen.* **2005**, *292*, 259–271.
6. Mahadevappa, D. S.; Ananda, S.; Murthy, A. S. A.; Rangappa, K. S. Oxidation of dimethylsulphoxide by sodium m-bromobenzene-sulphonamide: A kinetic and mechanistic study. *Tetrahedron* **1984**, *40*, 1673–1683.
7. Rangappa, K. S.; Ragavendra, M. P.; Mahadevappa, D. S.; Gowda, D. C. Sodium N-chlorobenzenesulfonamide as a selective oxidant for hexosamines in alkaline medium: A kinetic and mechanistic study. *J. Org. Chem.* **1998**, *63*, 531–536.
8. Vinod Kumar, C. H.; Jagadeesh, R. V.; Shivananda, K. N.; Sree Sandhya, Y.; Naga Raju, C. Catalysis and mechanistic studies of Ru(III), Os(VIII), Pd(II), and Pt(IV) metal ions on oxidative conversion of folic acid. *Ind. Eng. Chem. Res.* **2010**, *49*, 1550–1560.
9. Vinod Kumar, C. H.; Shivananda, K. N.; Jagadeesh, R. V.; Naga Raju, C. Ruthenium complex-catalyzed oxidative conversion of aliphatic amines to carboxylic acids using bromamine-T: Kinetic and mechanistic study. *J. Mol. Catal. A: Chem.*, **2009**, *311*, 23–28.
10. Shannon, S. S. Palladium-catalyzed oxidation of organic chemicals with O_2. *Science* **2005**, *309*, 1824.
11. Peterson, K. P.; Larock, R. C. Palladium-catalyzed oxidation of primary and secondary allylic and benzylic alcohols. *J. Org. Chem.* **1998**, *63*, 3185–3189.
12. Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. Palladium-catalyzed cross-coupling reactions in total synthesis. *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489.
13. Bishop, E.; Jennings, V. J. Titrimetric analysis with chloramine-T: The status of chloramine-T as a titrimetric reagent. *Talanta* **1958**, *1*, 197–199.
14. Hardy, F. F.; Johnston, J. P. The interactions of N-bromo-N-sodiobenzesulfonamide (chloramine-B) with p-nitrophenoxide ion. *J. Chem. Soc., Perkin Trans. 2* **1973**, 742–746.
15. Pryde, B. G.; Soper, F. G. The direct interchange of chlorine in the interaction of p-toluenesulfonamide and N-chloroacetalinide. *J. Chem. Soc.* **1962**, 1582.
16. Puttaswamy; Jagadeesh, R. V. Kinetics of oxidation of pantothenic acid by chloramine-T in perchloric acid and in alkaline medium catalyzed by OsO_4: A mechanistic approach. *Int. J. Chem. Kinet.* **2005**, *37*, 201–210.
17. Puttaswamy; Jagadeesh, R. V. Mechanistic studies of oxidation of thiols to disulfides by sodium N-chloro-p-toluenesulfonamide in an alkaline medium: A kinetic approach. *Ind. Eng. Chem. Res.* **2006**, *45*, 1563–1570.

18. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry,* 6th ed.; John Wiley and Sons: New York, 1999.
19. Wan, W. K.; Zaw, K.; Henry, P. M. Oxidation of olefins by palladium(II), 11: Kinetics and mechanism of the oxidation of allyl alcohol by $PdCl_{42}$ in aqueous solution. *Organometallics* **1998**, *7* (8), 1677–1683.
20. Kondarasaiah, M. H.; Ananda, S.; Puttaswamy; Made Gowda, N. M. Palladium(II)-catalyzed oxidation of primary amines by bromamine-T in alkaline medium: A kinetic and mechanistic study. *Synth. React. Inorg. Met. Org. Chem.* **2003**, *33*, 1145–1156.
21. Vogel, A. I. *Textbook of Quantitative Inorganic Analysis*, 4th ed.; ELBS-Longman: London, 1978.