European Journal of Chemistry 4 (1) (2013) 61-63

European Journal of Chemistry

Journal homepage: www.eurjchem.com

Synthesis of azoarenes by reductive dimerization of nitroarenes using ammonium bromide and magnesium

Malavalli Basavaraju Sridhara, Ramesh Suhas, and Dase Gowda Channe Gowda *

Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore-570006, Karnataka, India

**Corresponding author at: Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore-570006, Karnataka, India. Tel.: +91.0821.2419664; fax: +91.0821.2419361. E-mail address: dchannegowda@yahoo.co.in (D.C. Gowda).*

ARTICLE INFORMATION

Received: 02 January 2013
Received in revised form: 19 January 2013
Accepted: 20 January 2013
Online: 31 March 2013

KEYWORDS

Magnesium
Nitroarenes
Azocompounds
Ammonium bromide
Reductive dimerization
Catalytic transfer hydrogenation

ABSTRACT

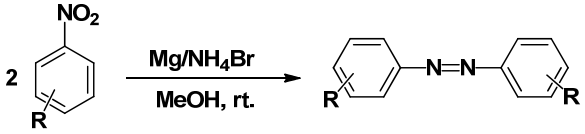
A simple and efficient protocol for the synthesis of symmetrically substituted azoarenes from nitroarenes by using ammonium bromide as hydrogen donor and magnesium powder as catalyst at room temperature in methanol media is described. Various azoarenes containing few additional substituents such as halogen, methyl, hydroxyl, methoxy, ethoxy etc. functions have been synthesized in a single step by the use of this reagent. The conversion is clean, rapid, chemo-selective and high yielding.

1. Introduction

Azoarenes are widely utilized as dyes, analytical reagents and as materials for non-linear and storage optics in laser dishes [1]. Recently, many studies have shown that azo compounds possess excellent optic memory and photoelectric properties [2]. They have long played a significant role in the development of mechanistic and synthetic organic chemistry [3]. In earlier, the preparation of azoarenes was directly obtained from nitroarenes by using Zn/NaOH [4], and $LiAlH_4$ [5]. Also, nitroarenes and aniline at high temperature in the presence of powdered alkali leads to azoarenes [6].

A variety of multi-step indirect routes are available for the synthesis of azoarenes, which include diazonium coupling, condensation of nitroarenes with azide, mild oxidation of anilines [7]. Furthermore, the preparation of azoarenes has been described in many other references [8-12]. Most of these methods have some limitations like cyclization, rearrangement and isomerization side reactions in the presence of strong acid and alkaline medium. Recently, Wada *et al*. [13] reported the newborn surface of dull metals in organic synthesis using bismuth-mediated one-step conversion of nitroarenes to azoxy and azoarenes. But this method forms a mixture of both azoxy and azoarenes.

There are many methodologies reported in the literature concerning reduction of organic compounds [14-16]. In comparison with all other reduction process, catalytic transfer hydrogenation [17,18] and metal mediated reactions [19,20] are gaining more potential advantages due to their simple workup and selectivity. The utility of magnesium [21-23] as a powerful reducing agent in organic synthesis and in the field of catalytic transfer hydrogenation for the removal of commonly used protecting groups in peptide synthesis [24] and also for various functional group transformation is reported [25,26]. In our laboratory, the substituted nitroarenes are directly converted into azoarenes by employing the systems like $HCOONH_4$/Pb [18], $HCOONHEt_3$/Pb [27], $HCOONHEt_3$/Mg [28], and CH_3COONH_4/Pb [29]. In this paper, we have developed another simple, efficient and cost-effective method for the synthesis of symmetrically substituted azoarenes from nitroarenes using ammonium bromide as hydrogen donor and magnesium powder as catalyst in methanol at room temperature and pressure is depicted in Scheme 1.



R = Cl, -OH, CH_3, OCH_3, OC_2H_5

Scheme 1

2. Experimental

2.1. Materials and methods

The ^1H NMR spectra were recorded on an AMX-400 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as internal standard. IR spectra were recorded on Shimadzu FTIR-8300 spectrometer. Elemental analysis was performed on a model Vario EL III elemental analyzer. The melting points were determined by using Thomas-Hoover melting point apparatus and are uncorrected. Thin layer chromatography was carried out on silica gel plates obtained from Whatman Inc. The substrates were either commercial products and were used as purchased or were prepared according to literature procedures. Magnesium metal powder was purchased from Himedia Pvt. Ltd., Mumbai (India) and ammonium bromide was

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
DOI:10.5155/eurjchem.4.1.61-63.732

purchased from Lobachemie Co Pvt. Ltd Mumbai (India) Ltd. All of the solvents used were analytical grade or were purified according to standard procedures.

2.2. General procedure for the synthesis of azoarenes from nitroarenes

A suspension of the nitroarenes (10 mmol) and ammonium bromide (20 mmol) in methanol (15 mL) taken in a round bottomed flask was stirred at room temperature. The reaction was initiated by the addition of magnesium power (10 mmol). The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the reaction mixture was filtered through a Celite pad and washed with methanol. The combined filtrate and washings were evaporated under reduced pressure and taken into chloroform or petroleum ether (2 x 25mL). The organic layer was washed with 50% saturated brine solution (2x15mL) and was dried over anhydrous sodium sulphate. The solvent was removed using rotary evaporator and the residue was purified either by preparative TLC or by column chromatography.

Diphenyldiazene (**1**): Color: Orange Red. M.p.: 66-68 °C (68 °C, [30]). Reaction time: 1.5 hr. Yield: 90%. IR (KBr, ν, cm^{-1}): 1620. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.48-8.12 (m, 10H, ArH). Anal. calcd. for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.37. Found C, 79.02; H, 5.52; N, 15.32%.

1,2 Di-o-tolyldiazene (**2**): Color: Yellow. M.p.: 53-55 °C (55 °C, [30]). Reaction time: 1.5 hr. Yield: 85%. IR (KBr, ν, cm^{-1}): 1600. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.32-7.90 (m, 8H, ArH), 2.31 (s, 6H, CH_3). Anal. calcd. for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32. Found C, 79.92; H, 6.69; N, 13.28%.

1,2 Di-m-tolyldiazene (**3**): Color: Yellow. M.p.: 55-57 °C (55 °C, [30]). Reaction time: 1.2 hr. Yield: 85%. IR (KBr, ν, cm^{-1}): 1592. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.29-7.87 (m, 8H, ArH), 2.33 (s, 6H, CH_3). Anal. calcd. for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32. Found C, 79.94; H, 6.67; N, 13.30%.

1,2 Di-p-tolyldiazene (**4**): Color: Yellow. M.p.: 144-146 °C (144 °C, [30]). Reaction time: 1.3 hr. Yield: 87%. IR (KBr, ν, cm^{-1}): 1598. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.32-7.90 (m, 8H, ArH), 2.33 (s, 6H, CH_3). Anal. calcd. for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32. Found C, 79.89; H, 6.63; N, 13.27%.

1,2-Bis(2-chlorophenyl)diazene (**5**): Color: Orange. M.p.: 135-138 °C (137 °C, [30]). Reaction time: 1.2 hr. Yield: 85%. IR (KBr, ν, cm^{-1}): 1625. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.45-7.92 (m, 8H, ArH). Anal. calcd. for $C_{12}H_8N_2Cl_2$: C, 57.39; H, 3.21.71; N, 11.12. Found C, 57.35; H, 3.19; N, 11.06%.

1,2-Bis(3-chlorophenyl)diazene (**6**): Color: Yellow. M.p.: 101-103 °C (101 °C, [30]). Reaction time: 1.2 hr. Yield: 90%. IR (KBr, ν, cm^{-1}): 1623. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.49-8.02 (m, 8H, ArH). Anal. calcd. for $C_{12}H_8N_2Cl_2$: C, 57.39; H, 3.21; N, 11.12. Found C, 57.36; H, 3.20; N, 11.05%.

1,2-Bis(4-chlorophenyl)diazene (**7**): Color: Red. M.p.: 185-187 °C (188 °C, [30]). Reaction time: 1.5 hr. Yield: 88%. IR (KBr, ν, cm^{-1}): 1620. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.49-7.92 (m, 8H, ArH). Anal. calcd. for $C_{12}H_8N_2Cl_2$: C, 57.39; H, 3.21; N, 11.12. Found C, 57.27 H, 3.18; N, 11.09%.

1,2-Bis(2-methoxyphenyl)diazene (**8**): Color: Red. M.p.: 130-133 °C (131 °C, [30]). Reaction time: 1.5 hr. Yield: 87%. IR (KBr, ν, cm^{-1}): 1585. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.10-7.92 (m, 8H, ArH), 3.62 (s, 6H, CH_3). Anal. calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H,5.82; N, 11.56. Found C, 69.35; H, 5.78; N, 11.48%.

1,2-Bis(3-methoxyphenyl)diazene (**9**): Color: Yellow. M.p.: 90-93 °C (91 °C, [30]). Reaction time: 1.5 hr. Yield: 90%. IR (KBr, ν, cm^{-1}): 1590. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.10-7.52 (m, 8H, ArH), 3.62 (s, 6H, CH_3). Anal. calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82; N, 11.56. Found C, 69.37; H, 5.76; N, 11.52%.

1,2-Bis(4-ethoxyphenyl)diazene (**10**): Color: Red. M.p.: 159-161 °C (160 °C, [30]). Reaction time: 1.5 hr. Yield: 88%. IR (KBr, ν, cm^{-1}): 1592. ^1H NMR (400 Mhz, $CDCl_3$, δ, ppm): 7.10-7.92 (m, 8H, ArH), 4.12 (q, 4H, CH_2), 1.38 (s, 6H, CH_3). Anal. calcd. for $C_{16}H_{18}N_2O_2$: C, 71.08; H, 6.71; N, 10.36. Found C, 70.95; H, 6.69; N, 10.28%.

4,4'-(Diazene-1,2-diyl)diphenol (**11**): Color: Dark Yellow. M.p.: 174-175 °C (173-175 °C, [30]). Reaction time: 2.0 hr. Yield: 90%. IR (KBr, ν, cm^{-1}): 1590. ^1H NMR (400 Mhz, $CDCl_3$, δ, ppm): 7.12-7.82 (m, 8H, ArH), 4.98 (s, 2H, OH). Anal. calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.70; N, 13.07. Found C, 67.22; H, 4.67; N, 12.97%.

1,2-Di(naphthalene-1-yl)diazene (**12**): Color: Orange. M.p.: 188-191 °C (190 °C, [30]). Reaction time: 1.5 hr. Yield: 90%. IR (KBr, ν, cm^{-1}): 1610. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.40-7.92 (m, 14H, ArH). Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 4.99; N, 9.92. Found C, 84.95; H, 5.02; N, 9.85%.

1,2-Di(naphthalene-2-yl)diazene (**13**): Color: Orange. M.p.: 207-209 °C (208 °C, [30]). Reaction time: 1.5 hr. Yield: 87%. IR (KBr, ν, cm^{-1}): 1610. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.40-8.42 (m, 14H, ArH). Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 4.99; N, 9.92. Found C, 84.92; H, 4.95; N, 9.85%.

1,2-Di(biphenyl-4-yl)diazene (**14**): Color: Pale Yellow. M.p.: 248-250 °C (250 °C, [30]). Reaction time: 2.0 hr. Yield: 85%. IR (KBr, ν, cm^{-1}): 1615. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.28-8.12 (m, 18H, ArH). Anal. calcd. for $C_{24}H_{18}N_2$: C, 86.19; H, 5.42; N, 8.37. Found C, 86.12; H, 5.35; N, 8.29%.

3. Results and discussion

We have synthesized a number of symmetrically substituted azoarenes directly from nitroarenes in a single step by using ammonium bromide as hydrogen donor and magnesium powder as catalyst in methanol. The functional groups such as Cl, CH_3, OCH_3, OH and OC_2H_5 are tolerated by the present system. The reduction of nitroarenes to the corresponding symmetrically substituted azoarenes was completed within 1-2 hours. The course of reaction was monitored by TLC and IR spectra. The disappearance of asymmetric and symmetric stretching bands near 1520 and 1345 cm^{-1} due to N=O of NO_2 and the appearance of a strong band between 1630-1575 cm^{-1} due to N=N stretching in the IR spectra clearly indicated the conversion of nitroarenes to azoarenes. All the azoarenes were characterized by comparison of their TLC, IR spectra, ^1H NMR spectra, elemental analysis and melting point with authentic samples. The yields of the products were virtually quantitative and analytically pure.

Control experiment was carried out by using nitroarenes with ammonium bromide but without magnesium powder does not yield the desired product. Furthermore, another attempted reduction was carried out by using nitroarenes with magnesium powder but without ammonium bromide also does not yield the desired product. Synthesis of unsymmetrically substituted azoarenes leads to the formation of mixtures, which need extensive purification and the yields were low (less than 30%).

4. Conclusion

In conclusion, we have developed a mild, convenient and cost-effective method for the synthesis of azoarenes from nitroarenes using readily available magnesium powder as catalyst in presence of ammonium bromide at room temperature. This system is superior to our own previously reported method for the synthesis of azoarenes in purity, time and yield wise

Acknowledgements

One of the authors (Malavalli Basavaraju Sridhara) gratefully acknowledges The University Grants Commission (UGC), New Delhi, India for the award of Post-doctoral fellowship.

References

[1]. Ikeda, T.; Stutsman, O. *Science* **1995**, *268*, 1873-1875.
[2]. Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658-660.
[3]. Little, R. D.; Venegas. *J. Org. Chem.* **1978**, *43*, 2921-2923.
[4]. Shine, H. J.; Chamness, J. T. *J. Org. Chem*. **1963**, *28,* 1232-1236.
[5]. Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1948**, *70*, 3738-3740.
[6]. Martynoff, M. *Compt. Rend. Acad. Sci. Paris* **1946**, *223*, 747-749.
[7]. Lang-Fugmann, S. In Houben-Weyl Methoden der Organischen Chemie, Band E/6d, Teil 1; Klamann, D., Ed.; Georg Thieme: Stuttgart, 1992; pp. 119-142.
[8]. Vogel, A. I.; Watling, A.; Watling, J. *J. Chem. Educ*. **1958**, *35*, 40-40.
[9]. Tadros, W.; Ishak, M. S.; Bassili, E. *J. Org. Chem*. **1959**, *24*, 627-629.
[10]. Moore, R. E.; Furst, A. *J. Org. Chem*. **1958**, *23*, 1504-1506.
[11]. Hutchins, R. O.; Lamson, D. W.; Rua, L.; Cynthia, M.; Bruce, M. *J. Org. Chem*. **1971**, *36*, 803-806.
[12]. Kabalka, G. W.; Varma, R. S. Comprehensive Organic Synthesis, Vol. 8; Pergamon Press: Oxford. 1991, pp. 363-380.
[13]. Wada, S.; Urano, M.; Suzuki, H. *J. Org. Chem*. **2002**, *67*, 8254-8257.
[14]. Comprehensive Organic Synthesis, Vol. 8; (Reduction) Fleming I., Eds; Pergamon Press: Oxford, 8, 1991, pp. 1-24.
[15]. Rylander, P. N. Hydrogenation Methods, Academic Press: New York. 1985, pp. 365.
[16]. Brieger, O.; Nestrick, T. *J. Chem. Rev*. **1974**, *74*, 567-580.
[17]. Johnstone, R. A. W.; Wibly, A.; Entwistle, I. D. *Chem. Rev*. **1985**, *85*, 129-170.
[18]. Gowda, S.; Gowda, D. C. *Synthesis* **2002**, *4,* 460-462.
[19]. Pitts, R. M.; Harison, M. R.; Moody, E. J. *J Chem. Soc. Perkin Trans I* **2001**, *9,* 955-977.
[20]. Banik, B. K.; Suhendra, M.; Banik, I.; Becker, F. F. *Synth. Commun*. **2000**, *30*, 3745-3754.
[21]. Youn, K. I.; Yon, H. G.; Pak, S. C. *Tetrahedron Lett*. **1986**, *27*, 2409-2410.
[22]. Proffit, A. J.; Watt, S. D.; Corey, E. J. *J. Org. Chem*. **1979**, *44*, 3972-3974.
[23]. Brettle, R.; Shiobib, M. S. *Tetrahedron Lett*. **1980**, *30*, 2915-2916.
[24]. Gowda, D. C. *Tetrahedron Lett.* **2002**, *43*, 311-313.
[25]. Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. *Indian J. Chem. Sect. B.* **2003**, *42*, 2882-2884.
[26]. Abiraj, K.; Gowda, D. C. *Synth. Commun*. **2004**, *34(4),* 599-605.
[27]. Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. *Tetrahedron Lett.* **2003**, *44*, 5835-5837.
[28]. Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. *Aust. J. Chem*. **2004**, *57*, 609-610.
[29]. Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. *Synth. Commun*. **2003**, *33*, 4221-4227.
[30]. Vogel, A. I. Text Book of Practical Organic Chemistry; Addison Wesley Longman Limited: UK, 1997, 1298.