J Incl Phenom Macrocycl Chem (2008) 62:111–115
DOI 10.1007/s10847-008-9445-1

ORIGINAL ARTICLE

Diazo reductive: a new approach to the synthesis of novel "upper rim" functionalized resorcin[4]arene Schiff-bases

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Received: 27 March 2008 / Accepted: 9 April 2008 / Published online: 29 April 2008
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Abstract The tetraaminoresorcin[4]arene was synthesized, which otherwise could not be easily synthesized by conventional method, by first introducing the azo group at the upper rim, followed by its reduction with $Na_2S_2O_4$. Tetraaminoresorcin[4]arene was then condensed with different aromatic aldehydes in ethanol at reflux temperature to obtain nine novel "upper rim" functionalized resorcin[4]arene Schiff-bases. All the nine Schiff-bases were characterized by m.p., elemental analysis, FT-IR, NMR and Mass spectral data.

Keywords Resorcin[4]arene · Azo · Upper rim functionalisation · $Na_2S_2O_4$ · Schiff-bases

Introduction

Resorcin[4]arenes (**1**) are cyclic tetramers readily formed by the acid-catalysed condensation of resorcinol with aldehydes [1]. The most stable crown conformer possesses a bowl-shaped molecular cavity formed by the four resorcinol units [1, 2]. Resorcin[4]arenes deliver a versatile molecular platform for the elaboration of more complicated host system by virtue of its conformational flexibility. This has been widely exploited as a basis for making macrocyclic host molecules in a variety of supramolecular systems, as well as being the basis for their spontaneous adhesion to hydrophilic surfaces and formation of hexameric capsules [3–6]. Their chemistry is mainly focused in (i) synthesis and application of host- guest complexes by inter molecular forces and (ii) construction of novel supramolecular assemblies, dendrimer, nano particles, nanocapsules and metal ion extraction agents [7–11]. Resorcin[4]arenes form a relatively shallow conical cavity that can be extended by suitable substitution and further functionalization. Interest in resorcin[4]arenes has grown rapidly also because of the numerous derivatization that can be created through relatively simple synthetic procedures by substitution at their upper rim, methylene bridges and –OH group at the extra annular position to alter their properties and applications.

Our focus in current the work is to be able to introduce amino functional groups at the upper rim which otherwise could not be achieved by conventional method of Nitration (HNO_3/H_2SO_4) and reduction with common reducing agents like Fe/HCl, Sn/HCl, hydrazine hydrate/raney nickel. In fact Cram et al. [12] also failed to obtain tetra nitro resorcin[4]arene by taking 2-nitro resorcinol and acetaldehyde as the starting materials.

Therefore to obtain amino group at the upper rim, we have first coupled the resorcin[4]arene with diazonium salt of p-aminobenzoic acid and subsequently breaking –N=N– group with sodium dithionite in alkaline medium to get the desired tetra amino product. The tetra amino resorcin[4]arenes was then condensed with different aromatic aldehydes to give corresponding Schiff-bases. Schiff base are versatile coordinating ligands and found to be excellent reagents for biological and industrial purposes [13, 14]. Binding properties of Schiff-bases of resocin[4]arene with various metal ions and guests is yet to be explored.

Experimental

Materials, instruments and methods

All reagents were obtained from Sigma Aldrich or BDH and used without further purification. Resorcin[4]arene was

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synthesized by earlier reported method [1, 11]. Melting points were taken in a single capillary tube using a Veego melting point apparatus (Model: VMP-DS, India) and were uncorrected. Elemental analysis was done on Perkin Elmer, Series II, 2400 elemental analyzer. IR spectra were recorded on Bruker tensor 27 Infrared spectrophotometer as KBr pellets and expressed in cm^{-1}. ^{1}HNMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker ARX 500 instrument, using tetramethylsilane as internal standard. Mass Spectra were recorded on JEOL SX 102/DA 6000 mass spectrometer using Xenon/argon (6 KV, 10 mA) as the FAB-gas.

Synthesis

Synthesis of tetra azo resorcin[4]arene (2)

p-amino benzoic acid (1.11 g, 0.0081 M) and 2 mL conc. HCl were added to 15 mL of water and the resulting solution was cooled to 0 °C. Then a solution of $NaNO_2$ (0.6 g, 0.0087 M) in 10 mL of water was added drop wise at such a rate to maintain the temperature below 5 °C. The resulting mixture was slowly added to a solution of resorcin[4]arene (1 g, 0.0018 M) and sodium hydroxide (0.8 g, 0.02 M) in 20 mL of water at 0 °C–5 °C. The reaction mixture was stirred for 2–4 h at the same temperature, and the product was obtained by salting out with sodium chloride. The solid obtained was dissolved in a solution of $NaHCO_3$ and reprecipitated by adding conc. HCl. The mixture was stirred overnight at room temperature, filtered as a red solid and washed with water followed by methanol and dried overnight at 80 °C to yield 72% as a red solid, mp > 280 °C(decompose). ^{1}HNMR (DMSO-d_6) δ 1.65 (d, 12H, CH_3), 4.67 (q, 4H, bridge CH), 9.78 (s, 12H, OH & COOH), 7.25–7.89 (m, 20H, ArH). IR (KBr) ν/cm^{-1} 3167 (OH), 1698 (C=O), 1517 (N=N), 853. MS-FAB:$(M + H)^+$1137. *Elemental analysis* for $C_{60}H_{48}O_{16}N_8$ cacld: C, 63.28; H, 4.22; N, 9.86. Found: C, 63.32; H, 4.21; N, 9.79.

Synthesis for tetra amino resorcin[4]arene (3)

The azo compound (**2**) (0.5 g) was dissolved in a mixture of NaOH (0.5 g) and 25 mL water. The resulting dark red solution was reduced by stirring with $Na_2S_2O_4$ (2.5 g, 14.4 m mole) for 1 h at 90 °C. The reaction mixture was cooled to room temperature and 20 mL conc. HCl was added. The resulting precipitate were filtered and washed with dil. HCl and methanol. The product was dried at reduced pressure to give 240 mg of **3**. The solid was unstable and used in the following reaction without further purification.

Synthesis of resorcin[4]arene Schiff-bases (4)

A mixture of (**3**) (1 g, 1.655 m mol) and different aromatic aldehydes (8.275 m mol) in 50 mL of ethanol was refluxed for 3–5 h at the boiling temperature. The precipitates obtained were filtered, washed with hot water and recrystallized in ethanol. The resulting solid was dried under vacuum to give yields of 60%–70% for different aldehydes **4a-i.**

Benzaldehyde based resorcin[4]arenes Schiff base (**4a**): Yield 66%; M.P. 135 °C; color: yellow. ^{1}HNMR ($CDCl_3$): δ = 1.65(d, 12H CH_3), 4.63(q, 4H bridge CH), 9.49(s, 8H –OH), 8.82(s, 4H –N=CH), 7.3–7.9(s, 24H ArH). IR (KBr): ν = 3,426 cm^{-1} (–OH), 1,634 cm^{-1} (–N=CH). MS-FAB: $(M + H)^+$958. Anal.calcd.for $C_{60}H_{52}N_4O_8$: C, 75.30; H, 5.48; N, 5.85. Found: C, 74.98; H, 5.44; N, 5.60.

Salisaldehyde based resorcin[4]arenes Schiff base (**4b**): Yield 68%; M.P. 170 °C; color: yellow. ^{1}HNMR ($CDCl_3$): δ = 1.65(d, 12H CH_3), 4.63(q, 4H bridge CH), 9.50(s, 12H –OH), 8.82(s, 4H –N=CH) 7.3–7.9(s, 20H ArH). IR (KBr): ν = 3,403 cm^{-1} (–OH), 1,604 cm^{-1} (–N=CH). MS-FAB: $(M + H)^+$1022. Anal.calcd.for $C_{60}H_{52}N_4O_{12}$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.49; H, 5.10; N, 5.55.

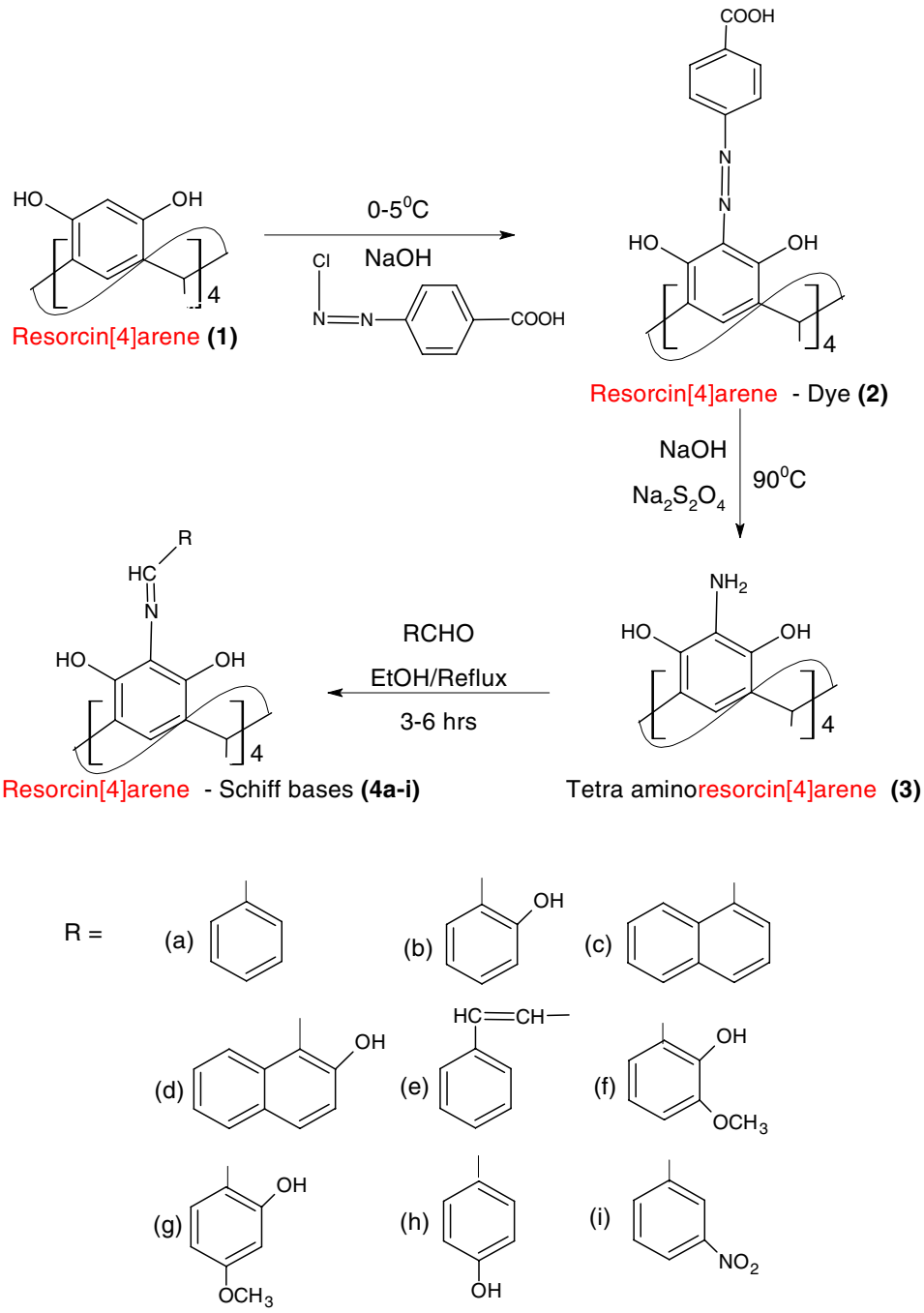
Naphthaldehyde based resorcin[4]arenes Schiff base (**4c**): Yield 70%; M.P. 145 °C; color: yellow. ^{1}HNMR ($CDCl_3$): δ = 1.64(d, 12H CH_3), 4.64(q, 4H bridge CH), 9.58 (s, 8H –OH), 8.88(s, 4H –N=CH) 7.3–7.9(s, 32H ArH). IR (KBr): ν = 3,346 cm^{-1} (–OH), 1,614 cm^{-1} (–N=CH). MS-FAB: $(M + H)^+$1158. Anal.calcd.for $C_{76}H_{60}N_4O_8$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.77; H, 5.10; N, 4.72.

2-hydroxy naphthaldehyde based resorcin[4]arenes Schiff base (**4d**): Yield 64%; M.P. 175 °C (decomp.); color: brown. ^{1}HNMR ($CDCl_3$): δ = 1.64(d, 12H CH_3), 4.62(q, 4H bridge CH), 9.50(s, 12H –OH), 8.82(s, 4H –N=CH) 7.3–7.9(s, 28H ArH). IR (KBr): ν = 3,473 cm^{-1} (–OH), 1,610 cm^{-1} (–N=CH). MS-FAB:$(M + H)^+$1222. Anal.calcd.for $C_{76}H_{60}N_4O_{12}$ C, 74.74; H, 4.95; N, 4.59. Found: C, 74.98; H, 4.94; N, 4.60.

Cinnamaldehyde based resorcin[4]arenes Schiff base (**4e**): Yield 62%; M.P. 160 °C; color: creamish. ^{1}HNMR ($CDCl_3$): δ = 1.65(d, 12H CH_3), 4.63(q, 4H bridge CH), 4.6(d, 8H –CH=CH–), 9.61(s, 8H –OH),8.89(s, 4H –N=CH), 7.3–7.9(s, 24H ArH). IR (KBr): ν = 3,463 cm^{-1} (–OH), 1,617 cm^{-1} (–N=CH), 931(CH=CH). MS-FAB:$(M + H)^+$1062. Anal.calcd.for $C_{68}H_{60}N_4O_8$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.90; H, 5.69; N, 5.18.

o-vanillin based resorcin[4]arenes Schiff base (**4f**): Yield 62%; M.P. 150 °C; color: light brown. ^{1}H NMR ($CDCl_3$): δ = 1.65(d, 12H CH_3), 3.72(s, 12H OCH_3), 4.63(q, 4H bridge CH), 9.60(s, 12 H –OH), 8.87(s, 4H –N=CH) 7.3–7.9(s, 16H ArH). IR (KBr): ν = 3,427 cm^{-1} (–OH), 1,623 cm^{-1} (–N=CH). MS-FAB:$(M + H)^+$1142. Anal.calcd.for $C_{64}H_{60}N_4O_{16}$: C, 67.36; H, 5.26; N, 4.91. Found: C, 67.42; H, 5.50; N, 4.92.

Scheme 1 Schematic route for synthesis of resorcin[4]arene Schiff-bases



Vanillin based resorcin[4]arenes Schiff base (**4g**): Yield 60%; M.P. 125 °C; color: yellow. ^{1}HNMR ($CDCl_3$): $\delta = 1.65$(d, 12H CH_3), 3.70(s, 12H OCH_3), 4.65(q, 4H bridge CH), 9.71(s, 12H –OH), 8.82(s, 4H –N=CH), 7.4–7.9(s, 16H ArH). IR (KBr): $\nu = 3{,}423$ cm^{-1} (–OH), 1,617 cm^{-1} (–N=CH). MS-FAB:$(M + H)^+$1142. Anal. calcd. for $C_{64}H_{60}N_4O_{16}$: C, 67.36; H, 5.26; N, 4.91. Found: C, 67.41; H, 5.50; N, 4.90.

p-hydroxy benzaldehyde based resorcin[4]arenes Schiff base (**4h**): Yield 66%; M.P. 127 °C; color: yellow. ^{1}HNMR ($CDCl_3$): $\delta = 1.64$(d, 12H CH_3), 4.64(q, 4H bridge CH), 9.68(s, 12H –OH), 8.89(s, 4H –N=CH), 7.3–7.9(s, 20H ArH). IR (KBr): $\nu = 3{,}363$ cm^{-1} (–OH), 1,610 cm^{-1} (–N=CH). MS-FAB:$(M + H)^+$1022. Anal.calcd.for $C_{60}H_{52}N_4O_{12}$: C, 70.58; H, 5.14; N, 5.49. Found: C, 70.39; H, 5.19; N, 5.45.

m-nitro benzaldehyde based resorcin[4]arenes Schiff base (**4i**): Yield 64%; M.P.160 °C; color: creamish. ^{1}HNMR ($CDCl_3$): $\delta = 1.63$(d, 12H CH_3), 4.64 (q, 4H bridge CH), 9.63(s, 8H –OH), 8.89(s, 4H –N=CH), 7.3–7.9(s, 20H ArH). IR (KBr): $\nu = 3{,}222$ cm^{-1} (–OH), 1,606 cm^{-1} (–N=CH),

1508 (N–O). MS-FAB:$(M + H)^+$1138. Anal.calcd.for $C_{60}H_{48}N_8O_{16}$: C, 63.38; H, 4.25; N, 9.85. Found: C, 62.29; H, 4.15; N, 9.70.

Results and discussion

In this article we report a new method for the derivatization of the resorcin[4]arenes at the upper rim by reaction with diazonium salts leading to the corresponding tetra azo compound in high yields which on reduction with $Na_2S_2O_4$. gives amino groups at all the four positions of resorcin[4]arenes Tetra amino substituted resorcin[4]arene, which is very useful intermediate, suitable for the preparation of many other derivatives or aminoresorcin[4]arenes based receptors, should usually be synthesized in two steps (i) nitration of the upper rim and (ii) reduction of corresponding nitro compound. During our attempts for nitration of resorcin[4]arenes we found that the reaction conditions normally used in 'classical' chemistry did not work in this case. To afford the introduction of amino groups at the upper rim of resorcin[4]arenes we carried out a diazo coupling reaction between resorcin[4]arenes (**1**) and diazonium salt to yield the corresponding tetra azo compound. The reaction was carried out using different diazonium salts of aniline, p-nitro aniline and p-amino benzoic acid, However quantitative yields were obtained with the diazonium salt of p-amino benzoic acid because of ease in isolation. The addition of the diazonium salt to a solution of (**1**) led to an immediate colour change (yellow to red) indicating the formation of an azo compound. Stirring the reaction at room temperature gave colored precipitates which were recrystallised using alcohol. The structure of azo compound was confirmed by ^{1}H NMR analysis, multiplet at δ 7.76–7.89 ppm due to the p-substituted phenyl rings, singlet at δ 9.87 (–OH & COOH group) and doublet at δ 1.65 ppm for CH_3 and quartet at d 4.67 ppm for CH. The IR spectra gave C=O stretching at 1,698 cm^{-1} and hydrogen bonded –OH at 3,167 cm^{-1}.

For reduction of the azo group we tried several different methods described in the literature [15, 16].The most efficient reduction of the azo compound (**2**) was achieved using $Na_2S_2O_4$ and NaOH in an aqueous solution [17, 18]. Stirring the reaction mixture at elevated temp. (90 °C) gave the expected product as a pale yellow powder in 90% yield. The compound (**3**) was not stable in air for long therefore the reaction with different aromatic aldehydes (benzaldehyde, salisaldehyde, naphthaldehyde, 2-hydroxy naphthaldehyde, cinnamaldehyde, *o*-vanillin, vanillin, *p*-hydroxy benzaldehyde, *m*-nitro benzaldehyde) was carried out quickly in alcohol to yield corresponding Schiff-bases (**4a–i**), which were duly characterized. The synthetic reaction sequence is given in Scheme 1.

^{1}H-NMR spectra of **4a–i** revealed a singlet for azo methine (–N=CH) group at δ 8.8–8.9 ppm, a doublet at 1.65 ppm for ($–CH_3$), a quartet at d 4.62–4.65 ppm for (–CH), a multiplet from 7.3 ppm to 7.9 ppm for aromatic protons (ArH), for (–OH) a singlet at δ 9.5–9.7 ppm. Compound **4f** and **4g** a singlet at δ 3.7 ppm for ($–OCH_3$), Compound **4e** a doublet at δ 4.6 ppm for (–CH=CH–). In the IR spectra, there is the typical absorption at 1,604–1,634 cm^{-1} for (–N=CH) and for (–OH) at 3,400–3,200 cm^{-1}.

Conclusion

A new approach was developed to synthesize the tetra amino resorcin[4]arene. This amino derivative can serve as a key intermediate for further functionalization to obtain resorcin[4]arene with specific receptor properties. Nine new resorcin[4]arene Schiff-bases were synthesized and characterized. Binding properties of Schiff-bases of resorcin[4]arenes with various metal ions and different guests is being explored.

Acknowledgements The authors gratefully acknowledge the financial assistance provided by Council of Scientific and Industrial Research (CSIR), New Delhi to carry out this work. The authors acknowledge CDRI (Lucknow), SAIF (IIT, Mumbai), IISC (Bangalore) for providing instrumental facilities and authors also acknowledge INFLIBNET, Ahmedabad for e-journals.

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