

Facile one pot synthesis of dioxazadibenzocyclodecene-6-one, 6-thione and other homologues

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Abstract

Previously unknown dioxazadibenzocyclodecene-6-one, -6-thione and other homologues were prepared *via* the intermediacy of a 1,9-dianion generated and used *in situ* from *N*-(2-hydroxymethylphenyl)salicylideneimine followed by treatment with a variety of dielectrophiles in a simple one-pot procedure. The products were characterized by satisfactory elemental analyses and spectral (IR, ¹H, ¹³C NMR and Mass) studies.

Keywords: Salicylaldehyde, *o*-aminobenzyl alcohol, *N*-(2-hydroxymethylphenyl)-salicylideneimine, dioxazadibenzocyclodecene-6-one

Introduction

Heterocyclic compounds hold a special place among pharmaceutically important natural and synthetic materials. Heterocyclic derivatives such as morphine alkaloids, β -lactam antibiotics and benzodiazepines are just a few familiar examples from various pharmaceuticals featuring a heterocyclic component.¹ The benzodiazepine nucleus is a well-studied traditional pharmacophoric scaffold that has emerged as a core structural unit of various sedative-hypnotic, muscle relaxant, anxiolytic, antihistaminic and anticonvulsant agents. A number of pharmaceutically important 1,4-benzodiazepin-5-ones have been reported;²⁻⁶ among them are the antibiotic Neothramicin, the antidepressant Flumazenil, and the antistaminic Clobenzepam. Imines have been relatively under utilized (yet easily prepared⁷) functional groups in the synthesis of heterocycles. Recently certain derivatives of imines have been employed in cycloaddition chemistry,⁸ and addition reactions to the imine moiety have been reported⁹ (primarily *via* activation with Lewis acids) opening new opportunities for the construction of azaheterocyclic compounds. Medium size polyheterocyclic rings containing N and O atoms are rare in the literature. Benzodiazepines,¹⁰ dibenzthiazocine¹¹ and dibenzoxazocine have been

synthesized. Monocyclic medium-ring nitrogen heterocycles are an extremely important class of compounds, which occur in a range of natural and unnatural products.¹² Medium sized rings are generally the most difficult to prepare using conventional cyclization methods.¹³

To the best of our knowledge there are no reports of the synthesis of ten-to-fifteen membered heterocycles shown in Scheme 1. This fact led us to carry out studies to design the synthesis of this scaffold. We describe here a cyclization reaction of dianions leading to previously unknown heterocycles. Strategies involving dianion reactions¹⁴⁻¹⁶ have become powerful and versatile tools in organic synthesis and have developed as a powerful method for preparing various types of carbocyclic and heterocyclic compounds *via* carbon-carbon and carbon-heteroatom bond forming processes. In our continuing studies on the synthesis of new heterocyclic ring systems¹⁷⁻¹⁹ using efficient intermolecular cyclization reactions *via* dianion intermediates we herein describe the preparation of novel dioxazadibenzocyclodecene-6-one, 6-thione and other homologues in good yields.

Results and Discussion

The reaction of equimolar amounts of salicylaldehyde and *o*-aminobenzyl alcohol in ethanol under reflux for 30 min afforded *N*-(2-hydroxymethylphenyl)-salicylideneimine,²⁰ **1** (Scheme 1). The structure of compound **1** was established from its spectral and analytical data. The IR spectrum showed peaks at 3400 cm⁻¹ for the hydroxyl group and at 2908 and 1618 cm⁻¹ for aromatic C-H and C=N groups, respectively. The ¹H NMR spectrum exhibited a singlet at 13.05 ppm for the phenolic-OH and a singlet at 7.12 ppm for the benzylic-OH, which were D₂O exchangeable. The downfield signal for the phenolic-OH group suggests intramolecular hydrogen bonding between -OH and the azomethine nitrogen. The azomethine proton of the CH=N group resonated at 8.61 ppm as a sharp singlet. Finally there was a multiplet in the range 6.93–7.53 ppm for aromatic protons and a sharp singlet at 4.87 ppm for benzylic CH₂ protons.

In order to assess the stability of *Z* and *E* forms of Schiff base **1**, quantum chemical investigations were carried out with the aid of the Density Functional Theory (DFT) method. The optimized geometries of *Z* and *E* forms of **1** (Figure 1) were obtained by the B3LYP functional, which combines Becke's three-parameter exchange functional²¹ and the no local correlation functional of Lee, Yang and Parr,²² together with the split-valence 6-31G basis set.²³ All the calculations were performed with Gaussian03 program.²⁴ It was found that *E*-form was more stable than *Z*-form by 2.9 kcal/mol. The hydrogen bond length in the *Z* form was 1.76 Å whereas for the *E* form it was 1.81 Å.

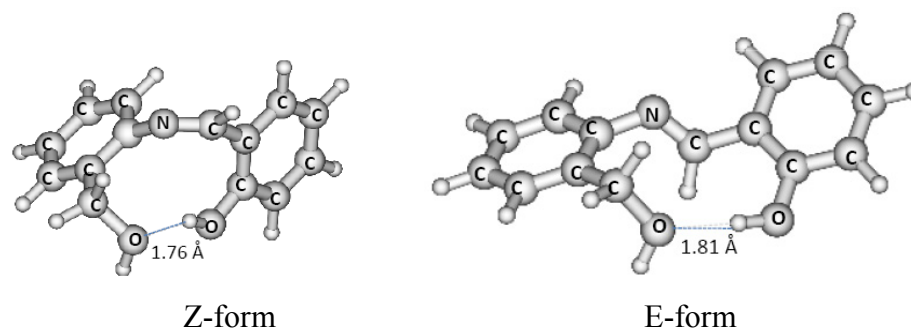
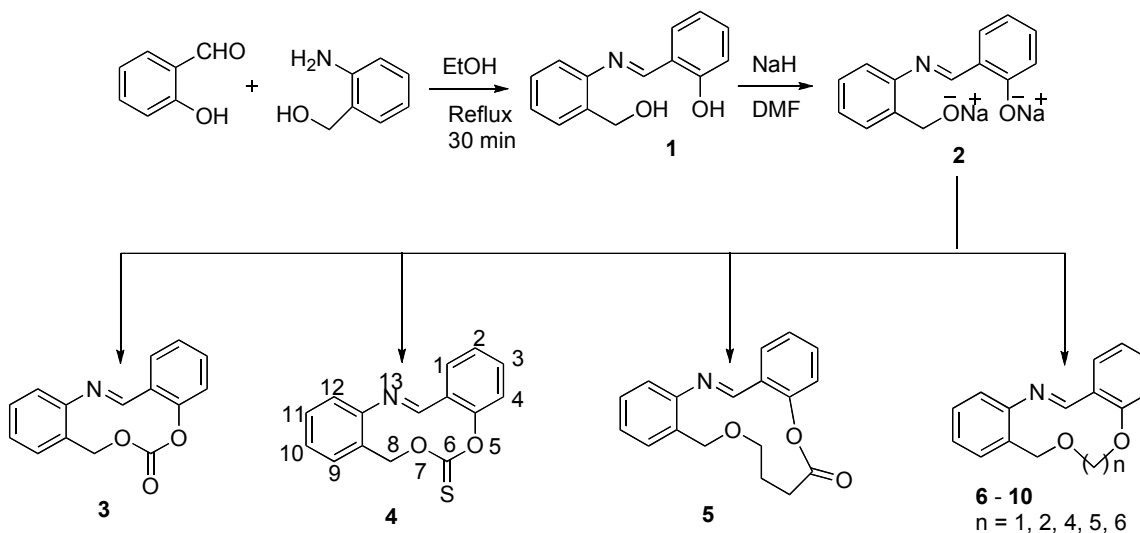


Figure 1. The optimized geometries of *Z* and *E* forms of Schiff base **1**.

Our synthesis involved the initial formation of dianion (**2**) from sequential deprotonation of the phenolic and benzylic OH groups of ligand (**1**) using sodium hydride in dry DMF. The 1,9-dianion thus generated was reacted with a variety of dielectrophiles such as ethyl chloroformate, carbon disulfide,²⁵ 4-chlorobutyl chloride and dibromoalkanes leading to the formation of compounds **3-10** (Scheme 1). The beauty of the reaction procedure resides in the *in situ* formation of a remote dianion and further cyclization so that the multi-step reaction sequence occurs in one pot. TLC analyses of all compounds confirmed their purity.



Scheme 1. Dioxazadibenzocyclodecene-6-one, -6-thione and other homologues.

The disappearance of absorption band and signals corresponding to -OH groups in both IR and ¹H NMR spectra and the appearance of new band in the region 1250-1275 cm⁻¹ is attributed to the formation of C-O-C bond.^{26,27} A comparison of the IR spectrum of the Schiff base²⁰ with those of heterocycles shows that the band in the region 1618 cm⁻¹ due to ν(C=N) is observed in all the compounds almost at the same position indicating that the C=N group is an integral part of the system. The stretching frequency for C=O and C=S groups appeared at 1755 and

1278 cm^{-1} , respectively. The ^1H NMR spectra of the compounds showed disappearance of the two -OH signals as singlets at 13.05 and 7.12 ppm suggesting deprotonation and formation of C-O-C bonds. Methylene protons attached to phenoxy oxygen in compound **7** resonated as a triplet in the region 4.66-3.89 ppm, and methylene protons attached to benzyloxy oxygen resonated as a triplet in the region 4.23-2.59 ppm, while methylene protons attached to methylene carbon resonated as a multiplet in the region 1.80-1.67 ppm as well as 1.61-1.25 ppm, respectively. In the ^{13}C NMR spectra the signal at 162.74 ppm is due to the azomethine carbon and signals in the region 116.86-160.62 ppm are due to aromatic carbons, signal in the region 60-66 ppm is due to benzylic carbon, signals at 170 and 193 ppm are due to carbonyl and thiocarbonyl carbons, respectively. Finally the new peaks of methylene carbons attached to oxygen as well as carbon are visible in their expected regions. Mass spectrometric data of the compounds established their monomeric nature.

Experimental Section

General Procedures. Chemicals were obtained from Sigma-Aldrich, Merck, Fluka and Lancaster, and were used as such without further purification. All solvents (AR or extra pure grade) used for spectroscopic and other physical studies were further purified by literature methods.²⁸ All operations were performed under a nitrogen atmosphere using standard glassware. Melting points were determined using a calibrated thermometer in a Buchi B-540 Melting Point apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on JASCO FT/IR-5300 spectrophotometer. NMR (^1H and ^{13}C) spectra were recorded on a JEOL AL 300 instrument. All chemical shifts are reported in parts per million relative to TMS as an internal standard in CDCl_3 . Mass spectra were recorded at 70 eV ionizing voltage on a JEOL SX-102 (FAB). Elemental analyses were performed by Central Drug Research Institute, Lucknow.

Synthesis of N-(2-hydroxymethylphenyl)salicylideneimine²⁰(1). To a stirred solution of *o*-aminobenzyl alcohol (5.66 g, 46 mmol) in absolute ethanol (50 mL) was added dropwise an ethanolic (50 mL) solution of salicylaldehyde (4.82 mL, 46 mmol) and the mixture refluxed for 30 min to give a yellowish brown solution. The excess solvent was removed under vacuum to leave a yellow solid, which was recrystallised to give **1** (6.265 g, 60%), mp 121 °C; ^1H NMR (300 MHz, CDCl_3) δ 4.87 (s, 2H, CH_2), 6.93-7.53 (m, 8H, ArH, and s, 1H, CH_2OH), 8.61 (s, 1H, $\text{CH}=\text{N}$), 13.05 (s, 1H, OH); ^{13}C NMR (75 MHz, CDCl_3) δ 61.40, 116.86, 117.56, 118.57, 119.36, 126.65, 127.20, 127.88, 128.40, 131.96, 132.99, 134.03, 146.19, 160.62, 162.74; IR (KBr) 3400, 2908, 1618 cm^{-1} ; MS (m/z): 227; Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2$: C, 73.99; H, 5.76; N, 6.16%. Found: C, 73.75; H, 5.69; N, 5.97%.

Synthesis of 5,7-dioxa-13-azadibenzocyclodecene-6-one (3). NaH (96 mg, 4 mmol) was stirred with DMF (3 mL) in an ice bath under N_2 atmosphere for 15 min, then *N*-(2-

hydroxymethylphenyl)salicylideneimine (454 mg, 2 mmol) dissolved in DMF (10 mL) was added slowly. Stirring was continued for 2 h. The ice bath was removed and the mixture was allowed to attain room temperature then ethyl chloroformate (217 mg, 2 mmol) in DMF (1 mL) was added. Stirring was continued for a further 2 h. Completion of reaction was confirmed by TLC. The solution was poured onto crushed ice and the product formed was extracted with dichloromethane. The extract was washed with water and brine and dried over MgSO₄. The drying agent was filtered off and the filtrate evaporated to leave a crude product, which was purified by column chromatography on silica gel (hexane/ethyl acetate 8:1) to give **3** (359 mg, 71%), mp 160 °C; ¹H NMR (300 MHz, CDCl₃) δ 4.87 (s, 2H, CH₂), 6.96-7.51 (m, 8H, ArH), 8.61 (s, 1H, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ 61.40, 116.86, 117.56, 118.57, 119.36, 126.65, 127.20, 127.88, 128.40, 131.96, 132.99, 134.03, 146.19, 160.62, 162.74, 170.80; IR (KBr) 1618, 1755 cm⁻¹. MS (*m/z*): 253; Anal. Calcd for C₁₅H₁₁NO₃: C, 71.14; H, 4.37; N, 5.53% Found: C, 71.35; H, 4.45; N, 5.38%

Synthesis of 5,7-dioxa-13-azadibenzocyclodecene-6-thione (4). Following the procedure described above, 454 mg (2 mmol) of *N*-(2-hydroxymethylphenyl)-salicylideneimine, 96 mg (4 mmol) of sodium hydride and 152 mg (2 mmol) of carbon disulfide afforded **4** (371 mg, 69%), mp 140 °C; ¹H NMR (300 MHz, CDCl₃) δ 4.87 (s, 2H, CH₂), 6.96-7.51 (m, 8H, ArH), 8.61 (s, 1H, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ 60.84, 116.28, 116.99, 118.18, 126.07, 127.32, 127.60, 128.10, 131.37, 132.41, 136.20, 145.60, 160.03, 162.16, 193.18; IR (KBr) 1618, 1278 cm⁻¹. MS (*m/z*): 269; Anal. Calcd for C₁₅H₁₁NO₂S: C, 66.89; H, 4.11; N, 5.20% Found: C, 66.68; H, 4.24; N, 5.36%

Synthesis of 5,10-dioxa-16-azadibenzocyclotridecene-6-one (5). Following the procedure described above for the preparation of **3**, 454 mg (2 mmol) of *N*-(2-hydroxymethylphenyl)salicylideneimine, 96 mg (4 mmol) of sodium hydride and 282 mg (2 mmol) of 4-chlorobutyl chloride afforded **5** (442 mg, 75%), mp 108 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.00 (t, *J*=6.6 Hz, 2H, CH₂), 2.44 (m, 2H, CH₂), 3.47 (t, *J*=6.0 Hz, 2H, CH₂), 5.19 (s, 2H, CH₂), 6.86-7.38 (m, 8H, ArH), 8.53 (s, 1H, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ 26.33, 29.72, 45.68, 61.40, 116.86, 117.56, 118.57, 119.36, 126.65, 127.20, 127.88, 128.40, 131.96, 132.99, 134.03, 146.19, 160.62, 162.74, 171.82; IR (KBr) 1620, 1255, 1733 cm⁻¹. MS (*m/z*): 295; Anal. Calcd for C₁₈H₁₇NO₃: C, 73.21; H, 5.80; N, 4.74% Found: C, 73.08; H, 5.67; N, 4.85%

Synthesis of 5,7-dioxa-13-azadibenzocyclodecene (6). Following the procedure described above for the preparation of **3**, 454 mg (2 mmol) of *N*-(2-hydroxymethylphenyl)salicylideneimine, 96 mg (4 mmol) of sodium hydride and 348 mg (2 mmol) of dibromomethane afforded **6** (334 mg, 70%), mp 88 °C; ¹H NMR (300 MHz, CDCl₃) δ 4.66 (s, 2H, OCH₂), 4.85 (s, 2H, OCH₂Ar), 6.70-7.52 (m, 8H, ArH), 8.60 (s, 1H, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ 63.14, 76.23, 115.08, 117.24, 118.30, 123.92, 128.28, 131.46, 132.40, 144.83, 162.05; IR (KBr) 1618, 1263 cm⁻¹. MS (*m/z*): 239; Anal. Calcd for C₁₅H₁₃NO₂: C, 75.30; H, 5.47; N, 5.85% Found: C, 75.49; H, 5.38; N, 5.67%

Synthesis of 5,8-dioxa-14-azadibenzocycloundecene (7). Following the procedure described above for the preparation of **3**, 454 mg (2 mmol) of *N*-(2-hydroxymethylphenyl)salicylideneimine, 96 mg (4 mmol) of sodium hydride and 376 mg (2 mmol) of 1,2-dibromoethane afforded **7** (364 mg, 72%), mp 85 °C; ¹H NMR (300 MHz, CDCl₃) δ 4.20 (t, *J*=6.9 Hz, 2H, OCH₂), 4.64 (t, *J*=7.3 Hz, 2H, OCH₂), 4.84 (s, 2H, OCH₂Ar), 6.67-7.51 (m, 8H, ArH), 8.59 (s, 1H, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ 61.87, 64.36, 67.45, 116.06, 118.21, 124.89, 129.34, 145.95, 159.54, 162.57; IR (KBr) 1616, 1263 cm⁻¹. MS (*m/z*): 253; Anal. Calcd for C₁₆H₁₅NO₂: C, 75.87; H, 5.96; N, 5.53% Found: C, 75.94; H, 5.76; N, 5.34%

Synthesis of 5,10-dioxa-16-azadibenzocyclotridecene (8). Following the procedure described above for the preparation of **3**, 454 mg (2 mmol) of *N*-(2-hydroxymethylphenyl)salicylideneimine, 96 mg (4 mmol) of sodium hydride and 432 mg (2 mmol) of 1,4-dibromobutane afforded **8** (387 mg, 69%), mp 72 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.46 (m, 2H, CH₂), 1.80 (m, 2H, CH₂), 3.34 (t, *J*=7.5 Hz, 2H, OCH₂), 4.26 (t, *J*=7.5 Hz, 2H, OCH₂), 4.84 (s, 2H, OCH₂Ar), 7.65-8.37 (m, 8H, ArH), 8.59 (s, 1H, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ 29.69, 62.96, 63.14, 67.48, 115.08, 117.24, 118.30, 123.92, 128.28, 131.46, 132.40, 144.83, 162.05; IR (KBr) 1618, 1261 cm⁻¹. MS (*m/z*): 281; Anal. Calcd for C₁₈H₁₉NO₂: C, 76.84; H, 6.80; N, 4.97% Found: C, 76.63; H, 6.57; N, 4.85%

Synthesis of 5,11-dioxa-17-azadibenzocyclotetradecene (9). Following the procedure described above for the preparation of **3**, 454 mg (2 mmol) of *N*-(2-hydroxymethylphenyl)salicylideneimine, 96 mg (4 mmol) of sodium hydride and 460 mg (2 mmol) of 1,5-dibromopentane afforded **9** (354 mg, 60%), mp 83 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.61 (m, 2H, CH₂), 1.67 (m, 2H, CH₂), 1.83 (m, 2H, CH₂), 2.59 (t, *J*=6.1 Hz, 2H, OCH₂), 4.02 (t, *J*=5.7 Hz, 2H, OCH₂), 4.75 (s, 2H, OCH₂Ar), 6.90-8.05 (m, 8H, ArH), 9.07 (s, 1H, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ 24.83, 38.14, 39.08, 63.14, 68.88, 69.00, 115.08, 117.24, 118.30, 123.92, 128.28, 131.46, 132.40, 144.83, 162.05. IR (KBr) 1619, 1250 cm⁻¹. MS (*m/z*): 295; Anal. Calcd for C₁₉H₂₁NO₂: C, 77.26; H, 7.16; N, 4.74% Found: C, 77.45; H, 7.38; N, 4.59%

Synthesis of 5,12-dioxa-18-azadibenzocyclopentadecene (10). Following the procedure described above for the preparation of **3**, 454 mg (2 mmol) of *N*-(2-hydroxymethylphenyl)salicylideneimine, 96 mg (4 mmol) of sodium hydride and 488 mg (2 mmol) of 1,6-dibromohexane afforded **10** (401 mg, 65%), mp 80 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.25 (m, 2H, CH₂), 1.35 (m, 2H, CH₂), 1.73 (m, 2H, CH₂), 1.85 (m, 2H, CH₂), 3.41 (t, *J*=6.6 Hz, 2H, OCH₂), 3.89 (t, *J*=7.2 Hz, 2H, OCH₂), 5.31 (s, 2H, OCH₂Ar), 6.78-7.51 (m, 8H, ArH), 8.62 (s, 1H, CH=N); ¹³C NMR (75 MHz, CDCl₃) δ 26.43, 26.66, 34.64, 66.27, 66.98, 67.66, 113.25, 116.83, 121.93, 123.12, 123.54, 128.16, 128.44, 134.54, 152.56, 162.05; IR (KBr): 1619, 1258 cm⁻¹. MS (*m/z*): 309; Anal. Calcd for C₂₀H₂₃NO₂: C, 77.64; H, 7.49; N, 4.52%; Found: C, 77.45; H, 7.28; N, 4.24%

Acknowledgements

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