Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2013, 2 (3): 433-437

(International Peer Reviewed Journal)

Synthesis of novel C_2-symmetric salen molecules

Ghanasham B. Sathe[1*], Vikas V. Vaidya[2], Ravindra G. Deshmukh[3], Maharudra B. Kekare[4], Vikas S. Kulkarni[5] , Atul C. Chaskar[6]

1. Dapoli Urban Bank Senior Science College, Dapoli, **INDIA**
2. Ruia College, Mumbai, **INDIA**
3. Konkan Dyanpeeth College, Karjat, **INDIA**
4. Patkar College, Mumbai, **INDIA**
5. Institute of Chemical Technology (ICT), Mumbai, **INDIA**
6. Sanghavi College of Engineering, Nashik, **INDIA**

Email: gbsathe47@gmail.com

Received on 24th April and finalized on 2nd May 2013.

ABSTRACT

The five Schiff base type salen molecules have been synthesized from the diamine and substituted salicylaldehydes in the molar ratio of 1:2. N, N'-dimethyl ethylenediamine was reacted with 1-cholo-2-nitrobenzene to obtain N, N'-dimethyl-N, N'-bis(2-nitrophenyl)ethane-1,2-diamine. It was further reduced to get N, N'-ethane-1, 2-diylbis (N-methylbenzene-1, 2-diamine). All the compounds were characterized by IR, ^{1}HNMR, ^{13}CNMR, and Mass Spectrometry.

Keywords: Schiff base, C_2- symmetric, Salens.

INTRODUCTION

Hugo Schiff described the condensation between an aldehyde and an amine to obtain the compounds, later known as Schiff base. [1] Active and well-designed Schiff bases are considered ''privileged ligands.'' [2] These ligands can coordinate with many metals and also stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations. [3] Stereogenic centres or other elements of chirality (planes, axes) can be introduced in the synthetic design. Schiff bases and their metal complexes have been prepared because of their interesting and important properties, e.g., ability to bind toxic and heavy metal atoms [4], undergo tautomerism [5], exhibit catalytic reduction [6] and photochromism [7] . When two equivalents of salicylaldehyde are condensed with a diamine, a particular chelating Schiff base is produced. The so-called salen ligands, with four coordinating sites and two axial sites open to ancillary ligands, are very much like porphyrins, but can be prepared with ease than the later ones. Although the term salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in the literature to describe the class of [O, N, N, O] tetradentate bis-Schiff bases [3].The ligand can act as a polydentate dianionic species, with the ability to co-ordinate with almost any element in the Periodic Table. This opens up a possibility to synthesize large number of metal-salen complexes, displaying catalytic activities in a

wide range of useful organic transformations. [8] Having the ability to modify the ligand structure allows any salen metal complex to be finely tuned, both sterically and electronically. Since many of these complexes have been shown to display high levels of stereocontrol, this is a huge advantage in a forever expanding, vital area of synthetic and asymmetric catalytic chemistry. [2] The preferential utilization of C_2-symmetric ligands was a concept developed in the early stages of asymmetric catalysis. [9]

In the present work, we report the synthesis and characterization of the new potentially hexadentate C_2-symmetric salen systems with N_4O_2 donor atoms derived from *N, N*'-dimethyl ethylenediamine precursor and substituted salicylaldehydes. Different substituents were used such as –H (σp= 0), -Br (σp= 0.26), -Cl (σp= 0.24), -OH (σp= -0.38)[13], - OCH_3 (σp= -0.28) [10] to study the effect of substituents on acidity of donor phenolic hydroxyl group. The structures of all products were confirmed by IR, ^{1}HNMR, ^{13}CNMR and Mass spectrometry analysis.

MATERIALS AND METHODS

All reagents used were obtained from Aldrich and Loba chemicals and are chemically pure or analytical reagent grade. Infrared spectra were recorded as KBr pellets using Nicolet Instruments Corporation, USA Model MAGMA-550 (4000-50 cm^{-1}) from IIT Mumbai. ^{1}HNMR and ^{13}CNMR spectra were obtained using Bruker Ultrashield^{TM} 300 MHz spectrometer with TMS as internal standard from Shivaji University. Mass spectra were recorded on Varian Inc, USA 410 Prostar Binary LC with 500 MS IT PDA Detectors from IIT Mumbai. Fig. 1 represents the sequence of reactions for the synthesis of salens. The composition and properties of the corresponding products are summarized in table 1.

Synthesis of *N, N*'-dimethyl-*N, N*'-bis(2-nitrophenyl)ethane-1, 2-diamine(Compound 1): *N, N*'-dimethyl ethylenediamine (0.84 gm, 9.55 mmol), 1-chloro-2-nitrobenzene (3.0 gm, 19.1 mmol) and sodium carbonate (2.02 gm, 19.1 mmol) were mixed in round bottom flask and fused at 150 ^oC for 4 hours. The resulting orange colored solid **(1)** was washed with 50% methanol (Yield 2.774 gm, 88 %).

Synthesis of *N, N*'-ethane-1, 2-diylbis (*N*-methylbenzene-1, 2-diamine) (Compound 2): A mixture of *N, N*'-dimethyl-*N, N*'- bis(2-nitrophenyl)ethane-1,2-diamine (2.5 gm, 7.5 mmol), tin powder (2.7 gm, 22.6 mmol) and 10 ml conc. HCl were refluxed for 2 hours at 110^oC. Reaction mixture was made alkaline and stirred by using mechanical stirrer for 10 minutes. The dark brown free organic amine **(2)** was then extracted with ether. (Yield 1.845 gm, 90%)

Synthesis of Salen molecules (Compound 3a-3e): A methanolic solution of *N,N*'-ethane-1,2-diylbis (*N*-methylbenzene-1,2-diamine) (2.5 gm, 9.25 mmol)was slowly added to a solution of salicylaldehyde (2.259 gm, 18.5 mmol)(**3a**), 5-bromosalicylaldehyde (3.722 gm, 18.5 mmol)(**3b**), 5-Chlorosalicylaldehyde (2.886 gm, 18.5 mmol)(**3c**), 5-methocysalicylaldehyde (2.812 gm, 18.5 mmol)(**3d**) & 2,5 –dihydroxy benzene (2.553 gm, 18.5 mmol)(**3e**). After stirring, the reaction mixture was refluxed for about 1 hour. The reaction mixture was taken in a beaker and the solvent was evaporated. The yellow/orange colored products were filtered and recrystallized from alcohol (3.7 gm, above 80%)

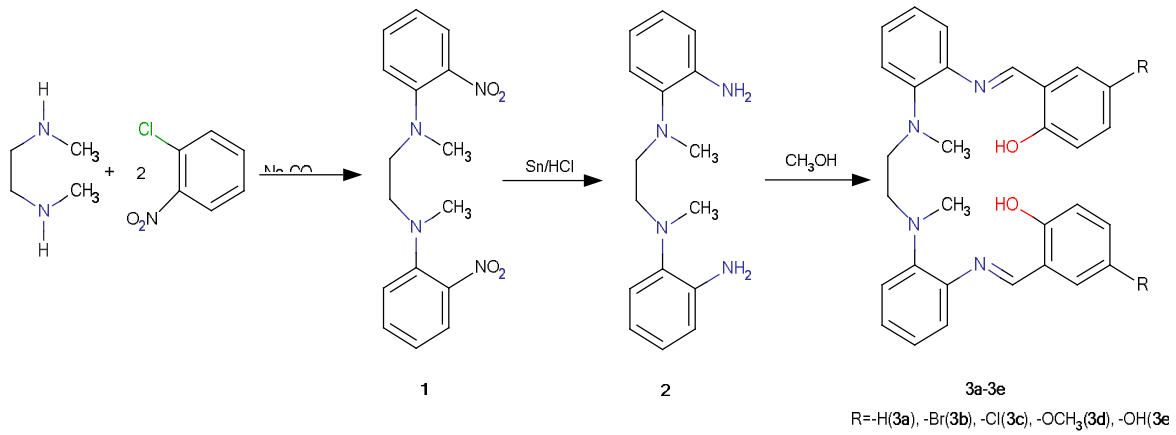

Figure 1: Synthetic Route for synthesis of Salens

Table 1. Spectral data of newly prepared compounds

Compound	Spectral data
1	IR (KBr cm^{-1}): 3004 □ (Ar-H), 2966, 2889 □ (CH_2 and CH_3), 1605 & 1561 □ (c=c), 1507 & 1346 □ (NO_2).^{1}HNMR (δ, 300 MHz, $CDCl_3$, ppm): 2.82(6H, S), 3.43(4H, S), 6.90- 7.7(8H, m). ^{13}CNMR (δ, 300 MHz, $CDCl_3$, ppm): 40.53 ($2CH_3$), 52.59 ($2CH_2$), 119.72, 120.21, 126.17, 133.21, 141.25, 145.42 (Ar) Mass: 330 (Base peak)
2	IR (KBr cm^{-1}): 3400 & 3300 □ (NH_2), 3051 & 3026 □ (Ar-H), 2970 & 2851 □ (CH_2 & CH_3), 1617 & 1500 □ (C=C). ^{1}HNMR (δ, 300 MHz, $CDCl_3$, ppm):2.7(6H, S), 2.9 (4H, S), 4.42 (4H, S,), 6.7-7.2(8H, m). ^{13}CNMR (δ, 300 MHz, CDCl3, ppm): 40.93($2CH_3$), 55.23($2CH_2$), 115.09, 117.81, 120.24, 124.49, 139.55, 141.93 Mass: 270(Base Peak), 149, 134.
3a	IR (KBr cm^{-1}): 3500-2300 broad □ (Ar-OH), 3057 □ (Ar-H), 2999 & 2966 □ (CH_2 & CH_3), 1616 □ (C=N), 1587 & 1566 □ (C=C), 1166 □ (C-O). ^{1}HNMR (δ, 300 MHz, $CDCl_3$, ppm): 2.7(6H, S), 3.23(4H, S), 6.94-7.33 (16H, m), 8.43(2H, CH=N, S), 13.65(2H, OH, S,). ^{13}CNMR (δ, 300 MHz, $CDCl_3$, ppm): 41.66, 53.57, 117.32, 118.81, 118.91, 119.53, 119.80, 122.18, 127.34, 132.02, 132.88, 141.60, 146.57, 161.09, 161.27 Mass: 478, 373(Base peak), 253, 226, 147.

3b IR (KBr cm^{-1}): 3411 broad □ (Ar-OH), 3063 □ (Ar-H), 2960 & 2918 □ (CH_2 & CH_3), 1618 □ (C=N), 1584 □ (C=C), 1184 □ (C-O). ^{1}HNMR (δ, 300 MHz, DMSO/$CDCl_3$, ppm): 2.72(6H, S), 3.23(4H, S), 6.28-7.42 (14H, m), 8.36(2H, CH=N, S), 13.68(2H, OH, S,). ^{13}CNMR (δ, 300 MHz, DMSO/$CDCl_3$, ppm): 41.34, 53.42, 109.99, 119.56, 119.84, 120.11, 121.78, 122.68, 127.98, .134.26, 135.67, 141.16, 146.85, 160.13, 160.53 Mass: 638/636/634, 490, 450(Base), 331, 267.

3c IR (KBr cm^{-1}) 3445 broad □ (Ar-OH), 1609 □ (C=N), 1578, 1510 □ (C=C), 1176 & 1164 □ (C-O), ^{1}HNMR (δ, 300 MHz, DMSO/$CDCl_3$, ppm): 2.72 (6H, S), 3.22 (4H, S), 6.88-7.29 (14H, m), 8.35 (2H, CH=N, S) 13.45 (2H, OH, S). ^{13}CNMR (δ, 300 MHz, DMSO/$CDCl_3$, ppm): 41.78, 53.69, 118.85, 119.47, 119.90, 120.15, 122.33, 123.28, 127.69, 130.84, 132.53, 136.77, 141.18, 159.43, 159.82, Mass: 546(Base), 466, 404.

3d IR (KBr cm^{-1}) 3450 broad □ (Ar-OH), 3046 □ (Ar-H) 1614 □ (C=N), 1513, 1157 □ (C-O), ^{1}HNMR (δ, 300 MHz, DMSO/$CDCl_3$, ppm): 2.74 (6H, S), 3.27 (4H, S), 3.82 (6H, S), 6.79-7.26 (14H, m), 8.37 (2H, CH=N, S) 12.90 (2H, OH, S), Mass: 538, 402, 282(Base).

3e IR (KBr cm^{-1}) 3445 broad □ (Ar-OH), 3031 □ (Ar-H), 2932 □ (CH_2 & CH_3), 1613 □ (C=N), 1513 □ (C-O), 1157 □ (C-O) ^{1}HNMR (δ, 300 MHz, DMSO/$CDCl_3$, ppm): 2.54 (6H, S), 3.09 (4H, S), 6.38-7.08 (14H,),8.30 (2H, CH=N, S) 9.09 (2H, OH, S), 12.59 (2H, OH, S), Mass: 508, 376(Base), 255.

RESULTS AND DISCUSSION

The salen type Schiff bases were prepared in three steps. In earlier study Hassen Keypour et al. [11] have reported synthesis of diamine derivative from ethylene diamine. In the first step due to electron withdrawing effect of nitro group nucleophilic substitution on aromatic ring was possible. The dinitro compound **(1)** was then reduced with Sn/HCl to yield diamine **(2)**. The six Schiff base ligand molecules were prepared by condensation of the diamine **(2)** and salicylaldehyde **(3a)**, 5-bromosalicylaldehyde **(3b)**, 5-chlorosalicylaldehyde **(3c**), 5- methoxysalicylaldehyde (**3d**) & 2, 5-dihydroxyl benzene **(3e)** in 1:2 ratios. The reactions yield intense orange-yellow colored solids with almost qunatitative yield. . The structural formulae of the salens were confirmed by IR, ^{1}H, ^{13}C and mass spectroscopy, with all the results in good agreement with designed compounds.

The ^{1}HNMR of all the Schiff bases show only a single ^{1}H imine resonance at 8.43 ppm, demonstrating the equivalence of the two imine environments. The peak at 13.65 ppm is ascribed to two symmetric highly acidic phenolic protons. The ^{13}CNMR spectra confirms that the imine carbon atoms (161.27 ppm) and appear in the region corresponding to aromatic ring carbons are chemically equivalent (161.27-117.32 ppm). Also two signals corresponding to 53.57 and 41.66 ppm in ^{13}CMR and 3.35 (s, 4H) and 2.72 (s, 6H) in ^{1}HNMR are assigned to two methylene and two methyl carbons respectively which again confirms symmetric structure of ligand molecule. The ^{1}HNMR chemical shifts of phenolic hydroxyl group (12.59-13.68 ppm) reveals that salens with electron withdrawing groups could act as potential ligands than those with electron releasing groups.

APPLICATIONS

The salens reported in this paper would prove exciting potential polydentate ligand applications. Further studies on this part are undergoing.

CONCLUSIONS

In the present study, we have been able to demonstrate that C_2-symmetric salens having potential ligand properties can be prepared in excellent yields and short reaction times.

ACKNOWLEDGMENTS

The authors are thankful to University Grants Commission (UGC), Delhi for the financial support.

REFERENCES

[1] Schiff, H., *Ann Suppl*., **1864**, 3, 343.
[2] Yoon, T. P.; Jacobsen, **2003,** 299, 1691.
[3] Cozzi, P. G., *Chem. Soc. Rev*., **2004**, 33, 410-421.
[4] Soliman, A.A.; Linert, W., *Thermochim Acta*; **1999,** 338:67.
[5] Pizzala, H.; Carles M.; Stone, W.; Thevand, A., *Mol Struct*, **2000,** 526:261.
[6] Gaber, M.; Issa, R., *Thermochim Acta*, **1989,** 155:309.
[7] Lambi, E.; Gegiou, D.; Hadjoudis, E., *J. Photochem Photobiol*, **1995,** 86:241.
[8] A. D. Garnovskii, A. L. Nivorozhkin, V. I. Minkin, *Coord. Chem. Rev.*, **1993,**126, l-69.
[9] Kim, G.-J.; Shin, J.-H., *Catal. Lett.*, **1999**, 63, 83.
[10] Matsui T., Hon C. K., Hepler L.G., *Can. J. Chem*., **1974**, 52, 2906
[11] H. Keypour, R. Azadbakht, S. Salehzadeh, H. Amiri Rudbari, H. Adams, *Tet Lett*, 50, **2009**, 169-171.