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Synthesis of New Macrocycles of Ortho-Methoxy Salicylaldehyde using Claisen-Schmidt Condensation

Shana Balchi [α] & Alireza Banaei [σ]

Abstract- In this research prepared some new families of macrocycles by reaction of ortho-methoxy salicylaldehyde sequently with ketone by claisen-Schmidt condensation. Claisen-Schmidt condensation proceed under base or acid catalysis, at moderate temperature, in high atom economy and with water as the sole by product. Macrocycle were characterized by IR, NMR and Mass spectroscopie.

Keywords: macrocyclic compounds, claisen-schmidt condensation, ortho-methoxy salicylaldehyde.

I. Introduction

Calixarenes, resorcinarenes, cyclotriveratrylenes, cucurbiturils, and crown ethers, exemplify families of macro cyclic compounds that found extensive use in supra molecular chemistry . Pedersen in 1967 he published two works that are now considered classics [1]. He describes the methods of synthesizing crown ether (cyclic polyethers). Discovered a simple method of synthesizing crown ether when he was trying to prepare a complexing agent for divalent cations. The donut-shaped molecules were the first in a series of extraordinary compounds that form stable structures with alkali metal ions and a hetero cyclic compound is a cyclic compound which has atoms of at least two different elements as members of its ring(s). Although heterocyclic compounds may be inorganic, most contain at least one carbon atom, and one or more atoms of elements other than carbon within the ring structure, such as sulfur, oxygen or nitrogen recently chemists try to produce new macro cycles by Claisen-Schmidt condensation. The reactions between a ketone and an aldehyde (crossed aldol condensation) or between two aldehydes also go by the name Claisen-Schmidt condensation [2]. Claisen-Schmidt condensations proceed under either acid or base catalysis, at moderate temperature, In high atom economy and with water as the sole byproduct. Chemo selectivity is also high. It was first reported in 1925 that arylaldehydes and cycloalkanones afford predominantly α , ά bisarylidene cycloalkanones instead of α-mono arylidene cycloalkanones. Subsequent workers have found that this applies even when the ratio of starting ketone to aldehyde is greater than 1:1the orientation of exocyclic bonds generated is exclusively trans with respect to the aryl ring and the carbonyl group of the cycloalkanone [3].

II. Results and Discussion

In this research prepared some new families of macro cycles by reaction of ortho-methoxy salicylaldehyde. These aspects of the Claisen-Schmidt condensation and green chemistry have been exploited in this work, to produce members of a new family of macro cycles in a single step as shown in Scheme above. Starting dialdehydes were prepared (step1), in each case by linking two ortho-methoxysalicylaldehyde molecules with bromoalkans, their derivatives or analogues, with flexible linear tethers. To such compoundsemployed Williamson etherification conditions that required long reaction times (100 hr athightemperatures). In the presence of ketone and base, Cyclization occurred through sequential Claisen-Schmidt condensations, at α position to the carbonyl group and macrocycles are obtaining meanto moderate yields.Workersfoundin 2004 during the investigation of α , ά bisary lidenecycloalkanones the tethering unit contained fewer than seven atoms, cyclization isdimeric macrocycleresulting from the condensation of two cyclohexanone molecules and two dialdehyde linkers. Against them we produce the monomer macrocycles.

Reaction of ortho-methoxy salicylaldehyde sequently with 1,2 dibromoetane , 1,3 dibromopropane and 1,4 dibroboetane under base catalysis(step1) and output compound (I–III).Consequently inter- and intra molecular cyclization of one flexible connector with one type of ketones, through two sequential Claisen-Schmidt condensations, (step2) and output compound (IV - X).

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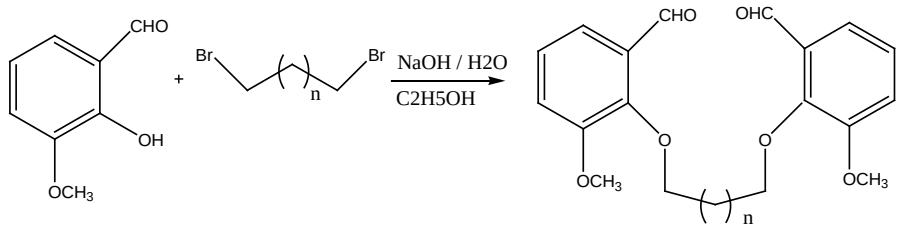
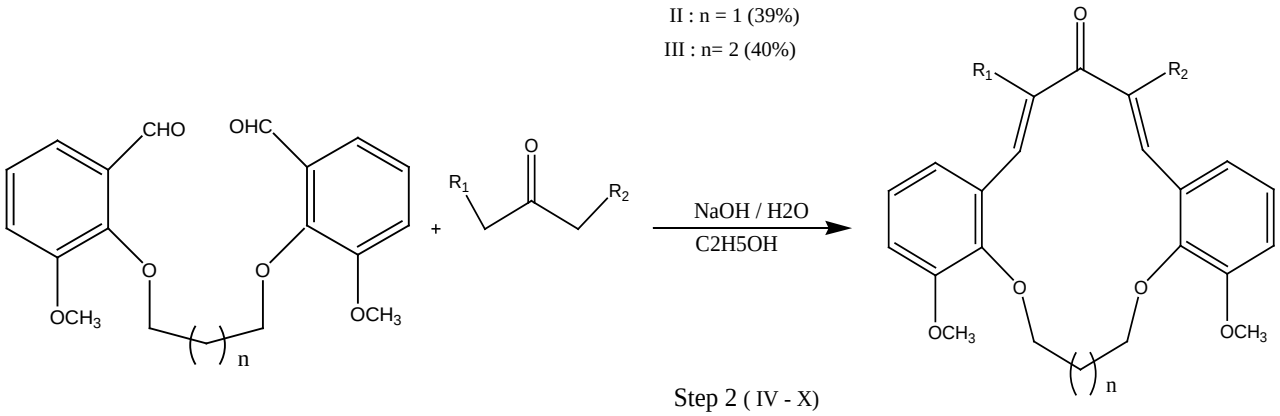


Step 1 (I- III)

I : n= 0 (36%)

II : n = 1 (39%)

III : n= 2 (40%)



Step 2 (IV - X)

I : n= 0, { IV = R1 = R2 = CH3 ; VII = R1 = CH3, R2 = H }

II : n = 1, { V = R1 = R2 = CH3 ; VIII = R1 = CH3, R2 = H ; X = R1 = H, R2 = H }

III : n= 2, VI = R1 = R2 = CH3

III. Experimental

a) Synthesis

The Synthesis of compound (I – III), to ortho-methoxy salicylaldehyde (24.4 g, 0.2 mol) in alcol (20 ml) was added sodium hydroxide (8.0g .02 mol) in water (400 ml) in three bollon then the mixture was warmed andin every of the bollonsequently1,2 dibromoetane1,3 dibromopropane and 1,4 dibroboetane (0.1 mol) was added. Sufficient alcohol (300 ml) to produce a homogeneous solution. The solution was refluxed under nitrogen for 100 hr and then cooled and let stand at 0°C The cream-colored crystals produced were washed with water of first two bollon and letter bollonproducedtan-colored crystals [3-4].

i. *Yield (36%) , Mp: 117.8- 118.3°C*

IR$\nu_{max(neat)/cm}^{-1}$: 2937.56 ,05/2785(CHO),1664.57(C=O), 785.03, 746.45

^{1}H-NMR ($CDCl_3$,TMS,300MHz) δ ppm : 3.905 (s,3H), 4.526 (s,2H), 7.183 (m,2H), 7.292-7.471 (m,1H), 10.547 (s,1H)

^{13}C-NMR($CDCl_3$,TMS,75MHz)δppm : 55.97,

117.94, 119.18, 124.33, 129.99, 151.11, 152.81, 190.57

MS m/z :[M =330],179,151,135,108,119

ii. *Yield (39%), Mp: 64.4 –66.7°C*

IR$\nu_{max(neat)/cm}^{-1}$: 2846.93, 2744.71(CHO), 1691.57(C=O), 734.88, 761.88

^{1}H-NMR ($CDCl_3$,TMS,300MHz) δ ppm : 2.309-2.317 (m,2H), 3.911(s,3H),4.400(t,2H), 7.318-7.190 (m,2H), 7.432-7.455 (m,1H) 10.489 (s,1H)

^{13}C-NMR (CDCl3,TMS,75MHz) δ ppm: 30.91, 56.04, 71.46, 118.04, 119.20, 124.19, 129.88, 151.62, 152.99, 190.27

MS m/z :[M = 344],151,165,193,122,137,108

iii. *Yield(40%),Mp: 111.3- 117.9°C*

IR$\nu_{max(neat)/cm}^{-1}$:2846.93,2765.74(CHO), 1672.14(C=O), 723.31, 765.74

^{1}H-NMR ($CDCl_3$,TMS,300MHz) δ ppm : 2.041(br.s,2H), 3.893(s,3H),4.218 (br.s,2H), 7.109- 7.147 (m,2H), 7.412-7.428 (m,1H), 10.465(s,1H)

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^{13}C-NMR ($CDCl_3$,TMS,75MHz) δ ppm: 26.69, 56.03, 74.46, 118.08, 119.08, 124.11, 129.94, 151.80, 153.05, 190.25
MS m/z:[M = 358],207,165,151,55

b) Synthesis

The Synthesis of compound (IV - X),to an ethanolic solution (95%, 1.83 L) of compound I (1.02g, 3.10 mmol) and diethyl keone (0.49 ml, 4.60 mmol) was added aqueous NaOH (1.87g in 3.75 ml H2O, 4.6 mmol). After stirring at rt for 6 d, abright yellow solution heterogeneous produce of the reaction. then it washed with 1.0 M HCL and water. and dried, then recrystallisation in etanol and produce cream- powder, compound (IV). The Synthesis of compound compound of (V – X) similar manner refered.

iv. *Yield (31.1%), Mp:128-127.7 °C*

IR$\nu_{max(neat)/cm}^{-1}$: 1622.62(C=O), 765.10,744.52
^{1}H-NMR (CDCl3,TMS,300MHz) δ ppm : 2.057 (s,3H) 3.913(s,3H) 4.477 (s,2H), 6.943- 6.972(m,2H), 7.091-7.146(m,1H), 7.867(s,1H)
^{13}C-NMR ($CDCl_3$,TMS,75MHz) δ ppm: 13.84, 55.78, 72.40, 112.42, 121.30, 123.54, 130.61, 130.66, 137.50, 145.93, 152.62, 202.58
MS m/z :[M = 380],335,203,191,175,91,83,43,57

v. *Yield (46.6%), Mp:140-138 °C*

IR$\nu_{max(neat)/cm}$-1: 1662.31(C=O), 758.02, 742.57
1H-NMR ($CDCl_3$,TMS,300MHz) δ ppm : 2.248 (s,3H), 2.307 (m,1H), 3.921(s,3H), 4.221 (t,2H), 6.973(d,1H), 7.070 (d,H), 7.117- 7.157(t,1H), 7.580 (s,1H)
13C-NMR ($CDCl_3$,TMS,75MHz) δ ppm: 15.08, 31.34, 55.58, 68023, 112.39, 121.95, 123.99, 130.91, 133.52, 137.33, 146.51, 153.51, 202.47
MS m/z :[M =394],336,321,91,43,57,191,103,131,380

vi. *Yield (35.1), Mp:142-140 °C*

IR$\nu_{max(neat)/cm}^{-1}$:1692.85(C=O), 798.53, 746.45
^{1}H-NMR ($CDCl_3$,TMS,300MHz) δ ppm : 1.968 (br,s,2H), 2.078 (s,3H), 3.891(s,3H),4.069 (br,s,2H), 6.937 (d,1H), 7.012 (d,1H), 7.077- 7.116 (t,1H), 7.504 (s,1H)
^{13}C-NMR ($CDCl_3$,TMS,75MHz) δ ppm:15.20, 26.56, 55.85, 72.89, 112.40, 121.90, 123.62, 130.57, 134.28, 138.14, 146.43, 152.97, 201.88
MS m/z :[M = 408],91,55,148,175,333

vii. *Yield (54%), Mp:140-138 °C*

IR$\nu_{max(neat)/cm}^{-1}$: 1635.46 (C=O), 732.95, 785.03
1H-NMR ($CDCl_3$,TMS,300MHz) δ ppm : 2.0721 (s,3H), 3.917 (s,6H), 4.403 (m,2H), 4.582 (m,2H), 6.651 (d,1H), 6.977 (s,3H), 7.075- 7.156 (m,2H), 7.697(s,H), 8.512 (d,H)
^{13}C-NMR ($CDCl_3$,TMS,75MHz) δ ppm:13.62, 55.86, 55.94, 72.14, 73.85, 112.88, 113.69, 117.93, 121.25, 123.08, 124.47, 126.91, 129.71, 129.78, 135.70, 137.16, 142.80, 146.21, 146.93, 151.94, 153.07, 200.83
MS m/z :[M=366],321,336,188,91,161,17

viii. *Yield (26.3%), Mp:169 -171°C*

IR$\nu_{max(neat)/cm}$-1: 1622.13(C=O), 767.67,731.02
^{1}H-NMR ($CDCl_3$,TMS,300MHz) δ ppm :
2.193(s,3H), 2.317 (m,2H), 3.915 (s,6H), 4.231 (t,4H), 6.777-6.820 (d,1H), 6.953-7.007(m,2H), 7.055 (d,1H), 7.122-7.169 (m,2H), 7.291- 7.334 (t,1H), 7.584 (s,1H), 8.104 (d,1H)
^{13}C-NMR ($CDCl_3$,TMS,75MHz) δ ppm: 14.85, 31.49, 50.84, 55.86, 68.79, 68.95, 68.79, 68.95, 112.30, 113.76, 118.01, 121.84, 124.05, 124.74, 127.30, 129.45, 130.78, 133.37, 137.00, 139.22, 146.56, 146.88, 152.85, 153.45, 199.94
MS m/z :[M=380],149,307,322,91,161,175,350

ix. *Yield (53%) , Mp: 131-129°C*

IR$\nu_{max(neat)/cm}^{-1}$: 28/1618 (C=O),792.74,67/740
^{1}H-NMR ($CDCl_3$,TMS,300MHz) δ ppm :2.342-2.392 (m,2H), 3.931)s,3H), 4.237 (t,2H), 6.750 (d,1H), 7-7.301 (m,3H), 8.135-8.092 (d,1H)

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