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Synthesis of some o.o'-Dihydroxy Schiff Bases

By

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Synthesis of some o,o'-Dihydroxy Schiff Bases

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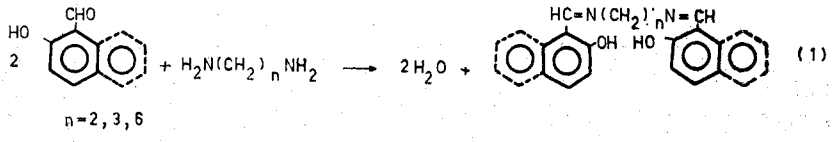
ABSTRACT

Some Schiff bases have been prepared by using o-hydroxy benzaldehyde and β-hdyroxy-α-naphthaldehyde with some diamines in medium of methyl alcohols. Their properties have been examined.

INTRODUCTION

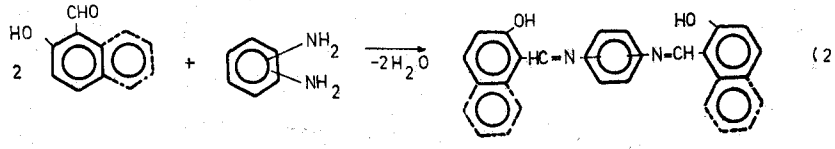
o,o'-dihydroxy schiff bases give very strong 5 or 6 membered chelate rings complexes with transition element cations (1, 2). In this work some o,o'-dihydroxy schiff bases like polymethylene dialdimine, polyethyleneamine dialdimine, 4,4'-(dialdimine), diphenyl methane and p-N,N-dimethyaminophenyl aldimine, have been prepared and their properties have been examined by spectrophotometrically.

Polymethylenedialdimines were obtained by condensation of polymethylene dialdimines with salicylaldehyde and ß-hydroxy-α-naphthaldehyde in medium of methyl alcohols (Equation-1).



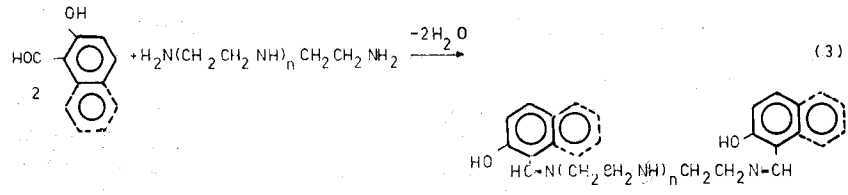
(1)

Phenylene dialdimines were obtained by condensation of phenylene diamine dihydrochlorides with salicylaldehyde and ß-hydroxy-α-naphthaldehyde in medium of pyridine (Equation-2).



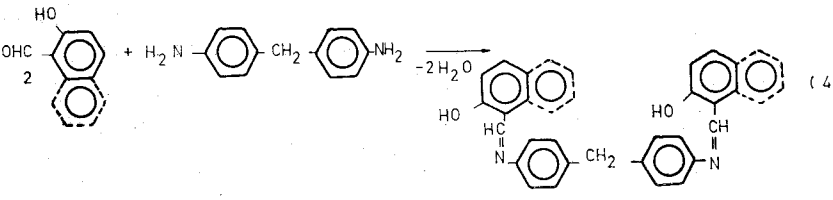
(2)

Polyethyleneamine dialdimines were obtained by condensation of polyethylene amines with salicylaldehyde ß-hydroxy -α- naphthaldehyde in medium of methylalcohol. Only salicylaldimines are liquid at room temperature and were purified by chromotographic method (Equation-3).



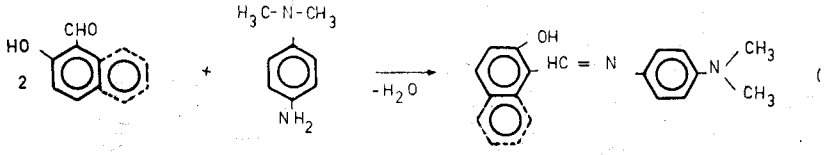
(3)

The compound 4,4'-(dialdimine) diphenylmethane were obtained by condensation of 4,4'-diamino diphenylmethane with salicylaldehyde and ß-hydroxy -α- naphthaldehyde in medium of methylalcohol (Equation-4).



(4)

p-N,N-dimethylaminophenylaldimines were obtained by condensation of N,N-dimethyl-p-phenylene diamine dihydrochloride with salicylaldehyde and ß-hydroxy -α- naphthaldehyde in medium of methylalcohol (Equation-5).



(5)

One of the striking properties of o-hydroxy schiff bases is to give intramolecular hydrogen bondings (like O - H.. N). Because of this hydrogen bonding in their I.R. Spectra a large brodeaning is observed in region of O - H vibrations, covering 3600–2800 cm^{-1} (3). This seems to be in great agreement with work done by Freedman (4).

Studies on the schiff bases also gave a sharp absorption band in the region of 1640–1633 cm^{-1} (5, 6) which is due to C = N double bond.

In their UV spectra all schiff bases showed absorption band round about 330–320 nm due to C = N double bond.

EXPERIMENTAL

Propane-1,3-disalicylaldimine:

24,42 g (0,2 M) salicylaldehyde dissolved in 50 cc methyl alcohol is placed in a 250 cc baloon 7,41 g (0,1 M) 1,3-diamino propane is added dropwise on to the solution which is stirred and cooled down to –10 °C. After little time yellow crystalls formed. They are filtered off and collected on a buchner funnel and recrystallized from petroleum ether. Yield 75% m.p 59 °C.

Propane-1,3-di (ß-hydroxy) -α- naphthaldimine:

34,4 g (0.2 M) ß-hydroxy -α- naphthaldehyde dissolved in 175 cc methylalcohol by heating is placed in a 250 cc baloon 7.41 g(0,1 M) 1,3-diamino propane is added dropwise on to the solution which is stirred and cooled down to –10° C. Yellow crystalls are filtered off and collected on a buchner funnel and recrystallized from chloroform. Yield 67% m.p 212 °C.

Hexane-1,6-disalicylaldimine:

24,42 g (0,2 M) salicylaldehyde dissolved 50 cc methyl alcohol is put in a 250 cc baloon. 11,62 g (0,1 M) 1,6-diaminohexane dissolved in 50 cc methyl alcohol is added dropwise on to the solution which is stirred and cooled down to –10 °C. Yellow crystalls are filtered off and collected on a buchner funnel and recrystallized from hot methyl alcohol. Yield 73% m.p 72–73 °C.

Hexane-1,6-di (ß-hydroxy) -α-naphthaldimine:

34.4 g (0.2 M) ß-hydroxy -α- naphthaldehyde dissolved in 150 cc methylalcohol by heating is placed in a 250 cc baloon. 11.62 g (0,1 M)

1,6-diamine hexane dissolved in 50 cc methylalcohol is added dropwise on to the solution which is stirred and cooled down to –10 °C. After some time, the yellow crystalls are filtered off and collected on a buchner funnel and recrystallized from hot ethylacetate. Yield 65% m.p 173 °C.

o-phenylene-disalicylaldimine:

24.42 g (0.2 M) salicylaldehyde placed in a 250 cc baloon, is dissolved in 50 cc methylalcohol. 10.8 g (0,1 M) o-phenylene diamine dissolved in 50 cc methylalcohol is added dropwise on to the solution which is stirred and cooled down to –10 °C. Orange crystalls are filtered off and collected on a buchner funnel and washed with mixture of diethylether and petroleum ether (1:1) and recrystallized from ethylalcohol. Yield 60% m.p 156 °C.

o-phenylene di (ß-hydroxy) -α-naphthaldimine:

34.4 g (0.2 M) ß-hydroxy -α- naphthaldehyde placed in a 250 cc baloon is dissolved in 50 cc methylalcohol by heating. 10.8 g (0.1 M) o-phenylene diamine dissolved in 50 cc methylalcohol is added dropwise on to the solution which is stirred when the resulting red coloured mixture is evaporated by an evaporator orange crystalls are formed. They are filtered off and collected on a buchner funnel and recrystallized from ethylacetate. Yield 65%. Decomp: 195–198 °C.

m-phenylene disalicylaldimine:

24.42 g (0.2 M) salicylaldehyde placed in a 250 cc baloon is dissolved in 50 cc methyl alcohol. 18.10 g (0.1 M) m-phenylene diamine dihydrochloride dissolved in mixture of 150 cc pyridine and methyl alcohol is added dropwise on to the solution which is stirred and cooled down to –10 °C. The resulting purple coloured mixture is added drop by drop on to 50 cc distilled water and stirred. Yellow crystalls are obtained. They are filtered off and coltected on a buchner funnel and washed with 50 cc water and recrystallized from 100 cc methyl alcohol. Yield 63% m.p 109. 5 °C.

m-phenylene di (ß-hydroxy) -α- naphthaldimine:

34.4 g (0.2 M) ß-hydroxy -α- naphthaldehyde placed in a 250 cc baloon is dissolved 175 cc methyl alcohol by heating. 18.10 g (0.1 M) m-phenylene diamine dihydrochloride dissolved in hot mixture of 50 cc methyl alcohol and pyridine (1:1) is added on to the above solution. The resulting red coloured solution is cooled down to –10 °C. After some

time, yellow crystalls are obtained. They are filtered off and collected on a buchner funnel and washed with the mixture of petroleum ether and diethylether (1:1). Yield 60%. Decomp at 222–225 °C.

p-phenylene disalicylaldimine:

24.42 g (0.2 M) salicylaldehyde placed in a 250 cc baloon is dissolved in 50 cc methyl alcohol. 18.10 g (0.1 M) p-phenylene diamine dihydrochloride dissolved in hot mixture of 50 cc pyridine and methyl alcohol (1:1) is added dropwise on the above solution. The resulting red coloured solution is cooled down to –10 °C. After some time oranges crystalls are obtained. They are filtered off and collected on a buchner funnel and washed through petroleum ether and recrystallized from hot chloroform. Yield 73% m.p 210–11 °C.

p-phenylene di (ß-hydroxy) -α- naphthaldimine:

34.4 g (0.2) ß-hydroxy -α- naphthaldehyde placed in a 250 cc baloon is dissolved in 175 cc ethyl alcohol by heating. 18.10 g (0.1 M) p-phenylene diamine dihydrochloride dissolved in hot mixture of 250 cc pyridine and ethy alcohol, is added dropwise on to the above solution is cooled down –10 °C. After some time red crystalls come down. They are filtered off and collected on a buchner funnel washed through benzene and dried. Yield 65%. Decomp at 298 °C.

N,N'bis (salicylidene) diethylenetriamine:

24.42 g (0.2M) salicylaldehyde placed in a 250 cc baloon is dissolved 50 cc methylalcohol. 10.3 g (01M) diethylenetriamine dissolved in 50 cc methylalcohol is added dropwise on to above solution which is stirred and cooled. Resulting red coloured solution is evaporated by an evaporater and 50 cc benzene is added. It is left over night and yellowish-orangeviscos liquid is seperated by chromotographically using a column of 3×10 silicium dioxide and eluated by 250 cc ethylalcohol. Then the eluate is evaporated. Yield 62–63%.

N,N'-bis [(ß-hydroxy) -α- naphthalydene] diethylenetriamine:

34.4 g (0.2 M) ß-hydroxy -α- naphthaldehyde placed in a 250 cc baloon is dissolved in hot 100 °C methylalcohol. 10.3 g (0.1 M) diethylene triamine dissolved in 50 cc methylalcohol is added dropwise on to the above solution which is stirred and cooled down to –10 °C. Yellow crystalls form. They are filtered off and collected on a buchner funnel and

washed with the mixture of chloroform and petroleum ether (1:9) and recrystallized from 100 cc methylalcohol. Yield 70–71%. m.p 151 °C.

N.N'—bis (salicylidene) triethylene tetramine:

24.42 g (0.2 M) salicylaldehyde placed in a 250 cc baloon is dissolved 50 cc methylalcohol. 14.6 g (0.1 M) triethylene tetramine dissolved in 50 cc methylalcohol is added dropwise on to the above solution which is stirred and cooled down to –10 °C. Yellow crystalls form. They are filtered off and collected on a buchner funnel and recrystallized from methylalcohol. Yield 81–82%. m.p. 102–103 °C.

N.N'-bis (ß-hydroxy) -α-naphthalydene triethylenetetramine:

34.4 g (0.2 M) ß-hydroxy -α- naphthaldehyde placed in a 250 cc baloon is dissolved in 150 cc hot methylalcohol. 14.6 g (0.1 M) triethylene tetramine dissolved in 50 cc methylalcohol is added dropwise on to the above solution which is stirred and cooled down to –10 °C. After the resulting dark yellow mixture is evaporated and waited 3–4 hours yellow crystalls form. They are filtered off and collected on a buchner funnel and washed with the mixture of diethyl ether and methylalcohol (1:1) and recrystallized from 100 cc methylalcohol. Yield 78%. m.p. 192 °C.

N.N'-bis (salicylidene) tetraethylenepentamine:

24.42 g (0.2 M) salicylaldehyde placed in a 250 cc baloon is dissolved in 50 cc methylalcohol. 18.9 g (0.1 M) tetraethylenepentamine dissolved in 50 cc methylalcohol is added dropwise on to the above solution which is stirred and cooled down to –10 °C. After the resulting red coloured solution is evaporated by an evaporater, 50 cc benzene is added. It is left over night and dark red viscos liquid is seperated by chromotographically using a column of 3×10 silicium dioxide and eluated by 250 cc ethylalcohol. Then the eluate is evaporated. Yield 69%.

N.N'-bis (salicylidene) pentaethylenehexamine:

24.42 g (0.2 M) salicylaldehyde placed in a 250 cc baloon is dissolved 50 cc methylalcohol. 22.6 g (0.1 M) pentaethylenehexamine dissolved in 50 cc methylalcohol is added dropwise on to the above solution which is stirred and cooled down to –10 °C. The resulting red colour solution is evaporated by an evaporator and 50 cc benzene is added. It is left over night and dark red viscos liquid seperated by chromotographically

using a column of silicium dioxide and eluated by 250 cc ethylalcohol. Then the eluate is evaporated. Yield 65–66%

4.4'-(disalicylaldimine) diphenylmethane:

24.42 g (0.2 M) salicylaldehyde placed in a 250 cc baloon is dissolved in 50 cc methylalcohol. 19.8 g (0.1 M) 4.4-diaminodiphenyl methane dissolved in 100 cc dimethylformamide is added dropwise on to the above solution which is stirred and cooled down to –10 °C. Yellow crystalls form. After some time they are filtered off a buchner funnel and washed with 50 cc methylalcohol. Yield 72–73%. m.p. 212–213 °C.

4.4'- di (ß-hydroxy) -α-naphaldymine diphenylmethane:

34.4 g(0.2 M) ß-hydroxy -α- naphthaldehyde placed in a 250 cc baloon is dissolved in 175 cc hot methylalcohol. 19.8 g (0.1 M) 4.4'-diamine diphenylmethane dissolved in 50 cc methylalcohol is added dropwise on to the above solution. Resulting dark yellow mixture is slowly poured in to 100 cc destilled water. Yellow crystall form. After some time they are filtered off a buchner funnel and washed with mixture of distilled water and methylalcohol (1:1) and recrystallized from 150 cc chloroform. Yield 68%. m.p. 198–200 °C.

p-N.N-dimethylaminophenyl salicylaldimine:

12.21 g(0.1M) salicylaldehyde placed in a 250 cc baloon is dissolved in 50 cc methylalcohol. 17.25 g (0.1 M) N.N-dimethyl-p-phenylene diamine hydrochloride dissolved hot mixture of 50 cc pyridine and methyl alcohol (1:1) is added dropwise on to the above solution which is stirred and cooled down to –10 °C. Orange crystalls form. They are filtered off a buchner funnel and recrystallized from methylalcohol. Yield 83–84%. m.p. 133–35 °C.

p-N.N-dimethylamino phenyl (ß-hydroxy) -α- naphthaldimine:

17.2 g (0.1 M) ß-hydroxy -α- naphthaldehyde placed in a 250 cc baloon is dissolved in 50 cc methylalcohol. 17.25 g (0.1 M) N.N-dimethyl-p-phenylenediamine dissolved in hot mixture of 50 cc pyridine and methylalcohol is added dropwise on to the above solution which is stirred and cooled down to –10 °C. Red crystalls form. They are filtered off a buchner funnel and recrystallized from methylalcohol. Yield 80%. m.p. 163–64 °C.

Yields, m.ps., and analytical data for the products are recorded in the table.

TABLE 1.

COMPOUND	Yield%	M.p.°C	Found %			Formula	Required %		
			C	H	N		C	H	N
Propane-1,3-disalicylaldimine	75	59	68.99	5.82	10.10	$C_{17}H_{18}N_2O_2$	72.34	6.38	9.93
Propane-1,3-di (β-hydroxy) -α-naphthaldime	67	212	78.87	5.25	7.10	$C_{25}H_{22}N_2O_2$	78.87	5.76	7.33
Hexane-1,6-disalicylaldimine	73	72–73	74.31	7.37	9.08	$C_{20}H_{24}N_2O_2$	74.07	7.41	8.64
Hexane-1,6-di(β-hydroxy)-α-naphthaldimine	65	173	75.10	6.40	6.82	$C_{28}H_{28}N_2O_2$	79.20	6.60	6.60
o-phenylene-disalicylaldimine	60	156	75.72	4.81	8.99	$C_{20}H_{16}N_2O_2$	75.95	5.06	8.86
o-phenylene-di(β-hydroxy)-α-naphthaldimine	65	195–98	80.47	4.71	7.33	$C_{28}H_{20}N_2O_2$	80.77	4.80	6.73
m-phenylene-disalicylaldimine	63	109.5	75.41	5.01	8.01	$C_{20}H_{16}N_2O_2$	75.95	5.06	8.86
m-phenylene-di(β-hydroxy)-α-naphthaldimine	60	222–25*	80.20	4.90	5.26	$C_{28}H_{20}N_2O_2$	80.77	4.80	6.73
p-pheynlene-disalicylaldimine	73	210–11	76.05	5.28	9.20	$C_{20}H_{16}N_2O_2$	75.95	5.06	8.86
p-phenylene-di(β-hydroxy)-α-naphthaldimine	65	298*	81.16	4.32	9.96	$C_{28}H_{20}N_2O_2$	80.70	4.80	6.73

N,N'-bis(salicylidene)diethylene triamine	62–63	–	67.47	6.33	13.43	$C_{18}H_{21}N_3O_2$	69.45	6.75	13.51
N,N'-bis [(β-hydroxy)-α-naphthalidene] diethylenetriamine	70–71	151	76.06	6.87	9.59	$C_{26}H_{25}N_3O_2$	75.91	6.08	10.22
N,N'-bis(salicylidene)triethylene tetramine	81–82	102–3	67.70	6.88	14.42	$C_{20}H_{26}N_4O_2$	67.80	7.34	15.82
N,N'-bis [(β-hydroxy)-α-naphthalidene]triethylenetetramine	78	192	73.33	6.94	12.42	$C_{28}H_{30}N_4O_2$	74.00	6.60	12.33
N,N'-bis(salicylidene)tetra-ethylenepentamine	69	–	67.14	7.50	16.88	$C_{22}H_{31}N_5O_2$	66.50	7.81	17.63
N,N'-bis(salicylidene) pentaethylenehexamine	65–66	–	65.47	7.95	18.17	$C_{24}H_{36}N_6O_2$	65.49	8.18	19.10
4,4'-(disalicylaldimine)diphenylmethane	72–73	212–13	79.65	5.20	7.04	$C_{27}H_{22}N_2O_2$	79.80	5.42	6.90
4,4'-di(β-hydroxy)-α-naphthaldimine diphenymethane	68	198–200	82.75	5.84	6.11	$C_{35}H_{26}N_2O_2$	83.00	5.14	5.53
p-N.N-dimethylamino-phenylsalicylaldimine	83–84	133–35	72.18	6.99	11.74	$C_{15}H_{16}N_2O$	75.00	6.67	11.67
p-N.N-dimethylaminophenyl(β-hydroxy)-α-naphthaldimine	80	163–64	78.59	6.25	9.73	$C_{19}H_{18}N_2O$	78.62	6.21	9.66

decomposition*

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ÖZET

o-hidroksi benzaldehit ve β-hidroksi -α- naftaldehitin metanollü ortamda bazı diaminler ile verdiği Schiff bazları hazırlandı ve özellikleri incelendi.