Convenient, Mild and One-Pot Synthesis of Double Schiff Bases from Three Component Reaction of Salicylaldehyde, Ammonium Acetate and Aliphatic Aldehydes Accelerated by NEt_3 as a Base

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A convenient and efficient procedure for one-pot preparation of double Schiff bases through a three component reaction of salicylaldehyde, ammonium acetate and aliphatic aldehyde was described. In this reaction, N,N′-bis(salicylidene)-1,1-diaminoalkanes was easily obtained in excellent yields and short reaction times under mild reaction condition.

Keywords: Schiff base; Salicylaldehyde; Three component; One pot; Aldehydes.

INTRODUCTION

Combinatorial chemistry is widely used in pharmaceutical research as a powerful tool for acceleration of the identification of novel therapeutic agents in drug discovery. In this field, multicomponent condensation reactions have been utilized very efficiently in conjugation with combinatorial chemistry to prepare large collections of molecules in a short reaction sequence.[1] Multicomponent reactions (MCR) are an attractive concept for high-throughput chemistry that provide the ability to rapidly generate new complex products from simple substrates.[2-4]

The history of MCR dates back to 1838 when Laurent and Gerhardt prepared benzoylazotid.[5] MCR, defined as one-pot reactions in which at least three functional groups join through covalent bonds, have been steadily gaining importance in synthetic organic chemistry.[6] The reagents employed may be different molecules or they may be different functional groups of the same reagent. Speed, diversity, efficiency and environmental amiability are some of the key features of this class of reactions.[7] In times where a premium is put on speed, diversity and efficiency in the drug discovery process MCR strategies offer significant advantages over conventional liner-type syntheses.[8,9]

Schiff base ligands have gained importance because of the physiological and pharmacological activities associated with them. They constitute an interesting class of chelating agents capable of coordination with metal ions given complex which serve as models for biological system.[10-12] Also these complexes find many important catalytic applications, ranging from asymmetric epoxidations,[13-16] reduction of aromatic ketones,[17] and asymmetric aziridination of olefins[18] to various types of polymerization[19-22] as well as their widespread use for preparation of the ion selective electrodes,[23-28] solid phase extraction of metal ions,[29] etc.

Schiff base compounds containing an imine group are usually formed by the condensation of primary amine and diamine with an active carbonyl compound in methanol solvent.[30] In solvent medium the reactants can interact effectively if they are in a homogenous solution, whereby the reactant molecules come together rapidly and continually. Moreover uniform heating or cooling of the mixture, if needed, can be carried out in solution relatively easily. It could be deeply and inseparably associated with the process of an organic reaction through the solvation of the reactants, products, transition state or other intervening species. Such intimate interactions between the solvent and the reaction partners are due to many factors that include electrostatic, steric and conformational effects among others.[31]

In continuation of our current efforts on research, we are focused on the development of the multicomponent reaction and the utilization of these processes toward the synthesis of double Schiff bases. In this study, we report a practical and efficient three component reaction by which N,N′-bis(salicylidene)-1,1-diaminoalkanes were synthesized by reacting the salicylaldehyde, ammonium salt and aliphatic aldehyde in the presence of a base at room temperature (Scheme I).

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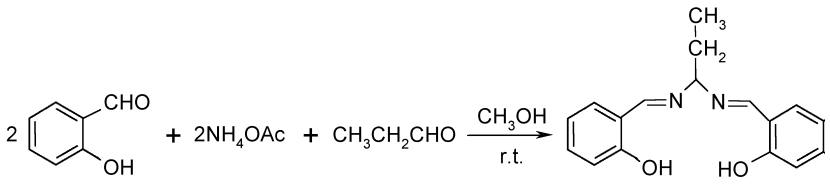
Scheme I



RESULTS AND DISCUSSION

The first time, the salicylaldehyde, ammonium acetate salt and propionaldehyde were reacted together in ratio 2:2:1, respectively, by stirring at room temperature in a methanol solution (Scheme I).

In this research, we were interested in studing various ammonium salts in the reaction. The results have been summarized in Table 1. As shown in this Table, ammonium acetate and ammonium benzoate were the most effective among the other ammonium salts in this reaction (entries 1 and 2 in Table 1). The reason for this behavior may be due to the usage of later pointed salts where strong acids were yielded in the reaction mixture that can be inefficient for progress of the reaction. When the reaction was done by using $(NH_4)_2C_2O_4$, no product was obtained even with an extension of the reaction time to several days (entry 6, Table 1).

When the above mentioned reaction was performed in the presence of a base, the reaction was remarkably enhanced, giving an excellent yield of the desired product. With respect to these results, we infer that the base may play a main role in the reaction. Thus the reaction of salicylaldehyde, propionaldehyde and NH_4OAc has been carried out in the presence of various bases at room temperature. Table 2 introduces the results of these investigations.

As can be seen in Table 2, by using the NEt_3, KOH and NaOH as a base, the reaction proceeded faster than the reaction either with other bases or without any base (compare entries 3, 4 and 5 *vs* 1, 2, 6 and 7 in Table 2).

Nothing that a solvent has the power to enhance or reduce the speed of a reaction, at times enormously, the changing of a solvent of a reaction can influence the rate of that reaction, and it can be powerful enough to change the reaction course itself. Thus in conjunction with this research, the reaction of salicylaldehyde, propionaldehyde and ammonium acetate has been considered in the presence of NEt_3 as a base in various solvents (Scheme II). The results are indicated in Table 3. As shown in this Table, these three component reactions proceeded with speed in order as follows: MeOH, EtOH > DMSO > DMF > CH_3CN > THF, $CHCl_3$, CH_2Cl_2.

Table 1. The reaction of salicylaldehyde and propionaldehyde with various ammonium salts at room temperature

Entry	Ammonium Salt	Time/hour	Yield/%
1	NH_4OAc	2	40
2	NH_4OOCPh	2.5	30
3	NH_4NO_3	4	17
4	NH_4Cl	4	15
5	NH_4SCN	7	10
6	$(NH_4)_2C_2O_4$	72	-
7	$(NH_4)_2SO_4$	6	5
8	$(NH_4)_6Mo_7O_{24}$	5	15

Table 2. Preparation of Schiff base in the presence of various bases at room temperature

Entry	Base	Time/min	Yield[a]/%
1	$NaOOCCH_3$	80	55
2	$NaHCO_3$	70	60
3	KOH	50	90
4	NaOH	50	90
5	NEt_3	45	95
6	Pyridine	115	45
7	None	120	40

[a] Isolated yield based on salicylaldehyde.

Scheme II

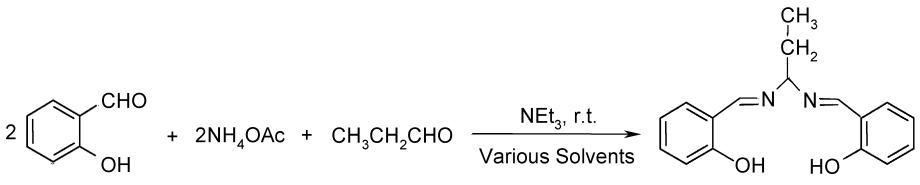


Table 3. Schiff base formation in various solvents at room temperature

Entry	Solvent	Time/min	Yield[a]/%
1	MeOH	45	95
2	EtOH	45	95
3	DMF	40	92
4	DMSO	40	95
5	THF	80	10
6	CH_3CN	70	10
7	$CHCl_3$	90	5
8	CH_2Cl_2	90	5

[a] Isolated product yield.

This sequence can probably be related to the polarity and ability of these solvents for hydrogen bonding formation with the transition state and intermediate of this reaction that can be influenced to dissolve and hamper their stability.

Finally, in order to elucidate the generality of this one-pot reaction, we employed several aliphatic aldehydes in the reaction with salicylaldehyde and ammonium acetate in the presence of NEt_3 base in ethanol solvent at room temperature (Scheme III).

The results of these reactions are shown in Table 4. As indicated in the Table, a lot of useful double Schiff bases were afforded in excellent yields and short reaction times from the one-pot reaction of various aldehydes with salicylaldehyde and ammonium acetate.

The structures of the products have been assigned by spectroscopic data. In the IR spectra, the characteristic Schiff base C=N stretching frequency is formed in the region between υ =1600-1700 cm^{-1} as a signal strong band. The OH stretching frequency is found at υ = 3000 cm^{-1} with a particular width. The stretching vibration of C-H in the alkyl groups appear in the region between υ = 2700-2800 cm^{-1} with sharp absorptions. In the ^1H NMR spectra, the broad signals with δ =12-13 ppm are assigned to the protons of the hydroxyl groups. Two protons of CH=N have the same chemical shifts in δ = 8.30-8.46 ppm, and the signal around the δ = 4.6-5.0 ppm is assigned to the protons of the NCHN. The UV spectra show about 2-3 maximum absorptions dependent on the particular structure of the compound.

CONCLUSION

In this study, we have shown that the NEt_3 base dramatically accelerates the rates of one-pot preparation of double Schiff base compounds. This method was carried out by a three-component reaction of two aldehydes and ammonium acetate at room temperature. The excellent yields of useful Schiff base products were successfully achieved in a short time with this mild, efficient and convenient method.

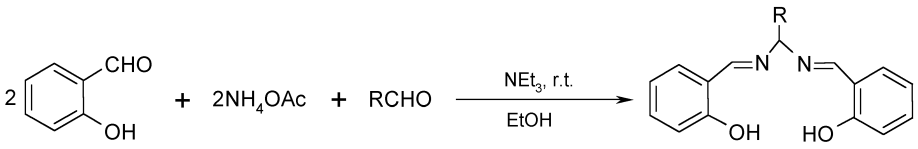
EXPERIMENTAL

Chemicals were purchased from the Merck Chemical Company in high purity. IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 Spectrophotometer and an Impact 400 Nickolet FTIR Spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ with (400 MHz) Spectrometer using TMS as an internal reference. Melting points obtained with a Yanagimoto micromelting point apparatus are uncorrected. The purity determination of the substrates and reactions monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

General Procedure for Synthesis of N,N′-bis(2-hydroxybenzylidene)-1,1-diaminoalkanes

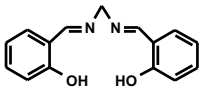
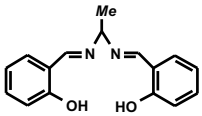
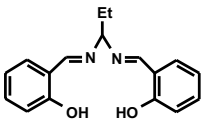
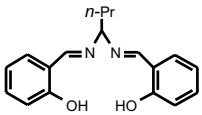
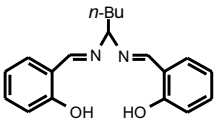
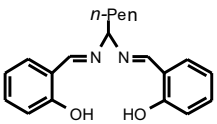
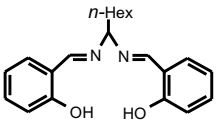
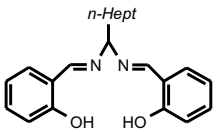
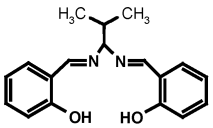
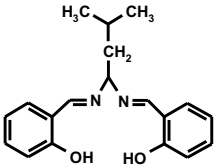
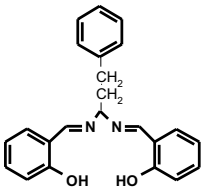
To a mixture of salicylaldehyde (0.4 g, 3.27 mmol) and propionaldehyde (R=C_2H_5, 0.095 g, 1.64 mmol) was added NH_4OAc (0.25 g, 3.27 mmol) in the presence of the NEt_3 (1 mL) as a base by stirring in one portion. The stirring of the mixture continued for 45 minutes. The progress of the reaction was monitored by TLC. After the comple-

Scheme III



R=H, Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *n*-Pent, *n*-Hex, *n*-Hept, *i*-Bu, $PhCH_2CH_2$

Table 4. The reaction of salicylaldehyde, ammonium acetate and different aldehydes in the presence of NEt_3 at room temperature in EtOH solvent

Entry	Aliphatic Aldehyde	Time (min)	M.P. (^oC)	Yield [a] (%)	Product
1	HCHO	45	116-118	95	
2	CH_3CHO	30	98-100	92	
3	CH_3CH_2CHO	45	92-94	95	
4	$CH_3(CH_2)_2CHO$	45	72-74	94	
5	$CH_3(CH_2)_3CHO$	35	82-84	96	
6	$CH_3(CH_2)_4CHO$	35	72-74	96	
7	$CH_3(CH_2)_5CHO$	30	82-84	95	
8	$CH_3(CH_2)_6CHO$	25	64-66	97	
9	$(CH_3)_2CHCHO$	20	74-76	98	
10	$(CH_3)_2CHCH_2CHO$	25	Oil	92	
11	$Ph(CH_2)_2CHO$	40	Oil	93	

[a] Isolated product yields.

tion of the reaction, the mixture became yellow. After cooling the reaction mixture, a solid product was formed, filtered off and washed with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, N,N′-bis(2-hydroxybenzylidene)-1,1-diaminopropane was obtained in 95% yield, m.p. = 92-94 °C. The Schiff base products were identified by spectroscopic data.

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminomethane

mp 116-118 °C; IR (KBr)/υ (cm^{-1}) 3150-3450 (br, OH); 1620 (s, C=N), 1587, 1501 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 4.46 (s, 2H), 6.9-7.6 (m, 8H), 8.6 (s, 2H); 12.70 (s, 2OH); ^{13}C NMR/$CDCl_3$/δ p.p.m: 85, 117.6, 119.9, 118.7, 133, 133.9, 161; MS: *m/z* = 243 (M^++1, 7), 242 (M^+, 8), 132 (14), 133 (100), 91 (17), 77 (44), 58 (60); UV ($CHCl_3$)/λ_{max} (nm) 320 (w), 260 (s); Anal. Calcd. For C. H. N.: C, 69.42; H, 5.78; N, 11.57. Found: C, 69.43; H, 5.8; N, 11.57.

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminoethane

mp = 98-100 °C; IR (neat)/υ (cm^{-1}) 3000-3300 (br, OH); 1625 (s, C=N), 1490.6, 1576 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 2.5 (d, 3H, CH_3), 4.5 (q, 1H, NCHN), 6.9-7.6 (m, 8H), 8.7 (s, 2H, C=N), 13.02 (s, 2OH); ^{13}C NMR/$CDCl_3$/δ p.p.m: 25.4, 84.2, 117.4, 119.4, 118.7, 132.9, 133, 161.3, 166; UV ($CHCl_3$)/λ_{max} (nm) 323 (w), 262 (s); MS: *m/z* = 269 (M^++1, 6), 298 (M^+, 10), 149 (100), 91 (20), 77 (30), 58 (55); Anal. Calcd. For C. H. N.: C, 71.64; H, 5.95; N, 10.45. Found: C, 71.64; H, 5.97; N, 10.45.

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminopropane

mp 92-94 °C; IR (KBr)/υ (cm^{-1}): 3150-3450 (br, OH), 1625 (s, C=N), 1501, 1587 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 4.8 (t, 1H, NCHN), 0.9 (t, 3H, CH_3), 1.99 (m, 2H, CH_2), 6.9-7.6 (m, 8H), 8.7 (s, 2H, C=N); 13.0 (s, 2OH); ^{13}C NMR/$CDCl_3$/δ p.p.m: 19, 20.2, 85, 116.4, 118.4, 119.6, 133, 133.7, 161.3; MS: *m/z* = 283 (M^+ + 1, 6%), 282 (M^+, 10), 162 (13), 161 (100), 91 (20), 77 (45), 58 (59); UV ($CHCl_3$)/λ_{max} (nm); Anal. Calcd. For C. H. N.: C, 72.34; H, 6.38; N, 9.93. Found: C, 72.35; H, 6.39; N, 9.93.

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminobutane

mp 72-74 °C; IR (KBr)/υ (cm^{-1}) 3100-3440 (br, OH); 1625 (s, C=N), 1502, 1576 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 0.9 (t, 3H, CH_3), 1.4 (m, 2H, CH_2), 1.9 (q, 2H, CH_2), 4.99 (t, 1H, NCHN), 6.9-7.7 (m, 8H), 8.7 (s, 2H, C=N), 13.0 (s, 2OH); ^{13}C NMR/$CDCl_3$/δ p.p.m: 15.3, 18, 20, 84, 117.4, 118.8, 119, 133, 133.7, 161. UV ($CHCl_3$)/λ_{max} (nm) 322 (w), 260 (s); MS: *m/z* = 297 (M^++1, 6), 296 (M^+, 7), 176 (15), 175 (100), 91 (17), 77 (45), 58 (55), 56 (30), 42 (15); Anal. Calcd. For C. H. N.: C, 72.97; H, 6.77; N, 9.46. Found: C, 72.98; H, 6.80; N, 9.46.

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminopentane

mp 82-84 °C; IR (KBr)/υ (cm^{-1}) 3250-3430 (br, OH); 1625 (s, C=N), 1491, 1577 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 0.9 (t, 3H, CH_3), 1.4 (m, 4H, $2CH_2$), 1.9 (q, 2H, CH_2), 4.99 (t, 1H, NCHN), 6.9-7.7 (m, 8H), 8.7 (s, 2H, C=N), 12.93 (s, 2OH); ^{13}C NMR/$CDCl_3$/δ p.p.m: 15.3, 17, 20, 82, 117, 118, 119, 133, 133.2, 165; UV ($CHCl_3$)/λ_{max} (nm) 320 (w), 260 (s); MS: *m/z* = 311 (M^++1, 5), 310 (M^+, 9), 190 (12), 189 (100), 91 (20), 77 (40), 58 (55), 56 (25), 42 (14); Anal. Calcd. For C. H. N.: C, 73.55; H, 7.09; N, 9.03. Found: C, 73.56; H, 7.10; N, 9.03.

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminohexane

mp 72-74 °C; IR (KBr)/υ (cm^{-1}) 3000-3350 (br, OH); 1629 (s, C=N), 1486, 1573 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 0.9 (t, 3H, CH_3), 1.4 (m, 6H, 3 CH_2), 1.9 (q, 2H, CH_2), 4.99 (t, 1H, NCHN), 6.9-7.7 (m, 8H), 8.5 (s, 2H, C=N), 13.1 (s, 2OH); ^{13}C NMR/$CDCl_3$/δ p.p.m: 12.3, 19, 21, 86, 118, 119, 120.5, 133, 133.2, 166; UV ($CHCl_3$)/λ_{max} (nm) 320 (w), 261 (s); MS: *m/z* = 325 (M^+ + 1, 3), 324 (M^+, 5), 202 (20), 175 (100), 91 (15), 77 (35), 58 (58), 42 (25); Anal. Calcd. For C. H. N.: C, 74.07; H, 7.40; N, 8.64. Found: C, 74.08; H, 7.41; N, 8.65.

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminoheptane

mp 82-84 °C; IR (KBr)/υ (cm^{-1}) 3250-3500 (br, OH), 1631 (s, C=N), 1491, 1571 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 0.8 (t, 3H, CH_3), 1.3 (m, 8H, $4CH_2$), 1.9 (q, 2H, CH_2), 5.0 (t, 1H, NCHN), 6.9-7.6 (m, 8H), 8.7 (s, 2H, C=N), 13.2 (s, 2OH); MS: *m/z* = 339 (M^+ + 1, 10%), 338 (M^+, 15), 220 (20), 220 (100), 91 (29), 77 (50), 58 (57), 56 (34), 42 (20); UV ($CHCl_3$)/λ_{max} (nm) 320 (w), 262 (s); Anal. Calcd. For C. H. N.: C, 74.55; H, 7.69; N, 8.28. Found: C, 74.56; H, 7.7; N, 8.28.

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminoctane

mp 64-66 °C; IR (KBr)/υ (cm^{-1}) 3300-3500 (br, OH), 1630 (s, C=N), 1491, 1571 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 0.89 (t, 3H, CH_3), 1.34 (m, 10H, 5 CH_2), 1.93 (m, 2H, CH_2), 4.89 (t, 1H, NCHN), 6.9-7.56 (m, 8H), 8.7 (s, 2H, C=N), 12.4 (s, 2OH). UV ($CHCl_3$)/λ_{max} (nm) 320 (w), 262 (s).

N,N′-bis(2-hydroxybenzylidene)-1,1-diaminoisobutane

mp 74-76 °C; IR (KBr)/υ (cm^{-1}) 3250-3520 (br, OH); 1615 (s, C=N), 1502, 1577 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 0.8 (d, 6H, CH_3), 2.0 (m, 1H, CH), 4.4 (t, 1H, NCHN), 6.9-7.2 (m, 8H), 8.2 (s, 2H, C=N), 12.9 (s, 2OH); ^{13}C NMR/$CDCl_3$/δ p.p.m: 18.4, 35.2, 92, 117.4, 119.4, 119.7, 133, 133.7, 161.3; UV ($CHCl_3$)/λ_{max} (nm) 323 (w), 242 (w), 262 (s); MS: *m/z* = 297 (M^+ + 1, 5), 296 (M^+, 6), 177 (12), 176 (100), 133 (11), 132 (58), 91 (18), 77 (42), 58 (58); Anal. Calcd. For C. H. N.: C, 72.97; H, 6.76; N, 9.45. Found: C, 72.97; H, 6.76; N, 9.45.

N,N′-bis(2-hydroxybenzylidene)-1,1-diamino-3-phenylpropane

Oil; IR (neat)/υ (cm^{-1}) 3000-3300 (br, OH), 1625 (s, C=N), 1490.6, 1576 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 0.9 (d, 6H, CH_3), 1.4 (m, 1H, CH_2), 1.9 (2H, CH_2), 4.99 (t, 1H, NCHN), 6.9-7.7 (m, 13H), 8.7 (s, 2H, C=N), 13.02 (s, 2OH); UV ($CHCl_3$)/λ_{max} (nm) 323 (w), 262 (s), 243 (sh).

N,N′-bis(2-hydroxybenzylidene)-1,1-diamino-3-methylbutane

Oil; IR (neat)/υ (cm^{-1}) 3300-3555 (br, OH), 1625 (s, C=N), 1490, 1577 (Ar); ^{1}H NMR/$CDCl_3$/δ p.p.m: 0.8 (d, 6H, CH_3), 2.0 (m, 1H, CH), 1.5 (t, 2H, CH_2), 4.4 (t, 1H, NCHN), 6.9-7.4 (m, 8H), 8.2 (s, 2H, C=N), 12.9 (s, 2OH); UV ($CHCl_3$)/λ_{max} (nm) 323 (w), 262 (s), 252 (sh).

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