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Synthesis of Some New Open-Chain Conjugated Azomethines and N-Aryl-1-Cyano-α-Methylcinnamylamines

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The reactivity of carbon-nitrogen double bond lies in between that of carbon-oxygen and carbon-carbon double bond. Some new open-chain conjugated azomethines, *i.e.*, α-methyl cinnamylideneanilines (3) have been prepared by condensation of α-methylcinnamaldehyde with a series of various substituted anilines. The addition of hydrocyanic acid to these open-chain conjugated azomethines leads to some new amines identified as N-aryl-1-cyano-α-methylcinnamylamines (4). All the products have been identified by their spectral data. The addition of hydrocyanic acid occurs at carbon-nitrogen double bond rather than carbon-carbon double bond of the azomethines indicating that the former is more reactive than the latter.

Key Words: Synthesis, Open-chain, Conjugated azomethines, N-Aryl-1-cyano-α-methylcinnamylamines.

INTRODUCTION

The reactivity of carbon-nitrogen double bond lies in between that of carbon-oxygen and carbon-carbon double bond, because of moderate electronegativity and presence of lone pair of electrons on the nitrogen atom[1]. In azomethines carbon-nitrogen double bond is polar and undergoes various types of reactions with N-sulphinyl anilines[2, 3], thioglycolic acid[4, 6], ketenes[7], Reformatsky reagent[8, 9], nitrile oxide[10], benzyne[11] and a series of some new microwave promoted reactions[12].

The survey of literature revealed that addition reactions of various open-chain conjugated azomethines has not been critically examined. Therefore to study the reactivity of carbon-nitrogen double bond in the presence of carbon-carbon double bond and its addition reactions some new open-chain conjugated azomethines, *i.e.*, α-methyl cinnamylideneanilines (3) have been prepared by condensation of α-methyl cinnamaldehyde (1) with a series of nine aromatic amines (2), having various substituents at *o*, *m*, *p*-positions (**Scheme-1**). These open-chain conjugated azomethines are potential electrophiles for the various addition reactions as having carbon-carbon and carbon-nitrogen double bonds in conjugation with carbon-carbon double bond.

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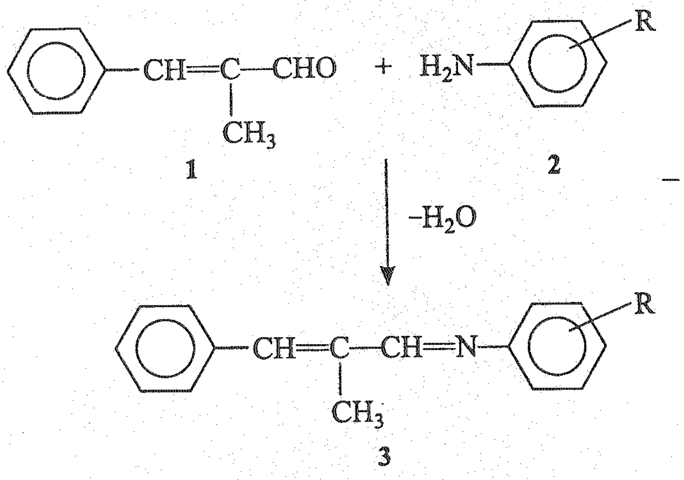


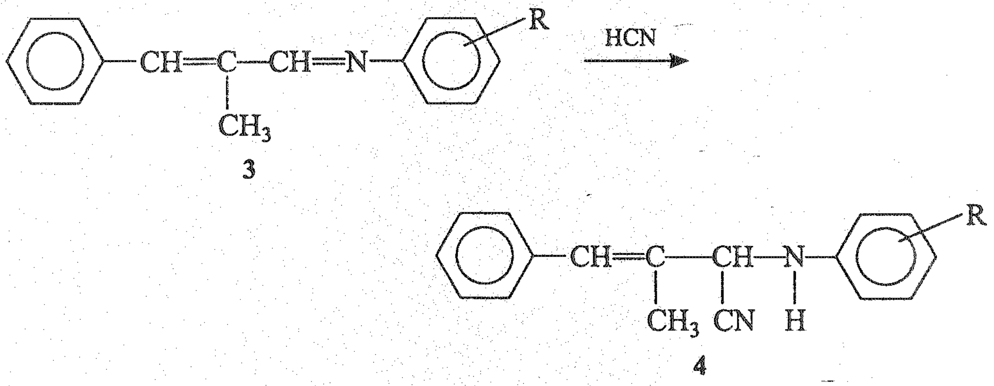
R = H, 4-CH_3, 4-OCH_3, 4-Br, 4-Cl, 4-OC_2H_5, 2-COOH, 3-NO_2, 4-SO_2NH_2

Scheme-1

The infrared spectra of all α-methylcinnamylideneanilines displays a sharp and strong absorption band in the region 1610–1598 cm^{-1}, that has been assigned to carbon-nitrogen double bond strecthings.

The ^1H NMR spectra of α-methylcinnamal-4-toluidine displayed a singlet at δ 8.76 (1H) which has been assigned to azomethinic proton. A multiplet at δ 7.04–7.45 (9H) has been assigned to aromatic protons. A singlet at δ 6.94 (1H) has been assigned to H_β proton of stryryl moiety. Another singlet at δ 2.33 (3H) has been assigned to methyl group of N-aryl ring and a split signal at δ 2.27 (3H) has been assigned to methyl group present at α-position of styryl bond.

The addition of hydrocyanic acid is carried out by adding 10% aqueous potassium cyanide slowly to 2 mmol of open-chain conjugated azomethine in methanol having glacial acetic acid (**Scheme-2**). The work up of the reaction mixture yields the products leading to some new amines identified as N-aryl-1-cyano-α-methyl cinnamylamines (**4**).



R = 4-CH_3, 4-OCH_3, 4-Br, 4-Cl, 4-OC_2H_5, 2-COOH, 3-NO_2, 4-SO_2NH_2

Scheme-2

The infrared spectra of all these N-aryl-1-cyano-α-methylcinnamylamines display a sharp and strong absorption band in the region 3368–3349 cm^{-1} of N—H strechings. Another band in the region 2223–2218 cm^{-1} is of C≡N strechings. Strong to medium intensity absorption bands in the regions 1370–1316 and 1298–1271 cm^{-1} have been assigned to C—N strechings.

The ^1H NMR spectra of N-(4-tolyl)-1-cyano-α-methylcinnamylamine displays a multiplet at δ 6.67–7.33 (9H) which has been assigned to aromatic protons. A singlet at δ 6.49 (1H) has been assigned to H_2 proton of styryl moiety. A singlet at δ 4.81 (1H) has been assigned to H_4 proton. A broad peak at δ 3.82 (1H) has been assigned to H_1 proton of secondary amine (N—H) functionality which disappears on shaking with deuterium oxide (D_2O exchange). A singlet at δ 2.26 (3H) and another singlet at δ 2.03 (3H) has been assigned to methyl group attached to phenyl group and another is of α-methyl group attached to styryl bond respectively.

From the addition reactions it has been concluded that the addition of hydrocyanic acid occurs at carbon-nitrogen double bond rather than carbon-carbon double bond of the open-chain conjugated azomethines. This indicates that the former is more reactive than the latter. Like other double bonds, the carbon-nitrogen double bond of azomethines also serves as an active centre for the variety of reactions. Also the azomethines which have electron withdrawing substituents at N-phenyl ring like 3-NO_2, 2-COOH, 4-SO_2NH_2 give poor yield. Therefore electron-withdrawing substituents on the N-aryl ring of these open-chain conjugated azomethines seems to inhibit the reaction.

EXPERIMENTAL

All the infrared spectra of the synthesized compounds have been recorded on FT-IR Perkin-Elmer spectrophotometer RX-I at the Department of Chemistry, Punjabi University, Patiala. The proton-magnetic resonance spectra have been run on a Bruker AC-300F NMR spectrometer 300 MHz and Hitachi R-1500 spectrometer 60 MHz using TMS as an internal standard and $CDCl_3$ + DMSO as a solvent by SAIF, Panjab University, Chandigarh and Department of Chemistry, Punjabi University, Patiala respectively. Mass spectra was recorded on mass spectrometer VG-70S by SAIF, Panjab University, Chandigarh. The elemental analyses have been carried out at the Microanalytical Laboratory by SAIF, Panjab University, Chandigarh. All melting points have been recorded by Gallen-Kamp apparatus and are uncorrected.

General procedure for the synthesis of open-chain conjugated azomethines (3a-3i): *Synthesis of α-methylcinnamal-4-chloroaniline* **(3d):** Freshly distilled α-methyl cinnamaldehyde (1.46 g, 0.01 mol) in ethanol (10 mL) was mixed with 4-chloroaniline (1.27 g, 0.01 mol) at room temperature in a 100 mL conical flask. The reaction mixture was stirred well for about 15 min and then cooled in an ice-bath. The yellow compound that separated was filtered at the suction pump and recrystallized from methanol to give yellow crystals (1.89 g) in 74% yield; m.p. 79°C. Analysis, %: Found: C, 74.87; H, 5.87; N, 5.01; $C_{16}H_{14}NCl$ requires: C, 75.14; H, 5.47; N, 5.47. IR (nujol): 1608, 884, 826, 753, 692 cm^{-1}, ^1H NMR (300 MHz) ($CDCl_3$ + DMSO): δ 8.76 (s, 1H, azomethinic), 7.04–7.45 (m 9H, aromatic), 6.94 (s, $1H_\beta$), 2.33 (s, 3H, Ar-CH_3), 2.27 (s, 3H, α-CH_3).

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF
α-METHYLCINNAMYLIDENEANILINES (3)

Compd.	R	Yield (%)	m.p. (°C)	m.f.	Anal. (%) Calcd. (Found)		
					C	H	N
a	H	72	45–46	$C_{16}H_{15}N$	86.87	6.78	6.33
					(86.98)	(6.21)	(6.21)
b	4-CH_3	78	66–68	$C_{17}H_{17}N$	86.80	7.23	6.38
					(86.52)	(7.01)	(6.11)
c	4-OCH_3	75	65	$C_{17}H_{17}NO$	84.64	7.05	5.80
					(83.98)	(7.11)	(5.62)
d	4-Cl	74	70	$C_{16}H_{14}NCl$	75.14	5.47	5.47
					(74.87)	(5.87)	(5.01)
e	4-Br	71	74–75	$C_{16}H_{14}NBr$	64.00	4.66	4.66
					(63.72)	(4.56)	(4.24)
f	4-OC_2H_5	78	78	$C_{18}H_{20}NO$	81.50	7.54	5.28
					(81.95)	(7.97)	(5.05)
g	2-COOH	65	150–151	$C_{17}H_{15}NO_2$	72.18	5.26	10.52
					(71.90)	(5.79)	(10.24)
h	3-NO_2	69	110	$C_{16}H_{14}N_2O_2$	76.98	5.66	5.28
					(77.11)	(5.13)	(5.45)
i	4-SO_2NH_2	60	135–136	$C_{16}H_{16}N_2O_2S$	64.00	5.33	9.33
					(64.12)	(5.78)	(9.08)

Synthesis of N-Aryl-1-Cyano-α-Methylcinnamylamines (4a-4g): *Synthesis of N-(4-tolyl)-1-cyano-α-methylcinnamylamine* **(4b):** In a 250 mL conical flask, fitted with a mechanical stirrer and a burette containing 10 mL of 10% aqueous potassium cyanide, placed a solution of α-methylcinnamal-4-toludine (4.7 g, 20 mmol) in methanol (50 mL) containing 5–6 mL of glacial acetic acid. To this reaction mixture an aqueous solution of potassium cyanide was added in small installments from the burette till the addition was complete. The reaction being exothermic, the flask was cooled occasionally by placing it in ice-cold water. The reaction mixture was stirred for 1 h and it was then allowed to stay overnight. The reaction mixture was then diluted with distilled water till turbidity appeared and it resulted in the separation of the crude product. After the filtration of crude product under suction pump and recrystallization from benzene/petroleum ether (1 : 1) mixture yellow crystalline N-(4-tolyl) 1-cyano-α-methylcinnamylamine (2.03 g) was obtained in 78% yield, m.p. 108°C. Analysis (%): Found: C, 82.43; H, 6.48; N, 10.81; $C_{18}H_{17}N_2$ requires: C, 82.75; H, 6.51; N, 10.72. IR (cm^{-1}) (nujol): 3349, 1612, 1518, 1388, 1319, 1271, 1260, 808; ^1H NMR (300 MHz) ($CDCl_3$ + DMSO): δ 6.67–7.33 (m, 9H, aromatic), 6.49 (s, 1H, H_4), 4.81 (s, 1H, H_2), 3.82 (broad, 1H, H_1, disappear on D_2O exchange), 2.26 (s, 3H, Ar-CH_3), 2.03 (s, 3H, α-CH_3).

TABLE-2
PHYSICAL AND ANALYTICAL DATA OF
N-ARYL-1-CYANO-α-METHYLCINNAMYLAMINES (4)

Compd.	R	Yield (%)	m.p. (°C)	m.f.	Anal. (%): Calcd. (Found)		
					C	H	N
a	H	72	89–90	$C_{17}H_{15}N_2$	82.59 (81.98)	6.07 (6.21)	11.33 (11.01)
b	4-CH_3	78	108	$C_{18}H_{17}N_2$	82.75 (82.43)	6.51 (6.48)	10.72 (10.81)
c	4-OCH_3	73	110–112	$C_{18}H_{17}N_2O$	77.97 (76.89)	6.13 (6.21)	10.10 (10.20)
d	4-Cl	75	95	$C_{17}H_{14}N_2Cl$	72.46 (72.32)	4.97 (4.72)	9.94 (9.72)
e	4-Br	71	98–99	$C_{17}H_{14}N_2Br$	62.57 (62.62)	4.29 (4.18)	8.58 (8.47)
f	4-OC_2H_5	76	113–115	$C_{19}H_{19}N_2O$	78.35 (78.12)	6.52 (6.80)	9.62 (9.58)
g	2-COOH	47	105	$C_{18}H_{15}N_2O_2$	74.22 (74.32)	5.15 (5.01)	9.62 (9.58)
h	3-NO_2	50	115–117	$C_{17}H_{14}N_3O_2$	69.86 (69.58)	4.79 (4.71)	14.38 (14.21)
i	4-SO_2NH_2	42	152–155	$C_{17}H_{16}N_3O_3S$	62.57 (62.22)	4.90 (4.78)	12.88 (12.71)

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