

A mild synthesis, characterization and spectral properties of some new substituted cinnamamides and substituted α - β unsaturated acids

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ABSTRACT

The present investigation deals with the evaluation of various Newly Substituted Cinnamamides bearing chloro, methoxy, methyl groups have been obtained by the condensation of substituted phenyl malon anilic acids(1a,2a) with selected different substituted aromatic aldehydes by using pyridine as a condensing agent and α - β unsaturated acids have been synthesized by the condensation reactions between the substituted malon anilic acids (1a,2a) and aromatic substituted aldehydes without any condensing agent. The structures of Newly Synthesized Novel substituted cinnamamides (3a-3f, 4a-4g) and substituted unsaturated acids (5a-5g, 6a-6g) were established on the basis of their Spectral Studies and Analytical data.

Key words: Substituted Cinnamamides, Substituted α - β Unsaturated Acids, Condensation, Spectral Evaluation.

INTRODUCTION

Cinnamamides are an important heterocyclic compounds have been studied extensively for the last few decades which have received considerable investigative attention with regards to their syn-thesis and their broad spectrum of biological activity. Substituted cinnamamides have been reported to possess anti-convulsant¹⁻², inhibitors of blood platelet aggregation³, insecticides⁴, melanin inhibitors⁵, activities. In the applications which gave reduced pigment deposit on the guinea pig skin after exposure to ultra violet radiations. α - β unsaturated acids have been evaluated as β -adrenergic blocking agents^{6,7}. substituted unsaturated acids have also been found to possess diuretics⁸, anti-inflammatory and anti-arteriosclerosis remedies⁹ activities. Some derivatives of unsaturated acids have been reported as bronchodilators¹⁰, fungicides¹¹, sympatholytics¹² activities.

In this laboratory by various workers a number of substituted cinnamamides & substituted α - β unsaturated acids have been synthesized¹³⁻²¹.

In the present study we have synthesized a series of some new substituted cinnamamides & substituted α - β unsaturated acids. They have been synthesized by the condensation of aliphatic and aromatic aldehydes with N(R) phenyl malon anilic acids (1a,2a) with and without any condensing agent as pyridine.

EXPERIMENTAL

Material and Methods

All the chemicals used in the synthesis were obtained from Sigma-Aldrich Company. All the melting points were taken in open capillary tubes and were uncorrected. Thin layer chromatography (TLC) was conducted with silica-gel-coated Al plates (Merck) to check the purity of the newly synthesized

compounds. The IR spectra were recorded in (KBr-disc) method on Perkin-Elmer spectrum RX-1 FT-IR spectro-photometer at Central Drug Research Institute (CDRI) Lucknow .

The identity of newly synthesized compounds was confirmed by analytical data, elemental analysis, molecular formula, molecular weight, melting point, yield%, colour are recorded in the Table -1 and IR Spectral data are recorded in the Table -2 .

General procedure of the Synthesis of N(R) phenyl malon anilic acid (1a, 2a)

To the substituted aniline (2-methoxy-5-methyl, 3-chloro-4-methoxy ; 0.025 mole) and diethyl malonate (0.05 mole) was added with the catalyst DMF and then refluxed for about 45 minutes, after cooling, filter the solution and then add ethanol (20 ml) with a solution of Na_2CO_3 (20 ml) to it, after that the reaction mixture was hydrolysed for 30-45 minutes, filtered and concentrated HCl was added to it, the solid product was separated, filtered, washed with cold water, recrystallized from saturated solution of NaHCO_3 , was identified as N(R) phenyl malon anilic acid (1a, 2a) .

General procedure of the Synthesis of Cinnamamides (3a-3f, 4a-4g)

A mixture of N(R) phenyl malon anilic acid (1a, 2a; 0.001mole) and substituted aldehyde (0.001 mole) in equimolar quantities (1:1), with a trace of pyridine was added. The reaction mixture was

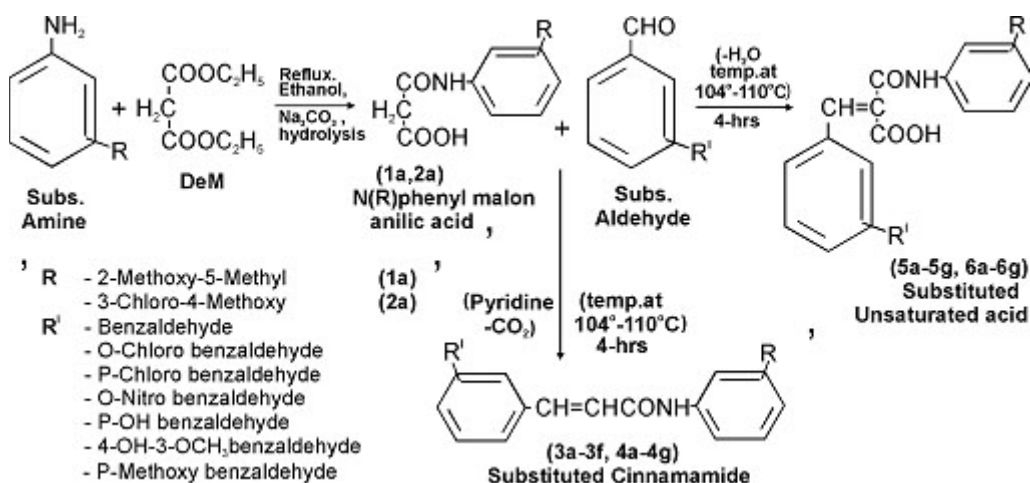
heated in an oil-bath at maintained temperature $104^\circ\text{--}110^\circ\text{C}$, brisk effervescence took place during refluxing, after cooling treated with (20 ml) solution of NaHCO_3 , filtered , thus the obtained residue was washed with hot water , recrystallized by aqueous ethanol, thus the analysed compound was identified to be N(R) phenyl Cinnamamide (3a-3f, 4a-4g).

General procedure of the Synthesis of α - β unsaturated acid (5a-5g, 6a-6g)

A mixture of N(R) phenyl malon anilic acid (1a, 2a ; 0.001 mole) and substituted aldehyde (0.001 mole) was heated in an oil-bath at $104^\circ\text{--}110^\circ\text{C}$ for 4-hours without any condensing agent, after cooling, and treated with saturated solution of NaHCO_3 (20 ml), filtered, NaHCO_3 extract gave a precipitate on acidification with concentrated HCl, filtered, washed with hot distilled water , recrystallized with aqueous ethanol. Thus the product obtained was identified to be benzal-N(R) phenyl malon anilic acid (5a-5g, 6a-6g).

RESULTS AND DISCUSSION

The IR spectrum of the newly synthesized compounds of substituted cinnamamides and substituted α - β unsaturated acids have been recorded in the frequency region $4000\text{--}450\text{ cm}^{-1}$ are furnished in the Table-2. The IR (KBr) spectrum of N(2-methoxy-5-methyl) phenyl 4-hydroxy cinnamamide ^{3e} shows stretching vibrations at 3021.5 cm^{-1} indicates -NH, absorption at 1680.9 cm^{-1} represents -CONH stretching vibrations, absorption



at 1598.7 cm^{-1} indicates $\text{C}=\text{C}$, absorption at 2362.0 cm^{-1} show $\text{HC}=\text{C}$ stretching vibrations, absorption at 670.9 cm^{-1} represents the mono substitutions. These observations are support to the assigned structures of compounds 3e&3f, 4b&4e and other compounds 3a-3d, 4a, 4c-4d, 4f-4g. The

IR Spectra of 2-chlorobenzal -N-(2-methoxy-5-methyl) phenyl malon anilic acid^{5b} shows stretching vibrations at 3021.9 cm^{-1} indicates NH , stretching vibrations at 1697.9 cm^{-1} represent CONH , stretching vibrations at 1598.0 cm^{-1} show $\text{C}=\text{C}$ and stretching vibrations at 2360.5 cm^{-1} indicates $\text{HC}=\text{C}$,

Table :1 Physical and Analytical data of Newly Synthesized Compounds

Compounds Codes	Molecular Formula	Molecular Weight	Melting Point $^{\circ}\text{C}$	Yield %	Colour	%N Cal.	(Found)
1a	$\text{C}_{11}\text{H}_{13}\text{N}_1\text{O}_4$	223.23	104 $^{\circ}$	40.72	tinge of rose	6.27	(6.30)
2a	$\text{C}_{10}\text{H}_{10}\text{N}_1\text{O}_4\text{Cl}_1$	243.64	132 $^{\circ}$	47.63	white	5.75	(5.79)
3a	$\text{C}_{17}\text{H}_{18}\text{N}_1\text{O}_2$	268.33	118 $^{\circ}$	35.98	shining ivory	5.22	(5.26)
3b	$\text{C}_{17}\text{H}_{17}\text{N}_1\text{O}_2\text{Cl}_1$	302.78	126 $^{\circ}$	38.99	light off white	4.62	(4.58)
3c	$\text{C}_{17}\text{H}_{17}\text{N}_1\text{O}_2\text{Cl}_1$	302.78	105 $^{\circ}$	41.59	light ivory	4.62	(4.66)
3d	$\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_4$	313.34	159 $^{\circ}$	30.74	dirty row silk	8.94	(8.92)
3e	$\text{C}_{17}\text{H}_{18}\text{N}_1\text{O}_3$	284.33	146 $^{\circ}$	84.34	dirty yellow	4.92	(4.96)
3f	$\text{C}_{17}\text{H}_{18}\text{N}_1\text{O}_4$	314.36	152 $^{\circ}$	56.80	ivory	4.45	(4.48)
4a	$\text{C}_{16}\text{H}_{14}\text{N}_1\text{O}_2\text{Cl}_1$	288.75	152 $^{\circ}$	30.36	light creamish	4.85	(4.89)
4b	$\text{C}_{16}\text{H}_{14}\text{N}_1\text{O}_2\text{Cl}_2$	323.20	141 $^{\circ}$	34.50	dirty white	4.33	(4.30)
4c	$\text{C}_{16}\text{H}_{14}\text{N}_1\text{O}_2\text{Cl}_2$	323.20	156 $^{\circ}$	43.60	crystalline white	4.33	(4.38)
4d	$\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{Cl}_1$	333.76	162 $^{\circ}$	39.34	light sporty yellow	8.39	(8.43)
4e	$\text{C}_{16}\text{H}_{15}\text{N}_1\text{O}_3\text{Cl}_1$	304.75	127 $^{\circ}$	54.52	pale cream	4.59	(4.56)
4f	$\text{C}_{17}\text{H}_{17}\text{N}_1\text{O}_4\text{Cl}_1$	334.78	137 $^{\circ}$	44.30	light row silk	4.18	(4.22)
4g	$\text{C}_{17}\text{H}_{17}\text{N}_1\text{O}_3\text{Cl}_1$	318.78	131 $^{\circ}$	32.65	dark morning glory	4.39	(4.41)
5a	$\text{C}_{18}\text{H}_{18}\text{N}_1\text{O}_4$	312.34	147 $^{\circ}$	43.36	shining light cream	4.48	(4.51)
5b	$\text{C}_{18}\text{H}_{17}\text{N}_1\text{O}_4\text{Cl}_1$	346.79	156 $^{\circ}$	41.37	pale cream	4.03	(4.05)
5c	$\text{C}_{18}\text{H}_{17}\text{N}_1\text{O}_4\text{Cl}_1$	346.79	148 $^{\circ}$	49.86	light pista	4.03	(4.07)
5d	$\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_6$	357.35	141 $^{\circ}$	52.67	dirty yellow	7.84	(7.90)
5e	$\text{C}_{18}\text{H}_{18}\text{N}_1\text{O}_5$	328.34	134 $^{\circ}$	38.84	dark sugar cane	4.26	(4.23)
5f	$\text{C}_{19}\text{H}_{20}\text{N}_1\text{O}_6$	358.37	127 $^{\circ}$	34.93	dirty cream	3.90	(3.93)
5g	$\text{C}_{19}\text{H}_{20}\text{N}_1\text{O}_5$	342.37	118 $^{\circ}$	32.79	shining wild yellow	4.09	(4.11)
6a	$\text{C}_{17}\text{H}_{15}\text{N}_1\text{O}_4\text{Cl}_1$	332.76	178 $^{\circ}$	49.30	pale cream	4.21	(4.25)
6b	$\text{C}_{17}\text{H}_{14}\text{N}_1\text{O}_4\text{Cl}_2$	367.21	189 $^{\circ}$	39.79	light pale cream	3.81	(3.78)
6c	$\text{C}_{17}\text{H}_{14}\text{N}_1\text{O}_4\text{Cl}_2$	367.21	182 $^{\circ}$	44.90	dirty brazen gold	3.81	(3.85)
6d	$\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_6\text{Cl}_1$	377.77	191 $^{\circ}$	47.46	silkish yellow	7.41	(7.38)
6e	$\text{C}_{17}\text{H}_{15}\text{N}_1\text{O}_5\text{Cl}_1$	348.76	161 $^{\circ}$	39.45	off white	4.01	(4.04)
6f	$\text{C}_{18}\text{H}_{17}\text{N}_1\text{O}_5\text{Cl}_1$	378.79	152 $^{\circ}$	35.94	dirty wheat sprig	3.69	(3.72)
6g	$\text{C}_{18}\text{H}_{17}\text{N}_1\text{O}_5\text{Cl}_1$	362.79	138	33.67	dirty pale cream	3.86	(3.90)

Table : 2 Spectral data of the Newly Synthesized Compounds

S. No.	Compounds codes	IR (Vibrations in Cm^{-1})
1.	3e	3021.5(-NH), 1680.8(-CONH), 1598.7(-C=C), 2362.0(HC=C), 670.9(mono subs.)
2.	3f	3021.3(-NH), 1672.7(-CONH), 1597.9(-C=C), 2363.8(HC=C), 670.8(mono subs.)
3.	4b	3021.9(-NH), 1680.0(-CONH), 1598.0(-C=C), 2361.7(HC=C), 671.1(mono subs.)
4.	4e	3021.8(-NH), 1680.6(-CONH), 1597.8(-C=C), 2361.5(HC=C), 671.0(mono subs.)
5.	5b	3021.9(-NH), 1697.9(-CONH), 1598.0(-C=C), 2360.5(HC=C), 671.6(mono subs.)
6.	5g	3020.3(-NH), 1686.2(-CONH), 1601.1(-C=C), 2363.6(HC=C), 670.0(mono subs.)
7.	6c	3021.7(-NH), 1683.8(-CONH), 1597.3(-C=C), 2359.3(HC=C), 671.9(mono subs.)
8.	6d	3022.4(-NH), 1656.2(-CONH), 1598.0(-C=C), 2360.2(HC=C), 672.4(mono subs.)

stretching vibrations at 671.6 show mono substitution ring. All the above observations are lent support to the assigned structure of compounds 5b&5g, 6c&6d and other compounds 5a, 5c-5f, 6a-6b, 6e-6g .

The above observations are agreed with the assigned structures of all the mentioned compounds, they were found to possess higher melting points shows thermal stability and also have characteristic colouring properties.

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