



Synthesis, Characterization and Fluorescence study of Certain Cinnamide Derivatives and α , β unsaturated acids

Kausik Ghosh, Arista Chaudhari* and D.S. Seth

Department of chemistry, Chemical research laboratory, St. John's college, agra-282002 (India).

Abstract: A series of Cinnamide were prepared by condensation of appropriate malonic acid derivatives with several aldehydes in presence of condensing agent and in its absence α , β Unsaturated acids were synthesized. The synthesized compounds were characterized by elemental analysis and I.R spectra.

Introduction:

Varley¹ was the first to have used pyridine in malonic acid-aldehyde condensations. Later, Several substituted Cinnammamides have been reported by condensing malonic derivatives such as N-phenyl malonamic acid, N-(2, 3 or 4 methyl)phenyl malonamic acids, N-(2, 3 or 4 -Cl) phenyl malonamic acids, N-(2- methoxy)phenyl malonamic acids, N-(2 and 4 ethoxy)phenyl malonamic acids, N-1- naphthyl, N-2- naphthyl, N-(2)-fluorenyl malonamic acids with aromatic aldehydes in the presence of pyridine. Various substituted N-phenyl cinnamide possess wide spectrum of biological activity. They have been useful as anticonvulsant drugs²⁻⁴, inhibitors of blood platelet aggregation⁵, insecticides⁶ and melanin inhibitors⁷, application of which gave a much reduced pigment deposit on the guinea pig skin after exposure to U.V radiations.

In the course of the present work N-(4-butyl) phenyl malonamic acid and N-(4-isopropyl) phenyl malonamic acid have been condensed with several aldehydes. It has been observed that all the condensation produced the expected α , β Unsaturated acids in the absence of condensing agent

Material and Method:

All reagents and solvents were procured from Sigma Aldrich. The identity of compounds was confirmed by M.P., Elemental analysis and I.R. spectral data. Melting Points were determined in open capillaries on Electro-thermal apparatus and were uncorrected. Infrared (IR) spectra were recorded on Perkin Elmer RX-1 using KBr wafers. Elemental analysis was performed

on Elementor Vario EL III at C.D.R.I., Lucknow. The analytical results of the elements were within ± 0.3 %.

Preparation of Substituted Cinnamamides and α , β Unsaturated acids

The general procedure adopted was to condense equimolecular quantities of malonamic acid and aldehyde in R.B flask in presence of pyridine. The mixture was then heated in an oil bath at 105°-110° C for four hours. The reaction mixture was first observed to melt to a clear solution with effervescence and afterwards it gets solidified. The solid product was extracted with a saturated solution of sodium bicarbonate and then filtered and washed with water 3-4 times. The filtrate gave no solid on acidification with Conc. HCl. The residue was purified by recrystallisation from ethanol and purity was checked by T.L.C (Methanol/Benzene). When the same procedure was carried out in absence of pyridine, then α , β Unsaturated acids were obtained.

Result:

The I.R spectrum on Perkin Elmer spectrophotometer of N-(4-butyl) phenyl cinnamide reveals absorption at 3290 cm^{-1} (-NH stretching), 1662 cm^{-1} (CONH group), 1610 cm^{-1} (-C=C- stretching for phenyl conjugation) 2956 cm^{-1} , 1532 cm^{-1} , 1440 cm^{-1} (aromatic characters). The I.R spectrum on Perkin Elmer spectrophotometer of Benzal N-(4-butyl) phenyl malonamic acid reveals absorption at 3285 cm^{-1} (-NH stretching), 1655 cm^{-1} (CONH group), 1605 cm^{-1} (-C=C- stretching for phenyl conjugation) 3300 cm^{-1} .

Table 1: Cinnamamide obtained by the condensation of N-(4-butyl) phenyl Malonamic acid with different aldehydes

S.NO	Aldehyde	Mol Formula of Cinnamamide	M.P °C	Yield %	Nitrogen	
					Found	Cal
1	Benzaldehyde	C ₁₉ H ₂₁ ON	149	54.94	5.22	5.01
2	2-methoxy benzaldehyde	C ₂₀ H ₂₃ O ₂ N	138	46.35	4.60	4.53
3	4-methoxy benzaldehyde	C ₂₀ H ₂₃ O ₂ N	141	49.66	4.61	4.53
4	3-nitro benzaldehyde	C ₁₉ H ₂₀ ON ₂	223	50.47	8.72	8.64
5	3-methoxy-4-hydroxy benzaldehyde	C ₂₀ H ₂₃ O ₃ N	118	40.88	4.44	4.30
6	3,4 dichloro benzaldehyde	C ₁₉ H ₁₉ ONCl ₂	177	44.11	4.15	4.02

Table 2: Cinnamamide obtained by the condensation of N-(4-isopropyl) phenyl Malonamic acid with different aldehydes

S.NO	Aldehyde	Mol Formula of Cinnamamide	M.P °C	Yield %	Nitrogen	
					Found	Cal
1	Benzaldehyde	C ₁₈ H ₁₉ ON	144	57.04	5.31	5.28
2	2-methoxy benzaldehyde	C ₁₉ H ₂₁ O ₂ N	132	51.19	4.80	4.74
3	4-methoxy benzaldehyde	C ₁₉ H ₂₁ O ₂ N	137	47.78	4.83	4.74
4	3-nitro benzaldehyde	C ₁₈ H ₁₈ O ₃ N ₂	210	51.94	9.52	9.03
5	3-methoxy-4-hydroxy benzaldehyde	C ₁₉ H ₂₁ O ₃ N	113	48.54	4.59	4.50
6	3,4 dichloro benzaldehyde	C ₁₈ H ₁₇ ONCl ₂	169	42.16	4.22	4.19

Table 3: α : β Unsaturated acids obtained by the condensation of N-(4-butyl) phenyl Malonamic acid with different aldehydes

S.NO	Aldehyde	Mol Formula of Cinnamamide	M.P °C	Yield %	Nitrogen	
					Found	Cal
1	Benzaldehyde	C ₂₀ H ₂₁ O ₃ N	190	47.46	4.45	4.33
2	2-methoxy benzaldehyde	C ₂₁ H ₂₃ O ₄ N	165	40.57	4.01	3.96
3	4-methoxy benzaldehyde	C ₂₁ H ₂₃ O ₄ N	167	37.68	4.02	3.96
4	3-nitro benzaldehyde	C ₂₀ H ₂₀ O ₅ N ₂	188	38.88	7.69	7.60
5	3-methoxy-4-hydroxy benzaldehyde	C ₂₁ H ₂₃ O ₅ N	251	44.32	3.82	3.79
6	3,4 dichloro benzaldehyde ⁶	C ₂₀ H ₁₉ O ₃ NCl ₂	231	36.55	3.62	3.57

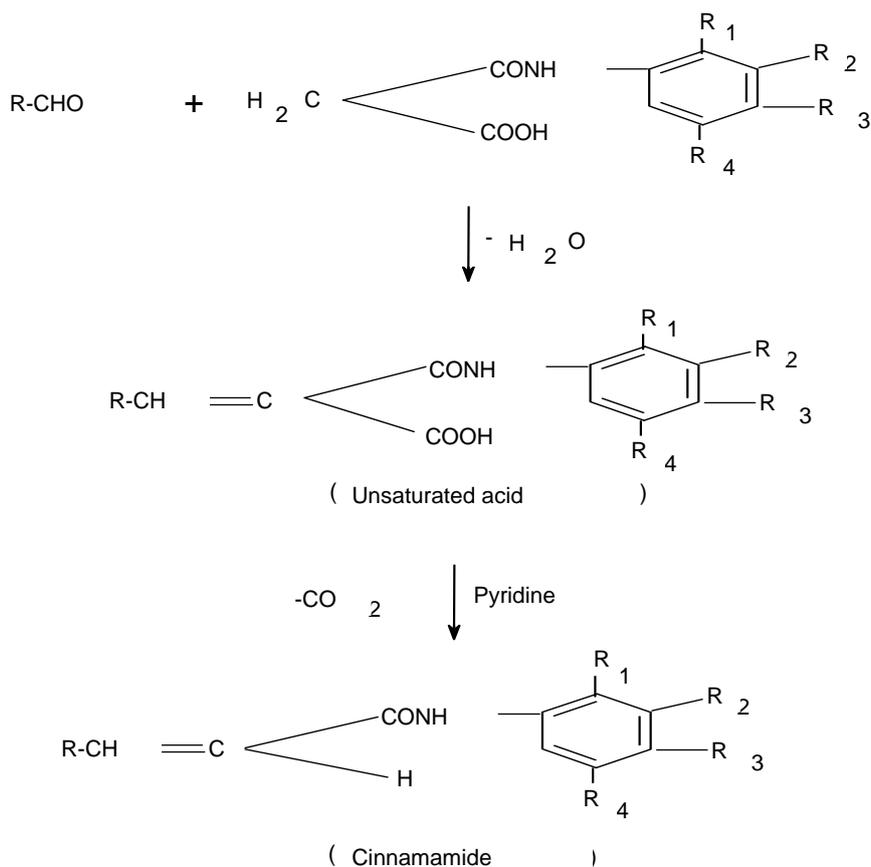
Table 4: α : β Unsaturated acids obtained by the condensation of N-(4-isopropyl) phenyl Malonamic acid with different aldehydes

S.NO	Aldehyde	Mol Formula of Cinnamamide	M.P °C	Yield %	Nitrogen	
					Found	Cal
1	Benzaldehyde	C ₁₉ H ₁₉ O ₃ N	182	48.85	4.63	4.53
2	2-methoxy benzaldehyde	C ₂₀ H ₂₁ O ₄ N	155	44.51	4.18	4.12
3	4-methoxy benzaldehyde	C ₂₀ H ₂₁ O ₄ N	161	41.54	4.18	4.12
4	3-nitro benzaldehyde	C ₁₉ H ₁₈ O ₅ N ₂	182	42.61	8.12	7.90
5	3-methoxy-4-hydroxy benzaldehyde	C ₂₀ H ₂₁ O ₅ N	234	39.66	4.01	3.93
6	3,4 dichloro benzaldehyde ⁶	C ₁₉ H ₁₇ O ₃ NCl ₂	217	42.55	3.82	3.70

Table 5: Fluorescence of Cinnamamide under ultra-violet light

S.NO	Name of the compound (Colour in day light)	Fluorescence under ultraviolet light	
		Alcoholic solution dropped on a chromatographic filter paper	Alcoholic solution adsorbed on a column of silica gel
1	N-(4-butyl) phenyl Cinnamamide(light yellow)	Dark yellow	Dark yellow
2	N-(4-butyl) phenyl-2- methoxyCinnamamide(super white)	No change	No change
3	N-(4-butyl) phenyl-4- methoxyCinnamamide(yellowish white)	Light yellow	Dark yellow
4	N-(4-butyl) phenyl-3-nitro Cinnamamide(yellowish white)	Dark yellow	Dark yellow

Reaction can be schematically represented as:



R = phenyl, 2-methoxy phenyl, 3-NO₂ phenyl, 3- methoxy, 4-hydroxy phenyl, 4-methoxy phenyl, 3, 4- dichloro phenyl (carboxylic -OH group), 2960 cm⁻¹, 1543 cm⁻¹, 1440 cm⁻¹ (aromatic characters).

The I.R spectrum on Perkin Elmer spectrophotometer of N-(4-isopropyl) phenyl Cinnamamide reveals absorption at 3300 cm^{-1} (-NH stretching), 1670 cm^{-1} (CONH group), 1600 cm^{-1} (-C=C- stretching for phenyl conjugation) 2950 cm^{-1} , 1522 cm^{-1} , 1430 cm^{-1} (aromatic characters). The I.R spectrum on Perkin Elmer spectrophotometer of Benzal N-(4-isopropyl) phenyl malonamic acid reveals absorption at 3285 cm^{-1} (-NH stretching), 1653 cm^{-1} (CONH group), 1600 cm^{-1} (-C=C- stretching for phenyl conjugation) 3310 cm^{-1} (carboxylic -OH group), 2962 cm^{-1} , 1534 cm^{-1} , 1444 cm^{-1} (aromatic characters).

The melting points, percentage yield and analytical results are reported in Table 1 - 4. Title compounds were observed under ultraviolet lamps (Phillips U.V Lamp, 80W;

high pressure mercury bulb) for their fluorescence and reported in Table V.

Acknowledgement: The authors thank the authorities of the CDRI, Lucknow for spectral and analytical data.

References:

- [1] Varley, *Bull.Chim.Soc.*, 1899,21, 143 and 414.
- [2] Kyowa Kakko Kogyo Co. Ltd., Ihra Chemical Industry Co.Ltd.,Jpn. Kokai Tokyo Koho JP 58, 92, 643,(83,92,643) 02 Jun 1983.
- [3] J.Li.Yiyao Gongye, 1985, 16(10), 465-7 (Ch).
- [4] S.Peng,W.Liu, J.Zhuo and Y.Pei, *J.Mol.Sci.*,1986, 4(2), 1637.
- [5] I.Katsumi,H.Kondo, K.Yamashita, T.Hidaka, K.Ho Soe, T.Yamashita and K.Watanabe, (Kanegafuchi.Chem. Ind.Co.) *Jpn.Kokai Tokyo Koho JP 61,57, 567 (8657,567)*,24 Mar 1987.
- [6] D.G.Kuhn (American Cyanamide Co.) U.S. US 4, 659, 857, 21 Apr. 1987.
- [7] K.Hori, K.Nakamura, M.Kawai, I.Mogi,G.Imokawa and N. Takaishi (Kao Corpn) *Jpn. Kokai Tokyo Koho JP. 6256, 459(87 56, 459)* 12 Mar 1987.