

Synthesis of 4-Styryl Coumarins by Using Coumarin-4-Acetic Acids

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Introduction

Coumarins-4-acetic acids on reaction with aldehydes like benzaldehyde, anisaldehyde give corresponding 4-styryl coumarins¹ and Benzocoumarin-4-acetic acids give similar products on reaction with aromatic aldehydes.

Experimental

All melting points are uncorrected. IR spectra were recorded on a FITR spectrometer and NMR (CD₃COOD) spectra on a 60MHz.

Coumarin-4-acetic acid preparation

On heating anhydrous citric acid and conc. H₂SO₄ in a water bath followed by cooling gave clear solution. Appropriate phenol or naphthol was added to it along with H₂SO₄. The reaction mixture was then kept for 48hrs. at room temperature and then poured into ice-water due to which solid compound got separated and which was then crystallized from appropriate solvent.

4-styryl coumarins (Ia to Ie and IIa to IIe)

Coumarin-4-acetic acid and appropriate aldehyde (vaniline/piperonal) on dissolving in piperidine followed by heating in an oil bath at 140^oC for 2 hrs. On cooling and dilution with water followed by acidification with diluted HCl, solid was obtained and it was crystallized from appropriate solvent.

Structure of IIa was established from its spectral data as given below

IR spectra

IIa 3055cm⁻¹ (phenolic -OH), 2983.7 and 2947 cm⁻¹ (Ar-C-H stretching), 1712 cm⁻¹ (>C=O), 1618.2cm⁻¹ (-OCH₃), 1600cm⁻¹ (aromatic), 881cm⁻¹(Ar-H)

NMR spectra

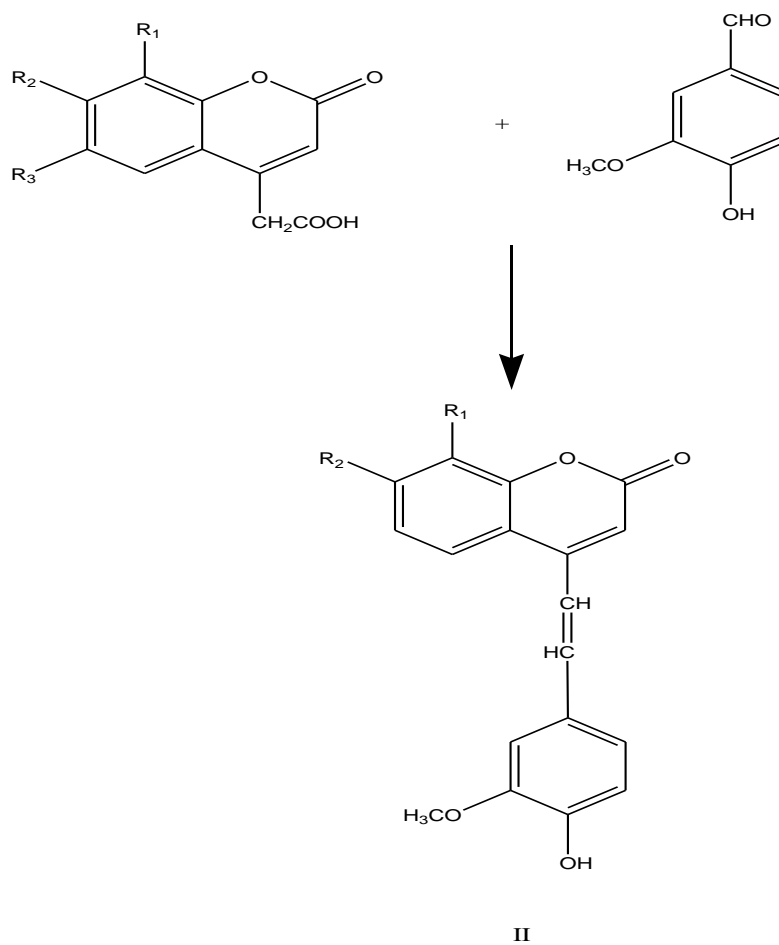
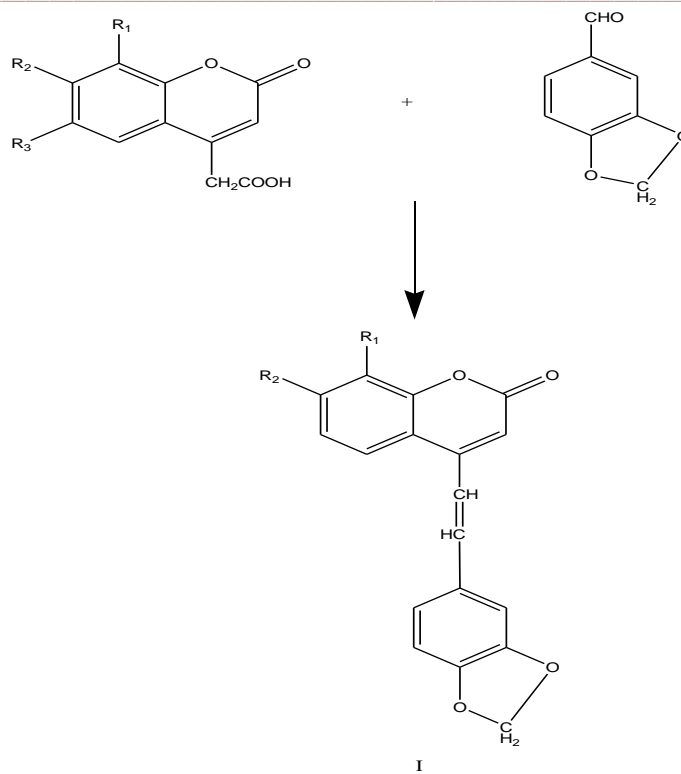
δ (CD₃COOD)

1.6 (3H, s, -CH₃), 2.0 (3H, s, -OCH₃), 2.3(2H, d, -CH=CH), 5.9 (-H of coumarin, s, -COCH=C-), 6.5-7.4 (6H, m, ArH), 10.2 (1H, s, -OH)

Physical data of compounds 1-10

No.	Compound No.	M.F.	M.P. ^o C	Solvent used
1	Ia	C ₁₉ H ₁₄ O ₄	130	Petroleum ether
2	Ib	C ₁₉ H ₁₄ O ₄	136	Petroleum ether
3	Ic	C ₂₂ H ₁₄ O ₄	152	Petroleum ether /Benzene
4	Id	C ₂₂ H ₁₄ O ₄	165	Benzene
5	Ie	C ₁₈ H ₁₂ O ₅	175	Benzene
6	IIa	C ₁₉ H ₁₆ O ₄	131	Petroleum ether
7	IIb	C ₁₉ H ₁₆ O ₄	136	Petroleum ether
8	IIc	C ₂₂ H ₁₆ O ₄	170	Petroleum ether/ Benzene
9	IId	C ₂₂ H ₁₆ O ₄	172	Benzene
10	IIe	C ₁₈ H ₁₄ O ₄	185	Benzene

All compounds gave satisfactory C, H analysis



$a = R_1 = R_3 = H, R_2 = -CH_3, b = R_1 = R_2 = -H, R_3 = -CH_3, c = R_1-R_2 = -Ph, R_3 = -H,$

$d = R_1 = -H, R_1 - R_2 = -Ph, e = R_1 = R_3 = -H, R_2 = -OH$

Reference

- [1] Gharade A.D. and Ghiya B. J., J. Indian Chem. Soc., 69, 1992, 397-398.