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NOTE

Synthesis of 1,2-Dihydronaphthalene by Cyclization of Dilactone

SUJATA S. DESHMUKH* and SHUBHRA BANERJEE
Department of Chemistry, Institute of Science, Nagpur-400 001, India

1,2-Dihydronaphthalene has been synthesised by acid cleavage and cyclisation in one step of dilactone, obtained from ferulic acid by its oxidative coupling.

During the studies in the process of synthesis of different 1-phenylnaphthalene systems (1) by one step cyclization with various reagents[1], the dilactone (2) obtained by oxidative coupling of ferulic acid (3) was found to cyclise with PPA and conc. H_2SO_4 to give the 1,2-dihydronaphthalene system.

1,2-Dihydronaphthalene system (4) is an important intermediate in the synthesis of cyclolignans. Cartwright and Haworth[2] established the dilactone structure (2) for the product of oxidative coupling of ferulic acid (3) and achieved its conversion to 1,2-dihydronaphthalene system. In the present work, the dilactone (2) was found to cleave and to cyclize into (4) very easily in one step with conc. H_2SO_4 and PPA which establishes this as a direct path towards the synthesis of different cyclolignans.

Charactersation of 1,2-dihydronaphthalene product (4) was done on the basis of its m.p., m.m.p. with the authentic sample,[3, 5] a broad peak at 3350 cm^{-1} for —OH phenolic absorption and a sharp peak at 1700 cm^{-1} for acid in the IR and λ_{max} 245 (log ε 4.38), 295 (log ε 3.96) and 340 mm (log ε 4.14) in the UV. The sample was insoluble for NMR.

Ferulic acid (3)

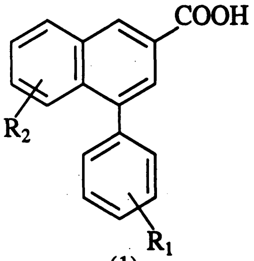
Knoevenagel reaction of vanilline (22.8 g) and malonic acid (46.8 g) in piperidine (80 mL) for 2 h yielded ferulic acid (26 g) as a white solid, crystallised from hot water, m.p. 170°C (lit. 173°C)[4].

Dehydroferulic acid dilactone (2)

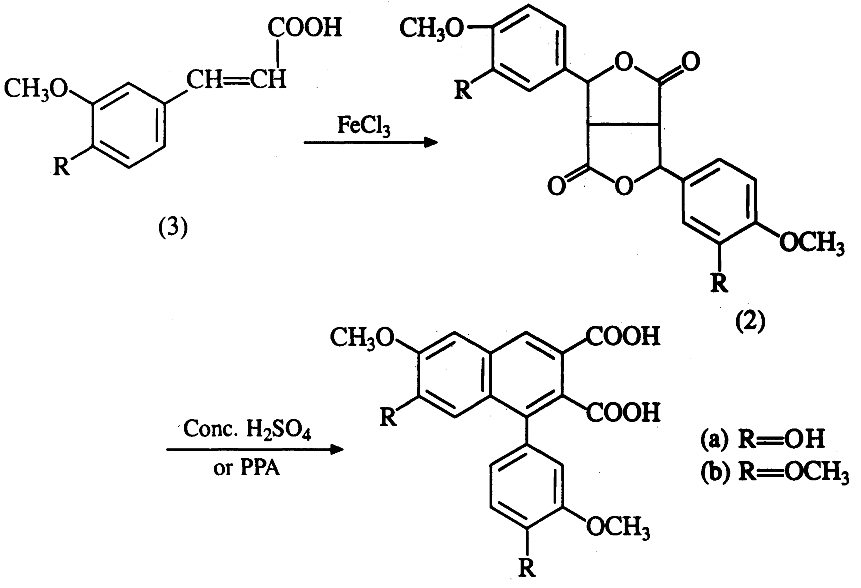
Ferulic acid (20 g) was subjected to oxidative coupling by passing air in its aq. methanolic solution (200 mL methanol and 1.5 lit. water) in presence of ferric chloride (40 g) for 10 h. The ferric salt was separated and decomposed with conc. HCl (50 mL) which yielded the dilactone (2) (4.5 g), crystallized from acetone as colorless plates, m.p. 208–209°C (lit. 208–209°C)[4], IR: 3420 (—OH phenolic), 1985 (sh) cm^{-1} (C=O lactone).

1,2-Dihyhydronaphthoic acid (4) : Cyclization with PPA

Dilactone (2) (1 g) was refluxed with PPA (prepared from 5–6 g P_2O_5 and 6–7



(1)



(4)

mL orthophosphoric acid) at 100°C for 1 h. The reaction mixture was poured in crushed ice when 1-(3-methoxy-4-hydroxyphenyl)-6-methoxy-7-hydroxy-1,2-dihydronaphthalene-2,3-dicarboxylic acid (4) was obtained as greenish brown solid crystallised from alcohol water mixture,[5] m.p. 234°C, eq. wt. 350.

Cyclization with conc. H_2SO_4

The same compound (4) was obtained when the dilactone[5] (2) (1 g) was cleaved with conc. H_2SO_4 (5 mL) at 0°C for 24 h; confirmed by its m.p., m.m.p. and eq. wt.

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