Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 89, Number 3, June 1980, pp. 301–307.

Reaction of β-naphthyl cinnamate with aluminum chloride

T MANIMARAN, T JAYACHANDRAN and
V T RAMAKRISHNAN*

Department of Organic Chemistry, University of Madras, Madras 600 025, India

*Present address: Department of Chemistry, University of Illinois, Chicago Circle, Illinois 60680, U.S.A.

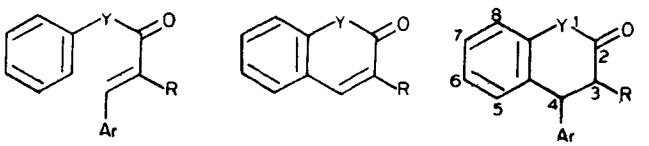
MS received 19 September 1979; revised 24 April 1980

Abstract. Reaction of β-naphthyl cinnamate with anhydrous aluminum chloride afforded 9-hydroxyphenalenone 5 by a Fries rearrangement followed by a dearylative cyclisation. 9-Hydroxy-3-phenyl-2,3-dihydrophenalen-1-one 7 was identified as an intermediate.

Keywords. Fries reaction; beta-naphthyl cinnamate; dearylative cyclization; 9-hydroxy-phenalen-1-one; aluminum chloride.

1. Introduction

In an earlier paper, we have described (Manimaran *et al* 1975) the synthesis of coumarins, thiacoumarins and carbostyrils 2 by the reaction of anhydrous aluminum chloride with the cinnamoyl derivatives 1 of phenols, thiophenols and anilines respectively. In continuation of this work, we have also studied (Manimaran and Ramakrishnan 1979) the reactions with α-phenylcinnamoyl compounds 1 (R = C_6H_5) which yielded 3-phenylcoumarins and related systems 2 (R = C_6H_5); likewise α-methylcinnamoyl compounds 1 (R = CH_3) afforded 3-methyl derivatives 2 (R = CH_3) (Manimaran *et al* 1979). These reactions are explained by invoking an intermediate 3,4-dihydroderivative 3, by its independent synthesis and further conversion to the final product 2 in the oxygen and nitrogen systems. Thus, in general, the steps involved in the reactions are cyclisation of 1 to 3 followed by dearylation of the C_4-aryl group to yield 2.



1 2 3

Y = O, S, NH
R = H, CH_3, C_6H_5

2. Results and discussion

However, the reaction of β-naphthyl cinnamate 4 with anhydrous aluminum chloride in chlorobenzene at 95° for 2 hr by a general procedure followed in other systems, afforded a product identified as the 9-hydroxyphenalenone 5. The formation of the phenalenone 5 could be rationalised as represented in chart 1.

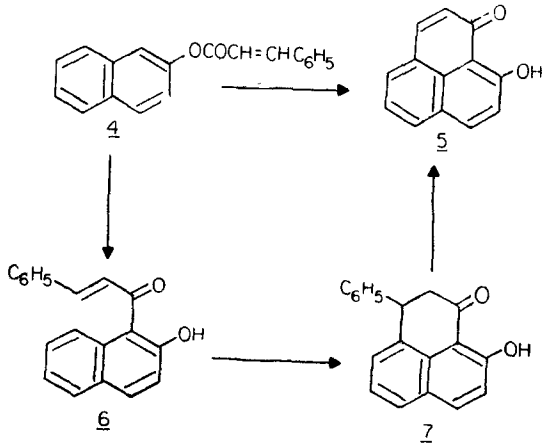


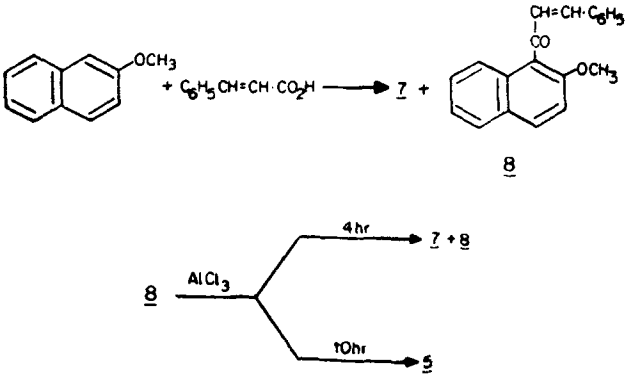
Chart 1.

Thus the action of aluminum chloride on β-naphthyl cinnamate 4 effects a Fries rearrangement to 6 followed by cyclisation to the dihydrophenalenone 7 which on dearylation could result in the product 5.

In order to gain a better understanding of the mechanism of the above reaction, efforts were made to isolate the possible intermediates 6 and 7. Hence it was felt that a milder reaction condition would be an ideal approach. Thus, the ester 4 was treated with aluminum chloride in carbon disulphide medium which afforded a mixture of the starting ester 4 and the dihydrophenalenone 7. The dihydro compound 7 on further treatment with aluminum chloride in chlorobenzene at 95° for 1 hr gave the phenalenone 5, thus establishing 7 as an intermediate in the above reaction. Since the chalcone 6 was not identified even in the above milder reaction condition, probably it is very unstable in the presence of aluminum chloride. Hence a different route was envisaged for the synthesis of the hydroxy-chalcone 6.

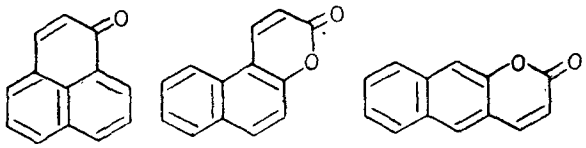
Treatment of β-naphthyl methyl ether with cinnamic acid afforded a mixture of the methoxy-chalcone 8 and the dihydrophenalenone 7, the latter being the predominant product. Whereas, this reaction has been reported by Koelsch and Anthes (1941) to give mainly the chalcone 8; in spite of their expectations and efforts, the dihydro compound 7 could not be obtained.

The methoxy-chalcone 8 on treatment with aluminum chloride in carbon disulphide at room temperature for 4 hr afforded a mixture of the starting material 8 and the dihydrophenalenone 7 whereas, mere increasing of the reaction time to 10 hr resulted in the formation of the phenalenone 5. Thus it is seen that the methoxy-chalcone 8 does give the dihydrophenalenone 7 and ultimately the phenalenone 5, implying that it is a highly reactive intermediate. Hence it could be assumed that the hydroxy-chalcone 6 would have also been formed as an intermediate in the reaction of β-naphthyl cinnamate with aluminum chloride yielding



the hydroxy-phenalenone 5. The Fries rearrangement would be normally expected to give products with migration of the acyl group to the 1-position of the naphthyl ring rather than to the 3-position and hence the structure 6 for the hydroxy-chalcone.

A parallel example is the formation of phenalenone 9 from 1-cinnamoyl-naphthalene (Williams and Schotter 1974). The coumarin structures A and B were discounted for the product of the reaction of β-naphthyl cinnamate with aluminum chloride, on the basis of spectral data and comparison with authentic samples of A and B (Narasimhan and Mali 1975).



9 A B

The dihydrophenalenone 7 on treatment with acetic anhydride afforded a semisolid identified as the acetate of the hydroxy-chalcone 6, resulting from the rupture of the C_3–C_{3a} bond. The mass spectral fragmentation for the dihydrophenalenone 7 is depicted in chart 2 and for the acetate in chart 3.

The NMR spectrum of the dihydrophenalenone 7 showed a two-line signal for the -OH proton, which was unaffected by double irradiation techniques at the other centres; this behaviour is probably due to the two tautomeric forms 7′ and 7″ for which examples are known (Jackman and Sternhell 1969); probably the existence of these tautomeric, hydrogen bonded structures prohibit the easy formation of the acetate for the hydroxy-compound 7. The C_2–C_3 protons were seen as a clear ABX spectra; $J_{gem} = 8$ Hz, $J_{trans} = 6$ Hz, $J_{cis} = 2$ Hz. Spin decoupling techniques simplified the 8-line signal of the methylene protons H_A and H_B into a simple *AB* quartet (J = 8 Hz) when irradiated at the region of the methine proton, whereas the 4-line signal of the methine proton H_X collapsed into a singlet on irradiation at the methylene region.

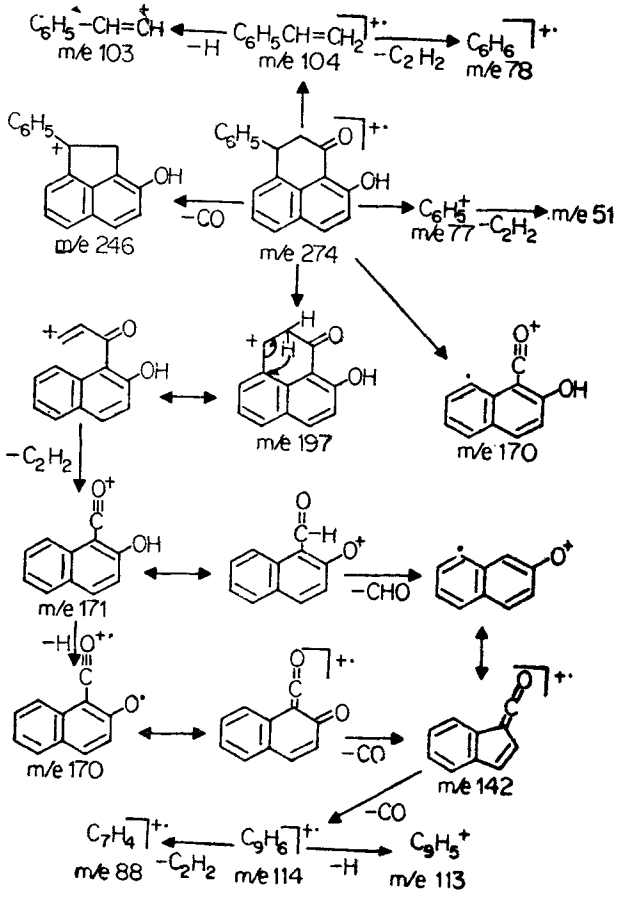

m/e 103
m/e 104
m/e 78
m/e 246
m/e 274
m/e 77
m/e 51
m/e 197
m/e 170
m/e 171
m/e 170
m/e 142
m/e 88
m/e 114
m/e 113

Chart 2.

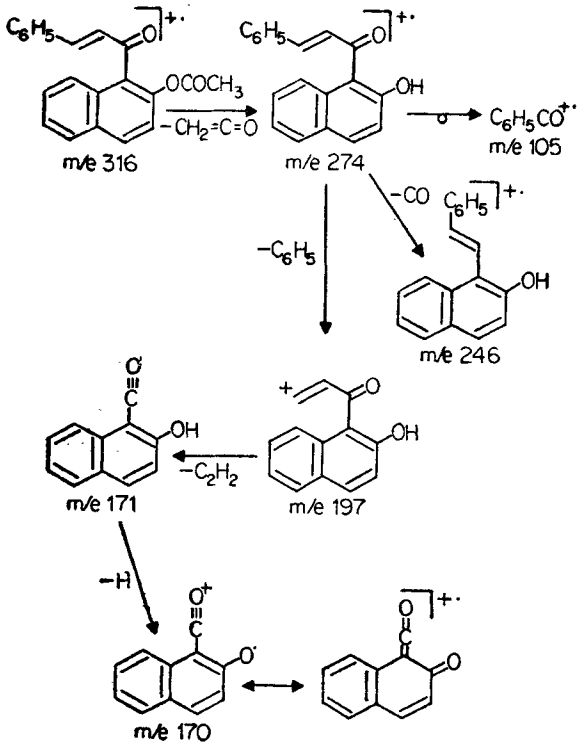
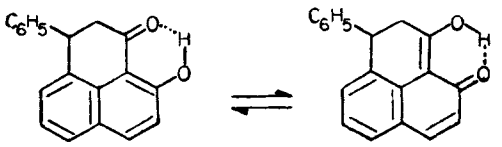


Chart 3.



7' 7''

3. Experimental

Melting points are uncorrected. The IR spectra were recorded on a Beckmann Model IR-20 spectrometer. NMR spectra were obtained for solutions in deuteriochloroform with JEOL PS-100 and Varian A-60 spectrometers using tetramethylsilane as internal standard. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E mass spectrometer.

3.1 *Reaction of β-naphthyl cinnamate with anhydrous aluminum chloride*

(a) A mixture of the ester 4 (2 g) and aluminum chloride (5 g) in chlorobenzene (25 ml) was heated at 95° for 2 hr. The reaction mixture was treated with iced hydrochloric acid, extracted with chloroform, dried ($MgSO_4$) and concentrated and the residue was chromatographed over a silica gel column. On elution with a mixture (1 : 9) of chloroform and benzene, 9-hydroxy-phenalenone 5 was obtained

as an yellow solid. (0·42 g, 30%); m.p. 200–201° lit. (Koelsch and Anthes 1941) m.p. 201°; ν_{max} (KBr) : 1620–30 cm^{-1}; δ 7·0–8·2 (7H, m, ArH) and 16·25 (1H, s, OH); m/e 196 (M^+), 169, 168, 145, 144, 107, 74, 59 and m* 144 (196 → 168).

(b) The above reaction was carried out with carbon disulphide (30 ml) as the solvent, instead of chlorobenzene, for 4 hr under reflux. Work-up of the reaction mixture as above furnished the phenalenone 5 (450 mg, 32%).

(c) The ester 4 (2 g) was stirred at room temperature with aluminum chloride (5 g) in carbon disulphide for 10 hr. Work-up followed by chromatography gave the starting ester 4 (900 mg) on elution with benzene. Using a mixture (1 : 19) of chloroform and benzene as eluant 9-hydroxy-3-phenyl-2,3-dihydrophenalen-1-one 7 (320 mg) was obtained; m.p. 113–114°. ν_{max} (KBr) 1640–50 cm^{-1}; δ (100 MHz) 2·88 (1H, q, C_2–H cis to C_3–H, $J_{gem} = 8$ Hz, $J_{cis} = 2$ Hz), 3·08 (1H, q, C_2-H trans to C_3–H, $J_{gem} = 8$ Hz, $J_{trans} = 6$ Hz), 5·52 (1H, q, C_3-H, $J_{trans} = 6$ Hz, $J_{cis} = 2$ Hz), 7–8 (10H, m, ArH) and 9·46, 9·54 (1H, 2s, OH) m/e 274 (M^+, 100%), 246(8), 197(20), 171(28), 170(96), 142(53), 115(20), 114(88), 113(20), 104(24), 103(18), 88(13), 78(15), 77(18). m* 118·6 (170 → 142) and 91·5 (142 → 114) (Found : C, 83·35; H, 5·30. $C_{19}H_{14}O_2$ requires C, 83·19; H, 5·14%).

3.2 *Reaction of 9-hydroxy-3-phenyl-2,3-dihydrophenalen-1-one 7*

A mixture of the compound 7 (1 g) and aluminum chloride (3 g) in chlorobenzene (25 ml) was heated at 95° for 75 min. Work-up and chromatography afforded 9-hydroxy-phenalen-1-one 5 (560 mg, 78%).

3.3 *Reaction of β-naphthyl methyl ether and cinnamic acid*

A mixture of cinnamic acid (14 g), β-naphthyl methyl ether (14 g) and phosphorus pentachloride (20 g) was heated in dry benzene (100 ml) under boiling condition for 5 min, then cooled and treated with aluminum chloride (14 g) which was added in small portions. The dark-red solution was boiled for 10 min and then decomposed with ice and dil. hydrochloric acid. The benzene layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried ($MgSO_4$), concentrated and the residue was chromatographed over a silica gel column. On elution with benzene, the dihydrophenalenone 7 was isolated (7·9 g, 32%). Elution with a mixture (1 : 9) of chloroform and benzene afforded 1-cinnamoyl-2-methoxy-naphthalene 8 (4·55 g, 18%); m.p. 140–141° (lit. m.p. 141°); ν_{max} (KBr) 1660–70 cm^{-1}; δ 3·9 (3H, s, OCH_3) and 7·2–8·2 (13 H, m).

3.4 *Reaction of 1-cinnamoyl-2-methoxy-naphthalene 8*

(a) The cinnamoyl naphthalene 8 (1 g) was stirred in carbon disulphide (30 ml) with anhydrous aluminum chloride (3 g) for 4 hr at room temperature. Work-up of the reaction mixture as above and chromatographic separation furnished 9-hydroxy-3-phenyl-2,3-dihydrophenalenone 7 (150 mg) in addition to the recovered 8 (420 mg).

(b) A second run of the above reaction was carried out with the reaction time increased to 10 hr. The reaction mixture was worked up which showed neither the starting material 8 nor the dihydro compound 7 on TLC; column chromatography of the residue gave 9-hydroxy-phenalen-1-one 5 (450 mg, 66%).

(c) When the above reaction was carried out with tetrachloroethane as solvent at 95° for 30 min, phenalenone 5(495 mg, 73%) was obtained after chromatography. The dihydro-phenalenone was not found in the reaction mixture unlike the reaction of phenyl cinnamate with aluminum chloride in tetrachloroethane which resulted only in the 4-phenyl-3,4-dihydrocoumarin (Christian and Amin 1960).

3.5 *Acetylation of 9-hydroxy-3-phenyl-2,3-dihydrophenalenone 7*

The dihydrophenalenone 7 (200 mg) was stirred with acetic anhydride (3 ml), in the presence of few crystals of *para*-toluene sulphonic acid, at room temperature for 10 hr. The TLC showed only the starting material 7. The reaction mixture was then heated at 95° for 15 hr, till the disappearance of 7 on TLC, poured over ice and extracted with chloroform. The organic layer was dried ($MgSO_4$), concentrated and the residue chromatographed to isolate 2-acetoxy-1-cinnamoyl-naphthalene as a semisolid (230 mg, 100%); ν_{max} ($CHCl_3$) 1640–50, 1755–65 cm^{-1}; δ 2·15 (3H, s, CH_3) and 7·0–8·2 (13 H, m); m/e 316 (M^+, 28%), 274 (100), 246 (11), 197 (73), 171 (8), 170 (90), 105 (71), 71 (36), 69 (34) (Found : C, 79·51; H, 5·40. $C_{21}H_{16}O_3$ requires C, 79·73; H, 5·10%).

Acknowledgements

We thank Prof. Walter Lwowski, New Mexico State University, USA, and Central Leather Research Institute, Madras, for spectral data and the University Grants Commission of India for financial support and Prof. S Swaminathan for his constant encouragement.

References

Christian C M and Amin G C 1960 *J. Sci. Ind. Res. (India)* **B19** 175

Jackman L M and Sternhell S 1969 *Applications of nuclear magnetic resonance spectroscopy in organic chemistry* (London : Pergamon) p. 382

Koelsch C F and Anthes J A 1941 *J. Org. Chem.* **6** 558

Manimaran T, Natarajan M and Ramakrishnan V T 1979 *Proc. Indian Acad. Sci.* **A88** Part 1 p. 125

Manimaran T and Ramakrishnan V T 1979 *Indian J. Chem.* (accepted for publication)

Manimaran T, Thiruvengadam T K and Ramakrishnan V T 1975 *Synthesis* p. 739

Narasimhan N S and Mali R S 1975 *Tetrahedron* **31** 1005

Williams H J and Schotter R G 1974 *Aust. J. Chem.* **27** 685