

Photo-Fries reaction of 1-naphthyl cinnamate

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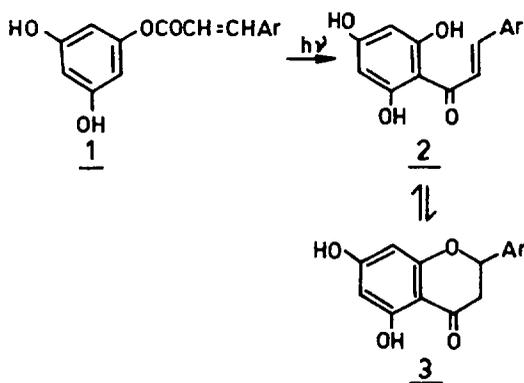
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Abstract. The photo-Fries reaction of 1-naphthyl cinnamate afforded 2-cinnamoyl-1-naphthol. Likewise, 1-naphthyl *p*-methyl-cinnamate gave 2-(*p*-methylcinnamoyl)-1-naphthol. The product chalcones were cyclised into the respective flavanones.

Keywords. 1-Naphthyl cinnamate; 1-naphthyl *p*-methylcinnamate; 1-naphthyl α -methylcinnamate; 2-cinnamoyl-1-naphthol; 2-(*p*-methylcinnamoyl)-1-naphthol; 7,8-benzoflavanone; photo-Fries reaction.

1. Introduction

The photo-Fries reaction of aryl esters is known since 1960 when the first report on the photolysis of phenyl acetate appeared (see Bellus 1971 for a review). Since then studies were initiated on the mechanistic aspect as well as the synthetic applications of the photo-Fries reaction. In such a study, the synthesis of naturally occurring chalcones (2) and flavanones (3) by the photo-Fries reaction of aryl cinnamates (1) have been reported (Ramakrishnan and Kagan 1970).

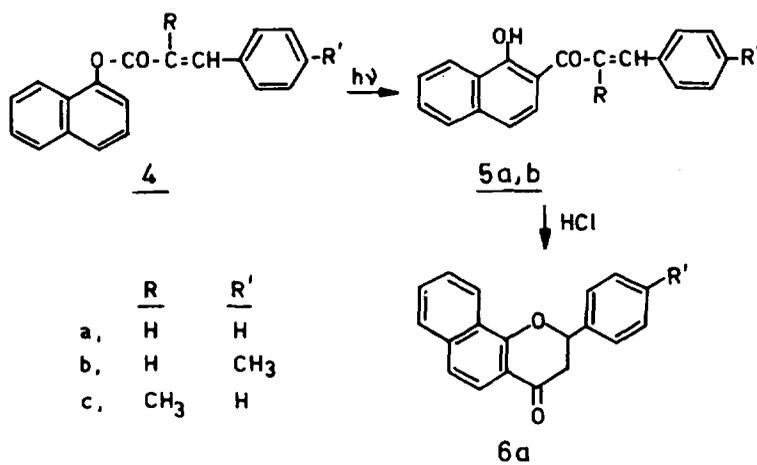


2. Results and discussion

We wish to report here the photo-Fries reaction of 1-naphthyl cinnamates (4). Irradiation (254 nm) of 1-naphthyl cinnamate (4a) in benzene solution in a Rayonet photochemical reactor for 10 hours furnished an orange red solid, mp 127–8°C. The

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infrared spectrum showed the carbonyl absorption at 1630 cm^{-1} . The $^1\text{H NMR}$ showed aromatic protons (13H) at $\delta 7.2\text{--}8.0$ and an hydroxy proton at $\delta 14.77$. The mass spectrum showed the molecular ion at m/e 274 and the elemental analysis agreed with the molecular formula $\text{C}_{19}\text{H}_{14}\text{O}_2$. Based on the above data, a chalcone structure obtained by Fries reaction is evident for the orange-red product (5a). However, the position of the cinnamoyl group in the product was perplexing since no clue could be obtained from the complex $^1\text{H NMR}$ spectrum. The possible positions of the cinnamoyl group are 2,4,5 and 7 of 1-naphthol, based on the mechanism of Fries reaction (Bellus 1971). The chalcone (5a) when treated with hydrogen chloride gas in methanol solution gave a pale yellow solid, m.p. $112\text{--}3^\circ\text{C}$, showing the characteristic signals for a CHCH_2 system with geminal as well as *cis* and *trans* couplings in the $^1\text{H NMR}$ spectrum; hence the flavanone structure is imperative and could arise only from the 2-cinnamoyl-1-naphthol. Thus the photo-Fries reaction of 1-naphthyl cinnamate (4a) afforded 2-cinnamoyl-1-naphthol (5a).



Likewise irradiation of 1-naphthyl *p*-methylcinnamate (4b) furnished an orange red solid, m.p. $147\text{--}8^\circ$, to which was assigned the chalcone structure, i.e. 2-(*p*-methylcinnamoyl)-1-naphthol (5b), based on its cyclisation into a flavanone with HCl gas. 1-Naphthyl α -methylcinnamate (4c) was also studied, which on irradiation furnished a mixture showing a yellow spot on TLC which however could not be separated by column or preparative thin layer chromatographic methods. While this study was in progress, a parallel report appeared on the photochemical reaction of 1-naphthylacetates, cyclohexane carboxylates and benzoates giving 2-acyl-1-naphthols, in connection with its synthetic usefulness for the synthesis of daunomycinone (Crouse *et al* 1981).

The photolysis of 2-naphthyl cinnamate in benzene, however, furnished only 2-naphthol. This marked difference in the photochemical reaction of 1-naphthyl and 2-naphthyl cinnamates is perplexing. Similarly, the interesting reaction observed (Manimaran *et al* 1980) with the 2-naphthyl cinnamate on treatment with anhydrous aluminium chloride while the 1-naphthyl cinnamate furnished only 1-naphthol under the same conditions is noteworthy. The explanation for such differences is not yet quite clear.

3. Experimental

Melting points are uncorrected. Beckmann IR-20, Varian A-60 and T-60 and Varian MS-30 were used. Tetramethylsilane was used as internal standard for NMR.

3.1 Preparation of 1-naphthyl *p*-methylcinnamate (4b)

p-Methylcinnamoyl chloride (8.1 g, 50 mmol, prepared from *p*-methylcinnamic acid) and thionyl chloride (7.5 ml) in dry benzene were added dropwise to a solution of 1-naphthol (7.2 g, 50 mmol) and pyridine (4 ml) in dry benzene. The reaction mixture was stirred for 14 hours at room temperature and worked up by washing with dil. HCl, an ice-cold solution of sodium hydroxide and water. The organic layer was dried (MgSO₄) and concentrated to get ester (4b) 11.5 g, 80% m.p. 109–111° (benzene-hexane); IR (KBr): 1720 cm⁻¹; ¹H NMR (CDCl₃-CCl₄): δ 2.42 (s, 3H, CH₃), 6.73 (d, α-H, *J* = 16 Hz), 7.1–8.0 (m, 11H, Ar-H), 8.0 (d, β-H, overlapping with Ar-H); *m/e* 288 (M⁺), 145, 143, 117, 91. Found: C, 83.60; H, 5.46; C₂₀H₁₆O₂ required C, 83.33; H, 5.55.

3.2 1-Naphthyl α-methylcinnamate (4c)

From α-methylcinnamoyl chloride and 1-naphthol (50 mmol) the ester (4c) was prepared (9.5 g, 66%) m.p. 98–9° (benzene-hexane); IR (KBr): 1750 cm⁻¹; ¹H NMR (CDCl₃-CCl₄): 2.37 (s, 3H, CH₃), 7.3–8.17 (m, 12H, ArH), 8.23 (s, β-H). *m/e*, 288 (M⁺), 145, 143, 117, 91, 77. Found: C, 83.40; H, 5.56; C₂₀H₁₆O₂ requires C, 83.33; H, 5.55.

1-Naphthyl cinnamate (4a) was prepared as above from cinnamoyl chloride (50 mmol) and 1-naphthol (50 mmol) in 87% yield; m.p. 108–9° (benzene-hexane) (lit. m.p. 109–110°) (Jean d' Ans and Zimmer 1952).

3.3 Irradiation of 1-naphthyl cinnamate (4a)

The ester (4a) (1.0 g) in dry benzene (100 ml), taken in a quartz vessel, was flushed with nitrogen and irradiated in a Rayonet photochemical reactor Model RPR-208 equipped with eight RUL-208 lamps of wavelength 254 nm. The reaction was followed by TLC when the solution turned yellow. The irradiation was stopped after 10 hours, even though the TLC showed the presence of starting material (4a), since the formation of 1-naphthol increased with increase in irradiation time (as per TLC). The solution was concentrated and the mixture (showing only 3 spots on TLC) was chromatographed over a column of silica gel. Elution with hexane furnished 2-cinnamoyl-1-naphthol (5a) as an orange-red solid (0.2 g, 20%) m.p. 127–8°; IR (CHCl₃): 1630 cm⁻¹; ¹H NMR (CDCl₃): δ 7.2–8.0 (m, 13H, Ar-H, α-H, β-H), 14.77 (s, 1H, OH); *m/e* 274 (M⁺), 197, 171, 143, 142, 131, 115, 103, 91, 77. Found: C, 83.30; H, 5.15; C₁₉H₁₄O₂ requires C, 83.20; H, 5.10.

On elution with a mixture of benzene-hexane (1:9) the ester (4a) was obtained (60 mg, 6%); a 1:1 mixture of benzene-hexane eluted only a small quantity of 1-naphthol (30 mg).

3.4 Irradiation of 1-naphthyl *p*-methylcinnamate (4b)

A solution of the ester 4b (1.0 g) in dry benzene (100 ml) taken in a quartz vessel, was irradiated with 254 nm light for 10 hours under nitrogen atmosphere. The reaction

mixture was concentrated and the residue chromatographed over a column of silica gel. Elution with hexane afforded 2-(*p*-methylcinnamoyl)-1-naphthol (**5b**), as an orange-red solid (0.35 g, 35%); m.p. 147–8°; IR (CHCl₃): 1630 cm⁻¹; ¹H NMR (CDCl₃-CCl₄): δ 2.37 (s, 3H, CH₃), 7.0–8.5 (m, 12H, Ar-H, α-H, β-H), 14.8 (s, 1H, OH); *m/e* 288 (M⁺), 197, 171, 145, 117, 102, 91. Found: C, 83.52; H, 5.48; C₂₀H₁₆O₂ requires C, 83.33; H, 5.55.

Elution with a 1:9 mixture of benzene-hexane gave the ester (**4b**) (0.1 g, 10%), while a 1:1 mixture of benzene-hexane gave 1-naphthol (70 mg).

3.5 Irradiation of 1-naphthyl α-methylcinnamate (**4c**)

The ester **4c** (1.0 g) in benzene solution (100 ml) was irradiated for 10 hr with 254 nm light. The yellow solution was concentrated and the residue chromatographed over a silica gel column. Elution with hexane furnished a brown liquid, showing a yellow spot on TLC, which, however, could not be purified further even by preparative TLC. Hence the suspected chalcone (**5c**) could not be characterized.

3.6 Treatment of the chalcone **5a** with HCl gas

The chalcone (**5a**, 0.5 g) was dissolved in methanol and HCl gas passed through the solution and kept at room temperature for 2 days. After concentration under reduced pressure the residue obtained was chromatographed over a column of silica gel. Elution first with hexane furnished the starting material (**5a**) (25 mg, 5%) while later elutions with a mixture of benzene and hexane (1:9) yielded 7,8-benzoflavanone (**6a**) as a pale yellow solid (45 mg, 9%); m.p. 112–113° IR (KBr): 1670 cm⁻¹; ¹H NMR (CDCl₃-CCl₄): δ 2.9–3.1 (m, 2H, CH₂), 5.5–5.75 (dd, 1H, CH-CH₂), 7.2–8.5 (m, 11H, Ar-H). Found C, 83.27; H, 5.08. C₁₉H₁₄O₂ requires C, 83.20; H, 5.10. The poor yield is probably due to loss of material in chromatography.

3.7 Treatment of 2-(*p*-methylcinnamoyl)-1-naphthol (**5b**) with HCl gas

Treatment of **5b** (500 mg) in methanol with HCl gas, as above, followed by chromatography over a silica gel column furnished a light brown solid (50 mg) mp 120–1°, tentatively identified as 4'-methyl-7,8-benzoflavanone (**6b**); IR (KBr): 1660–70 cm⁻¹; ¹H NMR (CDCl₃-CCl₄): δ 2.4 (s, 3H, CH₃), 2.85–3.2 (m, 2H, CH₂), 5.4–5.6 (dd, 1H, CH-CH₂), 7.1–8.2 (m, 10H, Ar-H).

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