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Photo-Fries and Fries reaction of 5,8-dihydro-1-naphthyl esters

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Abstract—Systematic studies were performed on the photo-Fries and the Fries reaction of aliphatic, aliphatic unsaturated, aromatic and aromatic unsaturated esters of 5,8-dihydro-1-naphthol. The Fries reaction of 5,8-dihydro-1-naphthyl acetate in various solvents is also reported.

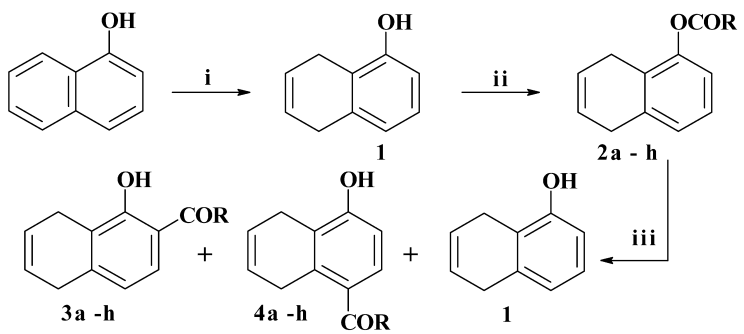
Since the observation of photo-Fries rearrangement in 1960, various aspects of the reaction have been studied.[1,2] Since then studies were initiated on the mechanistic aspects as well as the synthetic applications of photo-Fries reactions.[3–6] Crouse et al. have studied the photo-Fries reaction of esters of 1-naphthol and reported various substituted naphthoquinones derived from the photo-Fries product and their results provide a convenient method for the construction of tricyclic analogues of adriamycinone.[7] Recently, the photo-Fries reaction of tetrahydronaphthyl esters has also been reported.[8] Herein, we report the studies on photo-Fries reaction of 5,8-dihydronaphthyl esters. The 5,8-di-hydro-1-naphthol system will be of great interest in view of the isolated double bond.

In continuation of our interest on the photo-Fries reaction,[9,10] we have carried out the photochemical studies of various esters of 5,8-dihydro-1-naphthol (**1**). In the aliphatic series, the acetate (**2a**), crotonate (**2b**), and sorbate (**2c**) were prepared and their photochemistry studied. In the aromatic series, the benzoate (**2d**), 2-methylbenzoate (**2e**), 2-chlorobenzoate (**2f**), 1-naphthoate (**2g**), and cinnamate (**2h**) were studied and the results of the studies are discussed here.

The irradiation of 5,8-dihydro-1-naphthyl esters (**2a**–**h**) was carried out for 24 h in an Applied Photophysics Reactor at 254 nm in methanol in a quartz vessel (Scheme 1).

The products were separated by column chromatography over silica gel. The *ortho* rearrangement product **3** and the *para* product **4** were obtained in about 3:1 ratio respectively, in addition to the 5,8-dihydronaphthol **1**. The products were characterized by spectral and analytical data. Likewise, the crotonate **2b**, on irradiation, furnished the respective *ortho*- and *para*-rearrangement products **3b** and **4b**, in addition to 5,8-dihydronaphthol **1**. The sorbate **2c**, on irradiation also gave two products **3c** and **4c**.

Irradiation of the benzoate **2d** in methanol furnished a mixture, which was chromatographed to separate the two rearrangement products **3d** and **4d**: compound **3d** was found to be contaminated with the 5,8-dihydronaphthol **1**. The



Scheme 1. *Reagents and conditions*: (i) Li/NH_3, EtOH, 85%; (ii) RCOCl, benzene/pyridine, 80–90%; (iii) $h\nu$ (254 nm)/MeOH.

Keywords: photo-Fries; dihydro-1-naphthyl esters, aromatic esters; photolysis; rearrangement.

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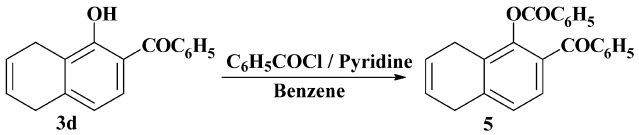
Table 1. Product distribution upon photolysis of 5,8-dihydro-1-naphthyl esters **2a–h**

Entry	Substrate **2**	R	% Yield of **3**	% Yield of **4**	% Yield of **1**
1	a	CH_3	40	12	25
2	b	$CH{=}CH{-}CH_3$	32	12.5	30
3	c	$(CH{=}CH)_2{-}CH_3$	32	12	30
4	d	C_6H_5	21.2[a]	10	30
5	e	$2\text{-}CH_3C_6H_4$	35	–	30
6	f	$2\text{-}ClC_6H_4$	25	10	40
7	g	1-Naphthyl	30	20	30
8	h	$CH{=}CH{-}C_6H_5$	15	–	40

Irradiation studies were carried out at 254 nm for 24 h in an Applied Photophysics Photochemical Reactor using absolute methanol as solvent.
[a] As benzoate.

mixture was benzoylated and the compound **3d** was isolated as its benzoyl derivative **5**. The 2-methylbenzoate **2e** on irradiation in benzene or methanol furnished only the *ortho* rearranged product **3e** along with the dihydronaphthol.



The 2-chlorobenzoate **2f** on photolysis furnished the two products **3f** and **4f** in addition to the dihydronaphthol. No cyclization product was isolated which can be expected in the light of other reports.[11] Irradiation of the ester **2f** in different solvents (benzene, ethanol, ethyl acetate) or at 300 nm gave the two rearranged products **3f** and **4f** only, with slight variation in their yields, but not any cyclized product. The 1-naphthoate **2g** gave the two products **3g** and **4g** as expected, on irradiation in methanol. The irradiation of the cinnamate **2h** in methanol furnished only the *ortho*-rearranged product **3h**, as observed earlier in similar systems[10] (Table 1).

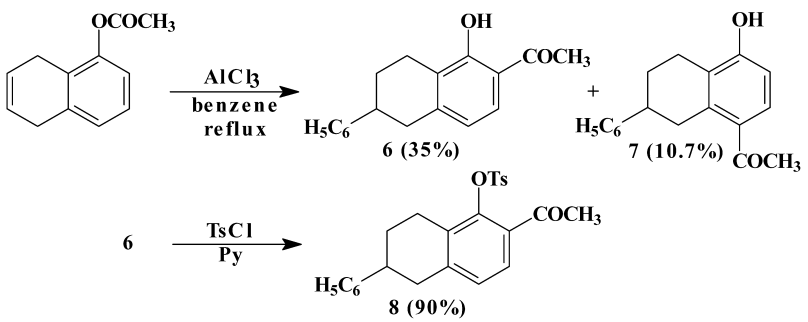
The esters **2a–h** were characterized by IR and ^{1}H NMR and were directly used for the irradiation studies, since they were found to be slowly undergoing decomposition. The products were characterized by IR, ^{1}H NMR, Mass spectra and elemental analysis. The ^{1}H NMR of the 2-acyl compounds **3a** invariably showed the C_4–H around δ 6.5, as a doublet with coupling constant ranging between 7 and 9 Hz; the C_6–H and C_7–H appeared around δ 5.8 as a complex signal due to the coupling between the adjacent olefinic and methylene protons; the C_5 and C_8 methylene protons appeared around δ 3.3 as a complex signal due to geminal and vicinal coupling. The Ar-OH appeared around δ 12, which was exchanged with D_2O.

The mass spectrum of products **3** and **4** invariably showed an intense molecular ion, in some cases as a base peak. The structure of compounds **3a**,[12] **3b**,[13] **3g**[14] and **4g**[13] were also confirmed by X-ray crystallographic studies. Thus the photo-Fries reaction of esters of 5,8-dihydro-1-naphthol gave in general, the *ortho* and *para*-rearrangement products in moderate yields. Invariably, 5,8-dihydro-1-naphthol was obtained in the irradiations, similar to the formation of phenol in the photolysis of phenyl esters. Aromatization of the dihydro-1-naphthol ring did not occur in any of the cases in the irradiation studies.

The Fries reaction of 2-naphthyl alkanoate is known.[15] The reaction of 2-naphthyl cinnamate in the presence of aluminium chloride has been studied by us earlier.[10] The reaction of 1-naphthyl cinnamate in presence of aluminium chloride gave only 1-naphthol. Hence the Fries reaction of 5,8-dihydro-1-naphthyl acetate (**2a**) was next studied. The treatment of **2a** with anhydrous aluminium chloride in either nitrobenzene or carbon disulfide at room temperature furnished 4-acetyl-5,8-dihydro-1-naphthol (**4a**) in 30–35% yield, along with the 5,8-dihydronaphthol **1** (40%).

When benzene was used as a solvent, the ester **2a**, in the presence of $AlCl_3$, gave two products **6** (35.7%) and **7** (10.7%), involving Fries rearrangement and arylation at double bond. The arylation has occurred similar to the earlier reports.[16,17] The structures of compounds **6** and **7** were established by spectral and analytical data and the structure of compound **6** was further confirmed by X-ray crystallographic studies[18] as its tosyl derivative **8** (Scheme 2).

In conclusion, irradiation of 5,8-dihydro-1-naphthyl esters in methanol at 254 nm furnished *ortho* and *para* rearranged products along with 5,8-dihydro-1-naphthol. The Fries



Scheme 2.

reaction of 5,8 dihydro-1-naphthyl acetate using benzene as the solvent, furnished the arylated Fries reaction product.

1. Experimental

Melting points were determined by using a Toshniwal melting point apparatus in an open capillary tube and are uncorrected. IR spectra were recorded in Nicolet Impact 400 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Jeol 400 MHz, Bruker 300 MHz, Bruker ARX 200 MHz and Jeol FX 90Q spectrometers, using TMS as internal standard. Mass spectra were obtained from a Jeol-DX-303 spectrometer. Microanalyses were performed in a Perkin–Elmer 240B elemental analyzer. Chromatography was performed on silica gel (ACME, 100–200 mesh).

1.1. General procedure for the preparation of 5,8-dihydro-1-naphthlyl esters (2a–h)

To a solution of 5,8-dihydronaphthol **1** (3.65 g, 25 mmol), and pyridine (2.40 mL, 30 mmol) in dry benzene (50 mL), was added dropwise a solution of the corresponding acid chloride (30 mmol) in dry benzene (30 mL), under cooling at 10°C. The reaction mixture was stirred overnight and washed with dil. $NaHCO_3$ solution, dil. NaOH solution and then several times with water. The organic layer was dried over anhydrous magnesium sulphate, the solvent removed under vacuum and the crude ester purified either by column chromatography using hexane–ethyl acetate (9:1) as an eluant or by recrystallization.

1.1.1. 5,8-Dihydro-1-naphthyl acetate[19] (2a). Following the general procedure, the reaction of 5,8-dihydro-1-naphthol (3.65 g, 25 mmol), with acetyl chloride (2.10 mL, 30 mmol) afforded the compound **2a** 4.2 g (90%) as a colourless liquid. ν_{max} (KBr) 3030, 2880, 2820, 1760, 1460, 1360, 1200 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 6.9 (m, 3H, Ar-*H*), 5.7 (m, 2H, Ar-H_6, Ar-H_7), 3.3 (m, 2H, 5-CH_2), 3.1 (m, 2H, 8-CH_2), 2.4 (s, 3H, CH_3).

1.1.2. 5,8-Dihydro-1-naphthyl crotonate[20] (2b). The crotonyl chloride was prepared by refluxing crotonic acid (2.6 g, 30 mmol) and thionyl chloride (5 mL) in dry benzene for 3 h. The solvent was removed under reduced pressure along with the excess of thionyl chloride. The crude crotonyl chloride was used in the next step without further purification.

Following the general procedure, treatment of 5,8-dihydro-1-naphthol (3.65 g, 25 mmol) with crotonyl chloride and pyridine (2.40 mL, 30 mmol), afforded the title compound **2b** (4.7 g, 88%) as a colourless liquid. ν_{max} (KBr) 3015, 2880, 1735, 1650, 1570, 1460, 1310, 1290, 1220 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 6.9 (m, 3H, Ar-*H*), 6.7 (m, 2H), 5.8 (m, 2H, Ar-H_6, Ar-H_7), 3.5 (m, 2H, 5-CH_2), 3.2 (m, 2H, 8-CH_2), 2.0 (d, J=6 Hz, 3H, CH_3).

1.1.3. 5,8-Dihydro-1-naphthyl-2,4-hexadienoate (2c). 2,4-Hexadienoyl chloride (sorbyl chloride) was prepared by refluxing 2,4-hexadienoic acid (3.4 g, 30 mmol) and thionyl chloride (5 mL) in dry benzene for 3 h. The solvent and the excess of thionyl chloride were removed under reduced pressure. The crude acid chloride was used for esterification of 5,8-dihydro-1-naphthol (3.65 g, 2.5 mmol) to afford the title compound **2c** (4.9 g 82%) as a white solid. Mp 58–60°C; ν_{max} (KBr) 3000, 1720, 1630, 1450, 1320, 1210, 1110, 990 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.45 (1H, m, Ar-*H*), 7.15 (1H, m, Ar-*H*), 6.95 (2H, m, Ar-*H*, CH=C*H*), 6.26 (2H, m), 5.97 (1H, m), 5.87 (2H, m, H_6, H_7), 3.43 (2H, bs, 5-CH_2), 3.2 (2H, bs, 8-CH_2), 1.9 (3H, d, J=5.1 Hz, CH*Me*); *m/z* (EI) 240 (M+, 33), 144 (13), 128 (8), 117 (5), 116 (6), 115 (22), 96 (14), 95 (100), 67 (61), 66 (8), 65 (21), 51 (10).

1.1.4. 5,8-Dihydro-1-naphthyl benzoate (2d). The treatment of 5,8-dihydro-1-naphthol (3.4 g, 25 mmol), with benzoyl chloride (3.5 mL, 30 mmol) furnished the ester **2d** (4.6 g, 75%) as a colourless liquid. ν_{max} (KBr) 3020, 2880, 2820, 1730, 1450, 1060, 1020, 700 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 8.1 (2H, m, Ar-*H*), 7.4 (4H, m, Ar-*H*), 6.9 (2H, m, Ar-*H*), 5.8 (2H, m, H_6, H_7), 3.3 (4H, m, 5 and 8-CH_2).

1.1.5. 5,8-Dihydro-1-naphthyl 2-methylbenzoate (2e). The 2-methylbenzoyl chloride was prepared by refluxing *o*-toluic acid (4 g, 30 mmol), and thionyl chloride (5 mL) in dry benzene for 3 h. The crude 2-methylbenzoyl chloride was treated with 5,8-dihydro-1-naphthol (3.65 g, 25 mmol) to afford the ester **2e** (5.6 g, 85%) as a colourless and viscous liquid. ν_{max} (KBr) 3000, 2870, 2825, 1728, 1610, 1450, 1320, 1125, 985,870 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.85 (1H, m, Ar-*H*), 7.23 (6H, m, Ar-*H*), 5.8 (2H, m, H_6, H_7), 3.3 (4H, m, 5 and 8-CH_2), 2.4 (3H, s, CH_3).

1.1.6. 5,8-Dihydro-1-naphthyl 2-chlorobenzoate (2f). The 2-chlorobenzoyl chloride, obtained from *o*-chlorobenzoic acid (4.7 g, 30 mmol) and 5,8-dihydro-1-naphthol (3.65 g, 25 mmol) in the presence of pyridine (2.40 mL, 30 mmol) in dry benzene furnished the ester **2f** (5.8 g, 82%) as a viscous liquid. ν_{max} (KBr) 3010, 2860, 1740, 1460, 1280, 1200, 970, 850 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.9 (1H, m, Ar-*H*), 7.20 (6H, m, Ar-*H*), 5.8 (2H, m, H_6, H_7), 3.3 (4H, m, 5 and 8-CH_2).

1.1.7. 5,8-Dihydro-1-naphthyl 1-naphthoate (2g). The 1-naphthoyl chloride, prepared by refluxing 1-naphthoic acid (5.2 g, 30 mmol) and thionyl chloride (5 mL) in dry benzene for 3 h, on treatment with 5,8-dihydro-1-naphthol (3.65 g, 25 mmol) in the presence of pyridine (2.40 mL, 30 mmol) furnished the ester **2g** (4.3 g, 58%) as a crystalline solid. Mp 100–102°C; ν_{max} (KBr) 3010, 2890, 2860, 1730, 1450, 1300, 1210, 960, 850, 810 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 8.90 (3H, m, Ar-*H*), 8.4 (1H, m, Ar-*H*), 7.8 (2H, m, Ar-*H*), 7.5 (3H, m, Ar-*H*), 5.8 (2H, m, H_6, H_7), 3.0 (4H, m, 5 and 8-CH_2); *m/z* (EI) 300 (M+, 11.4), 155 (100), 127 (38.2), 115 (6.32).

1.1.8. 5,8-Dihydro-1-naphthyl cinnamate (2h). The treatment of cinnamoyl chloride, from cinnamic acid (4.5 g, 30 mmol) and thionyl chloride (5 mL), with 5,8-dihydro-1-naphthol (3.65 g, 25 mmol) in the presence of pyridine (2.4 mL, 30 mmol) afforded the ester **2h** (5.4 g, 78%) as a colourless solid. Mp 122–124°C; ν_{max} (KBr) 1720, 1620, 1450, 1310, 1210, 1140, 1020, 870, 800, 750, 710 cm^{-1}; δ_H

(90 MHz, $CDCl_3$) 7.9 (1H, d, J=16 Hz, H_β), 7.65 (2H, m, Ar-*H*), 7.45 (3H, m, Ar-*H*), 7.0 (3H, m, Ar-*H*), 6.6 (1H, d, J=16 Hz, H_α), 5.9 (2H, m, H_6, H_7), 3.45 (2H, m, 5-CH_2), 3.25 (2H, m, 8-CH_2); *m/z* (EI) 276 (M+, 3), 144 (2), 131 (100), 115 (4.3), 103 (27), 91 (2).

1.2. General procedure for the irradiation of 5,8-dihydro-1-naphthyl esters (2a–h)

A solution of 5,8-dihydro-1-naphthyl ester **3** (1.0 g) in methanol or benzene (150 mL) was purged with nitrogen for half an hour in a quartz vessel and irradiated at 254 nm using Applied Photo-physics photochemical reactor. The course of the reaction was followed by TLC. After the disappearance of the starting material, the solvent was removed under vacuum. The residue obtained was chromatographed over a column of silica gel and eluted with a mixture of hexane–ethyl acetate (9:1), to isolate the products.

1.3. Irradiation of 5,8-dihydro-1-naphthyl acetate (2a)

Photolysis of the ester **2a** (1 g, 5.3 mmol) in methanol (150 mL) at 254 nm for 24 h gave the products **3a**, **4a** and 5,8-dihydro-1-naphthol **1** (25%).

1.3.1. 2-Acetyl-5,8-dihydro-1-naphthol (3a). Yield: 0.4 g (40%); mp 98–100°C; [Found: C, 75.95; H, 6.11. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%]; ν_{max} (KBr) 3020, 1620, 1490, 1430, 1410, 1360, 1320, 1270, 990, 840, 800 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 12.5 (1H, s, D_2O exchanged, Ar-O*H*), 7.46 (1H, d, J=9 Hz, Ar-H_3), 7.56 (1H, d, J=9 Hz, Ar-H_4), 5.80 (2H, m, H_6, H_7), 3.3 (4H, bs, 5 and 8-CH_2), 2.5 (3H, s, CH_3); *m/z* (EI) 188 (M+, 100), 187 (25), 186 (34), 173 (82), 171 (55), 155 (11), 145 (37), 127 (16), 115 (43), 105 (4), 91 (10), 86 (5).

1.3.2. 4-Acetyl-5,8-dihydro-1-naphthol (4a). Yield: 0.12 g (12%); mp 154–156°C; [Found: C, 76.20; H, 6.23. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%]; ν_{max} (KBr) 3035, 1640, 1495, 1400, 1420, 1350, 1250 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 13.0 (1H, s, D_2O exchanged, Ar-O*H*), 7.40 (1H, d, J=9 Hz, Ar-H_3), 7.20 (1H, d, J=9 Hz, Ar-H_2), 5.75 (2H, m, H_6, H_7), 3.28 (4H, bs, 5 and 8-CH_2), 2.35 (3H, s, CH_3); *m/z* (EI) 188 (M+, 100), 173 (30), 145 (47), 127 (45), 115 (85), 91 (30), 77 (30), 63 (46), 57 (18).

1.4. Irradiation of 5,8-dihydro-1-naphthyl crotonate (2b)

Photolysis of the ester **2b** (1.0 g, 4.67 mmol) in methanol at 254 nm for 24 h afforded the compounds **3b**, **4b** and 5,8-dihydro-1-naphthol (30%).

1.4.1. 2-Crotonyl-5,8-dihydro-1-naphthol (3b). Yield: 0.32 g (32%); mp 126–128°C; [Found: C, 78.07; H, 6.42. $C_{14}H_{14}O_2$ requires C, 78.48; H, 6.59%]; ν_{max} (KBr) 3400, 3050, 3000, 2900, 1630, 1590, 1420, 1350, 1300, 790 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 13.0 (1H, s, D_2O exchanged, Ar-O*H*), 7.50 (1H, d, J=9 Hz, Ar-H_3), 6.8–7.3 (2H, m, Ar-*H*), 6.6 (1H, d, J=9 Hz, H_4), 5.80 (2H, m, H_6 and H_7), 3.30 (4H, bs, H_5 and H_8), 2.0 (3H, d, J=6 Hz, CH_3); *m/z* (EI) 214 (M+, 18), 199 (100), 173 (25), 127 (7), 115 (21), 105 (3), 99 (6), 91 (7).

1.4.2. 4-Crotonyl-5,8-dihydro-1-naphthol (4b). Yield: 0.125 g (12.5%); mp 198–200°C; [Found: C, 78.01; H, 6.32. $C_{14}H_{14}O_2$ requires C, 78.48; H, 6.59%]; ν_{max} (KBr) 3420, 3048, 3000, 2950, 1650, 1450, 980 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 13.2 (1H, s, D_2O exchanged, Ar-O*H*), 7.57 (1H, d, J=9 Hz, Ar-H_3), 7.0–7.20 (2H, m, H_α and H_β), 6.6 (1H, d, J=9 Hz, Ar-H_2), 5.75 (2H, m, H_6 and H_7), 3.50 (4H, bs, H_5 and H_8), 2.2 (3H, dd, J=6.1, 1.0 Hz, CH_3).

1.5. Irradiation of 5,8-dihydro-1-naphthyl 2,4-hexadienoate (2c)

Photolysis of **2c** (1 g, 4.16 mmol) in MeOH (150 mL) at 254 nm, for 24 h furnished the rearranged compounds **3c**, **4c** and 5,8-dihydro-1-naphthol (30%).

1.5.1. 2-(2,4-Hexadienoyl)-5,8-dihydro-1-naphthol (3c). Yield: 0.32 g (32%); mp 128–130°C; [Found: C, 79.35; H, 6.58. $C_{16}H_{16}O_2$ requires C, 79.97; H, 6.71%]; ν_{max} (KBr) 3450, 1620, 1610, 1600, 1575, 1400 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 12.8 (1H, s, D_2O exchanged, Ar-O*H*), 7.50 (1H, d, J=9 Hz, H_3), 6.80 (1H, m), 6.50 (1H, d, J=9 Hz, H_4), 6.20 (3H, m), 5.8 (2H, m, H_6 and H_7), 3.20 (4H, bs, H_5 and H_8), 1.8 (3H, d, J=6 Hz, CH_3); *m/z* (EI) 240 (M+, 0.3), 239 (5), 238 (49), 223 (18), 171 (25), 170 (100), 115 (76), 114 (48), 89 (16), 77 (5), 67 (29), 66 (24), 65 (43), 52 (14).

1.5.2. 4-(2,4-Hexadienoyl)-5,8-dihydro-1-naphthol (4c). Yield: 0.12 g (12%); mp 108–110°C; [Found: C, 79.49; H, 6.65. $C_{16}H_{16}O_2$ requires C, 79.97; H, 6.71%]; ν_{max} (KBr) 3420, 1635, 1612, 1600, 1560, 1500 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 12.5 (1H, s, Ar-O*H*), 7.26 (1H, d, J=7.8 Hz, H_3), 6.69 (1H, d, J=8.2 Hz, H_2), 6.67 (1H, m), 6.49 (1H, m), 6.20 (2H, m), 5.88 (2H, bs, H_6 and H_7), 3.56 (2H, m, 5-CH_2), 3.32 (2H, m, 8-CH_2), 1.88 (3H, d, J=6 Hz, CH_3).

1.6. Irradiation of 5,8-dihydro-1-naphthyl benzoate (2d)

Photolysis of the ester **2d** (1 g, 4 mmol) in MeOH at 254 nm, for 24 h furnished 2-benzoyl-5,8-dihydro-1-naphthol (**3d**), 4-benzoyl-5,8-dihydro-1-naphthol (**4d**) and 5,8-dihydro-1-naphthol (30%). The separation of the *ortho* rearranged product was difficult by column chromatography, since its R_f value and that of 5,8-dihydro-1-naphthol were same. Hence the mixture of compounds **3d** and **1** was treated with benzoyl chloride (1.0 g) in the presence of pyridine (2 mL) using dry benzene as solvent at room temperature. After completion of the reaction, the solvent was removed and the residue was chromatographed over a silica gel column and eluted with hexane–ethyl acetate (9:1) to isolate the benzoyl derivative **5** as a colourless solid.

1.6.1. 2-Benzoyl-5,8-dihydro-1-naphthyl benzoate (5). Yield: 0.3 g (21%); mp 142–144°C; [Found: C, 81.25; H, 5.07. $C_{24}H_{18}O_3$ requires C, 81.34; H, 5.12%]; ν_{max} (KBr) 3020, 2890, 1720, 1630, 1600, 1590, 1420, 1350 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.7 (5H, m, Ar-*H*), 7.3 (7H, m, Ar-*H*), 5.9 (2H, m, H_6 and H_7), 3.4 (2H, m, 5-CH_2), 3.3 (2H, m, 8-CH_2); *m/z* (EI) 354 (M+, 4), 353 (7), 352 (35), 249 (49), 247 (30), 246 (7), 105 (100), 77 (90).

1.6.2. 4-Benzoyl-5,8-dihydro-1-naphthol (4d). Yield: 0.1 g (10%); mp 184–186°C; [Found: C, 81.60; H, 5.57.

$C_{17}H_{14}O_2$ requires C, 81.58; H, 5.63%]; ν_{max} (KBr) 3400, 3020, 2980, 1630, 1590, 1500, 1420, 970, 860 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 12.5 (1H, s, Ar-O*H*), 7.7 (4H, m, Ar-*H*), 7.0 (3H, m, Ar-*H*), 5.8 (2H, m, H_6 and H_7) 3.3 (4H, bs, 5 and 8-CH_2); *m/z* (EI) 250 (M+, 100), 171 (26), 145 (18), 127 (12), 115 (35), 105 (94), 91 (9), 77 (82).

1.7. Irradiation of 5,8-dihydro-1-naphthyl 2-methylbenzoate (2e)

Photolysis of the ester **2e** (1 g, 3.8 mmol) in benzene (150 mL) at 254 nm, for 24 h furnished, the *ortho* rearranged product (**3e**) along with 5,8-dihydro-1-naphthol **1** (30%).

1.7.1. 2-(2-Methylbenzoyl-5,8-dihydro-1-naphthol (3e). Yield: 0.35 g (35%); mp 78–80°C; [Found: C, 81.20; H, 5.98. $C_{18}H_{16}O_2$ requires C, 81.79; H, 6.10%]; ν_{max} (KBr) 3400, 3025, 2890, 1630, 1590, 880, 870 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 12.8 (1H, s, Ar-O*H*), 8.53 (1H, d, *J*= 7.5 Hz, Ar-H_3), 7.65 (1H, m, Ar-*H*), 7.30 (2H, m, Ar-*H*), 7.10–7.75 (4H, m), 6.56 (1H, d, *J*=7.5 Hz, Ar-H_4), 5.90 (2H, m, H_6 and H_7), 3.40 (4H, bs, 5 and 8-CH_2), 2.31 (3H, s, Ar-CH_3); δ_c (75 MHz, $CDCl_3$) 204.0, 161.4, 143.9, 138.1, 135.2, 130.7, 129.6, 129.8, 127.3, 125.9, 118.9, 117.0, 113.4, 30.21, 23.6, 19.5; *m/z* (EI) 264 (M+, 65), 263 (12), 249 (69), 247 (65), 245 (21), 223 (15), 173 (13), 172 (14), 171 (35), 170 (53), 119 (51), 115 (48), 114 (18), 91 (100), 90 (13), 77 (10), 65 (57), 51 (22).

1.8. Irradiation of 5,8-dihydro-1-naphthyl 2-chlorobenzoate (2f)

Photolysis of ester **2f** (1 g, 3.5 mmol) in MeOH at 254 nm, for 24 h furnished the products **3f**, **4f** and 5,8-dihydro-1-naphthol **1** (40%).

1.8.1. 2-Chlorobenzoyl-5,8-dihydro-1-naphthol (3f). Yield: 0.25 g (25%); mp 112–114°C; [Found: C, 72.08; H, 4.70. $C_{17}H_{13}ClO_2$ requires C, 71.71; H, 4.60%]; ν_{max} (KBr) 3420, 3020, 2980, 1620, 1600, 1520, 1480 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 12.2 (1H, s, Ar-O*H*), 7.55 (4H, m, Ar-*H*), 7.0 (1H, d, *J*=9 Hz, H_3), 6.7 (1H, d, *J*=9 Hz, H_4), 5.9 (2H, m, H_6 and H_7), 3.4 (2H, bs, 8-CH_2), 3.2 (2H, bs, 5-CH_2); *m/z* (EI) 286 (M+2, 32), 284 (M+, 88), 283 (15), 282 (15), 250 (15), 249 (82), 247 (56), 173 (33), 171 (23), 145 (35), 141 (33), 139 (100), 115 (39), 111 (39), 91 (10).

1.8.2. 4-(2-Chlorobenzoyl)-5,8-dihydro-1-naphthol (4f). Yield: 0.1 g (10%); mp 210–212°C; [Found: C, 71.36; H, 4.52. $C_{17}H_{13}ClO_2$ requires C, 71.71; H, 4.60%]; ν_{max} (KBr) 3400, 3020, 2990, 1640, 1600, 1580, 1420 cm^{-1}; δ_H (300 MHz, DMSO-d_6) 10.6 (1H, s, Ar-O*H*), 7.5 (4H, m, Ar-*H*), 7.05 (1H, d, *J*=9.0 Hz, H_3), 6.7 (1H, d, *J*=9.0 Hz, H_2), 5.9 (2H, m, H_6 and H_7), 3.25 (2H, m, 8-CH_2), 3.2 (2H, m, 5-CH_2); *m/z* (EI) 286 (M+2, 16), 284 (M+, 24), 283 (24), 282 (2), 251 (53), 249 (48), 231 (25), 175 (6), 145 (32), 141 (33) 139 (100), 127 (14), 115 (25), 111 (32), 91 (7.7).

1.9. Irradiation of 5,8-dihydro-1-naphthyl α-naphthoate (2g)

Photolysis of **2g** (0.64 g, 2.1 mmol) in benzene (150 mL) at 254 nm, for 24 h furnished the compounds **3g**, **4g** and 5,8-dihydro-1-naphthol **1** (30%).

1.9.1. 2-(1-Naphthoyl)-5,8-dihydro-1-naphthol (3g). Yield: 0.19 g (30%); mp 130–132°C; [Found: C, 84.42; H, 5.30. $C_{21}H_{16}O_2$ requires C, 83.98; H, 5.37%]; ν_{max} (KBr) 3420, 3200, 2990, 1630, 1620, 1590 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 12.87 (1H, s, D_2O exchanged, Ar-O*H*), 7.98 (3H, m, Ar-*H*), 7.51 (4H, m, Ar-*H*), 7.08 (1H, bs, Ar-*H*), 6.49 (1H, bs, Ar-H_4), 5.9 (1H, bs, H_6), 5.85 (1H, bs, H_7), 3.40 (4H, bs, 5 and 8CH_2); δ_c (75 MHz, $CDCl_3$) 203.3, 161.5, 144.1, 136.0, 133.5, 130.8, 130.6, 130.4, 128.4, 127.1, 126.5, 126.1, 125.5, 125.4, 124.5, 124.4, 123.8, 122.9, 118.9, 117.6, 30.3, 23.6; *m/z* (EI) 300 (M+, 100), 283 (5), 281 (9), 173 (18), 172 (50), 171 (36), 155 (35), 144 (15), 128 (27), 127 (49), 77 (11).

1.9.2. 4-(1-Naphthoyl)-5,8-dihydro-1-naphthol (4g). Yield: 0.125 g (20%); mp 206–208°C; [Found: C, 84.08; H, 5.40. $C_{21}H_{16}O_2$ requires C, 83.98; H, 5.37%]; ν_{max} (KBr) 3400, 3000, 2920, 2850, 1620, 1420, 1330 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.40 (1H, s, Ar-O*H*), 8.02 (3H, m, Ar-*H*), 7.50 (4H, m, Ar-*H*), 7.06 (1H, m, Ar-*H*), 6.66 (1H, m, Ar-*H*), 5.9 (2H, m, H_6 and H_7), 3.72 (2H, m, 5-CH_2), 3.25 (2H, m, 8-CH_2); δ_c (75 MHz, DMSO-d_6) 158.49, 138.4, 137.0, 133.2, 132.5, 130.6, 130.1, 128.4, 128.2, 128.1, 127.3, 127.1, 126.3, 125.32, 124.8, 124.2, 123.0, 122.2, 111.1, 28.3, 23.9; *m/z* (EI) 300 (M+, 100), 299 (13), 283 (13), 281 (13), 172 (15), 171 (91), 156 (11), 155 (77), 145 (16), 144 (10), 143 (13), 128 (20), 127 (82), 126 (37), 77 (17), 51 (16).

1.10. Irradiation of 5,8-dihydro-1-naphthyl cinnamate (2h)

Photolysis of the ester **2h** (1 g, 3.62 mmol) in MeOH at 254 nm, for 24 h furnished only the *ortho* rearranged product **3h** in low yield along with 5,8-dihydro-1-naphthol **1** (40%).

1.10.1. 2-Cinnamoyl-5,8-dihydro-1-naphthol (3h). Yield: 0.15 g (15%); mp 116–118°C; [Found: C, 82.08; H, 5.50. $C_{19}H_{16}O_2$ requires C, 82.58; H, 5.83 %]; ν_{max} (KBr) 3040, 1630, 1570, 1580, 1420, 1350, 1280, 1120, 760 cm^{-1}; δ_H (90 MHz, $CDCl_3$) 13.0 (1H, s, D_2O exchanged, Ar-O*H*), 7.5 (5H, m, Ar-*H*), 7.3 (3H, m, Ar-*H*), 6.6 (1H, d, *J*=9 Hz, H_4), 5.80 (2H, m, H_6 and H_7), 3.3 (4H, bs, 5 and 8-CH_2); *m/z* (EI) 276 (M+, 63), 275 (33), 257 (8), 199 (36), 197 (15), 173 (14), 172 (34), 171 (51), 170 (100), 144 (22), 131 (43), 115 (37), 103 (36), 91 (16).

1.11. Reaction of 5,8-dihydro-1-naphthyl acetate (2a) with $AlCl_3$ in benzene

Anhydrous aluminium chloride (4.2 g, 32 mmol) was added in portion to the solution of the ester **2a** (1 g, 5.3 mmol) in dry benzene (30 mL) at room temperature. Then the reaction mixture was refluxed on a water bath. After the disappearance of the starting material monitered by tlc, the reaction mixture was cooled and ice water (50 mL) added. The organic layer was separated and washed several times with dil. HCl and water and dried over magnesium sulphate. After distilling off the solvent, the residue was chromatographed over a silica gel column and eluted with

hexane–ethyl acetate (4:1), to obtain the compounds **6** and **7**.

1.11.1. 2-Acetyl-6-phenyl-5,6,7,8-tetrahydro-1-naphthol (6). Yield: 0.5 g (35.7%); mp 118–120°C; [Found: C, 80.80; H, 6.73. $C_{18}H_{18}O_2$ requires C, 81.17; H, 6.81%]; ν_{max} (KBr) 3400, 3000, 2910, 1620, 1500, 1390, 1320, 800 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 12.90 (1H, s, Ar-O*H*), 7.50 (1H, d, *J*=8.3 Hz, H_3), 7.32 (5H, m, Ar-*H*), 6.65 (1H, d, *J*=8.3 Hz, H_4), 3.0 (4H, m), 2.9 (1H, m), 2.8 (3H, s, CH_3), 2.2 (1H, m), 1.90 (1H, m); δ_c (75 MHz, DMSO-d_6) 203.9, 160.6, 146.2, 128.6, 127.3, 126.8, 126.3, 119.4, 39.8, 38.3, 29.6, 26.4, and 23.1; *m/z* (EI) 266 (M+, 48), 251 (16), 175 (16), 162 (100), 147 (18), 115 (10), 104 (5), 91 (26).

1.11.2. 4-Acetyl-6-phenyl-5, 6, 7, 8-tetrahydro-1-naphthol (7). Yield: 0.15 g (10.7%); mp 218–220°C; [Found: C, 81.76; H, 7.01. $C_{18}H_{18}O_2$ requires C, 81.17; H, 6.81%]; ν_{max} (KBr) 3100, 2920, 1625, 1540, 1250, 1010, 810, 700 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.20 (1H, s, Ar-O*H*), 7.65 (1H, d, *J*=8.4 Hz, H_3), 7.3 (5H, m, Ar-*H*), 6.75 (1H, d, *J*=8.4 Hz, H_2), 3.25 (2H, m), 2.9 (2H, m), 2.70 (1H, m), 2.4 (3H, s, CH_3), 2.0 (1H, m), 1.8 (1H, m); *m/z* (EI) 266 (M+, 63), 251 (37), 190 (27), 175 (100), 162 (77), 147 (20), 133 (80, 115 (13), 91 (68).

1.11.3. 2-Acetyl-6-phenyl-5,6,7,8-tetrahydronaphthalen-1-yl 4-toluene sulphonate (8). To a suspension of NaH (0.038 g, 0.8 mmol) in THF (20 mL) was added dropwise a solution of the naphthol **6** (0.1 g, 0.37 mmol) in THF (20 mL), followed by the addition of *p*-toluenesulfonyl chloride (0.15 g, 0.75 mmol) in THF (5 mL) under nitrogen atmosphere at room temperature. After completion of the reaction, the reaction mixture was quenched with dil. NH_4Cl solution. The organic layer was separated, dried and chromatographed to obtain compound **8** and it was recrystallized from hexane–ethyl acetate mixture (1:1).

Yield: 0.14 g (90%); mp 98–100°C; ν_{max} (KBr) 3020, 1695, 1610, 1380, 1200, 1020, 900, 800, 790 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.75 (2H, d, *J*=8 Hz, Ar-*H*), 7.20–7.40 (8H, m, Ar-*H*), 7.10 (1H, d, *J*=8 Hz, H_4), 3.1 (1H, m), 2.46 (6H, s, 2CH_3), 2.91 (3H, m), 2.62 (1H, m), 2.1 (1H, m), 1.74 (1H, m); δ_c (75 MHz, $CDCl_3$) 198.9, 145.5, 145.3, 144.1, 142.9, 132.9, 132.4, 132.0, 129.7, 128.3, 128.2, 127.4, 126.5, 126.2, 126.2, 39.3, 29.4, 29.2, 24.1, 21.5; δ_c (75 MHz, DEPT-135, $CDCl_3$) 129.7, 128.3, 128.2, 126.4, 39.3, 37.4 (↓), 29.2 (↓), 24.1(↓), 21.5.

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