Reaction of 2-Acetyltetralone with some Esters of Benzoic Acid

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In order to investigate the pharmacological screening of a number of pyran-4-ones their synthesis by cyclization with sulphuric acid of the corresponding 1,3,5-triketones has been carried out with high yields. In the course of preparation of the latter the reaction of 2-acetyltetralone with some esters of benzoic acid derivatives has been studied and in particular, for a number of them, an interesting nucleophilic substitution of a chlorine atom with an alkoxy group on a benzenic nucleus has been evidenced.

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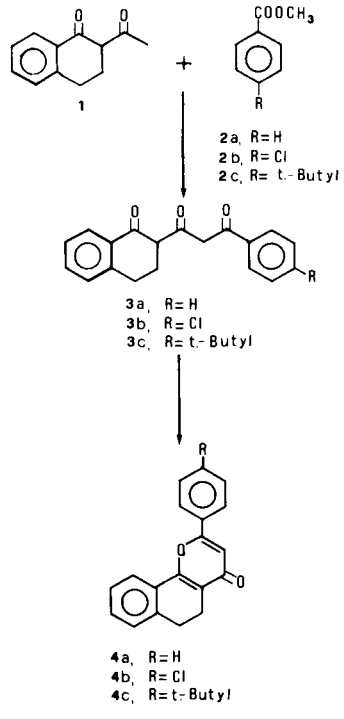
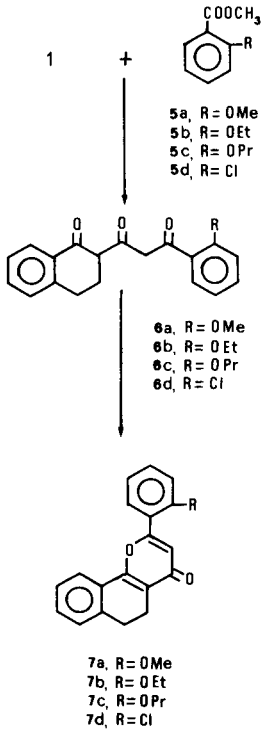
In a previous paper [1] we described the synthesis of 1-(4-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione and its succeeding cyclization to 5,6-dihydro-2-(4-methoxyphenyl)-4*H*-naphtho[1,2-*b*]pyran-4-one. Taking into account the synthetic utility of 1,3,5-triketones for a rapid synthesis of the corresponding pyran-4-ones, pharmacologically interesting [2], we have continued our study in order to synthesize the latter compounds. The triketones have been obtained by reaction of 2-acetyltetralone (**1**) with esters of benzoic acid. When **1** was allowed to react with the esters **2a, 2b, 2c** (Scheme 1), and **5a, 5b, 5c** (Scheme 2), in the presence of sodium hydride and using 1,2-dimethoxyethane as solvent, were obtained the following compounds: 1-phenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**3a**), 1-(4-chlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**3b**), 1-(4-*t*-butylphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**3c**), 1-(2-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**6a**), 1-(2-ethoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**6b**), and 1-(2-propoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**6c**). On the other hand when compound **1** was allowed to react, under the same experimental conditions, with methyl 2-chlorobenzoate (**5d**), the tlc analysis revealed two major components: the faster running compound has been shown to be the expected compound 1-(2-chlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**6d**). The slower running compound was found to be identical to compound **6a**. In fact the analytical, tlc and spectroscopic data were identical to the triketone obtained by reaction of **1** with **5a**. To explain the formation of **6a**, it has been supposed that in the course of a Claisen-type reaction the leaving methoxyl group causes an aromatic nucleophilic substitution of chlorine in position 2. In the presence of other solvents such as dioxane, the reaction has always led to the same products so excluding that the methoxyl group arises from the solvent (1,2-dimethoxyethane). The reaction of **1** with methyl 2,5-dichlorobenzoate (**8a**), performed under the same experimental conditions, gave the 1-(2,5-dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**9a**) and the 1-(5-chloro-2-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**9b**) as the main product (Scheme 3). In this case the substitution of the halogen is favoured by the presence of the chlorine atom in position 5. As expected, the reaction of **1** with ethyl 2,5-dichlorobenzoate (**8b**) and with propyl 2,5-dichlorobenzoate (**8c**), performed at the same conditions, gave in both cases **9a** and respectively 1-(5-chloro-2-ethoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**9c**) and 1-(5-chloro-2-propoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**9d**). The substitution of the chlorine atom becomes lower as the size of the alkoxy group increases. In fact the amounts of **9a** were: 4.06 g (18%), in the reaction with propyl 2,5-dichlorobenzoate, 2.40 g (11%) in the reaction with ethyl 2,5-dichlorobenzoate and even lower 1.90 g (8.6%) using methyl 2,5-dichlorobenzoate. The structures of all

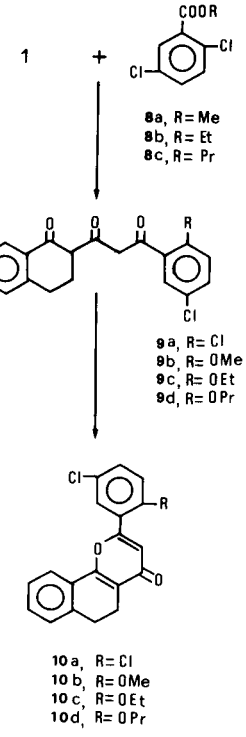
SCHEME 1



SCHEME 2



SCHEME 3



the triketones obtained have been supported by spectroscopic evidence. The nmr spectra showed signals characteristic of the keto-enolic structures. At this point, all the triketones obtained have been easily transformed, with high yields, in one step, into the corresponding 4*H*-naphtho[1,2-*b*]pyran-4-ones by cyclization with sulphuric acid. Compounds **4a** [3], **4b, 4c, 7d, 10a, 10b, 10c** and **10d** have been obtained using sulphuric acid at 96%, while the products **7a, 7b** and **7c** have been prepared using sulphuric acid at 80%. The nmr spectra evidenced, among the others, signals of about δ 7.00 (singlet, olefinic H). It is interesting to point out that some 4*H*-naphtho[1,2-*b*]pyran-4-ones occur naturally. Eleutherinol was extracted from bulbs of *Eleutherine bulbosa* (Mill.) [4]. Among the metabolites of *Aspergillus niger*, flavasperone was found [5] and synthesized in a ten-stage process from 3,5-dimethoxybenzoic acid [6]. Moreover, other naphto[1,2-*b*]pyran-4-ones are present in *Comanthus parviccirrus timorensis* [7]. All the 4*H*-naphtho[1,2-*b*]pyran-4-ones have been identified on the basis of their analytical and spectral data. These later compounds will be submitted for pharmacological screening.

EXPERIMENTAL

Melting points have been determined on Büchi 510 apparatus and are uncorrected. Infrared spectra have been recorded in nujol mulls with a Perkin-Elmer 137 IR spectrophotometer. The nmr spectra have been obtained with a Varian EM-360 at 60 MHz with tetramethylsilane as internal standard. Mass spectra have been recorded on a Jeol JMS-10SG-2 mass spectrometer. Elemental analyses have been carried out by the Kurt Eder service (Genève, Suisse).

Synthesis of the 1,3,5-Triketones. General Procedure.

A suspension of sodium hydride (dispersion 55-60% in oil) 10.5 g (0.25 mole) in 100 ml of 1,2-dimethoxyethane was added dropwise to a stirred solution of 2-acetyltetralone (**1**) 9.41 g (0.05 mole) and 0.075 mole of benzoic ester in 100 ml of 1,2-dimethoxyethane. The mixture was refluxed for 6 hours. Most of the solvent was then removed under reduced pressure and the pasty residue was cooled to 0° in an ice-water bath. Diethyl ether (150 ml) was added. After stirring the mixture for a few minutes, 100 ml of cold water was added initially, the water was added dropwise until the excess sodium hydride was destroyed. The two layers were separated. The ethereal layer was extracted with two 100 ml of cold 1% aqueous sodium hydroxide. Then 200 g of crushed ice and successively 50 ml of 12*N* hydrochloric acid were added at the aqueous extracts combined. The mixture was stirred for 20 minutes. After filtration, the resinous product obtained was dissolved in chloroform and then washed with water until neutral. After drying (anhydrous sodium sulfate), the solvent was evaporated *in vacuo*. The residue treated with ethanol yielded a crude product. The products **3c** and **6c** more soluble in ether, were recovered by slow evaporation of the solvent in refrigerator; crystals so obtained were dissolved in chloroform and the obtained solution washed with water and then dried with anhydrous sodium sulphate. After evaporation of the solvent, the residue was crystallized from ethanol. The crude product obtained from the reaction of **1** with **5d**, chromatographed over a column of silica gel (cycloexane/ethyl acetate 95:5) gave **6d** and **6a**. To separate **9a** from **9b**, from **9c** and from **9d** respectively, the crude products obtained by reactions of **1** with **8a, 8b and 8c**, were chromatographed as above.

1-Phenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**3a**).

This compound was obtained in a yield of 65% from reaction of **1** with **2a**, mp 98-99° (ethanol); ir (nujol): 1585, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.40-3.20 (m, 4H, C^3-H and C^4-H), 7.10-7.80 and 7.80-8.30 (2m, 9H, aromatic H), 4.20, 6.30, 6.40, 15.15, 15.55 and 16.30 (6s, 3H, C^2-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 292 (M^+).

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.88; H, 5.66.

1-(4-Chlorophenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**3b**).

This compound was obtained in a yield of 68% from reaction of **1** with **2b**, mp 128-129° (ethanol); ir (nujol): 1585, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.45-3.20 (m, 4H, C^3-H and C^4-H), 7.10-7.70 and 7.75-8.20 (2m, 4H, aromatic H), 7.45 and 7.90 (2d, J = 9 Hz, 4H, aromatic H), 4.20, 6.25, 6.35, 15.15, 15.55 and 16.30 (6s, 3H, C^2-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 326 (M^+).

Anal. Calcd. for $C_{19}H_{15}ClO_3$: C, 69.83; H, 4.63; Cl, 10.85. Found: C, 69.72; H, 4.66; Cl, 10.96.

1-(4-*t*-Butylphenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**3c**).

This compound was obtained in a yield of 64% from reaction of **1** with **2c**, mp 100-101° (ethanol); ir (nujol): 1585, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.30 (s, 9H, $C(CH_3)_3$), 2.50-3.00 (m, 4H, C^3-H and C^4-H), 7.15-8.25 (m, 4H, aromatic H), 7.55 and 7.90 (2d, J = 9 Hz, 4H, aromatic H), 4.20, 6.35, 15.15, 15.60 and 16.35 (5s, 3H, C^2-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 348 (M^+).

Anal. Calcd. for $C_{23}H_{24}O_3$: C, 79.27; H, 6.96. Found: C, 79.44; H, 6.77.

1-(2-Methoxyphenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphtalenyl)-1,3-propanedione (**6a**).

This compound was obtained in a yield of 66% from reaction of **1** with **5a**, mp 92-93° (ethanol); ir (nujol): 1580, 1600 cm^{-1}; ^{1}H-nmr (deuterio-

chloroform): δ 2.30-3.20 (m, 4H, C³-H and C⁴-H), 3.95 (s, 3H, OCH_3), 6.90-7.70 and 7.80-8.20 (2m, 8H, aromatic H), 3.90, 4.25, 6.75, 15.25, 15.65 and 16.20 (6s, 3H, C²-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 322 (M^+).

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.56; H, 5.82.

1-(2-Ethoxyphenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**6b**).

This compound was obtained in a yield of 63% from reaction of **1** with **5b**, mp 133-134° (ethanol); ir (nujol): 1580, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.50 (t, J = 7 Hz, 3H, OCH_2-CH_3), 2.30-3.10 (m, 4H, C³-H and C⁴-H), 4.15 (q, J = 7 Hz, 2H, OCH_2-CH_3), 6.90-7.50 and 7.70-8.10 (2m, 8H, aromatic H), 4.25, 6.80, 15.00, 15.45 and 15.95 (5s, 3H, C²-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 336 (M^+).

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 74.97; H, 6.00. Found: C, 75.11; H, 6.23.

1-(2-Propoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**6c**).

This compound was obtained in a yield of 62% from reaction of **1** with **5c**, mp 84-85° (ethanol); ir (nujol): 1585, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.00 (t, J = 7 Hz, 3H, OCH_2-CH_2-CH_3), 1.85 (sext, J = 7 Hz, 2H, OCH_2-CH_2-CH_3), 2.35-3.05 (m, 4H, C³-H and C⁴-H), 3.90 (t, J = 7 Hz, 2H, OCH_2-CH_2-CH_3), 6.85-7.50 and 7.65-8.10 (2m, 8H, aromatic H), 4.20, 6.75, 15.05, 15.50 and 16.05 (5s, 3H, C²-H and CO-CH_2-CO, keto-enolic structure; ms: m/z 350 (M^+).

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.39; H, 6.33. Found: C, 75.50; H, 6.47.

1-(2-Chlorophenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**6d**) and 1-(2-Methoxyphenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**6a**).

These compounds were obtained from reaction of **1** with **5d**. Compound **6d** had mp 97-98° (from ethanol, yield 42%); ir (nujol): 1580, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.20-3.20 (m, 4H, C³-H and C⁴-H), 7.00-8.25 (m, 8H, aromatic H), 4.25, 6.25, 15.10, 15.25 and 16.15 (5s, 3H, C²-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 326 (M^+).

Anal. Calcd. for $C_{19}H_{15}ClO_3$: C, 69.83; H, 4.63; Cl, 10.85. Found: C, 70.07; H, 4.86; Cl, 10.68.

The yield of compound **6a** was 17%.

1-(2,5-Dichlorophenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**9a**) and 1-(5-Chloro-2-methoxyphenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**9b**).

These compounds were obtained from reaction of **1** with **8a**. Compound **9a** had mp 118-119° (ethanol); ir (nujol): 1580, 1605 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.30-3.20 (m, 4H, C³-H and C⁴-H), 7.10-8.20 (m, 7H, aromatic H), 4.25, 6.30, 15.10 and 15.20 (4s, 3H, C²-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 361 (M^+).

Anal. Calcd. for $C_{19}H_{14}Cl_2O_3$: C, 63.17; H, 3.88; Cl, 19.64. Found: C, 62.99; H, 4.10; Cl, 19.80.

Compound **9b** had mp 137-138° (from ethanol, yield 41%); ir (nujol): 1585, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.45-3.10 (m, 4H, C³-H and C⁴-H), 3.90 (s, 3H, OCH_3), 7.15-7.60 and 7.75-8.10 (2m, 7H, aromatic H), 6.70, 6.85, 7.00, 15.10 and 15.40 (5s, 3H, C²-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 356 (M^+).

Anal. Calcd. for $C_{20}H_{17}ClO_4$: C, 67.32; H, 4.80; Cl, 9.94. Found: C, 67.34; H, 5.13; Cl, 10.15.

Compound **9a** and 1-(5-Chloro-2-ethoxyphenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**9c**).

These compounds were obtained from reaction of **1** with **8b**. Compound **9c** had mp 149-150° (from ethanol, yield 21%) ir (nujol): 1585, 1600 cm^{-1} ^{1}H-nmr (deuteriochloroform): δ 1.55 (t, J = 7 Hz, 3H, OCH_2-CH_3), 2.45-3.20 (m, 4H, C³-H and C⁴-H), 4.20 (q, J = 7 Hz, 2H, OCH_2-CH_3), 6.80-7.60 and 7.80-8.20 (2m, 7H, aromatic H), 4.30, 6.95, 15.10 and 15.40 (4s, 3H, C²-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 370 (M^+).

Anal. Calcd. for $C_{21}H_{19}ClO_4$: C, 68.01; H, 5.17; Cl, 9.56. Found: C, 68.17; H, 5.10; Cl, 9.30.

Compound **9a** and 1-(5-Chloro-2-propoxyphenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**9d**).

These compounds were obtained from reaction of **1** with **8c**. Compound **9d** had mp 134-135° (from acetic acid, yield 7.6%); ir (nujol): 1580, 1600 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.10 (t, J = 7 Hz, 3H, OCH_2-CH_2-CH_3), 1.95 (sext, J = 7 Hz, 2H, OCH_2-CH_2-CH_3), 2.40-3.10 (m, 4H, C³-H and C_4-H), 4.10 (t, J = 7 Hz, 2H, OCH_2-CH_2-CH_3), 7.15-7.75 and 7.85-8.25 (2m, 7H, aromatic H), 4.35, 6.90, 7.05, 15.15, 15.50 and 16.00 (6s, 3H, C²-H and CO-CH_2-CO, keto-enolic structure); ms: m/z 384 (M^+).

Anal. Calcd. for $C_{22}H_{21}ClO_4$: C, 68.67; H, 5.46; Cl, 9.10. Found: C, 68.87; H, 5.69; Cl, 9.22.

Synthesis of 4*H*-Naphtho[1,2-*b*]pyran-4-ones. General Procedure.

The 1,3,5-triketones (1 g) were added slowly in 15 ml of stirred 96% sulphuric acid at 0°. After 40 minutes at this temperature the reaction mixtures were poured into ice-water. The resulting precipitates were collected on a funnel and washed with water until neutral. The drying (at room temperature) products were crystallized from ethanol, except **7a**, **7b** and **7c** which were crystallized from cyclohexane. The compounds **7a**, **7b** and **7c** were synthesized using sulphuric acid at 80% instead of 96%.

5,6-Dihydro-2-phenyl-4*H*-naphtho[1,2-*b*]pyran-4-one (**4a**) [3].

This compound was obtained in a yield of 81% by cyclization of **3a** using sulphuric acid at 96%. Compound **4a** had mp 174-175° (ethanol); ir (nujol): 1610, 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.90 (s, 4H, C⁵-H and C⁶-H), 6.75 (s, 1H, C³-H), 7.25-7.75 and 7.75-8.10 (2m, 9H, aromatic H); ms: m/z 274 (M^+).

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15. Found: C, 83.10; H, 5.32.

2-(4-Chlorophenyl)-5,6-dihydro-4*H*-naphtho[1,2-*b*]pyran-4-one (**4b**).

This compound was obtained in a yield of 82% by cyclization of **3b** using sulphuric acid at 96%. Compound **4b** had mp 185-186° (ethanol); ir (nujol): 1620, 1645 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.85 (s, 4H, C⁵-H and C⁶-H), 6.85 (s, 1H, C³-H), 7.30-8.10 (m, 4H, aromatic H); 7.50 and 7.85 (2d, J = 9 Hz, 4H, aromatic H); ms: m/z 308 (M^+).

Anal. Calcd. for $C_{19}H_{13}ClO_2$: C, 73.91; H, 4.24; Cl, 11.48. Found: C, 73.83; H, 4.44; Cl, 11.78.

2-(4-*t*-Butylphenyl)-5,6-dihydro-4*H*-naphtho[1,2-*b*]pyran-4-one (**4c**).

This compound was obtained in a yield of 81% by cyclization of **3c** using sulphuric acid at 96%. Compound **4c** had mp 146-147° (ethanol); ir (nujol): 1615, 1650 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.49 (s, 9H, $C(CH_3)_3$), 2.93 (s, 4H, C⁵-H and C⁶-H), 6.90 (s, 1H, C³-H), 7.30-8.20 (m, 4H, aromatic H); 7.65 and 7.95 (2d, J = 9 Hz, 4H, aromatic H); ms: m/z 330 (M^+).

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.59; H, 6.72. Found: C, 83.59; H, 6.99.

5,6-Dihydro-2-(2-methoxyphenyl)-4*H*-naphtho[1,2-*b*]pyran-4-one (**7a**).

This compound was obtained in a yield of 78% by cyclization of **6a** using sulphuric acid at 80%. Compound **7a** had mp 132-133° (cyclohexane); ir (nujol): 1610, 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.85 (s, 4H, C⁵-H and C⁶-H), 3.85 (s, 3H, OCH_3), 6.80-7.60 and 7.60-7.90 (2m, 8H, aromatic H); 7.05 (s, 1H, C³-H); ms: m/z 304 (M^+).

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 79.00; H, 5.18.

5,6-Dihydro-2-(2-ethoxyphenyl)-4*H*-naphtho[1,2-*b*]pyran-4-one (**7b**).

This compound was obtained in a yield of 68% by cyclization of **6b** using sulphuric acid at 80%. Compound **7b** had mp 126-127° (cyclohexane); ir (nujol): 1610, 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.50 (t, J = 7 Hz, 3H, OCH_2-CH_3), 2.90 (s, 4H, C⁵-H and C⁶-H), 4.15 (q, J = 7 Hz, 2H, OCH_2-CH_3), 6.90-7.50 and 7.70-7.90 (2m, 8H, aromatic H); 7.10 (s, 1H, C³-H); ms: m/z 318 (M^+).

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.21; H, 5.70. Found: C, 79.48; H, 5.73.

5,6-Dihydro-2-(2-propoxyphenyl)-4*H*-naphtho[1,2-*b*]pyran-4-one (**7c**).

This compound was obtained in a yield of 65% by cyclization of **6c** using sulphuric acid at 80%. Compound **7c** had mp 112-113°

(cyclohexane); ir (nujol): 1610, 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.00 (t, J = 7 Hz, 3H, OCH_2-CH_2-CH_3), 1.80 (sext, J = 7 Hz, 2H, OCH_2-CH_2-CH_3), 2.80 (s, 4H, C^5-H and C^6-H), 4.00 (t, J = 7 Hz, 2H, OCH_2-CH_2-CH_3), 6.80-7.60 and 7.60-7.90 (2m, 8H, aromatic H); 7.05 (s, 1H, C^3-H); ms: m/z 332 (M^+).

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.48; H, 6.07. Found: C, 79.62; H, 6.17.

2-(2-Chlorophenyl)-5,6-dihydro-4*H*-naphtho[1,2-*b*]pyran-4-one (**7d**).

This compound was obtained in a yield of 82% by cyclization of **6d** using sulphuric acid at 96%. Compound **7d** had mp 155-156° (ethanol); ir (nujol): 1615, 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.90 (s, 4H, C^5-H and C^6-H), 6.70 (s, 1H, C^3-H), 7.20-8.00 (m, 8H, aromatic H); ms: m/z 308 (M^+).

Anal. Calcd. for $C_{19}H_{13}ClO_2$: C, 73.91; H, 4.24; Cl, 11.48. Found: C, 74.06; H, 4.44; Cl, 11.63.

2-(2,5-Dichlorophenyl)-5,6-dihydro-4*H*-naphtho[1,2-*b*]pyran-4-one (**10a**).

This compound was obtained in a yield of 84% by cyclization of **9a** using sulphuric acid at 96%. Compound **10a** had mp 173-174° (ethanol); ir (nujol): 1615, 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.90 (s, 4H, C^5-H and C^6-H), 6.75 (s, 1H, C^3-H), 7.30-8.10 (m, 7H, aromatic H); ms: m/z 342 (M^+).

Anal. Calcd. for $C_{19}H_{12}Cl_2O_2$: C, 66.49; H, 3.52; Cl, 20.66. Found: C, 66.69; H, 3.57; Cl, 20.78.

2-(5-Chloro-2-methoxyphenyl)-5,6-dihydro-4*H*-naphtho[1,2-*b*]pyran-4-one (**10b**).

This compound was obtained in a yield of 81% by cyclization of **9b** using sulphuric acid at 96%. Compound **10b** had mp 173-174° (ethanol); ir (nujol): 1615, 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 2.85 (s, 4H, C^5-H and C^6-H), 3.90 (s, 3H, OCH_3), 6.90 (s, 1H, C^3-H), 7.00-8.00 (m, 7H, aromatic H); ms: m/z 338 (M^+).

Anal. Calcd. for $C_{20}H_{15}ClO_3$: C, 70.90; H, 4.46; Cl, 10.47. Found: C, 71.00; H, 4.64; Cl, 10.33.

2-(5-Chloro-2-ethoxyphenyl)-5,6-dihydro-4*H*-naphtho[1,2-*b*]pyran-4-one (**10c**).

This compound was obtained in a yield of 88% by cyclization of **9c** using sulphuric acid at 96%. Compound **10c** had mp 155-156° (ethanol); ir (nujol): 1610, 1640 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.50 (t, J = 7 Hz, 3H, OCH_2-CH_3), 2.90 (s, 4H, C^5-H and C^6-H), 4.20 (q, J = 7 Hz, 2H, OCH_2-CH_3), 6.90-8.20 (m, 7H, aromatic H); 7.23 (s, 1H, C^3-H); ms: m/z 352 (M^+).

Anal. Calcd. for $C_{21}H_{17}ClO_3$: C, 71.48; H, 4.87; Cl, 10.05. Found: C, 71.39; H, 5.07; Cl, 10.20.

2-(5-Chloro-2-propoxyphenyl)-5,6-dihydro-4*H*-naphtho[1,2-*b*]pyran-4-one (**10d**).

This compound was obtained in a yield of 76% by cyclization of **9d** using sulphuric acid at 96%. Compound **10d** had mp 142-143° (ethanol); ir (nujol): 1610, 1635 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.05 (t, J = 7 Hz, 3H, OCH_2-CH_2-CH_3), 1.90 (sext, J = 7 Hz, 2H, OCH_2-CH_2-CH_3), 2.90 (s, 4H, C^5-H and C^6-H), 4.10 (t, J = 7 Hz, 2H, OCH_2-CH_2-CH_3), 6.95-8.10 (m, 7H, aromatic H); 7.25 (s, 1H, C^3-H); ms: m/z 366 (M^+).

Anal. Calcd. for $C_{22}H_{19}ClO_3$: C, 72.03; H, 5.22; Cl, 9.67. Found: C, 71.92; H, 5.42; Cl, 9.78.

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