

4,5-Dihydro-3H-naphtho[1,8-*bc*]furans

Takaaki Horaguchi,* Hiroaki Yagoh and Kiyoshi Tanemura

Department of Chemistry, Faculty of Science, Niigata University,
Ikarashi, Niigata 950-21, Japan

Tsuneo Suzuki

Nippon Dental University, Niigata,
Hamaura-cho, Niigata 951, Japan

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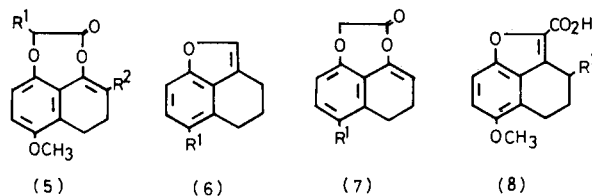
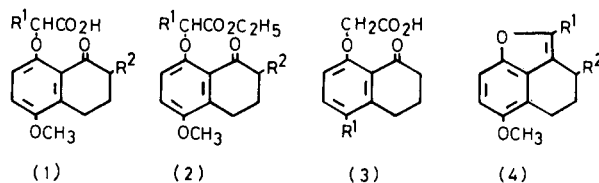
4,5-Dihydro-3H-naphtho[1,8-*bc*]furans **4** and **6** which have various substituents (R^1 and R^2) have been synthesized from 8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetic acids **1** and **3** or their ethyl esters **2**. The reaction of acids **1** and **3** with sodium acetate in acetic anhydride gave a mixture of furans **4** and **6** and lactones **5** and **7**. The ratios of the products were varied according to the types of substituents (R^1 and R^2) in acids **1** and **3**. As the substituent R^1 ($R^2 = \text{hydrogen}$) in acids **1** was changed from hydrogen to a methyl, ethyl or isopropyl group, production of furans **4** became more difficult. However, when a phenyl group was used as the substituent, furan **4** was obtained in good yield. Similarly, as the substituent R^2 ($R^1 = \text{hydrogen}$) in acids **1** was changed from hydrogen to a methyl, ethyl or isopropyl group, furan formation was more difficult. In contrast, acids **3** which had electron-withdrawing substituents such as chlorine, bromine or a nitro group at the 4-position afforded furans **6** in good yield. 4,5-Dihydro-3H-naphtho[1,8-*bc*]furans **4** and 4,5-dihydro-3H-naphtho[1,8-*bc*]furan-2-carboxylic acids **8** were synthesized from the reaction of esters **2** and potassium hydroxide in dioxane. When the substituents R^1 or R^2 in esters **2** were varied from hydrogen to a methyl, ethyl or isopropyl group the total yields of furans **4** and furancarboxylic acids **8** were reduced.

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Introduction.

Benzofurans may be readily synthesized by the treatment under reflux with sodium acetate in acetic anhydride [2] of 2-acylphenoxyacetic acids or by heating of their esters with bases such as potassium carbonate [3] or potassium hydroxide [4]. We recently applied the methods to the synthesis of 4,5-dihydro-3H-naphtho[1,8-*bc*]furans. The reaction of naphthoxyacetic acid **1a** with sodium acetate in acetic anhydride gave a 1:1 mixture of naphtho[1,8-*bc*]furan **4a** and lactone **5a** [5]. Furthermore, naphtho[1,8-*bc*]furan **4a** and naphtho[1,8-*bc*]furan-2-carboxylic acid **8a** were obtained in good yield from the reaction of ethyl naphthoxyacetate **2a** with potassium hydroxide in dioxane [6]. The lactone formation is attributed to restricted rotation of the carbonyl group around the single bond between the benzene ring and the carbonyl group [7] since such lactones are not produced in benzofuran synthesis from 2-acylphenoxyacetic acids. There were only a few literature reports on naphtho[1,8-*bc*]furans [8] before, but recently there appeared several reports on natural products having the naphtho[1,8-*bc*]furan structure [9] or about preparation of naphtho[1,8-*bc*]furans [10]. Therefore, we examined the two synthetic methods mentioned above and they were generally applicable to synthesis of naphtho[1,8-*bc*]furans **4** and **6** which had various substituents (R^1 and R^2) in the molecule, and we investigated the relationship between facility of furan-ring formation and

various types of substituents. Initially, the substituent R^1 in acids **1** and esters **2** was changed from hydrogen to a



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|--|------------------------|-------------------------------------|
| (1), (2), (4), (5) | (3), (6), (7) | (8) |
| a; $R^1 = \text{H}$, $R^2 = \text{H}$ | a; $R^1 = \text{H}$ | a; $R^1 = \text{H}$ |
| b; $R^1 = \text{CH}_3$, $R^2 = \text{H}$ | b; $R^1 = \text{Cl}$ | b; $R^1 = \text{CH}_3$ |
| c; $R^1 = \text{C}_2\text{H}_5$, $R^2 = \text{H}$ | c; $R^1 = \text{Br}$ | c; $R^1 = \text{C}_2\text{H}_5$ |
| d; $R^1 = \text{CH}(\text{CH}_3)_2$, $R^2 = \text{H}$ | d; $R^1 = \text{NO}_2$ | d; $R^1 = \text{CH}(\text{CH}_3)_2$ |
| e; $R^1 = \text{Ph}$, $R^2 = \text{H}$ | | |
| f; $R^1 = \text{H}$, $R^2 = \text{CH}_3$ | | |
| g; $R^1 = \text{H}$, $R^2 = \text{C}_2\text{H}_5$ | | |
| h; $R^1 = \text{H}$, $R^2 = \text{CH}(\text{CH}_3)_2$ | | |

steric effects of the substituent R^2 at the cyclization step of the furan ring, that is, the anion **9** could not easily attack the carbonyl carbon atom of the six-membered cyclic ketone because of steric repulsion between acid anhydride residue and R^2 . Though lactone formation is also suppressed by the inductive effect of the substituent R^2 , furan-ring formation appears to be much more strongly controlled by the steric effect.

Thirdly, the substituent effect of R^1 on the benzene ring in acids **3** was examined. In the case of $R^1 =$ hydrogen furan **4a** and lactone **5a** was obtained in a 1:1.4 ratio [5], while the ratios of the products were 4.4:1 and 6.8:1 for $R^1 =$ chlorine and $R^1 =$ bromine respectively. When a nitro group was introduced as the substituent R^1 , furan **6d** was exclusively produced. The results show that electron-withdrawing groups make furan-ring formation favourable because the carbonyl carbon atom of the six-membered cyclic ketone is activated toward anion attack. Thus, furan-ring formation is difficult in some cases compared with benzofuran synthesis, however, the method using sodium acetate and acetic anhydride is still useful for the synthesis of naphtho[1,8-*bc*]furans.

Finally, the reaction of esters **2a-h** and potassium hydroxide in dioxane was examined as a synthetic method of naphtho[1,8-*bc*]furans. The results are summarized in Table 2. The substituent R^2 was taken as hydrogen and R^1 was varied from hydrogen to a methyl, ethyl, isopropyl or phenyl group. When R^1 in esters **2** was hydrogen or a methyl group furans **4a-b** were obtained in yields above 84%. However, in the cases of $R^1 =$ ethyl and $R^1 =$ isopropyl the yields of furans **4c-d** were poor because of saponification of the starting esters **2c-d**. In contrast, using a phenyl group as the substituent R^1 furan **4e** was obtained in 90% yield. Next, the substituent R^1 was taken as hydrogen and R^2 was varied from hydrogen to a methyl, ethyl or an isopropyl group. In the cases of $R^2 =$ hydrogen, methyl and ethyl the total yields of furans **4a** and **4f-g** and furancarboxylic acids **8a-c** were above 73%. In contrast, when an isopropyl group was used as the substituent R^2 the yields of furan **4h** and furancarboxylic acid **8d** were low (47%) probably due to saponification of the starting ester **2h** prior to cyclization. The results show that the acidity of the methyne proton in esters **2** is the most important factor to determine facility of furan-ring formation and that the steric effect of R^2 in esters **2** is also operative at the cyclization step of furan ring. The trend of the results obtained in naphtho[1,8-*bc*]furan synthesis using sodium acetate in acetic anhydride are in accordance with those employing potassium hydroxide in dioxane. The latter method is better in naphtho[1,8-*bc*]furan synthesis than the former.

EXPERIMENTAL

The melting points were uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated anhydrous sodium sulfate was employed as the drying agent. The ir spectra were determined on a Hitachi EPI-G grating ir spectrophotometer. The nmr spectra (1H and ^{13}C nmr) were determined at 90 MHz on a JEOL JNM-FX 90Q FT NMR spectrometer, using tetramethylsilane as the internal standard. Ether refers to diethyl ether.

2-(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy)propionic Acid (**1b**).

A mixture of 8-hydroxy-5-methoxy-1,2,3,4-tetrahydro-1-naphthalenone **11** [11] (3.0 g, 15.6 mmoles), ethyl 2-bromopropionate (6.0 g, 33.1 mmoles), potassium phosphate (8.0 g, 37.7 mmoles) and dimethyl sulfide (20 ml) was stirred at 60° for 6 hours. The mixture was extracted with ether. The extract was washed, dried, and evaporated. The residue was dissolved in ethanol and saponified with 1M aqueous potassium hydroxide. The alkaline solution was acidified with 6M hydrochloric acid and the resulting precipitates were extracted with ether. The extract was washed, dried, and evaporated to give **1b** (3.3 g, 80%); it formed colorless needles from acetone, mp 141-142°; ir (potassium bromide): 1760 (CO_2H), and 1650 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.72 (d, J = 7 Hz, 3H, CH_3CH), 2.08 (t, J = 6 and 6 Hz, 2H, C_6H_2), 2.60-3.00 (m, 4H, C_5-H_2 and C_7-H_2), 3.84 (s, 3H, OCH₃), 4.79 (q, J = 7 Hz, 1H, CH_2CH), 6.85 (d, J = 9 Hz, 1H, C_2-H or C_3-H), 7.05 (d, J = 9 Hz, 1H, C_2-H or C_3-H) and 11.75 (br s, 1H, CO_2H); ^{13}C nmr (deuteriochloroform): δ 18.8 (q), 22.2 (t), 23.5 (t), 40.3 (t), 56.2 (q), 76.6 (d), 114.0 (d), 116.9 (d), 123.2 (s), 136.3 (s), 151.4 (s), 152.1 (s), 172.8 (s) and 200.7 (s).

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.39; H, 6.27.

2-(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy)butyric Acid (**1c**).

Compound **1c** (73%) was prepared from the reaction of **11** with ethyl 2-bromobutyrate in a manner similar to the synthesis of **1b**; it formed colorless needles from ether-hexane, mp 67-69°; ir (potassium bromide): 1740 (CO_2H) and 1660 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.08 (t, J = 7 Hz, 3H, CH_2CH_2), 1.98-2.29 (m, 4H, CH_2CH_2 and C_6-H_2), 2.60-3.00 (m, 4H, C_5-H_2 and C_7-H_2), 3.84 (s, 3H, OCH₃), 4.79 (t, J = 5 Hz, 1H, $CHCO_2H$), 6.85 (d, J = 9 Hz, 1H, C_2-H or C_3-H), 7.05 (d, J = 9 Hz, 1H, C_2-H or C_3-H) and 11.60 (br s, 1H, CO_2H); ^{13}C nmr (deuteriochloroform): δ 8.8 (q), 22.1 (t), 23.4 (t), 26.1 (t), 40.1 (t), 56.1 (q), 80.9 (d), 113.8 (d), 116.7 (d), 123.0 (s), 136.0 (s), 151.5 (s), 151.8 (s), 172.8 (s) and 201.3 (s).

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.49; H, 6.59.

2-(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy)-3-methylbutyric Acid (**1d**).

Compound **1d** (59%) was prepared from the reaction of **11** with ethyl 2-bromo-3-methylbutyrate in a manner similar to the synthesis of **1b**; it formed colorless needles from ether-hexane, mp 123-124°; ir (potassium bromide): 1750 (CO_2H) and 1660 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.10 (d, J = 7 Hz, 3H, CH_2CH_2CH), 1.15 (d, J = 7 Hz, 3H, CH_2CH_2CH), 2.02-2.93 (m, 7H, CH_2CH_2CH , C_5-H_2 , C_6-H_2 and C_7-H_2), 3.83 (s, 3H, OCH₃), 4.74 (d, J = 4 Hz, 1H, $CHCO_2H$), 6.85 (d, J = 9 Hz, 1H, C_2-H or C_3-H), 7.04 (d, J = 9 Hz, 1H, C_2-H or C_3-H); ^{13}C nmr (deuteriochloroform): δ 17.1 (q), 18.8 (q), 22.1 (t), 23.3 (t), 31.9 (d), 40.1 (t), 56.1 (q), 84.4 (d), 113.8 (d), 116.6 (d), 123.2 (s), 135.9 (s), 151.5 (s), 151.8 (s), 172.2 (s) and 201.6 (s).

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.55; H, 6.72.

2-(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy)-2-phenylacetic Acid (**1e**).

Compound **1e** (18%) was prepared from the reaction of **11** with ethyl 2-bromo-2-phenylacetate in a manner similar to the synthesis of **1b**; it formed colorless needles from acetone, mp 163-164°; ir (potassium bromide): 1750 (CO_2H) and 1650 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.92-2.21 (m, 2H, C_6-H_2), 2.61-2.96 (m, 4H, C_5-H_2 and C_7-H_2), 3.78 (s, 3H, OCH₃), 5.52 (s, 1H, $CHCO_2H$), 6.61 (d, J = 9 Hz, C_2-H or C_3-H), 6.88 (d, J = 9 Hz, 1H, C_2-H or C_3-H) and 7.31-7.59 (m, 5H, Ph-H₅); ^{13}C nmr (deuteriochloroform): δ 22.2 (t), 23.6 (t), 40.5 (t), 56.1 (q), 81.5 (d), 114.0 (d), 116.5

(d), 122.9 (s), 126.8 (d), 128.9 (d), 135.8 (s), 136.3 (s), 151.1 (s), 152.1 (s), 170.4 (s) and 200.6 (s).

Anal. Calcd. for $C_{19}H_{18}O_5$: C, 69.92; H, 5.56. Found: C, 69.73; H, 5.36.

4-Methoxy-7-methyl-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetic Acid (1f).

Compound **1f** (67%) was prepared from the reaction of 8-hydroxy-5-methoxy-2-methyl-1,2,3,4-tetrahydro-1-naphthalenone **15** and ethyl bromoacetate in a manner similar to the synthesis of **1b**; it formed colorless needles from acetone, mp 119-120°; ir (potassium bromide) 1790, 1700 (CO_2H) and 1670 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.23 (d, J = 7 Hz, 3H, $CHCH_3$), 1.55-3.25 (m, 5H, C_5-H_2 , C_6-H_2 and C_7-H), 3.85 (s, 3H, OCH_3), 4.67 (s, 2H, OCH_2CO_2H), 6.80 (d, J = 9 Hz, 1H, C_2-H or C_3-H), and 7.04 (d, J = 9 Hz, 1H, C_2-H or C_3-H); ^{13}C nmr (deuteriochloroform): δ 15.3 (q), 22.9 (t), 30.3 (t), 43.4 (d), 56.0 (q), 68.6 (t), 114.1 (d), 116.0 (d), 122.7 (s), 135.4 (s), 151.5 (s), 152.1 (s), 170.1 (s) and 203.3 (s).

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.76; H, 6.24.

7-Ethyl-4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetic Acid (1g).

Compound **1g** (61%) was prepared from the reaction of 8-hydroxy-5-methoxy-2-ethyl-1,2,3,4-tetrahydro-1-naphthalenone (obtained [15] from 5,8-dimethoxy-1,2,3,4-tetrahydro-1-naphthalenone) with ethyl bromoacetate in a manner similar to the synthesis of **1b**; it formed colorless needles from ether, mp 93-94°; ir (potassium bromide): 1780, 1760 (CO_2H) and 1660 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 0.98 (t, J = 7 Hz, 3H, CH_2CH_3), 1.17-3.23 (m, 7H, C_5-H_2 , C_6-H_2 , C_7-H and CH_2CH_3), 3.84 (s, 3H, OCH_3), 4.68 (s, 2H, OCH_2CO_2H), 6.80 (d, J = 9 Hz, 1H, C_2-H or C_3-H) and 7.04 (d, J = 9 Hz, 1H, C_2-H or C_3-H); ^{13}C nmr (deuteriochloroform): δ 11.5 (q), 22.3 (t), 22.6 (t), 26.9 (t), 49.9 (d), 56.0 (q), 68.7 (t), 114.2 (d), 115.9 (d), 122.8 (s), 135.2 (s), 151.6 (s), 152.1 (s), 170.1 (s) and 203.2 (s).

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.98; H, 6.58.

7-Isopropyl-4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetic Acid (1h).

Compound **1h** (46%) was prepared from the reaction of 8-hydroxy-5-methoxy-2-isopropyl-1,2,3,4-tetrahydro-1-naphthalenone (obtained [15] from 5,8-dimethoxy-1,2,3,4-tetrahydro-1-naphthalenone) with ethyl bromoacetate in a manner similar to the synthesis of **1b**; it formed colorless needles from ether, mp 88-89°; ir (potassium bromide): 1780, 1750 (CO_2H) and 1670 (CO); 1H nmr (deuteriochloroform): δ 0.94 (d, J = 7 Hz, 3H, $CHCH_3CH_3$), 0.96 (d, J = 7 Hz, 3H, $CHCH_3CH_3$), 1.84-3.22 (m, 6H, C_5-H_2 , C_6-H_2 , C_7-H and $CHCH_3CH_3$), 3.84 (s, 3H, OCH_3), 4.69 (s, 2H, OCH_2CO_2H), 6.80 (d, J = 9 Hz, 1H, C_2-H or C_3-H) and 7.04 (d, J = 9 Hz, 1H, C_2-H or C_3-H); ^{13}C nmr (deuteriochloroform): δ 18.9 (d), 20.8 (q), 21.8 (t), 23.1 (t), 26.8 (d), 54.8 (d), 56.0 (q), 68.8 (t), 114.2 (d), 115.9 (d), 123.2 (s), 135.1 (s), 151.5 (s), 152.1 (s), 170.1 (s) and 203.5 (s).

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.50; H, 6.78.

4-Chloro-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetic Acid (3b).

Compound **3b** (65%) was prepared from the reaction of 5-chloro-8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone (obtained from 5-nitro-8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone [12]) with ethyl bromoacetate in a manner similar to the synthesis of **1b**; it formed colorless needles from benzene, mp 135-136°; ir (potassium bromide): 1775 (CO_2H) and 1660 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 2.06-2.20 (m, 2H, C_6-H_2), 2.71 (t, J = 6 Hz, 2H, C_7-H_2), 3.02 (t, J = 6 Hz, 2H, C_5-H_2), 4.71 (s, 2H, OCH_2CO_2H), 6.83 (d, J = 9 Hz, 1H, C_2-H), 7.56 (d, J = 9 Hz, 1H, C_3-H) and 11.20 (br s, 1H, CO_2H); ^{13}C nmr (deuteriochloroform): δ 21.8 (t), 28.0 (t), 40.0 (t), 67.9 (t), 114.7 (d), 123.6 (s), 127.8 (s), 135.5 (d), 144.5 (s), 156.9 (s), 169.1 (s) and 199.1 (s).

Anal. Calcd. for $C_{12}H_{11}ClO_4$: C, 56.60; H, 4.35. Found: C, 56.78; H, 4.30.

4-Bromo-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetic Acid (3c).

Compound **3c** (63%) was prepared from the reaction of 5-bromo-8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone (obtained from 5-nitro-8-hydroxy-

xy-1,2,3,4-tetrahydro-1-naphthalenone [12]) with ethyl bromoacetate in a manner similar to the synthesis of **1b**; it formed colorless needles from benzene, mp 131-132°; ir (potassium bromide): 1760 (CO_2H) and 1670 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 2.06-2.27 (m, 2H, C_6-H_2), 2.71 (t, J = 6 Hz, 2H, C_7-H_2), 3.01 (t, J = 6 Hz, 2H, C_5-H_2), 4.71 (s, 2H, OCH_2CO_2H), 6.78 (d, J = 9 Hz, 1H, C_2-H), 7.74 (d, J = 9 Hz, 1H, C_3-H) and 10.75 (br s, 1H, CO_2H); ^{13}C nmr (deuteriochloroform): δ 22.2 (t), 31.6 (t), 40.4 (t), 68.2 (t), 116.3 (d), 117.3 (s), 124.8 (s), 138.9 (d), 146.5 (s), 158.5 (s), 169.2 (s) and 198.9 (s).

Anal. Calcd. for $C_{12}H_{11}BrO_4$: C, 48.19; H, 3.71. Found: C, 48.02; H, 3.65.

4-Nitro-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetic Acid (3d).

Compound **3d** (41%) was prepared from the reaction of 5-nitro-8-hydroxy-1,2,3,4-tetrahydro-1-naphthalenone [12] and ethyl bromoacetate in a manner similar to the synthesis of **1b**; it formed pale yellow needles from benzene, mp 134-135°; ir (potassium bromide): 1730 (CO_2H) and 1665 cm^{-1} (CO); 1H nmr (deuterioacetone): δ 2.05-2.26 (m, 2H, C_6-H_2), 2.71 (t, J = 6 Hz, 2H, C_7-H_2), 3.18 (t, J = 6 Hz, 2H, C_5-H_2), 4.93 (s, 2H, OCH_2CO_2H), 7.22 (d, J = 9 Hz, 1H, C_2-H), 8.13 (d, J = 9 Hz, 1H, C_3-H) and 9.40 (br s, 1H, CO_2H); ^{13}C nmr (deuterioacetone): δ 22.2 (t), 31.6 (t), 40.4 (t), 68.2 (t), 116.3 (d), 117.3 (s), 124.8 (s), 138.9 (d), 146.5 (s), 158.5 (s), 169.2 (s) and 198.9 (s).

Anal. Calcd. for $C_{12}H_{11}NO_6$: C, 54.34; H, 4.18; N, 5.28. Found: C, 54.51; H, 4.10; N, 5.43.

Ethyl 2-(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy)propionate (2b).

An ethanolic solution (50 ml) of **1b** (2.0 g, 7.58 mmoles) was refluxed for 6 hours in the presence of a few drops of sulfuric acid. After removal of the ethanol the residue was extracted with ether. The extract was washed with 1M aqueous potassium carbonate then with water, dried and evaporated. The residue was distilled under reduced pressure to give **2b** (2.1 g, 95%), colorless oil, bp 176-177° (1.2 Torr); ir (neat): 1750 ($CO_2C_2H_5$) and 1690 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.26 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.66 (d, J = 7 Hz, 3H, CH_3CH), 1.90-2.18 (m, 2H, C_6-H_2), 2.61 (t, J = 6 Hz, 2H, C_5-H_2 or C_7-H_2), 2.86 (t, J = 6 Hz, 2H, C_2-H_2 or C_7-H_2), 3.81 (s, 3H, OCH_3), 4.21 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.58 (q, J = 7 Hz, 1H, CH_3CH), 6.83 (d, J = 9 Hz, 1H, C_2-H or C_3-H) and 6.94 (d, J = 9 Hz, 1H, C_2-H or C_3-H); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 18.5 (q), 22.3 (t), 23.6 (t), 40.6 (t), 55.9 (q), 60.8 (t), 76.4 (d), 117.6 (d), 125.2 (s), 135.0 (s), 151.4 (s), 152.0 (s), 172.5 (s) and 197.1 (s).

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.47; H, 6.85.

Ethyl 2-(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy)butyrate (2c).

Compound **2c** (95%) was prepared by esterification of **1c** in a manner similar to the synthesis of **2b**, colorless oil, bp 182-183° (1.3 Torr); ir (neat): 1760, 1730 ($CO_2C_2H_5$) and 1690 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.12 (t, J = 7 Hz, 3H, CH_3CH_2CH), 1.25 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.90-2.20 (m, 4H, C_6-H_2 and CH_3CH_2CH), 2.61 (t, J = 7 Hz, 2H, C_5-H_2 or C_7-H_2), 2.86 (t, J = 6 Hz, 2H, C_5-H_2 or C_7-H_2), 3.80 (s, 3H, OCH_3), 4.21 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.49 (t, J = 6 Hz, 1H, CH_3CH_2CH), 6.72 (d, J = 9 Hz, 1H, C_2-H or C_3-H) and 6.91 (d, J = 9 Hz, 1H, C_2-H or C_3-H); ^{13}C nmr (deuteriochloroform): δ 9.3 (q), 14.2 (q), 22.3 (t), 23.7 (t), 26.2 (t), 40.7 (t), 55.9 (q), 60.8 (t), 80.2 (d), 115.0 (d), 124.6 (s), 135.1 (s), 151.4 (s), 151.9 (s), 171.7 (s) and 196.9 (s).

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.40; H, 7.18.

Ethyl 2-(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy)-3-methylbutyrate (2d).

Compound **2d** (95%) was prepared by esterification of **1d** in a manner similar to the synthesis of **2b**, colorless oil, bp 183-184° (1.2 Torr); ir (neat): 1750, 1730 ($CO_2C_2H_5$) and 1690 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.12 (d, J = 7 Hz, 3H, CH_3CH_2CH), 1.17 (d, J = 7 Hz, 3H, CH_3CH_2CH), 1.24 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.90-3.00 (m, 7H, CH_3CH_2CH , C_5-H_2 , C_6-H_2 and C_7-H_2), 3.79 (s, 3H, OCH_3), 4.21 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.36 (d, J = 7 Hz, 1H, $OCHCO_2$), 6.61 (d, J = 9 Hz, 1H, C_2-H or C_3-H) and 6.89 (d, J = 9 Hz, 1H, C_2-H or C_3-H); ^{13}C nmr (deu-

teriochloroform): δ 14.2 (q), 17.7 (q), 18.6 (q), 22.3 (t), 23.7 (t), 31.9 (d), 40.8 (t), 55.9 (q), 60.6 (t), 82.9 (d), 112.6 (d), 115.0 (d), 124.0 (s), 135.2 (s), 150.8 (s), 152.2 (s), 171.0 (s) and 196.5 (s).

Anal. Calcd. for $C_{18}H_{14}O_5$: C, 67.48; H, 7.55. Found: C, 67.35; H, 7.54.

Ethyl 2-(4-Methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxy)-2-phenylacetate (**2e**).

Compound **2e** (95%) was prepared by esterification of **1e** in a manner similar to the synthesis of **2b**; it formed colorless needles from benzene-hexane, mp 92-93°; ir (potassium bromide): 1730 ($CO_2C_2H_5$) and 1670 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.18 (t, J = 7 Hz, 3H, CH_2CH_3), 1.90-2.16 (m, 2H, C_2-H_2), 2.63 (t, J = 6 Hz, 2H, C_5-H_2 or C_7-H_2), 2.86 (t, J = 6 Hz, 2H, C_5-H_2 or C_7-H_2), 3.77 (s, 3H, OCH₃), 4.18 (q, J = 7 Hz, 2H, CH_2CH_3), 5.56 (s, 1H, CHCO₂), 6.70 (d, J = 9 Hz, 1H, C_2-H or C_5-H), 6.86 (d, J = 9 Hz, 1H, C_2-H or C_5-H), 7.24-7.40 (m, 3H, Ph-H₃) and 7.62-7.74 (m, 2H, Ph-H₂); ^{13}C nmr (deuteriochloroform): δ 14.0 (q), 22.2 (t), 23.6 (t), 40.6 (t), 55.8 (q), 61.2 (t), 81.2 (d), 114.8 (d), 115.8 (d), 124.9 (s), 127.3 (d), 128.5 (d), 135.2 (s), 136.0 (s), 150.9 (s), 151.8 (s), 170.1 (s) and 197.0 (s).

Anal. Calcd. for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 71.39; H, 6.17.

Ethyl 4-Methoxy-7-methyl-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetate (**2f**).

Compound **2f** (95%) was prepared by esterification of **1f** in a manner similar to the synthesis of **2b**, colorless oil, bp 173-174° (1.1 Torr); ir (neat): 1760, 1740 ($CO_2C_2H_5$) and 1690 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 1.20 (d, J = 6 Hz, 3H, $CHCH_3$), 1.29 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.50-3.22 (m, 5H, C_5-H_2 , C_6-H_2 and C_7-H), 3.81 (s, 3H, OCH₃), 4.25 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.54 (d, J = 9 Hz, 1H, C_2-H or C_5-H) and 6.93 (d, J = 9 Hz, 1H, C_2-H or C_5-H); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 15.3 (q), 23.1 (t), 30.4 (t), 43.3 (d), 55.8 (q), 61.0 (t), 68.6 (t), 114.4 (d), 115.5 (d), 124.9 (s), 134.5 (s), 151.9 (s), 169.3 (s) and 200.0 (s).

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.52; H, 6.78.

Ethyl 7-Ethyl-4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetate (**2g**).

Compound **2g** (95%) was prepared by esterification of **1g** in a manner similar to the synthesis of **2b**, colorless oil, bp 179-180° (1.4 Torr); ir (neat): 1760, 1740 ($CO_2C_2H_5$) and 1690 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 0.98 (t, J = 7 Hz, 3H, CH_2CH_3), 1.29 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.44-3.20 (m, 7H, C_5-H_2 , C_6-H_2 , C_7-H and CH_2CH_3), 3.81 (s, 3H, OCH₃), 4.25 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.64 (s, 2H, OCH₂CO₂), 6.81 (d, J = 9 Hz, 1H, C_2-H or C_5-H) and 6.93 (d, J = 9 Hz, 1H, C_2-H or C_5-H); ^{13}C nmr (deuteriochloroform): δ 11.6 (q), 14.2 (q), 22.6 (t), 27.1 (t), 50.0 (d), 55.9 (q), 61.0 (t), 68.8 (t), 114.4 (d), 115.6 (d), 125.2 (s), 134.4 (s), 151.9 (s), 169.3 (s) and 199.7 (s).

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.37; H, 7.17.

Ethyl 7-Isopropyl-4-methoxy-8-oxo-5,6,7,8-tetrahydro-1-naphthoxyacetate (**2h**).

Compound **2h** (95%) was prepared by esterification of **1h** in a manner similar to the synthesis of **2b**, colorless oil, bp 182-183° (1.2 Torr); ir (neat): 1760, 1740 ($CO_2C_2H_5$) and 1690 cm^{-1} (CO); 1H nmr (deuteriochloroform): δ 0.93 (d, J = 6 Hz, 3H, $CHCH_3CH_3$), 0.96 (d, J = 6 Hz, 3H, $CHCH_3CH_3$), 1.28 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.76-3.20 (m, 6H, C_5-H_2 , C_6-H_2 , C_7-H and $CHCH_3CH_3$), 3.81 (s, 3H, OCH₃), 4.24 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.65 (s, 2H, OCH₂CO₂), 6.79 (d, J = 9 Hz, 1H, C_2-H or C_5-H) and 6.91 (d, J = 9 Hz, 1H, C_2-H or C_5-H); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 18.9 (q), 21.0 (q), 22.1 (t), 23.2 (t), 26.7 (d), 55.0 (d), 55.8 (q), 61.0 (t), 68.5 (t), 114.3 (d), 115.1 (d), 125.4 (s), 134.2 (s), 151.7 (s), 169.3 (s) and 199.9 (s).

Anal. Calcd. for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.29; H, 7.42.

General Procedure for Reaction of Acids **1a-h** with Sodium Acetate in Acetic Anhydride.

A mixture of the acid (2.00 mmoles), acetic anhydride (7.5 ml) and sodium acetate (2.3 g, 28.1 mmoles) was refluxed at 150° for 1 hour. The mixture was poured into ice-water (200 ml), stirred for 5 minutes to de-

compose excess of acetic anhydride and extracted with ether. The extract was washed with aqueous 1M potassium carbonate (30 ml \times 3) and then with water, dried and evaporated. The resulting oil was chromatographed and eluted with benzene. The first fraction gave a furan and the second fraction afforded a lactone.

6-Methoxy-2-methyl-4,5-dihydro-3H-naphtho[1,8-bc]furan (**4b**).

Colorless needles from methanol, mp 43-44.5°; 1H nmr (deuteriochloroform): δ 1.80-2.06 (m, 2H, C_2-H_2), 2.33 (s, 3H, CH₃), 2.54-2.84 (m, 4H, C_3-H_2 and C_5-H_2), 3.82 (s, 3H, OCH₃), 6.69 (d, J = 9 Hz, 1H, C_7-H or C_8-H) and 7.06 (d, J = 9 Hz, 1H, C_7-H or C_8-H); ^{13}C nmr (deuteriochloroform): δ 12.2 (q), 19.9 (t), 21.7 (t), 23.6 (t), 56.6 (q), 107.2 (d), 107.9 (d), 111.5 (s), 118.5 (s), 130.3 (s), 147.6 (s), 148.2 (s) and 151.3 (s).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C 76.95; H, 7.02.

2-Ethyl-6-methoxy-4,5-dihydro-3H-naphtho[1,8-bc]furan (**4c**).

This compound was obtained as colorless oil, bp 133° (1.5 Torr); 1H nmr (deuteriochloroform): δ 1.29 (t, J = 7 Hz, 3H, CH_2CH_3), 1.80-2.08 (tt, J = 5 and 5 Hz, 2H, C_4-H_2), 2.60-2.86 (m, 6H, CH_2CH_3 , C_3-H_2 and C_5-H_2), 3.82 (s, 3H, OCH₃), 6.70 (d, J = 9 Hz, 1H, C_7-H or C_8-H) and 7.07 (d, J = 9 Hz, 1H, C_7-H or C_8-H); ^{13}C nmr (deuteriochloroform): δ 12.4 (q), 20.1 (t), 20.8 (t), 21.8 (t), 23.7 (t), 56.7 (q), 107.3 (d), 108.0 (d), 110.6 (s), 118.7 (s), 130.4 (s), 147.6 (s), 151.3 (s) and 153.3 (s).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.25; H, 7.46. Found: C, 77.53; H, 7.39.

2-Isopropyl-6-methoxy-4,5-dihydro-3H-naphtho[1,8-bc]furan (**4d**).

This compound was obtained as a colorless oil, bp 136° (1.4 Torr); 1H nmr (deuteriochloroform): δ 1.33 (d, J = 6 Hz, 6H, $CHCH_3CH_3$), 1.80-2.06 (m, 2H, C_4-H_2), 2.73 (t, J = 6 Hz, 2H, C_3-H_2 or C_5-H_2), 2.79 (t, J = 6 Hz, 2H, C_3-H_2 or C_5-H_2), 2.90-3.20 (m, 1H, $CHCH_3CH_3$), 3.82 (s, 3H, OCH₃), 6.71 (d, J = 9 Hz, 1H, C_7-H or C_8-H) and 7.08 (d, J = 9 Hz, 1H, C_7-H or C_8-H); ^{13}C nmr (deuteriochloroform): δ 20.6 (t), 21.2 (q), 21.8 (t), 23.7 (t), 28.1 (d), 56.9 (q), 107.3 (d), 108.1 (d), 109.5 (s), 118.9 (s), 130.4 (s), 147.4 (s), 151.2 (s) and 156.7 (s).

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.01; H, 7.70.

6-Methoxy-2-phenyl-4,5-dihydro-3H-naphtho[1,8-bc]furan (**4e**).

This compound was obtained as colorless plates from methanol, mp 84-85°; 1H nmr (deuteriochloroform): δ 1.86-2.14 (m, 2H, C_2-H_2), 2.83 (t, J = 6 Hz, 2H, C_3-H_2 or C_5-H_2), 2.98 (t, J = 6 Hz, 2H, C_3-H_2 or C_5-H_2), 3.82 (s, 3H, OCH₃), 6.77 (d, J = 9 Hz, 1H, C_7-H or C_8-H), 7.16 (d, J = 9 Hz, 1H, C_7-H or C_8-H) and 7.10-7.80 (m, 5H, Ph-H₅); ^{13}C nmr (deuteriochloroform): δ 21.5 (t), 22.1 (t), 23.5 (t), 56.6 (q), 107.6 (d), 109.3 (d), 113.1 (s), 119.2 (s), 125.3 (d), 127.3 (d), 128.5 (d), 130.5 (s), 131.8 (s), 147.5 (s), 148.6 (s) and 151.2 (s).

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.58; H, 6.02.

6-Methoxy-3-methyl-4,5-dihydro-3H-naphtho[1,8-bc]furan (**4f**).

This compound was obtained as a colorless oil, bp 122° (1.5 Torr); 1H nmr (deuteriochloroform): δ 1.33 (d, J = 7 Hz, 3H, CH₃), 1.44-3.16 (m, 5H, C_3-H , C_4-H_2 and C_5-H_2), 3.85 (s, 3H, OCH₃), 6.80 (d, J = 9 Hz, 1H, C_7-H or C_8-H), 7.16 (d, J = 9 Hz, 1H, C_7-H or C_8-H) and 7.28 (d, J = 2 Hz, 1H, C_2-H); ^{13}C nmr (deuteriochloroform): δ 19.7 (q), 21.6 (t), 27.1 (d), 32.6 (t), 56.7 (q), 108.0 (d), 109.3 (d), 119.3 (s), 122.9 (s), 128.6 (s), 138.4 (d), 148.5 (s) and 151.3 (s).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.07; H, 6.87.

3-Ethyl-6-methoxy-4,5-dihydro-3H-naphtho[1,8-bc]furan (**4g**).

This compound was obtained as a colorless oil, bp 130° (1.4 Torr); 1H nmr (deuteriochloroform): δ 1.05 (t, J = 7 Hz, 3H, CH_2CH_3), 1.20-3.00 (m, 7H, CH_2CH_3 , C_3-H , C_4-H_2 and C_5-H_2), 3.85 (s, 3H, OCH₃), 6.80 (d, J = 9 Hz, 1H, C_7-H or C_8-H), 7.16 (d, J = 9 Hz, 1H, C_7-H or C_8-H) and 7.31 (d, J = 1 Hz, 1H, C_2-H); ^{13}C nmr (deuteriochloroform): δ 11.8 (q), 20.9 (t), 27.1 (t), 29.5 (t), 33.9 (d), 56.7 (q), 107.9 (d), 109.3 (d), 119.3 (s), 121.3 (s), 128.7 (s), 138.6 (d), 148.4 (s) and 151.2 (s).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.50; H, 7.38.

3-Isopropyl-6-methoxy-4,5-dihydro-3H-naphtho[1,8-bc]furan (**4h**).

This compound was obtained as a colorless oil, bp 140° (1.3 Torr); ¹H nmr (deuteriochloroform): δ 1.03 (d, J = 7 Hz, 6H, CHCH₃CH₃), 1.74-3.02 (m, 6H, C₃-H, C₄-H₂, C₅-H₂ and CHCH₃CH₃), 6.79 (d, J = 9 Hz, 1H, C₇-H or C₈-H), 7.16 (d, J = 9 Hz, 1H, C₇-H or C₈-H) and 7.29 (d, J = 2 Hz, 1H, C₂-H); ¹³C nmr (deuteriochloroform): δ 19.7 (q), 20.4 (q), 21.0 (t), 26.2 (t), 30.3 (d), 39.0 (d), 56.8 (q), 107.9 (d), 109.3 (d), 119.5 (s), 119.9 (s), 129.1 (s), 138.9 (d), 148.3 (s) and 151.2 (s).

Anal. Calcd. for C₁₅H₁₈O₂: C, 78.23; H, 7.88. Found: C, 77.98; H, 7.83.

6-Chloro-4,5-dihydro-3H-naphtho[1,8-bc]furan (6b).

This compound was obtained as colorless needles from methanol, mp 43-44°; ¹H nmr (deuteriochloroform): δ 1.84-2.10 (m, 2H, C₄-H₂), 2.74 (dt, J = 1 and 6 Hz, C₃-H₂), 2.85 (t, J = 6 Hz, 2H, C₅-H₂), 7.14 (s, 2H, C₇-H and C₈-H) and 7.29 (t, J = 1 Hz, 1H, C₂-H); ¹³C nmr (deuteriochloroform): δ 19.7 (t), 23.5 (t), 24.6 (t), 109.4 (d), 116.8 (s), 124.8 (s), 124.8 (d), 129.0 (s), 130.1 (s), 138.7 (d) and 151.5 (s).

Anal. Calcd. for C₁₁H₉ClO: C, 68.58; H, 4.71. Found: C, 68.43; H, 4.61.

6-Bromo-4,5-dihydro-3H-naphtho[1,8-bc]furan (6c).

This compound was obtained as a pale yellow oil, bp 93° (0.7 Torr); ¹H nmr (deuteriochloroform): δ 1.86-2.12 (m, 2H, C₄-H₂), 2.74 (dt, J = 1 and 6 Hz, 2H, C₃-H), 2.82 (t, J = 6 Hz, 2H, C₅-H₂), 7.08 (d, J = 9 Hz, 1H, C₇-H or C₈-H), 7.27 (t, J = 1 Hz, 1H, C₂-H), and 7.31 (d, J = 9 Hz, 1H, C₇-H or C₈-H); ¹³C nmr (deuteriochloroform): δ 19.7 (t), 23.7 (t), 26.9 (t), 109.9 (d), 114.0 (s), 116.7 (s), 127.5 (d), 129.2 (s), 132.2 (s), 138.4 (d) and 151.9 (s).

Anal. Calcd. for C₁₁H₉BrO: C, 55.72; H, 3.83. Found: C, 55.92; H, 3.70.

6-Nitro-4,5-dihydro-3H-naphtho[1,8-bc]furan (6d).

This compound was obtained as colorless needles from methanol, mp 108-109°; ¹H nmr (deuteriochloroform): δ 1.90-2.16 (m, 2H, C₄-H₂), 2.81 (dt, J = 1 and 6 Hz, 2H, C₃-H₂), 3.31 (t, J = 6 Hz, 2H, C₅-H₂), 7.26 (d, J = 6 Hz, 1H, C₇-H or C₈-H), 7.43 (t, J = 1 Hz, 1H, C₂-H) and 8.07 (d, J = 6 Hz, 1H, C₇-H or C₈-H); ¹³C nmr (deuteriochloroform): 19.4 (t), 23.5 (t), 26.1 (t), 109.1 (d), 118.4 (s), 121.9 (d), 128.9 (s), 131.2 (s), 140.3 (d), 141.6 (s) and 155.2 (s).

Anal. Calcd. for C₁₁H₉NO₃: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.81; H, 4.62; N, 6.98.

Lactone 5b.

This compound was obtained as colorless needles from benzene-hexane, mp 76-77°; ir (potassium bromide): 1760 cm⁻¹ (CO₂); ¹H nmr (deuteriochloroform): δ 1.56 (d, J = 7 Hz, 3H, CH₃), 2.12-3.21 (m, 4H, CH₂-CH₂), 3.79 (s, 3H, OCH₃), 4.76 (q, J = 7 Hz, 1H, CH₃CH), 5.80-5.92 (m, 1H, C = CH) and 6.78 (s, 2H, Ph-H₂); ¹³C nmr (deuteriochloroform): δ 16.5 (q), 21.3 (t), 56.1 (q), 73.5 (d), 112.6 (d), 114.5 (d), 116.9 (d), 118.7 (s), 127.4 (s), 145.3 (s), 148.8 (s), 151.3 (s) and 168.7 (s).

Anal. Calcd. for C₁₄H₁₄O₄: C, 68.28; H, 5.73. Found: C, 68.10; H, 5.72.

Lactone 5c.

This compound was obtained as colorless needles from benzene-hexane, mp 83-84°; ir (potassium bromide): 1770 cm⁻¹ (CO₂); ¹H nmr (deuteriochloroform): δ 1.05 (t, J = 7 Hz, 3H, CH₃CH₂), 1.97 (dq, J = 7 and 7 Hz, 2H, CH₂CH₂), 2.30-3.20 (m, 4H, CH₂CH₂), 3.79 (s, 3H, OCH₃), 4.47 (t, J = 7 Hz, 1H, OCHCO₂), 5.80-5.90 (m, 1H, C = CH) and 6.80 (s, 2H, Ph-H₂); ¹³C nmr (deuteriochloroform): δ 9.3 (q), 21.2 (t), 21.3 (t), 24.0 (t), 56.1 (q), 78.6 (d), 112.6 (d), 114.5 (d), 116.7 (d), 118.9 (s), 127.4 (s), 145.4 (s), 149.1 (s), 151.4 (s) and 168.3 (s).

Anal. Calcd. for C₁₅H₁₆O₄: C, 69.21; H, 6.20. Found: C, 69.01; H, 6.08.

Lactone 5d.

This compound was obtained as colorless needles from benzene-hexane, mp 79-80°; ir (potassium bromide): 1780 cm⁻¹ (CO₂); ¹H nmr (deuteriochloroform): δ 1.04 (d, J = 5 Hz, 3H, CH₃CH₂CH), 1.11 (d, J = 5 Hz, 3H, CH₃CH₂CH), 2.12-3.20 (m, 5H, CH₂CH₂ and CH₃CH₂CH), 3.79 (s, 3H, OCH₃), 4.19 (d, J = 8 Hz, 1H, CHCO₂), 5.78-5.90 (m, 1H, C = CH), 6.74 (d, J = 9 Hz, 1H, Ph-H), 6.85 (d, J = 9 Hz, 1H, Ph-H); ¹³C nmr (deuteriochloroform): δ 17.4 (q), 18.8 (q), 21.2 (t), 21.3 (t), 29.2 (d), 56.1 (q), 82.2 (d), 112.7 (d), 114.4 (d), 116.6 (d), 119.1 (s), 127.4 (s), 145.4 (s), 149.2 (s),

151.4 (s) and 167.6 (s).

Anal. Calcd. for C₁₆H₁₈O₄: C, 70.05; H, 6.61. Found: C, 69.90; H, 6.66.

Lactone 5e.

This compound was obtained as colorless plates from benzene-hexane, mp 191-192°; ir (potassium bromide): 1760 cm⁻¹ (CO₂); ¹H nmr (deuteriochloroform): δ 2.20-3.20 (m, 4H, CH₂CH₂), 3.79 (s, 3H, OCH₃), 5.66 (s, 1H, OCHCO₂), 5.86-6.00 (m, 1H, C = CH), 6.75 (d, J = 9 Hz, 1H, Ph-H), 6.87 (d, J = 9 Hz, 1H, Ph-H) and 7.42 (s, 5H, Ph-H₂); ¹³C nmr (deuteriochloroform): δ 21.3 (t), 21.5 (t), 56.3 (q), 79.9 (d), 113.1 (d), 114.6 (d), 117.5 (d), 119.3 (s), 127.7 (d), 128.4 (d), 129.0 (d) 134.3 (s), 145.6 (s), 148.7 (s), 151.8 (s) and 167.4 (s).

Anal. Calcd. for C₁₉H₁₆O₄: C, 74.01; H, 5.23. Found: C, 74.08; H, 5.31.

Lactone 5f.

This compound was obtained as colorless needles from benzene-hexane, mp 61-62°; ir (potassium bromide): 1770 cm⁻¹ (CO₂); ¹H nmr (deuteriochloroform): δ 1.97 (s, 3H, CH₃), 2.18-2.80 (m, 4H, CH₂CH₂), 3.79 (s, 3H, CH₃), 4.63 (s, 2H, OCH₂CO₂), 6.68 (d, J = 9 Hz, 1H, Ph-H) and 6.80 (d, J = 9 Hz, 1H, Ph-H); ¹³C nmr (deuteriochloroform): δ 16.8 (q), 21.0 (t), 28.6 (t), 56.0 (q), 69.1 (t), 111.6 (d), 116.8 (d), 119.4 (s), 124.8 (s), 126.6 (s), 139.0 (s), 148.3 (s), 151.3 (s) and 167.8 (s).

Anal. Calcd. for C₁₄H₁₄O₄: C, 68.28; H, 5.73. Found: C, 68.12; H, 5.72.

Lactone 5g.

This compound was obtained as colorless needles from benzene-hexane, mp 59-60°; ir (potassium bromide): 1780 cm⁻¹ (CO₂); ¹H nmr (deuteriochloroform): δ 1.08 (t, J = 7 Hz, 3H, CH₂CH₃), 2.18-2.80 (m, 4H, CH₂CH₂), 2.60-2.80 (m, 2H, CH₂CH₃), 3.79 (s, 3H, OCH₃), 4.64 (s, 2H, CH₂CO₂), 6.68 (d, J = 9 Hz, 1H, Ph-H) and 6.80 (d, J = 9 Hz, 1H, Ph-H); ¹³C nmr (deuteriochloroform): δ 12.4 (q), 21.4 (t), 23.7 (t), 26.3 (t), 56.0 (q), 69.0 (t), 111.7 (d), 116.9 (d), 119.5 (s), 126.8 (s), 130.6 (s), 138.5 (s), 148.5 (s), 151.3 (s) and 167.9 (s).

Anal. Calcd. for C₁₅H₁₆O₄: C, 69.21; H, 6.20. Found: C, 69.08; H, 5.96.

Lactone 5h.

This compound was obtained as colorless needles from benzene-hexane, mp 114-115°; ir (potassium bromide): 1770 cm⁻¹ (CO₂); ¹H nmr (deuteriochloroform): δ 1.06 (d, J = 7 Hz, 6H, CHCH₃CH₃), 2.10-2.76 (m, 4H, CH₂CH₂), 3.30 (m, 1H, CHCH₃CH₃), 3.80 (s, 3H, CH₃), 4.66 (s, 2H, OCH₂CO₂), 6.68 (d, J = 9 Hz, 1H, Ph-H) and 6.80 (d, J = 9 Hz, 1H, Ph-H); ¹³C nmr (deuteriochloroform): δ 20.3 (q), 21.5 (t), 21.7 (t), 27.1 (d), 56.1 (q), 68.8 (t), 111.8 (d), 119.5 (s), 126.9 (s), 134.5 (s), 137.5 (s), 148.6 (s), 151.2 (s) and 168.0 (s).

Anal. Calcd. for C₁₆H₁₈O₂: C, 70.05; H, 6.61. Found: C, 69.94; H, 6.48.

General Procedure for Reaction of Esters 2a-h with Potassium Hydroxide in Dioxane.

A mixture of the ester (3.60 mmoles), powdered potassium hydroxide (1.00 g, 18.0 mmoles) and dioxane (20 ml) was refluxed for 1 hour. Water (40 ml) was added to the mixture and it was poured into 2M hydrochloric acid (200 ml). After 15 minutes the mixture was extracted with ether. The extract was washed with aqueous 1M potassium carbonate (30 ml × 3) then with water, dried and evaporated to give a furan. Hydrochloric acid (6M) was added to the alkaline solution and the resulting precipitates were extracted with ether. The extract was washed, dried and evaporated to give a mixture of a furancarboxylic acid and a naphthoxyacetic acid. The ratio of the acidic products was determined by ¹H nmr spectrometry.

6-Methoxy-3-methyl-4,5-dihydro-3H-naphtho[1,8-bc]furan-2-carboxylic Acid (8b).

This compound was obtained as colorless needles from acetone, mp 220-221°; ir (potassium bromide): 1700 cm⁻¹ (CO₂H); ¹H nmr (deuterioacetone): δ 1.31 (d, J = 7 Hz, 3H, CH₃), 1.86-2.08 (m, 2H, C₄-H₂ or C₅-H₂), 2.72-2.92 (m, 2H, C₄-H₂ or C₅-H₂), 3.40-3.70 (m, 1H, C₃-H), 3.87 (s, 3H, OCH₃), 7.11 (d, J = 9 Hz, 1H, C₇-H, or C₈-H) and 7.27 (d, J = 9 Hz, 1H, C₇-H or C₈-H).

Anal. Calcd. for C₁₄H₁₄O₄: C, 68.28; H, 5.73. Found: C, 68.01; H, 5.62.

3-Ethyl-6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylic Acids (**8c**).

This compound was obtained as colorless needles from acetone, mp 205-206°; ir (potassium bromide): 1700 cm⁻¹ (CO₂H); ¹H nmr (deuterioacetone): δ 1.03 (t, J = 7 Hz, 3H, CH₂CH₃), 1.48-3.40 (m, 7H, C₃-H, C₄-H₂ and CH₂CH₃), 3.87 (s, 3H, OCH₃), 7.10 (d, J = 9 Hz, 1H, C₇-H or C₈-H) and 7.28 (d, J = 9 Hz, 1H, C₇-H or C₈-H).

Anal. Calcd. for C₁₅H₁₆O₄: C, 69.22; H, 6.20. Found: C, 68.98; H, 6.27.

3-Isopropyl-6-methoxy-4,5-dihydro-3*H*-naphtho[1,8-*bc*]furan-2-carboxylic Acid (**8d**).

This compound was obtained as colorless needles from acetone, mp 181-182°; ir (potassium bromide): 1680 cm⁻¹ (CO₂H); ¹H nmr (deuterioacetone): δ 0.97 (d, J = 6 Hz, 3H, CHCH₃CH₃), 1.04 (d, J = 6 Hz, 3H, CHCH₃CH₃), 1.54-3.26 (m, 6H, C₃-H, C₄-H₂, C₅-H₂ and CHCH₃CH₃), 3.87 (s, 3H, OCH₃), 7.10 (d, J = 9 Hz, 1H, C₇-H or C₈-H) and 7.28 (d, J = 9 Hz, 1H, C₇-H or C₈-H).

Anal. Calcd. for C₁₆H₁₈O₄: C, 70.06; H, 6.61. Found: C, 70.15; H, 6.70.

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