

Photocyclization Reactions. Part 2 [1].
 Synthesis of Dihydrobenzofuranols Using Photocyclization of
 Ethyl 2-Formylphenoxyacetates and Ethyl 2-Acetylphenoxyacetates
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Photocyclization reactions were carried out on ethyl 2-formylphenoxyacetates **1a-e** and ethyl 2-acetylphenoxyacetates **2a-e** in acetonitrile. Irradiation of **1a-e** gave dihydrobenzofuranols **3** in 20-46% yields. Similarly, irradiation of **2a-e** afforded dihydrobenzofuranols **6** and their derivatives **7**, **8** in 40-86% yields. Substituent effects on photocyclization and reaction pathways are discussed.

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Introduction.

Carbonyl compounds which possess γ -hydrogen atoms undergo a very facile photoelimination under irradiation, called a Norrish type II reaction, to produce alkenes and smaller carbonyl compounds [2]. In the reactions cyclobutanols are also formed as by-products by intramolecular cyclization of intermediate 1,4-biradicals. By using this type of photocyclization dihydrobenzofuranols have been prepared from carbonyl compounds which possess δ -hydrogen [3]. In the previous paper [1], we investigated synthesis of dihydrobenzofuranols by photocyclization reactions of 2-alkoxybenzaldehydes, 2'-alkoxyacetophenones, 2-formylphenoxyacetic acids and 2-acetylphenoxyacetic acids. Electron-withdrawing substituents such as ethoxycarbonyl and cyano groups were useful for furan-ring formation. In this paper, we report synthesis of dihydrobenzofuranols by photocyclization reactions of ethyl 2-formylphenoxyacetates **1a-e** and ethyl 2-acetylphenoxyacetates **2a-e** and discuss substituent effects of R in the cyclization step.



- a, R = H
 b, R = CH₃
 c, R = C₂H₅
 d, R = CH(CH₃)₂
 e, R = Ph

Figure 1

Results and Discussion.

Ethyl 2-formylphenoxyacetates **1a-e** for photocyclization reactions were prepared by the reactions of 2-hydroxybenzaldehyde with ethyl bromoacetate, ethyl 2-bromo-

propanoate, ethyl 2-bromobutanoate, ethyl 2-bromo-3-methylbutanoate or ethyl 2-bromo-2-phenylacetate. Similarly, ethyl 2-acetylphenoxyacetates **2a-e** were synthesized from the reactions of 2'-hydroxyacetophenone and the corresponding bromoesters. The results are summarized in Table 1.

Photocyclization reactions of **1a-e** were carried out with 400-W high-pressure mercury lamp in acetonitrile. The results are shown in Scheme 1 and Table 2. When **1a** (R = H) was irradiated in acetonitrile dihydrobenzofuranol **3a** (46%) was obtained along with pinacol **5a** (22%). Unlike photoreactions of 2-alkoxybenzaldehydes and 2'-alkoxyacetophenones, rearranged products such as dihydroisobenzofuranols [1] were not obtained. Pinacol **5a** was a mixture (50:50 ratio) of *d,l* and *meso* isomers. The dihydrobenzofuranol **3a** was a mixture (60:40 ratio) of *cis* and *trans* isomers with regard to the ethoxycarbonyl and hydroxyl groups. The stereochemistry of two isomers was determined by comparing coupling constants ($J = 6.8$ Hz and $J = 3.1$ Hz) between C₂-H and C₃-H of **3a** with general values (*cis* isomers = 5.5-7.4 Hz, *trans* isomers = 2.0-4.8 Hz) in dihydrobenzofuran derivatives [3a,4]. Favorable formation of the *cis* isomer suggests that there is attractive interaction between the ethoxycarbonyl and hydroxyl groups in

the cyclization step of intermediate 1,5-biradicals **11** (Scheme 3) in spite of steric hindrance. The reason why rearranged products such as dihydroisobenzofuranols are not obtained in photocyclization reactions of esters may be attributed to an electronic effect of the ethoxycarbonyl group rather than a steric effect in the cyclization step, that is, 1,5-biradicals **11** stabilized by conjugation with the ethoxycarbonyl group would not be reactive enough to form spiro-ring [1,4g]. Therefore, furan-ring formation is predominant. In photocyclization reactions of **1b-d** (R = CH₃, C₂H₅, CH(CH₃)₂) dihydrobenzofuranols **3b-d** (20-26%) and ethyl acrylates derivatives **4b-d** (9-25%) were obtained. Though *cis* and *trans* isomers with regard

Scheme 1

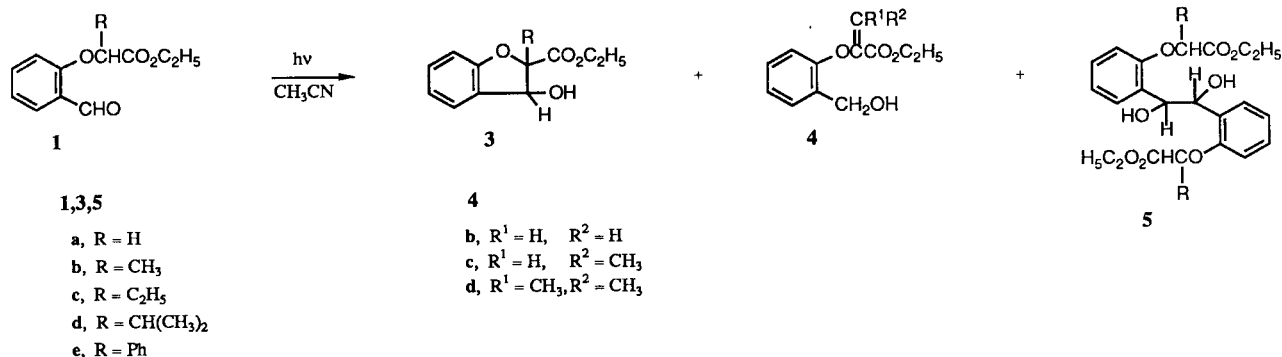


Table 1

Synthesis of Ethyl 2-Formylphenoxyacetates 1a-e and Ethyl 2-Acetylphenoxyacetates 2a-e

Starting material [a]	Product	R	Reagent	Solvent	Temperature	Yield (%)
B	1a	H	BrCH ₂ CO ₂ C ₂ H ₅	Acetone	Reflux	75
B	1b	CH ₃	CH ₃ CHBrCO ₂ C ₂ H ₅	Acetone	Reflux	74
B	1c	C ₂ H ₅	C ₂ H ₅ CHBrCO ₂ C ₂ H ₅	Acetone	Reflux	93
B	1d	CH(CH ₃) ₂	(CH ₃) ₂ CHCHBrCO ₂ C ₂ H ₅	DMSO	60°	64
B	1e	Ph	PhCHBrCO ₂ C ₂ H ₅	Acetone	Reflux	82
A	2a	H	BrCH ₂ CO ₂ C ₂ H ₅	Acetone	Reflux	64 [1]
A	2b	CH ₃	CH ₃ CHBrCO ₂ C ₂ H ₅	Acetone	Reflux	75
A	2c	C ₂ H ₅	C ₂ H ₅ CHBrCO ₂ C ₂ H ₅	Acetone	Reflux	95
A	2d	CH(CH ₃) ₂	(CH ₃) ₂ CHCHBrCO ₂ C ₂ H ₅	DMSO	60°	59
A	2e	Ph	PhCHBrCO ₂ C ₂ H ₅	Acetone	Reflux	35 [b]

[a] B and A are 2-hydroxybenzaldehyde and 2'-hydroxyacetophenone respectively. [b] The compound was prepared by ethylation of the corresponding carboxylic acid[1]. The value shows overall yield from 2'-hydroxyacetophenone and bromoester.

Table 2

Photocyclization Reactions of Ethyl 2-Formylphenoxyacetates 1 [a]

Starting material	R	Irradiation time (minutes)	Conversion (%)	Product yield (%)		
				3a-e (cis:trans) [b]	4b-d	5a-e
1a	H	120	97	46 (60:40)		22 (50:50) [c]
1b	CH ₃	70	93	20 [d]	25	0
1c	C ₂ H ₅	45	94	26 [d]	25 (40:60) [e]	0
1d	CH(CH ₃) ₂	60	92	22 [d]	9	0
1e	Ph	70	91	36 (84:16)		0

[a] An acetonitrile solution (500 ml) of 1 (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] *Cis* and *trans* isomers with regard to the ethoxycarbonyl and hydroxyl groups. [c] Two isomers (*dl* and *meso*) were obtained in 50:50 ratio. [d] Only one isomer was obtained and the stereochemistry was not determined. [e] Isomer ratio (*cis*:*trans*) with regard to the methyl and ethoxycarbonyl groups was determined from the ¹H nmr spectrum of the mixture.

to the ethoxycarbonyl and hydroxyl groups were possible for dihydrobenzofuranols **3b-d**, only one isomer was produced in each reaction, showing stereoselectivity in the cyclization step. The stereochemistry of the products is presumed to be *cis* because the ethoxycarbonyl and hydroxyl groups have attractive interaction in the cyclization step, however, we have no evidence to determine the

stereochemistry. When **1e** (R = Ph) was used as the starting material *cis* and *trans* isomers of dihydrobenzofuranol **3e** (36%) were obtained and the isomer ratio was 84:16 judging from anisotropy of the phenyl ring which shielded C₃-H at the *cis* position in the ¹H nmr spectra [3a-b, 3d]. Thus, dihydrobenzofuranols were prepared by photocyclization reactions of ethyl 2-formylphenoxyacetates but

the yields were not necessarily good because by-products such as pinacols, ethyl acrylates or other polymeric materials were produced.

Next, photocyclization reactions of ethyl 2-acetylphenoxyacetates **2a-e** were examined. The results are summarized in Scheme 2 and Table 3. When **2a** (R = H) was irradiated in acetonitrile *cis* and *trans* isomers of dihydrobenzofuranol **6a** with regard to the ethoxycarbonyl and hydroxyl groups were obtained in good yield (84%) and the isomer ratio was 75:25 [1]. In the case of **2b** (R = CH₃) dihydrobenzofuranol **6b** and its dehydrated product **7b** were produced in 53% yield, however, formation of ethyl acrylate **9b** (27%) lowered the yield of furan derivatives. Compound **7b** would be formed by dehydration of **6b** during isolation procedure after irradiation. Though *cis* and *trans* isomers were possible for **6b**, only one isomer was obtained. The stereochemistry of **6b** is not clear. On photocyclization reaction of **2c** (R = C₂H₅) no dihydrobenzofuranol **6c** was isolated and its dehydrated compound **7c** (48%) and ethyl acrylate **9c** (20%) were obtained. Compound **9c** was a mixture of *cis* and *trans* isomers (40:60 ratio) with regard to the ethoxycarbonyl and methyl groups judging from the ¹H nmr spectrum in which

ethoxycarbonyl group in **9c** deshielded hydrogen at the *cis* position. In the case of **2d** (R = CH(CH₃)₂) three products of dihydrobenzofuranol **6d** (35%), its dehydrated product **7d** (25%), and benzofuran **8d** (16%) were obtained and the total yield was good (76%). In this case only one isomer of dihydrobenzofuranol **6d** was isolated. No production of ethyl acrylate **9d** suggests that the ketyl radical in the 1,5-biradical intermediate can not abstract methyl-hydrogen of the isopropyl group because of steric hindrance. The effect made the yield of benzofuran derivatives good. We expected high yield of dihydrobenzofuranol **6e** in the photocyclization reaction of **2e** since formation of ethyl acrylate was not possible. However, the yield of dihydrobenzofuranol **6e** was only 38% because 2'-hydroxyacetophenone (39%) was produced by cleavage of the ether bond of **2e**. Using ethyl 2-acetylphenoxyacetates as the starting materials, the yields of dihydrobenzofuranols and their analogues were moderate to good.

Finally, we discuss reaction pathways in the photocyclization reactions of **1** and **2**. The mechanisms in this type of photoreactions have been well studied [2,3c,3e-h]. The plausible pathways of product formation are summarized in Scheme 3. Irradiation of esters **1, 2** produces

Scheme 2

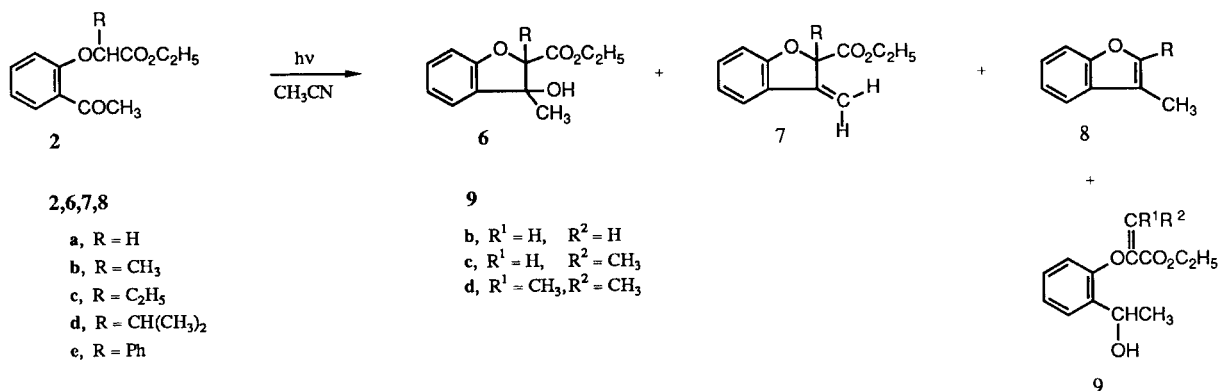


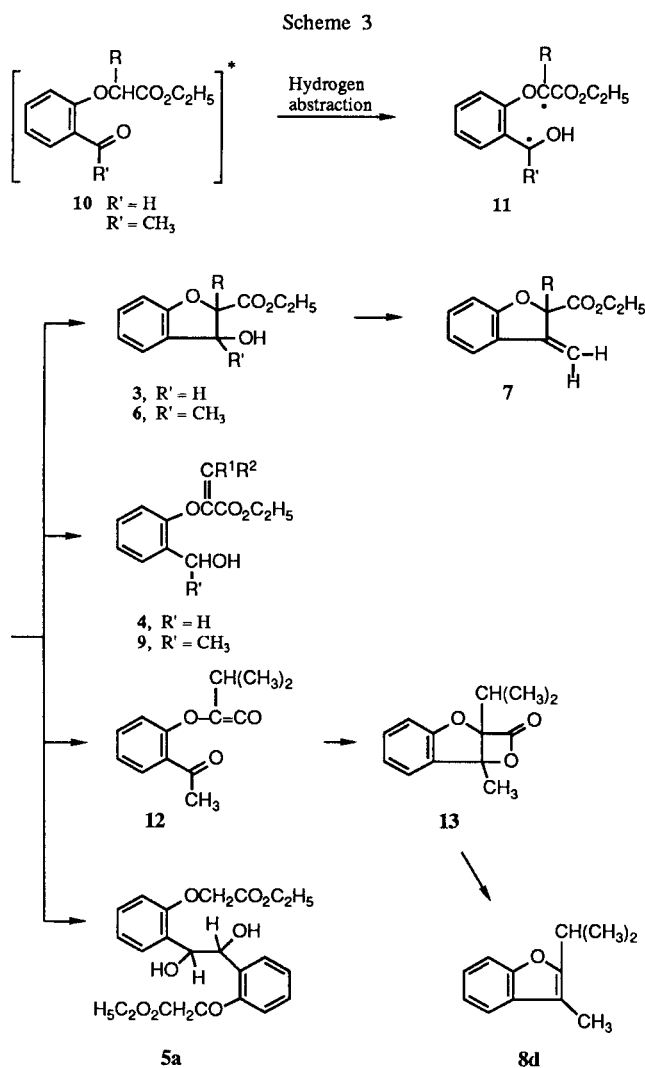
Table 3

Photocyclization Reactions of Ethyl 2-Acetylphenoxyacetates **2a-e** [a]

Starting material	R	Irradiation time (minutes)	Conversion (%)	Product yield (%)			
				6a-e (<i>cis:trans</i>) [b]	7a-e	8a-e	9b-d
2a	H	120	96	86 (75:25)	0	0	
2b	CH ₃	150	84	47 [c]	6	0	27
2c	C ₂ H ₅	90	84	0	48	0	20 (40:60) [d]
2d	CH(CH ₃) ₂	180	77	35 [c]	25	16	0
2e [e]	Ph	180	77	38 [c]	2	0	

[a] An acetonitrile solution (500 ml) of **2** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] *Cis* and *trans* isomers with regard to the ethoxycarbonyl and hydroxyl groups. [c] Only one isomer was obtained and the stereochemistry was not determined. [d] Isomer ratio (*cis:trans*) with regard to the methyl and ethoxycarbonyl groups was determined from the ¹H nmr spectrum of the mixture. [e] The yield of dihydrobenzofuranol **6e** was low because 2'-hydroxyacetophenone was produced in 39% yield.

(n, π^*) excited triplet state **10** after intersystem crossing (ISC). The carbonyl oxygen of **10** abstracts δ -hydrogen to give intermediate 1,5-biradicals **11**. Intramolecular cyclization of **11** affords *cis* and *trans* isomers of dihydrobenzofuranols **3**, **6** which are partly converted to compounds **7** by dehydration during isolation procedure. On the other hand, intermolecular coupling of **11** gives pinacols **5** which are produced when R and R' are hydrogen. If the ketyl radical of **11** abstracts hydrogen of R, ethyl acrylates **4**, **9** would be obtained. In contrast, production of **8d** is not so clear. However, **11** probably give ketene **12** by elimination of ethanol, which is converted to benzofuran **8d** through formation of β -lactone **13** and the following decarboxylation [5].



From the above results photocyclization reactions are useful to synthesize dihydrobenzofuranols and their analogues which are difficult to prepare by ionic reactions under acidic and basic conditions. The ethoxycarbonyl

group has effects to suppress spirocyclization reactions of intermediate 1,5-biradicals.

EXPERIMENTAL

The melting points are uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated anhydrous sodium sulfate was employed as the drying agent. Ether refers to diethyl ether. Acetonitrile was dried by distilling over phosphorus pentoxide, then over potassium carbonate. Photoreactions were carried out with 400-W high-pressure mercury lamp (Riko UVL-400 HA) in a pyrex cylindrical vessel equipped with a nitrogen inlet. The ir spectra were determined on a Hitachi Model 270-30 IR spectrometer. The ¹H and ¹³C nmr spectra were determined at 90 MHz on a JEOL-FX 90Q FT NMR spectrometer, using tetramethylsilane as the internal standard.

Ethyl 2-Formylphenoxyacetate **1a**.

A mixture of 2-hydroxybenzaldehyde (3.0 g, 24.5 mmoles), ethyl bromoacetate (9.6 g, 57.4 mmoles), tripotassium phosphate (12.0 g, 56.5 mmoles) and acetone (50 ml) was refluxed for 3 hours. After removal of insoluble materials by filtration the acetone was evaporated. The residue was chromatographed and eluted with benzene (95)-ether (5) to give **1a** (3.8 g, 75%). It formed colorless crystals from benzene-hexane, mp 43-44° [lit [6] mp 45-46°]; ir (potassium bromide): 1760 (CO₂CH₂CH₃), 1685 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.28 (t, J = 7.1 Hz, 3H, CO₂CH₂CH₃), 4.25 (q, J = 7.1 Hz, 2H, CO₂CH₂CH₃), 4.75 (s, 2H, OCH₂), 6.88 (d, J = 8.5 Hz, 1H, Ar-H), 7.04 (dd, J = 7.6 and 7.6 Hz, 1H, Ar-H), 7.42-7.62 (m, 1H, Ar-H), 7.83 (dd, J = 1.8 and 7.6 Hz, 1H, Ar-H), 10.55 (d, J = 0.6 Hz, 1H, CHO); ¹³C nmr (deuteriochloroform): δ 14.1 (q), 61.5 (t), 65.8 (t), 112.9 (d), 121.8 (d), 125.6 (s), 128.4 (d), 135.7 (s), 160.3 (s), 168.2 (s), 189.4 (d).

Anal. Calcd. for C₁₁H₁₂O₄: C, 63.45; H, 5.81. Found: C, 63.19; H, 5.83.

Ethyl 2-(2-Formylphenoxy)propanoate **1b**.

Compound **1b** (74%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 119-120° at 1.1 Torr; ir (neat): 1745 (CO₂CH₂CH₃), 1685 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.22 (t, J = 7.2 Hz, 3H, CO₂CH₂CH₃), 1.68 (d, J = 6.7 Hz, 3H, OCHCH₃), 4.20 (q, J = 7.2 Hz, 2H, CO₂CH₂CH₃), 4.90 (q, J = 6.7 Hz, 1H, OCHCH₃), 6.86 (d, J = 8.5 Hz, 1H, Ar-H), 7.02 (dd, J = 7.6 and 7.6 Hz, 1H, Ar-H), 7.32-7.50 (m, 1H, Ar-H), 7.82 (dd, J = 2.0 and 7.6 Hz, 1H, Ar-H), 10.57 (s, 1H, CHO); ¹³C nmr (deuteriochloroform): δ 14.1 (q), 18.4 (q), 61.4 (t), 73.4 (d), 113.6 (d), 121.6 (d), 125.7 (s), 128.2 (d), 135.6 (d), 160.2 (s), 171.2 (s), 189.5 (d).

Anal. Calcd. for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 65.03; H, 6.46.

Ethyl 2-(2-Formylphenoxy)butanoate **1c**.

Compound **1c** (93%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 138-140° at 0.9 Torr; ir (neat): 1740 (CO₂CH₂CH₃), 1680 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.11 (t, J = 7.6 Hz, 3H, CHCH₂CH₃), 1.23 (t, J = 7.0 Hz, 3H, CO₂CH₂CH₃), 1.92-2.24 (m, 2H, CHCH₂CH₃), 4.22 (q, J = 7.0 Hz, 2H, CO₂CH₂CH₃), 4.73 (t, J = 6.2 Hz, 1H, CHCH₂CH₃), 6.88 (d, J = 8.5 Hz, 1H, Ar-H), 7.05 (dd, J = 7.6 and 7.6 Hz, 1H, Ar-H), 7.40-7.60 (m, 1H, Ar-H), 7.86 (dd, J = 1.5 and 7.6 Hz, 1H, Ar-H), 10.60 (d, J = 0.9 Hz, 1H, CHO); ¹³C nmr

(deuteriochloroform): δ 9.5 (q), 14.1 (q), 26.1 (t), 61.3 (t), 78.1 (d), 113.6 (d), 121.6 (d), 125.8 (s), 128.2 (d), 135.7 (d), 160.4 (s), 170.6 (s), 189.3 (d).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.80; H, 6.79.

Ethyl 2-(2-Formylphenoxy)-3-methylbutanoate **1d**.

A mixture of 2-hydroxybenzaldehyde (2.0 g, 16.3 mmoles), ethyl 2-bromo-3-methylbutanoate (7.0 g, 33.4 mmoles), tripotassium phosphate (7.0 g, 32.9 mmoles) and dimethyl sulfoxide (30 ml) was stirred at 60° for 1 hour. After removal of insoluble materials by filtration the filtrate was poured into water and extracted with ether. The extract was washed, dried and evaporated. The residue was chromatographed and eluted with benzene (95)-ether (5) to give **1d** (2.7 g, 64%) as a colorless oil, bp 132-133° at 1.1 Torr; ir (neat): 1750 ($CO_2CH_2CH_3$), 1690 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.12 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.22 (t, J = 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.05-2.75 (m, 1H, $CH(CH_3)_2$), 4.21 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 4.57 (d, J = 4.7 Hz, 1H, OCHCH), 6.82 (d, J = 8.5 Hz, 1H, Ar-H), 7.03 (dd, J = 7.6 and 7.6 Hz, 1H, Ar-H), 7.28-7.57 (m, 1H, Ar-H), 7.85 (dd, J = 2.0 and 7.6 Hz, 1H, Ar-H), 10.62 (d, J = 0.9 Hz, 1H, CHO); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 17.6 (q), 18.8 (q), 31.8 (d), 61.3 (t), 81.9 (d), 113.3 (d), 121.6 (d), 125.9 (s), 128.4 (d), 135.6 (d), 160.6 (s), 170.2 (s), 189.5 (d).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.99; H, 7.25.

Ethyl (2-Formylphenoxy)phenylacetate **1e**.

Compound **1e** (82%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**; ir (neat): 1750 ($CO_2CH_2CH_3$), 1695 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.15 (t, J = 7.3 Hz, 3H, $CO_2CH_2CH_3$), 4.15 (q, J = 7.3 Hz, 2H, $CO_2CH_2CH_3$), 5.75 (s, 1H, OCH), 6.85-7.07 (m, 2H, Ar-H₂), 7.26-7.61 (m, 6H, Ar-H and Ph-H_s), 7.86 (dd, J = 1.7 and 7.6 Hz, 1H, Ar-H), 10.68 (d, J = 0.6 Hz, 1H, CHO); ^{13}C nmr (deuteriochloroform): δ 13.9 (q), 61.8 (t), 79.2 (d), 113.7 (d), 121.9 (d), 125.9 (s), 127.0 (d), 128.5 (d), 128.9 (d), 129.2 (d), 134.8 (s), 135.6 (d), 159.6 (s), 169.0 (s), 189.4 (d).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 72.04; H, 5.65.

Ethyl 2-(2-Acetylphenoxy)propanoate **2b**.

Compound **2b** (75%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 122-123° at 0.7 Torr; ir (neat): 1750 ($CO_2CH_2CH_3$), 1675 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.21 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.66 (d, J = 6.8 Hz, 3H, OCHCH₃), 2.68 (s, 3H, COCH₃), 4.18 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 4.92 (q, J = 6.8 Hz, 1H, OCHCH₃), 6.80 (d, J = 8.4 Hz, 1H, Ar-H), 6.96 (dd, J = 7.5 and 7.5 Hz, 1H, Ar-H), 7.22-7.42 (m, 1H, Ar-H), 7.72 (dd, J = 2.0 and 7.5 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 18.4 (q), 31.9 (q), 61.4 (t), 72.9 (d), 112.9 (d), 121.4 (d), 129.2 (s), 130.5 (d), 133.3 (d), 156.8 (s), 171.3 (s), 199.4 (s).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.91; H, 6.72.

Ethyl 2-(2-Acetylphenoxy)butanoate **2c**.

Compound **2c** (95%) was obtained as a colorless oil in a manner similar to the synthesis of **1a**, bp 135-136° at 1.3 Torr; ir (neat): 1750 ($CO_2CH_2CH_3$), 1680 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.10 (t, J = 7.3 Hz, 3H, OCHCH₂CH₃), 1.22 (t, J =

7.3 Hz, 3H, $CO_2CH_2CH_3$), 1.90-2.24 (m, 2H, OCHCH₂CH₃), 2.70 (s, 3H, COCH₃), 4.20 (q, J = 7.3 Hz, 2H, $CO_2CH_2CH_3$), 4.76 (t, J = 6.0 Hz, 1H, OCHCH₂CH₃), 6.80 (d, J = 8.4 Hz, 1H, Ar-H), 6.98 (dd, J = 7.5 and 7.5 Hz, 1H, Ar-H), 7.31-7.50 (m, 1H, Ar-H), 7.73 (dd, J = 2.0 and 7.5 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 9.7 (q), 14.1 (q), 26.1 (t), 31.9 (q), 61.3 (t), 77.9 (d), 112.7 (d), 121.4 (d), 129.2 (s), 130.6 (d), 133.3 (d), 157.1 (s), 170.7 (s), 199.5 (s).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.91; H, 7.28.

Ethyl 2-(2-Acetylphenoxy)-3-methylbutanoate **2d**.

Compound **2d** (59%) was obtained as a colorless oil in a manner similar to the synthesis of **1d**, bp 123-124° at 0.7 Torr; ir (neat): 1750 ($CO_2CH_2CH_3$), 1675 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.11 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.13 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.22 (t, J = 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.20-2.50 (m, 1H, $CH(CH_3)_2$), 2.72 (s, 3H, COCH₃), 4.20 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 4.61 (d, J = 5.1 Hz, 1H, OCHCH), 6.80 (d, J = 8.1 Hz, 1H, Ar-H), 6.99 (dd, J = 7.5 and 7.5 Hz, 1H, Ar-H), 7.29-7.49 (m, 1H, Ar-H), 7.72 (dd, J = 2.0 and 7.5 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 18.1 (q), 18.8 (q), 31.6 (d), 32.0 (q), 61.2 (t), 81.6 (d), 112.5 (d), 121.3 (d), 129.3 (s), 130.6 (d), 133.3 (d), 157.1 (s), 170.3 (s), 199.9 (s).

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.96; H, 7.41.

Ethyl (2-Acetylphenoxy)phenylacetate **2e**.

Ethanol solution (50 ml) of (2-acetylphenoxy)phenylacetic acid (2.0 g, 7.40 mmoles) [1] was refluxed for 3 hours in the presence of concentrated sulfuric acid (0.5 ml). The solution was extracted with ether. The extract was washed with a 5% aqueous potassium carbonate solution, then with water, dried and evaporated. The residue was chromatographed and eluted with benzene (95)-ether (5) to give **2e** (1.6 g, 73%); ir (neat): 1750 ($CO_2CH_2CH_3$), 1680 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.16 (t, J = 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.76 (s, 3H, COCH₃), 4.17 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 5.76 (s, 1H, OCHPh), 6.78-7.05 (m, 2H, Ar-H₂), 7.26-7.79 (m, 7H, Ar-H₂ and Ph-H_s); ^{13}C nmr (deuteriochloroform): δ 13.9 (q), 32.0 (q), 61.7 (t), 79.2 (d), 113.2 (d), 121.6 (d), 127.2 (d), 128.2 (d), 128.9 (d), 129.4 (s), 130.6 (d), 133.3 (d), 134.9 (s), 156.3 (s), 169.1 (s), 199.5 (s).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.23; H, 6.34.

General Procedure for Photocyclization Reactions of Esters **1a-e** and **2a-e**.

An acetonitrile solution (500 ml) of the starting material (2.00 mmoles) was deoxygenated by bubbling nitrogen gas for 1 hour and then irradiated under monitoring by high performance liquid chromatography (hplc). The irradiation was stopped when the ester almost disappeared. After irradiation the acetonitrile was evaporated under reduced pressure below 40°. The residue was chromatographed and eluted with benzene-ether to give a variety of products.

Ethyl *cis*-3-Hydroxy-2,3-dihydro-2-benzofurancarboxylate *cis*-**3a**.

Compound *cis*-**3a** was obtained as colorless crystals from benzene-hexane, mp 80-82°; ir (potassium bromide): 3480 (OH), 1735 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 0.93 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 2.60 (broad s, 1H, OH), 3.97 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 4.72 (d, J = 6.8 Hz, 1H, C₂-H), 5.08 (broad s, 1H, C₃-H), 6.61-7.16 (m, 4H, Ar-H₄); ^{13}C nmr

(deuteriobenzene): δ 14.1 (q), 61.3 (t), 73.4 (d), 85.1 (d), 110.9 (d), 121.6 (d), 126.1 (d), 127.7 (s), 131.1 (d), 160.1 (s), 167.9 (s).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.60; H, 5.72.

Ethyl *trans*-3-Hydroxy-2,3-dihydro-2-benzofurancarboxylate **trans-3a**.

Compound **trans-3a** was obtained as a colorless oil, ir (neat): 3450 (OH), 1740 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriobenzene): δ 0.83 (t, $J = 7.1$ Hz, 3H, $CO_2CH_2CH_3$), 2.90 (d, $J = 7.0$ Hz, 1H, OH), 3.82 (q, $J = 7.1$ Hz, 2H, $CO_2CH_2CH_3$), 4.95 (d, $J = 3.1$ Hz, 1H, C_2-H), 5.32 (dd, $J = 3.1$ and 7.0 Hz, 1H, C_3-H), 6.60-7.20 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriobenzene): δ 13.9 (q), 61.5 (t), 76.4 (d), 88.0 (d), 111.0 (d), 121.7 (d), 125.9 (d), 127.6 (s), 131.0 (d), 160.4 (s), 169.7 (s).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.57; H, 5.70.

Ethyl 3-Hydroxy-2-methyl-2,3-dihydro-2-benzofurancarboxylate **3b**.

Compound **3b** was initially obtained as a mixture with **4b**. Catalytic hydrogenation of the mixture with palladium-charcoal in ethanol converted **4b** to ethyl 2-(2-methylphenoxy)propanoate. From the mixture **3b** was isolated as a colorless oil by chromatography; ir (neat): 3480 (OH), 1735 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.29 (t, $J = 7.0$ Hz, 3H, $CO_2CH_2CH_3$), 1.54 (s, 3H, C_2-CH_3), 3.27 (d, $J = 7.5$ Hz, 1H, OH), 4.22 (q, $J = 7.0$ Hz, 2H, $CO_2CH_2CH_3$), 4.96 (d, $J = 7.5$ Hz, 1H, C_3-H), 6.86-7.02 (m, 2H, Ar-H₂), 7.17-7.42 (m, 2H, Ar-H₂); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 22.2 (q), 61.7 (t), 79.4 (d), 91.5 (s), 111.0 (d), 121.5 (d), 126.2 (d), 126.6 (s), 131.0 (d), 159.0 (s), 170.4 (s).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.65; H, 6.23.

Ethyl 2-Ethyl-3-hydroxy-2,3-dihydro-2-benzofurancarboxylate **3c**.

Compound **3c** was obtained as a colorless oil; ir (neat): 3470 (OH), 1740 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 0.99 (t, $J = 7.3$ Hz, 3H, CH_2CH_3), 1.33 (t, $J = 7.3$ Hz, 3H, $CO_2CH_2CH_3$), 1.80-2.34 (m, 2H, CH_2CH_3), 2.60 (d, $J = 7.5$ Hz, 1H, OH), 4.32 (q, $J = 7.3$ Hz, 2H, $CO_2CH_2CH_3$), 5.03 (d, $J = 7.5$ Hz, 1H, C_3-H), 6.84-7.45 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 8.2 (q), 14.2 (q), 29.3 (t), 61.6 (t), 78.6 (d), 95.1 (s), 111.0 (d), 121.4 (d), 126.0 (d), 126.9 (s), 131.0 (d), 159.2 (s), 169.9 (s).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.90; H, 6.96.

Ethyl 3-Hydroxy-2-isopropyl-2,3-dihydro-2-benzofurancarboxylate **3d**.

Compound **3d** was obtained as colorless crystals from benzene-hexane, mp 95-96°; ir (potassium bromide): 1735 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 0.74 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.06 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.32 (t, $J = 7.1$ Hz, 3H, $CO_2CH_2CH_3$), 2.39 (septet, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 2.64 (broad s, 1H, OH), 4.28 (q, $J = 7.1$ Hz, 2H, $CO_2CH_2CH_3$), 5.19 (s, 1H, C_3-H), 6.84-7.02 (m, 2H, Ar-H₂), 7.18-7.40 (m, 2H, Ar-H₂); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 15.9 (q), 18.1 (q), 34.8 (d), 61.4 (t), 77.1 (d), 97.1 (s), 110.0 (d), 121.2 (d), 125.5 (d), 127.1 (s), 130.8 (d), 160.2 (s), 170.3 (s).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.27; H, 7.35.

Ethyl *cis*-3-Hydroxy-2-phenyl-2,3-dihydro-2-benzofurancarboxylate **cis-3e**.

Compound **cis-3e** was obtained as colorless crystals from benzene-hexane, mp 112.5-113.5°; ir (potassium bromide): 3500 (OH), 1730 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.19 (t, $J = 7.0$ Hz, 3H, $CO_2CH_2CH_3$), 3.98 (d, $J = 7.0$ Hz, 1H, OH), 4.17 (q, $J = 7.0$ Hz, 2H, $CO_2CH_2CH_3$), 5.44 (d, $J = 7.0$ Hz, 1H, C_3-H), 6.74-7.36 (m, 7H, Ar-H₂ and Ph-H₅), 7.65-7.76 (m, 2H, Ar-H₂); ^{13}C nmr (deuteriochloroform): δ 14.0 (q), 62.3 (t), 80.9 (d), 94.3 (s), 111.0 (d), 122.1 (d), 125.9 (d), 126.3 (s), 128.4 (d), 128.5 (d), 131.1 (d), 137.5 (s), 158.9 (s), 169.3 (s).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.53; H, 5.85.

Ethyl *trans*-3-Hydroxy-2-phenyl-2,3-dihydro-2-benzofurancarboxylate **trans-3e**.

Compound **trans-3e** was obtained as a colorless oil; 1H nmr (deuteriochloroform): δ 1.17 (t, $J = 7.1$ Hz, 3H, $CO_2CH_2CH_3$), 1.60 (broad s, 1H, OH), 4.16 (q, $J = 7.1$ Hz, 2H, $CO_2CH_2CH_3$), 5.78 (s, 1H, C_3-H), 6.90-7.72 (m, 9H, Ar-H₄ and Ph-H₅); ^{13}C nmr (deuteriochloroform): δ 13.9 (q), 62.4 (t), 76.5 (d), 94.6 (s), 111.0 (d), 122.1 (d), 126.2 (d), 126.5 (d), 127.3 (s), 128.5 (d), 131.1 (d), 133.7 (s), 158.6 (s), 171.0 (s).

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.66; H, 5.52.

Ethyl 3-Hydroxy-2,3-dimethyl-2,3-dihydro-2-benzofurancarboxylate **6b**.

Compound **6b** was obtained as colorless crystals from benzene-hexane, mp 67-68°; ir (potassium bromide) 3450 (OH), 1740 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriobenzene): δ 0.98 (t, $J = 7.1$ Hz, 3H, $CO_2CH_2CH_3$), 1.36 (s, 3H, C_2-CH_3), 1.55 (s, 3H, C_3-CH_3), 2.90 (broad s, 1H, OH), 4.01 (q, $J = 7.1$ Hz, 2H, $CO_2CH_2CH_3$), 6.64-7.17 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriobenzene): δ 14.1 (q), 20.6 (q), 21.3 (q), 61.2 (t), 81.5 (s), 94.5 (s), 111.2 (d), 121.4 (d), 124.0 (d), 130.7 (d), 131.6 (s), 158.6 (s), 170.5 (s).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.24; H, 6.72.

Ethyl 2-Methyl-3-methylene-2,3-dihydro-2-benzofurancarboxylate **7b**.

Compound **7b** was obtained as a colorless oil; ir (neat): 1735 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.25 (t, $J = 7.0$ Hz, 3H, $CO_2CH_2CH_3$), 1.75 (s, 3H, C_2-CH_3), 4.21 (q, $J = 7.0$ Hz, 2H, $CO_2CH_2CH_3$), 5.21 (d, $J = 0.9$ Hz, 1H, =CH₂), 5.50 (d, $J = 0.9$ Hz, 1H, =CH₂), 6.80-7.43 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 14.0 (q), 24.8 (q), 61.9 (t), 88.9 (s), 102.6 (t), 110.8 (d), 121.2 (d), 124.3 (s), 131.0 (d), 147.7 (s), 161.2 (s), 170.8 (s).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.36; H, 6.34.

Ethyl 2-Ethyl-3-methylene-2,3-dihydro-2-benzofurancarboxylate **7c**.

Compound **7c** was obtained as a colorless oil; ir (neat): 1740 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 0.96 (t, $J = 7.3$ Hz, 3H, CH_2CH_3), 1.25 (t, $J = 7.1$ Hz, 3H, $CO_2CH_2CH_3$), 1.90-2.32 (m, 2H, CH_2CH_3), 4.21 (q, $J = 7.1$ Hz, 2H, $CO_2CH_2CH_3$), 5.23 (d, $J = 0.7$ Hz, 1H, =CH₂), 5.53 (d, $J = 0.7$ Hz, 1H, =CH₂), 6.80-7.40 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 7.7 (q), 14.0 (q), 31.9 (t), 61.7 (t), 92.1 (s).

102.8 (t), 110.6 (d), 121.0 (d), 121.1 (d), 124.8 (s), 130.9 (d), 146.2 (s), 161.7 (s), 170.6 (s).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.16; H, 6.75.

Ethyl 3-Hydroxy-2-isopropyl-3-methyl-2,3-dihydro-2-benzofurancarboxylate **6d**.

Compound **6d** was obtained as colorless crystals from benzene-hexane, mp 108-111° dec; ir (potassium bromide): 3380 (OH), 1760, 1735 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 0.57 (d, J = 6.6 Hz, 3H, $CH(CH_3)_2$), 1.04 (d, J = 6.6 Hz, 3H, $CH(CH_3)_2$), 1.34 (t, J = 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.24 (s, 1H, OH), 2.43 (septet, 1H, $CH(CH_3)_2$), 4.31 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 6.80-7.27 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 17.0 (q), 18.7 (q), 19.6 (q), 33.0 (d), 61.2 (t), 80.7 (s), 99.9 (s), 110.3 (d), 121.3 (d), 122.3 (d), 130.8 (d), 131.4 (s), 159.5 (s), 170.2 (s).

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.01; H, 7.54.

Ethyl 2-Isopropyl-3-methylene-2,3-dihydro-2-benzofurancarboxylate **7d**.

Compound **7d** was obtained as a colorless oil; ir (neat): 1755, 1735 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 0.81 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.10 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.26 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 2.48 (septet, J = 6.8 Hz, 1H, $CH(CH_3)_2$), 4.22 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 5.28 (s, 1H, =CH₂), 5.55 (s, 1H, =CH₂), 6.76-7.42 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 14.0 (q), 15.2 (q), 17.4 (q), 36.9 (d), 61.7 (t), 94.7 (s), 102.9 (t), 110.5 (d), 120.8 (d), 121.0 (d), 125.1 (s), 130.8 (d), 145.6 (s), 162.1 (s), 170.8 (s).

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.94; H, 7.14.

2-Isopropyl-3-methylbenzofuran **8d**.

Compound **8d** was obtained as a colorless oil; 1H nmr (deuteriochloroform): δ 1.32 (d, J = 6.8 Hz, 6H, $CH(CH_3)_2$), 2.16 (s, 3H, C_3-CH_3), 3.16 (septet, J = 6.8 Hz, 1H, $CH(CH_3)_2$), 7.08-7.44 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 7.7 (q), 21.9 (q), 26.5 (d), 107.5 (s), 110.6 (d), 118.6 (d), 121.9 (d), 122.9 (d), 130.7 (s), 153.8 (s), 158.5 (s).

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.56; H, 8.21.

Ethyl 3-Hydroxy-3-methyl-2-phenyl-2,3-dihydro-2-benzofurancarboxylate **6e**.

Compound **6e** was obtained as colorless crystals from benzene-hexane, mp 101-104°; ir (potassium bromide): 3500 (OH), 1715 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.22 (t, J = 7.0 Hz, 3H, $CO_2CH_2CH_3$), 1.29 (s, 3H, C_3-CH_3), 3.60 (broad s, 1H, OH), 4.26 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 6.90-7.46 (m, 9H, Ar-H₄ and Ph-H₅); ^{13}C nmr (deuteriochloroform): δ 13.9 (q), 25.0 (q), 62.2 (t), 83.5 (s), 95.0 (s), 110.6 (d), 122.2 (d), 123.4 (d), 125.7 (d), 128.2 (d), 128.4 (d), 130.2 (d), 132.3 (s), 135.5 (s), 157.5 (s), 171.2 (s).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.57; H, 6.17.

Ethyl 3-Methylene-2-phenyl-2,3-dihydro-2-benzofurancarboxylate **7e**.

Compound **7e** was obtained as a colorless oil; ir (neat): 1745 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.26 (t, J =

7.1 Hz, 3H, $CO_2CH_2CH_3$), 4.26 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 5.49 (s, 1H, =CH₂), 5.80 (s, 1H, =CH₂), 6.82-7.60 (m, 9H, Ar-H₄ and Ph-H₅); ^{13}C nmr (deuteriochloroform): δ 14.0 (q), 62.3 (t), 92.2 (s), 106.7 (t), 110.9 (d), 121.1 (d), 121.5 (d), 124.6 (s), 126.3 (d), 128.5 (d), 128.6 (d), 131.0 (d), 138.8 (s), 145.0 (s), 160.5 (s), 169.7 (s).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.02; H, 5.86.

d,l- and *meso*-Pinacol **5a**.

One isomer was obtained as colorless crystals from benzene, mp 133-134°; ir (potassium bromide): 3520 (OH), 1730 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.28 (t, J = 7.1 Hz, 6H, $CO_2CH_2CH_3$ and $CO_2CH_2CH_3$), 3.68 (broad s, 2H, OH and OH), 4.25 (q, J = 7.1 Hz, 4H, $CO_2CH_2CH_3$ and $CO_2CH_2CH_3$), 4.54 (s, 4H, OCH₂ and OCH₂), 5.31 (s, 2H, $CHOH$ and $CHOH$), 6.62-7.24 (m, 8H, Ar-H₄ and Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 61.4 (t), 65.5 (t), 74.4 (d), 111.4 (d), 121.6 (d), 128.4 (d), 129.2 (d), 130.0 (s), 155.4 (s), 168.9 (s).

Anal. Calcd. for $C_{22}H_{26}O_8$: C, 63.15; H, 6.26. Found: C, 62.87; H, 6.37.

Another isomer was obtained as colorless crystals from benzene-hexane, mp 74-75°; ir (potassium bromide): 3550, 3470 (OH), 1755, 1740 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.29 (t, J = 7.1 Hz, 6H, $CO_2CH_2CH_3$ and $CO_2CH_2CH_3$), 4.10 (broad s, 2H, OH and OH), 4.25 (q, J = 7.1 Hz, 4H, $CO_2CH_2CH_3$ and $CO_2CH_2CH_3$), 4.29 (d, J = 15.6 Hz, 2H, OCH₂), 4.52 (d, J = 15.6 Hz, 2H, OCH₂), 5.14 (s, 2H, $CHOH$ and $CHOH$), 6.49-7.34 (m, 8H, Ar-H₄ and Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 61.3 (t), 65.5 (t), 74.4 (d), 111.4 (d), 121.5 (d), 128.3 (d), 129.0 (d), 129.7 (s), 155.3 (s), 168.8 (s).

Anal. Calcd. for $C_{22}H_{26}O_8$: C, 63.15; H, 6.26. Found: C, 63.43; H, 6.11.

Ethyl 2-(2-Hydroxymethylphenoxy)propenoate **4b**.

Compound **4b** was obtained as a mixture with **3b** and difficult to isolate; 1H nmr (deuteriochloroform): δ 1.31 (t, J = 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.80 (broad s, 1H, CH_2OH), 4.28 (q, J = 7.0 Hz, 2H, $CO_2CH_2CH_3$), 4.66 (s, 2H, CH_2OH), 5.01 (d, J = 2.0 Hz, 1H, =CH₂), 5.75 (d, J = 2.0 Hz, 1H, =CH₂), 6.90-7.50 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 14.0 (q), 60.0 (t), 61.6 (t), 104.8 (t), 118.1 (d), 124.6 (d), 128.7 (d), 129.3 (d), 132.3 (s), 150.0 (s), 152.9 (s), 162.7 (s).

Catalytic hydrogenation of the mixture with 7% palladium-charcoal converted **4b** into ethyl 2-(2-methylphenoxy)propanoate in 77% yield, colorless oil; ir (neat): 1755, 1735 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.21 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.60 (d, J = 6.8 Hz, 3H, OCHCH₃), 2.27 (s, 3H, Ar-CH₃), 4.18 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 4.71 (q, J = 6.8 Hz, 1H, OCHCH₃), 6.58-7.17 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 16.2 (q), 18.6 (q), 61.0 (t), 73.1 (d), 112.2 (d), 121.3 (d), 126.6 (d), 127.6 (s), 131.0 (d), 156.0 (s), 172.2 (s).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.92; H, 7.62.

Ethyl *cis*- and *trans*-2-(2-Hydroxymethylphenoxy)-2-butenate *cis*-**4c**, *trans*-**4c**.

These compounds were obtained as a mixture (oil) and difficult to isolate each component.

Compound *cis*-**4c** had ir (neat): 3460 (OH), 1725 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriochloroform): δ 1.15 (t, J = 7.2 Hz,

3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.12 (d, $J = 7.7$ Hz, 3H, = CHCH_3), 3.20 (broad s, 1H, OH), 4.14 (q, $J = 7.2$ Hz, 1H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.71 (s, 2H, CH_2OH), 6.08 (q, $J = 7.7$ Hz, 1H, = CHCH_3), 6.60-7.39 (m, 4H, Ar-H₄).

Compound *trans*-**4c** had ir (neat): 3460 (OH), 1725 cm^{-1} ($\text{CO}_2\text{CH}_2\text{CH}_3$); ^1H nmr (deuteriochloroform): δ 1.18 (t, $J = 7.0$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.84 (d, $J = 7.3$ Hz, 3H, = CHCH_3), 3.20 (broad s, 1H, OH), 4.13 (q, $J = 7.0$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.77 (s, 2H, CH_2OH), 6.60-7.39 (m, 4H, Ar-H₄), 6.68 (q, $J = 7.3$ Hz, 1H, = CHCH_3), 6.60-7.39 (m, 4H, Ar-H₄).

Catalytic hydrogenation of the mixture (*cis*-**4c** and *trans*-**4c**) with palladium-charcoal gave ethyl 2-(2-methylphenoxy)butanoate as a colorless oil in 70% yield; ir (neat): 1755, 1730 cm^{-1} ($\text{CO}_2\text{CH}_2\text{CH}_3$); ^1H nmr (deuteriochloroform): δ 1.09 (t, $J = 7.5$ Hz, 3H, CHCH_2CH_3), 1.23 (t, $J = 7.1$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.83-2.14 (m, 2H, CHCH_2CH_3), 2.29 (s, 3H, Ar-CH₃), 4.19 (q, $J = 7.1$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.55 (t, $J = 6.2$ Hz, 1H, CHCH_2CH_3), 6.56-7.18 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 9.6 (q), 14.1 (q), 16.3 (q), 26.3 (t), 61.0 (t), 77.9 (d), 111.8 (d), 121.1 (d), 126.6 (d), 127.5 (s), 131.0 (d), 156.3 (s), 171.8 (s).

Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3$: C, 70.25; H, 8.16. Found: C, 70.46; H, 8.37.

Ethyl 2-(2-Hydroxymethylphenoxy)-3-methyl-2-butenolate **4d**.

Compound **4d** was obtained as a colorless oil; ir (neat): 3460 (OH), 1720 cm^{-1} ($\text{CO}_2\text{CH}_2\text{CH}_3$); ^1H nmr (deuteriochloroform): δ 1.10 (t, $J = 7.1$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.90 (s, 3H CH_3), 2.26 (s, 3H, CH_3), 3.04 (broad s, 1H, OH), 4.10 (q, $J = 7.1$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.75 (s, 2H, CH_2OH), 6.60-7.36 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 13.8 (q), 19.7 (q), 20.2 (q), 60.7 (t), 61.6 (t), 112.5 (d), 122.1 (d), 128.7 (d), 129.5 (d), 129.6 (s), 136.0 (s), 139.9 (s), 155.2 (s), 163.2 (s).

Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C, 67.18; H, 7.25. Found: C, 67.31; H, 7.34.

Ethyl 2-[2-(1-Hydroxyethyl)phenoxy]propionate **9b**.

Compound **9b** was obtained as a colorless oil; ir (neat): 3450 (OH), 1730 cm^{-1} ($\text{CO}_2\text{CH}_2\text{CH}_3$); ^1H nmr (deuteriochloroform): δ 1.28 (t, $J = 7.1$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.50 (d, $J = 6.6$ Hz, 3H, CHCH_3), 2.76 (broad s, 1H, OH), 4.25 (q, $J = 7.1$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.99 (d, $J = 2.0$ Hz, 1H, = CH), 5.14 (q, $J = 6.6$ Hz, 1H, CHCH_3), 5.73 (d, $J = 2.0$ Hz, 1H, = CH), 6.80-7.56 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 14.1 (q), 23.2 (q), 61.8 (t), 65.0 (d), 105.0 (t), 118.0 (d), 124.6 (d), 126.9 (d), 128.3 (d), 136.4 (s), 150.2 (s), 152.4 (s), 162.6 (s).

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4$: C, 66.09; H, 6.83. Found: C, 65.83; H, 6.73.

Ethyl *cis*- and *trans*-2-[2-(1-Hydroxyethyl)phenoxy]-2-butenolate *cis*-**9c**, *trans*-**9c**.

These compounds were obtained as a mixture (oil) and difficult to isolate each component.

Compound *cis*-**9c** had ir (neat): 3460 (OH), 1725 cm^{-1} ($\text{CO}_2\text{CH}_2\text{CH}_3$); ^1H nmr (deuteriochloroform): 1.14 (t, $J = 7.0$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.55 (d, $J = 6.4$ Hz, 3H, CHOHCH_3), 2.12 (d, J

= 7.5 Hz, 3H, = CHCH_3), 3.10 (broad s, 1H, OH), 4.15 (q, $J = 7.0$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.18 (q, $J = 6.4$ Hz, 1H, CHOHCH_3), 6.06 (q, $J = 7.5$ Hz, 1H, = CHCH_3), 6.56-7.42 (m, 4H, Ar-H₄).

Compound *trans*-**9c** had ir (neat): 3460 (OH), 1725 cm^{-1} ($\text{CO}_2\text{CH}_2\text{CH}_3$); ^1H nmr (deuteriochloroform): 1.17 (t, $J = 7.1$ Hz, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.58 (d, $J = 6.6$ Hz, 3H, CHOHCH_3), 1.82 (d, $J = 7.3$ Hz, 3H, = CHCH_3), 3.32 (broad s, 1H, OH), 4.13 (q, $J = 7.1$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.28 (q, $J = 6.6$ Hz, 1H, CHOHCH_3), 6.56-7.42 (m, 5H, Ar-H₄ and CHOHCH_3).

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