

Photocyclization Reactions. Part 1. Synthesis of
Dihydrobenzofuranols Using Photocyclization of 2-
Alkoxybenzaldehydes, 2'-Alkoxyacetophenones, 2-

Formylphenoxyacetic Acids and 2-Acetylphenoxyacetic Acids

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Photocyclization reactions were carried out on 2-alkoxybenzaldehydes **1a-f**, 2'-alkoxyacetophenones **2a-h**, 2-formylphenoxyacetic acids **1i-l** and 2-acetylphenoxyacetic acids **2i-m**. Irradiation of **1a-f** and **2a-h** in acetonitrile gave the corresponding dihydrobenzofuranols **3, 5** and dihydroisobenzofuranols **4, 6**. Using carboxylic acids **1i-l**, **2i-m** as starting materials, decarboxylation occurred immediately to give the corresponding ethers **1a-d**, **2a-e**. Further irradiation of the solution afforded dihydrobenzofuranols **3, 5** and dihydroisobenzofuranols **4, 6**. Substituent effects on photocyclization and reaction pathways are discussed.

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Introduction.

It is well-known that irradiation of aromatic carbonyl compounds such as benzophenone or acetophenone in the presence of alcohols or amines gives photoreduction products [1]. The reactions proceed through hydrogen abstraction from alcohols or amines by the excited carbonyl group. On the other hand, carbonyl compounds which possess γ -hydrogen atoms undergo a very facile photoelimination, called a Norrish type II reaction, to produce alkenes and smaller carbonyl compounds [2]. In the reactions cyclobutanols are also formed by intramolecular cyclization of intermediate 1,4-biradicals. In aromatic ketones γ -hydrogen abstraction occurs from (n, π^*) excited triplet state of the carbonyl group [3]. By using this type of photocyclization dihydrobenzofuranols have been prepared from carbonyl compounds [4]. For example, Pappas *et al.* [4a] prepared *cis* and *trans* isomers of 2-phenyl-2,3-dihydro-3-benzofuranol by irradiation of 2-benzyloxybenzaldehyde **1** ($R^1 = \text{Ph}$, $R^2 = \text{H}$) in acetonitrile. However, there are few literatures which investigate systematic synthesis of dihydrobenzofuranols and substituent effects on photocyclization. Therefore, in this paper we report synthesis of dihydrobenzofuranols and substituent effects on photocyclization from 2-alkoxybenzaldehydes **1a-f**, 2'-alkoxyacetophenones **2a-h**, 2-formylphenoxyacetic acids **1i-l** and 2-acetylphenoxyacetic acids **2i-m**.

Results and Discussion.

2-Alkoxybenzaldehydes **1c-f** and 2'-alkoxyacetophenones **2b-h** for photocyclization reactions were prepared as shown in Table 1. Compounds **1a-b** and **2a** are commer-

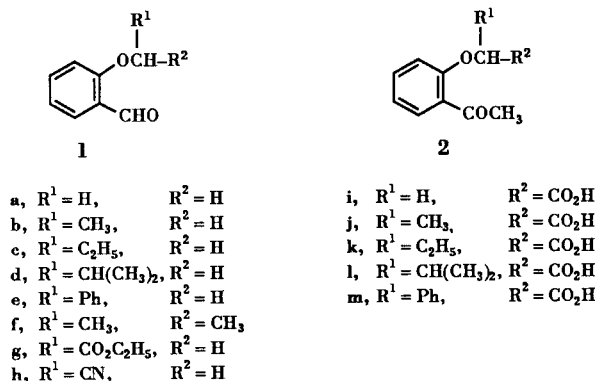


Figure 1

cially available. For example, compounds **1c-f** were obtained from the reactions of 2-hydroxybenzaldehyde with 1-iodopropane, 1-bromo-2-methylpropane, chloromethylbenzene or 2-iodopropane in the presence of tripotassium phosphate as a base. Similarly, compounds **2b-h** were prepared by the reactions of 2'-hydroxyacetophenone with iodoethane, 1-iodopropane, 1-bromo-2-methylpropane, chloromethylbenzene, 2-iodopropane, ethyl bromoacetate or bromoacetonitrile in the presence of tripotassium phosphate.

Carboxylic acids **1j-l**, **2i-m** were prepared as shown in Table 2. Compound **1i** is commercially available. Reactions of 2-hydroxybenzaldehyde with ethyl 2-bromopropionate, ethyl 2-bromobutanoate or ethyl 2-bromo-3-methylbutanoate gave the corresponding carboxylic acids **1j-l** after hydrolysis of the esters with potassium hydroxide. However, synthesis of **1m** was difficult because of

Table 1
Synthesis of 2-Alkoxybenzaldehydes **1c-f** and 2'-Alkoxyacetophenones **2b-h**

Starting material [a]	Product	R ¹	R ²	Reagent	Solvent	Temperature	Yield (%)
B	1c	C ₂ H ₅	H	CH ₃ CH ₂ CH ₂ I	Acetone	Reflux	56
B	1d	CH(CH ₃) ₂	H	(CH ₃) ₂ CHCH ₂ Br	DMSO	60°	82
B	1e	Ph	H	PhCH ₂ Cl	DMSO	60°	63
B	1f	CH ₃	CH ₃	(CH ₃) ₂ CHI	Acetone	Reflux	60
A	2b	CH ₃	H	CH ₃ CH ₂ I	DMSO	60°	89
A	2c	C ₂ H ₅	H	CH ₃ CH ₂ CH ₂ I	Acetone	Reflux	83
A	2d	CH(CH ₃) ₂	H	(CH ₃) ₂ CHCH ₂ Br	DMSO	60°	83
A	2e	Ph	H	PhCH ₂ Cl	Acetone	Reflux	83
A	2f	CH ₃	CH ₃	(CH ₃) ₂ CHI	DMSO	60°	87
A	2g	CO ₂ C ₂ H ₅	H	BrCH ₂ CO ₂ C ₂ H ₅	Acetone	Reflux	64 [b]
A	2h	CN	H	BrCH ₂ CN	DMSO	60°	93

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

Table 2
Synthesis of 2-Formylphenoxyacetic Acids **1j-l** (R² = CO₂H) and 2-Acetylphenoxyacetic Acids **2i-m** (R² = CO₂H)

Starting material [a]	Product	R ¹	Reagent	Solvent	Temperature	Yield (%)
B	1j	CH ₃	CH ₃ CHBrCO ₂ C ₂ H ₅	Acetone	Reflux	46
B	1k	C ₂ H ₅	CH ₃ CH ₂ CHBrCO ₂ C ₂ H ₅	Acetone	Reflux	43
B	1l	CH(CH ₃) ₂	(CH ₃) ₂ CHCHBrCO ₂ C ₂ H ₅	DMSO	60°	47
A	2i	H	BrCH ₂ CO ₂ C ₂ H ₅	Acetone	Reflux	84
A	2j	CH ₃	CH ₃ CHBrCO ₂ C ₂ H ₅	Acetone	Reflux	65
A	2k	C ₂ H ₅	CH ₃ CH ₂ CHBrCO ₂ C ₂ H ₅	Acetone	Reflux	79
A	2l	CH(CH ₃) ₂	(CH ₃) ₂ CHCHBrCO ₂ C ₂ H ₅	DMSO	60°	28
A	2m	Ph	PhCHBrCO ₂ C ₂ H ₅	Acetone	Reflux	48

[a] B and A are 2-hydroxybenzaldehyde and 2'-hydroxyacetophenone respectively.

Table 3
Photocyclization Reactions of 2-Alkoxybenzaldehydes **1a-f** [a]

Starting material	R ¹	R ²	Irradiation time (minutes)	Conversion (%)	Product yield (%)	
					3a-f	4a-f
1a	H	H	90	97	27	0
1b	CH ₃	H	60	92	28 (20:80)	0
1c	C ₂ H ₅	H	75	88	28 (0:100)	0
1d	CH(CH ₃) ₂	H	70	83	29 (0:100)	0
1e	Ph	H	60	88	40 (63:37)	0
1f	CH ₃	CH ₃	45	97	0	24

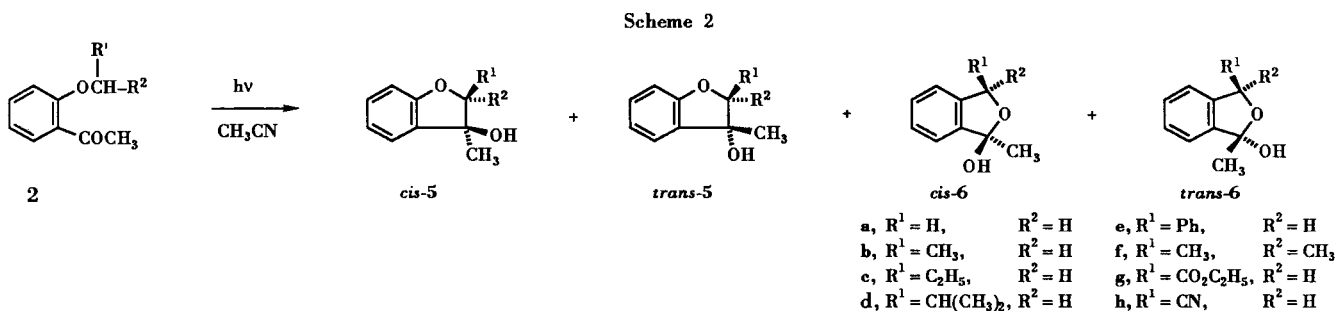
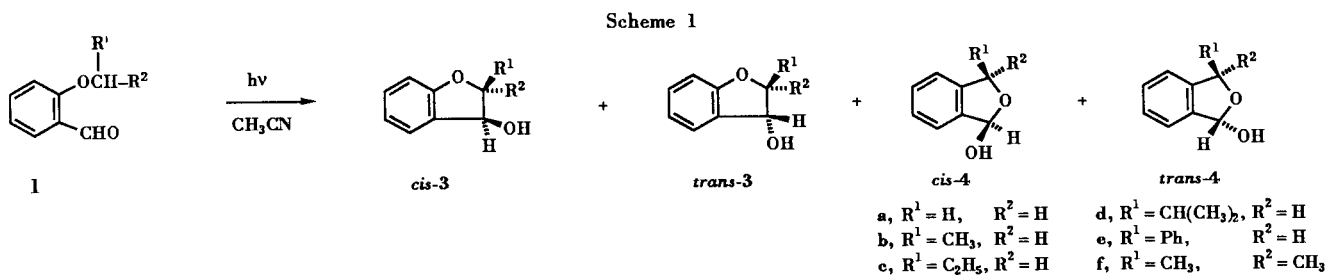
[a] An acetonitrile solution (500 ml) of **1a-f** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] *Cis* and *trans* isomers with regard to the R¹ and hydroxyl group.

decomposition during hydrolysis. Carboxylic acids **2i-m** were similarly obtained from the reactions of 2'-hydroxyacetophenone and the corresponding bromoesters.

When 2-alkoxybenzaldehydes **1a-e** were irradiated with 400-W high-pressure mercury lamp in acetonitrile, dihydrobenzofuranols **3a-e** (27-40%) were obtained along with a small amount (*ca.* 10%) of pinacols which were not further investigated. In the case of **1f** only isobenzofuranol **4f** was produced. The results are shown in Scheme 1 and Table 3. It seems that dihydroisobenzofuranols **4** were produced in every reaction but decomposed during isolation procedure except for **4f**. The yields (27-40%) of dihydrobenzofuranols **3a-e** were not necessarily good, however, photocyclization reactions are convenient to prepare this type of compounds. In the case of dihydrobenzofuranols **3b-e**, *cis* and *trans* isomers with regard to the R¹ and hydroxyl group are possible. In general, coupling constants between C₂-H and C₃-H in dihydrobenzofurans are 5.5-7.4 Hz for *cis* isomers and 2.0-4.8 Hz for *trans* isomers [4a,5-6]. Configurations of **3b-e** were determined by comparing these coupling constants with general values in literatures (see Experimental). In the reaction of **1b** (R¹ = CH₃, R² = H) *cis* and *trans* isomers, *cis*-**3b**, *trans*-**3b** were obtained in a 20:80 ratio. Furthermore, when **1c** (R¹ = C₂H₅, R² = H) and **1d** (R¹ = CH(CH₃)₂, R² = H) were used only *trans* isomers of **3c** and **3d** were produced. The results suggest that intramolecular cyclization of 1,5-biradical intermediates (*vide infra*) proceeds as the substituent R¹ and hydroxyl group become apart each other probably because of a steric requirement. In contrast, using **1e** (R¹ = Ph, R² = H) as the starting material *cis* isomer of **3e**

was obtained predominantly in spite of a bulky phenyl group, showing attractive interaction between the hydroxyl and phenyl groups in the cyclization step. The effect of a phenyl group is different from that of alkyl groups.

Using 2'-alkoxyacetophenones **2a-h** as the starting materials, dihydrobenzofuranols **5a-h** and dihydroisobenzofuranols **6b-c**, **6f** were obtained (Scheme 2 and Table 4). Dihydroisobenzofuranols **6b-c** were a mixture of *cis* and *trans* isomers with regard to the R¹ and hydroxyl group and difficult to purify enough because of instability. The stereochemistry of dihydroisobenzofuranols **6b-c** is not clear. The yields (36-89%) of dihydrobenzofuranols **5** became better than those from 2-alkoxybenzaldehydes, especially, in the case of R¹ = CO₂C₂H₅ and CN the yields were high. The yield of dihydrobenzofuranol **5f** was low probably because of steric hindrance in the cyclization step. In contrast, stereoselectivity of *cis* and *trans* isomers with regard to the R¹ and hydroxyl group in dihydrobenzofuranols became lower, showing that bulk of methyl and hydroxyl groups of 1,5-biradicals is similar in the acetonitrile solution. Table 4 shows that formation of dihydrobenzofuranols **5** and dihydroisobenzofuranols **6** is competing and the substituent R¹ such as phenyl, ethoxycarbonyl and cyano groups which stabilize 1,5-biradicals suppresses production of dihydroisobenzofuranols and makes dihydrobenzofuranol formation favorable. The stereochemistry of dihydrobenzofuranols **5** was determined by considering an anisotropic effect of C₃-CH₃ for C₂-H in ¹H nmr spectra. Generally, in dihydrobenzofurans C₃-CH₃ shield C₂-H at the *cis* position and deshield C₂-H at the *trans* position by anisotropy of the methyl group [6]. In the



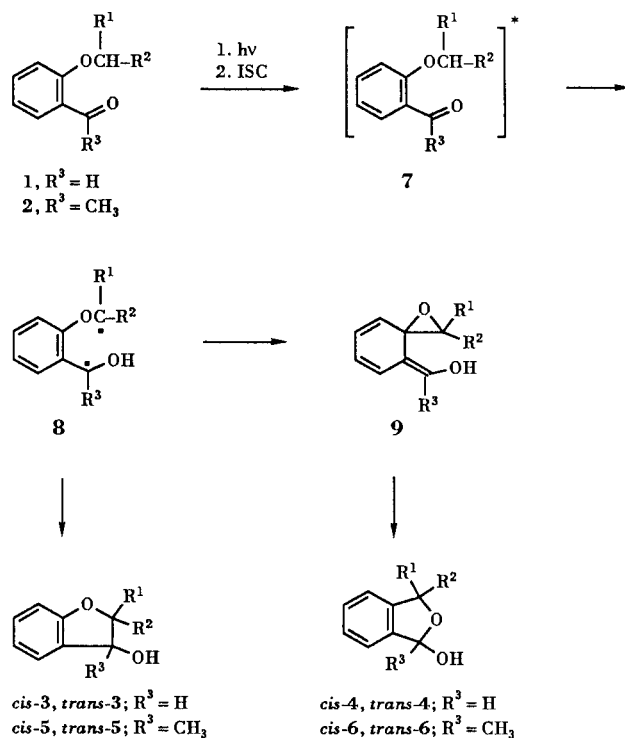
cis isomers with regard to the R¹ and hydroxyl group, the chemical shifts of C₂-H appear at a higher magnetic field than those of *trans* isomers. The assignments were also supported by determining NOE effect of both isomers of **5b**. Irradiation of C₃-CH₃ in the *cis* isomer *cis-5b* showed 25% NOE effect for C₂-H, and in contrast irradiation of C₃-CH₃ in the *trans* isomer *trans-5b* gave 12% NOE effect for C₂-H.

The mechanisms of photocyclization reactions through γ - or δ -hydrogen abstraction have been well studied [2-3,4j,5]. The plausible mechanisms of photocyclization from 2-alkoxybenzaldehydes **1a-f** and 2'-alkoxyacetophenones **2a-h** are shown in Scheme 3.

Irradiation of ethers **1**, **2** produces (n, π^*) excited triplet state **7** after intersystem crossing process. The carbonyl group of **7** abstracts δ -hydrogen to give 1,5-biradicals **8** which afford a variety of products. For example, intramolecular cyclization of **8** immediately produces *cis* and *trans* dihydrobenzofuranols **3**, **5**. In contrast, novel rearrangement is necessary for formation of dihydroisobenzofuranols **4**, **6**. The possible intermediates for dihydroisobenzofuranol formation are spiroenols **9** which were initially suggested by Wagner *et al.* [7,4j]. By irradiation of 2-benzyloxyacetophenone in benzene they obtained 2'-benzoylacetophenone as a major product which was formed through spiroenol **9** (R¹ = Ph, R² = H, R³ = CH₃) followed by spiro-ring cleavage and oxidation by oxygen. However, in this study we isolated dihydroisobenzofuranols **4**, **6**.

Next we examined photocyclization reactions of 2-formylphenoxyacetic acids **1i-l**. The results are summarized in Table 5. When carboxylic acids **1i-l** were irradiated, decarboxylation reactions occurred immediately to give the corresponding ethers **1a-d**. Further irradiation of the solution afforded dihydrobenzofuranols **3a-d** and dihydroiso-

Scheme 3



benzofuranols **4b-c** along with a small amount of pinacols (ca. 10%). In the reactions product yields and isomer ratios of dihydrobenzofuranols **3a-d** were almost the same with those from 2-alkoxybenzaldehydes **1a-d**. Dihydroisobenzofuranols **4b-c** were a mixture of *cis* and *trans* isomers and the stereochemistry was not determined. The results in Table 5 suggest that photocyclization products from 2-formylphenoxyacetic acids **1i-l** and 2-alkoxybenzaldehydes **2a-d** were obtained from the common 1,5-biradical intermediates such as **8**.

Table 4
Photocyclization Reactions of 2'-Alkoxyacetophenones **2a-h** [a]

Starting material	R ¹	R ²	Irradiation time (minutes)	Conversion (%)	Product yield (%)	
					5a-h	6a-h
					<i>(cis:trans)</i> [b]	
2a	H	H	120	88	37	0 [c]
2b	CH ₃	H	60	88	43 (67:33)	46 (60:40) [d]
2c	C ₂ H ₅	H	75	97	38 (57:43)	52 (60:40) [d]
2d	CH(CH ₃) ₂	H	110	90	36 (42:58)	-[e]
2e	Ph	H	70	94	56 (78:22)	-[e]
2f	CH ₃	CH ₃	75	81	7	52
2g	CO ₂ C ₂ H ₅	H	120	96	86 (75:25)	0
2h	CN	H	300	73	89 [f]	0

[a] An acetonitrile solution (500 ml) of **2a-h** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] *Cis* and *trans* isomers with regard to the R¹ and hydroxyl group. [c] The compound was not isolated because of instability. [d] Two stereoisomers were obtained as a mixture and the ratios were determined from the ¹H nmr spectra. [e] The compounds were difficult to purify. [f] Only one isomer was obtained and the stereochemistry was not determined.

Table 5
Photocyclization Reactions of 2-Formylphenoxyacetic Acids **1i-1** ($R^2 = \text{CO}_2\text{H}$) [a]

Starting material	R^1	Decarboxylation time (minutes)	Irradiation time (minutes)	Product yield (%)	
				3a-d ($R^2 = \text{H}$) (<i>cis:trans</i>) [b]	4a-d ($R^2 = \text{H}$)
1i	H	20	60	32	0 [c]
1j	CH_3	15	40	23 (20:80)	15 (55:45) [d]
1k	C_2H_5	20	50	22 (0:100)	12 (55:45) [d]
1l	$\text{CH}(\text{CH}_3)_2$	25	40	35 (0:100)	-[e]

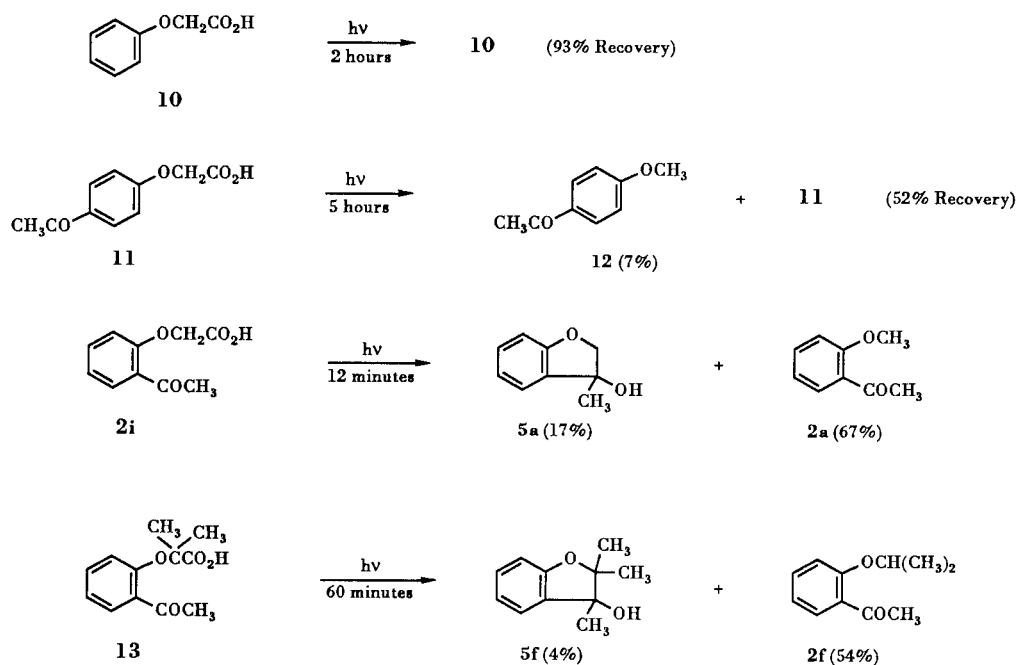
[a] An acetonitrile solution (500 ml) of **1i-1** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. In all cases conversion is 100%. [b] *Cis* and *trans* isomers with regard to the R^1 and hydroxyl group. [c] The compound was not isolated because of instability. [d] Two stereoisomers were obtained as a mixture and the ratios were determined from the ^1H nmr spectra. [e] The compound was difficult to purify.

Table 6
Photocyclization Reactions of 2-Acetylphenoxyacetic Acids **2i-m** ($R^2 = \text{CO}_2\text{H}$) [a]

Starting material	R^1	Decarboxylation time (minutes)	Irradiation time (minutes)	Product yield (%)	
				5a-d ($R^2 = \text{H}$) (<i>cis:trans</i>) [b]	6a-d ($R^2 = \text{H}$)
2i	H	12	120	38	0 [c]
2j	CH_3	12	60	30 (67:37)	11 (60:40) [d]
2k	C_2H_5	12	60	34 (56:44)	20 (60:40) [d]
2l	$\text{CH}(\text{CH}_3)_2$	15	130	39 (45:55)	-[e]
2m	Ph	30	120	64 (65:35)	-[e]

[a] An acetonitrile solution (500 ml) of **2i-m** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. In all cases conversion is 100%. [b] *Cis* and *trans* isomers with regard to the R^1 and hydroxyl group. [c] The compound was not isolated because of instability. [d] Two stereoisomers were obtained as a mixture and the ratios were determined from the ^1H nmr spectra. [e] The compounds were difficult to purify.

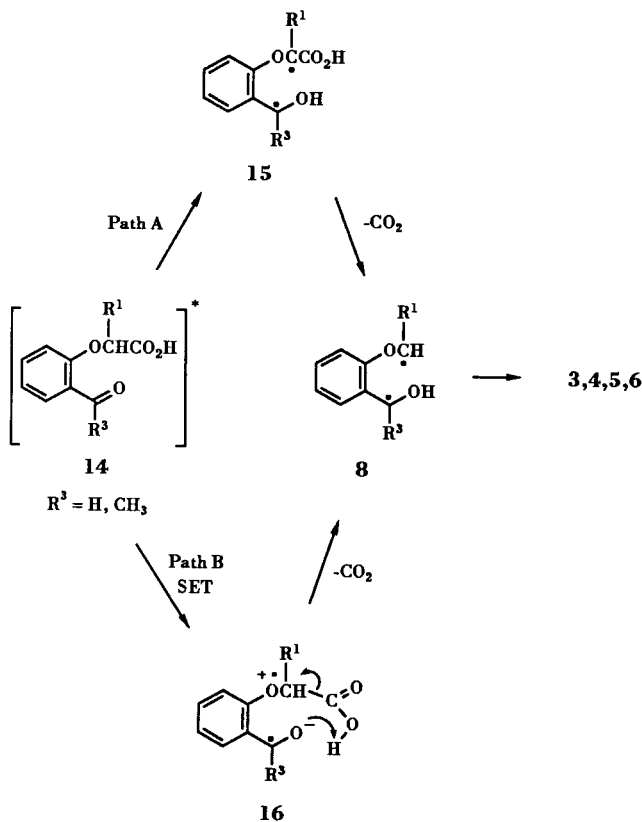
Scheme 4



Finally, photocyclization reactions of 2-acetylphenoxyacetic acids **2i-m** were examined. The results are summarized in Table 6. Photoreactions of **2i-m** proceed through immediate decarboxylation as well as those of 2-formylphenoxyacetic acids **1i-l**. The product yields and isomer ratios of dihydrobenzofuranols **5a-e** were almost the same with those from 2'-alkoxyacetophenones **2a-e**. A small amount of dihydroisobenzofuranols **6b-c** was also obtained as a mixture of *cis* and *trans* isomers.

To examine decarboxylation process some carboxylic acids were irradiated. Though phenoxyacetic acid **10** was irradiated for 2 hours no methoxybenzene was obtained and 93% of the starting material being recovered. In the case of 4-acetylphenoxyacetic acid **11** decarboxylation product **12** was only 7% yield after 5 hours with recovery of 52% starting material. In contrast, decarboxylation of 2-acetylphenoxyacetic acid **2i** was complete after 12 minutes to give 2'-methoxyacetophenone **2a** (67%) and dihydrobenzofuranol **5a** (17%). These results show that the acetyl group at the *ortho*-position is necessary for the facile decarboxylation reaction. When 2-(2-acetylphenoxy)-2-methylpropanoic acid **13** which possess no δ -hydrogen was irradiated, decarboxylation time (60 minutes) was longer than that of 2-acetylphenoxyacetic acids **2i-m**.

Scheme 5



From the above results two pathways are possible for decarboxylation process as shown in Scheme 5. The first one (Path A) is similar to photocyclization reactions of 2-alkoxybenzaldehydes **1a-f** and 2'-alkoxyacetophenones **2a-h**. The (n, π^*) excited triplet state **14** of starting carboxylic acids abstract δ -hydrogen to produce 1,5-biradicals **15**, which give intermediate biradicals **8** by decarboxylation. The following pathways are the same with photocyclization of 2-alkoxybenzaldehydes and 2'-alkoxyacetophenones. The second mechanism may be single electron transfer process (SET, Path B). Davidson *et al.* [8] suggested excited charge transfer complex in decarboxylation reaction of phenoxyacetic acid in the presence of benzophenone. In the cases of 2-acetylphenoxyacetic acids the similar process would occur intramolecularly to give ion radicals **16**, which afford the intermediate biradicals **8** after loss of carbon dioxide. The decarboxylation of carboxylic acids **1i-l**, **2i-m** would occur through both paths, however, path A is probably the main process because decarboxylation time of **2i-m** is shorter than that of **13**.

Photocyclization reactions of 2-alkoxybenzaldehydes, 2'-alkoxyacetophenones, 2-formylphenoxyacetic acids and 2-acetylphenoxyacetic acids are useful to synthesize dihydrobenzofuranol derivatives which are difficult to prepare by ionic reactions under basic or acidic conditions. Especially ethoxycarbonyl and cyano groups which stabilize intermediate 1,5-biradicals make furan-ring formation favorable.

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.

2-Propoxybenzaldehyde **1c**.

A mixture of 2-hydroxybenzaldehyde (2.0 g, 16.4 mmol), 1-iodopropane (5.6 g, 32.9 mmol), tripotassium phosphate (5.2 g, 24.5 mmol) and acetone (30 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 **1c** (1.5 g, 56%) as a colorless oil, bp 89° at 1.8 Torr (lit [9] bp 87° at 0.3 Torr); IR (neat): 1685 cm⁻¹ (Ar-CO); ¹H NMR (deuteriochloroform): δ 1.07 (t, J = 7.0 Hz, 3H, CH₂CH₂CH₃), 1.65-2.05 (m, 2H, CH₂CH₂CH₃), 4.02 (t, J = 6.4 Hz, 2H, CH₂CH₂CH₃), 6.90-7.06 (m, 2H, Ar-H), 7.42-7.61 (m, 1H, Ar-H), 7.81 (dd, J = 1.7 and 8.0 Hz, 1H, Ar-H), 10.51 (d, J = 0.6 Hz, 1H, CHO); ¹³C NMR (deuteriochloroform): δ 10.5 (q), 22.5 (t), 70.2 (t).

112.7 (d), 120.5 (d), 125.2 (s), 128.2 (d), 135.8 (d), 161.6 (s), 189.7 (d).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.92; H, 7.48.

2-Isobutoxybenzaldehyde **1d**.

A mixture of 2-hydroxybenzaldehyde (2.0 g, 16.4 mmoles), 1-bromo-2-methylpropane (4.5 g, 32.8 mmoles), tripotassium phosphate (7.0 g, 33.0 mmoles) and dimethyl sulfoxide (30 ml) was stirred at 60° for 1 hour. The following treatment was carried out in a manner similar to the synthesis of **1c** to give **1d** (2.4 g, 82%) as a colorless oil, bp 80° at 0.9 Torr (lit [9] bp 117° at 1-2 Torr); ir (neat): 1690 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.06 (d, J = 6.5 Hz, 6H, $CH_2CH(CH_3)_2$), 1.93-2.37 (m, 1H, $CH_2CH(CH_3)_2$), 3.83 (d, J = 6.2 Hz, 2H, $CH_2CH(CH_3)_2$), 6.90-7.07 (m, 2H, Ar-H₂), 7.42-7.61 (m, 1H, Ar-H), 7.82 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 10.54 (d, J = 0.6 Hz, 1H, CHO); ^{13}C nmr (deuteriochloroform): δ 19.2 (q), 28.3 (d), 74.9 (t), 112.6 (d), 120.5 (d), 125.2 (s), 128.2 (d), 135.8 (d), 161.7 (s), 189.6 (d).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.88; H, 7.93.

2-Benzoyloxybenzaldehyde **1e**.

Compound **1e** (63%) was obtained in a manner similar to the synthesis of **1d**. It formed colorless crystals from hexane, mp 44-46° (lit [10] mp 47-48°); ir (potassium bromide): 1680 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 5.15 (s, 2H, OCH_2Ph), 6.87-7.07 (m, 2H, Ar-H₂), 7.19-7.60 (m, 6H, Ar-H and Ph-H₃), 7.84 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 10.54 (s, 1H, CHO); ^{13}C nmr (deuteriochloroform): δ 70.4 (t), 113.1 (d), 120.9 (d), 125.2 (s), 127.2 (d), 128.1 (d), 128.3 (d), 128.6 (d), 135.8 (d), 136.1 (s), 161.0 (s), 189.3 (d).

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 78.95; H, 5.84.

2-Isopropoxybenzaldehyde **1f**.

Compound **1f** (60%) was obtained as a colorless oil in a manner similar to the synthesis of **1c**, bp 83° at 1.8 Torr (lit [11] bp 130-131° at 15 Torr); ir (neat): 1690 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.40 (d, J = 6.2 Hz, 6H, $CH(CH_3)_2$), 4.68 (septet, J = 6.2 Hz, 1H, $CH(CH_3)_2$), 6.89-7.05 (m, 2H, Ar-H₂), 7.42-7.61 (m, 1H, Ar-H), 7.82 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 10.49 (d, J = 0.6 Hz, 1H, CHO); ^{13}C nmr (deuteriochloroform): δ 21.9 (q), 71.2 (d), 114.3 (d), 120.4 (d), 125.9 (s), 128.1 (d), 135.7 (d), 160.6 (s), 189.7 (d).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.88; H, 7.49.

2'-Ethoxyacetophenone **2b**.

Compound **2b** (89%) was obtained in a manner similar to the synthesis of **1d**. It formed colorless crystals from benzene-hexane, mp 39-40°; ir (potassium bromide): 1665 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.47 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 2.63 (s, 3H, $COCH_3$), 4.12 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 6.87-7.04 (m, 2H, Ar-H₂), 7.33-7.51 (m, 1H, Ar-H), 7.73 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 14.7 (q), 31.9 (q), 64.2 (t), 112.6 (d), 120.4 (d), 128.5 (s), 130.3 (d), 133.6 (d), 158.5 (s), 199.3 (s).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.94; H, 7.50.

2'-Propoxyacetophenone **2c**.

Compound **2c** (83%) was obtained in a manner similar to the synthesis of **1c**. It formed colorless crystals from benzene-hexane, mp 38-39°; ir (potassium bromide): 1670 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.08 (t, J = 6.8 Hz, 3H, $OCH_2CH_2CH_3$), 2.24-2.67 (m, 2H, $OCH_2CH_2CH_3$), 2.64 (s, 3H, $COCH_3$), 4.02 (t, J = 6.4 Hz, 2H, $OCH_2CH_2CH_3$), 6.89-7.05 (m, 2H, Ar-H₂), 7.34-7.54 (m, 1H, Ar-H), 7.74 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 10.8 (q), 22.6 (t), 32.0 (q), 70.2 (t), 112.4 (d), 120.4 (d), 128.6 (s), 130.4 (d), 133.5 (d), 158.6 (s), 199.8 (s).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.26; H, 8.05.

2'-Isobutoxyacetophenone **2d**.

Compound **2d** (83%) was obtained as a colorless oil in a manner similar to the synthesis of **1d**, bp 87° at 2.5 Torr; ir (neat): 1690 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.07 (d, J = 6.6 Hz, 6H, $OCH_2CH(CH_3)_2$), 1.92-2.38 (m, 1H, $OCH_2CH(CH_3)_2$), 2.65 (s, 3H, $COCH_3$), 3.82 (d, J = 6.4 Hz, 2H, $OCH_2CH(CH_3)_2$), 6.88-7.05 (m, 2H, Ar-H₂), 7.33-7.53 (m, 1H, Ar-H), 7.74 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 19.4 (q), 28.3 (d), 32.0 (q), 75.0 (t), 112.4 (d), 120.3 (d), 128.4 (s), 130.3 (d), 133.6 (d), 158.6 (s), 199.1 (s).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.78; H, 8.25.

2'-Benzoyloxyacetophenone **2e**.

Compound **2e** (83%) was obtained as a colorless oil in a manner similar to the synthesis of **1c**, bp 139° at 0.7 Torr (lit [12] mp 40°); ir (neat): 1670 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 2.58 (s, 3H, $COCH_3$), 5.14 (s, 2H, OCH_2), 6.89-7.06 (m, 2H, Ar-H₂), 7.28-7.52 (m, 6H, Ar-H and Ph-H₃), 7.74 (dd, J = 1.5 and 8.0 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 32.0 (q), 70.8 (t), 113.0 (d), 120.9 (d), 127.5 (d), 128.2 (d), 128.7 (d), 129.0 (s), 130.4 (d), 133.4 (d), 136.3 (s), 158.0 (s), 199.6 (s).

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.39; H, 6.45.

2'-Isopropoxyacetophenone **2f**.

Compound **2f** (87%) was obtained as a colorless oil in a manner similar to the synthesis of **1d**, bp 82° at 2.7 Torr; ir (neat): 1680 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 1.40 (d, J = 6.0 Hz, 6H, $CH(CH_3)_2$), 2.62 (s, 3H, $COCH_3$), 4.68 (septet, J = 6.0 Hz, 1H, $CH(CH_3)_2$), 6.89-7.02 (m, 2H, Ar-H₂), 7.32-7.51 (m, 1H, Ar-H), 7.71 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 22.0 (q), 32.0 (q), 70.6 (d), 113.7 (d), 120.2 (d), 129.4 (s), 130.4 (d), 133.3 (d), 157.3 (s), 199.7 (s).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.96; H, 8.19.

2'-Cyanomethoxyacetophenone **2h**.

Compound **2h** (93%) was obtained in a manner similar to the synthesis of **1d**. It formed colorless crystals from benzene-hexane, mp 82-83°; ir (neat): 1660 cm^{-1} (Ar-CO); 1H nmr (deuteriochloroform): δ 2.60 (s, 3H, $COCH_3$), 4.89 (s, 2H, CH_2CN), 6.94-7.20 (m, 2H, Ar-H₂), 7.36-7.56 (m, 1H, Ar-H), 7.74 (dd, J = 1.5 and 7.7 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 31.5 (q), 54.2 (t), 113.4 (d), 114.8 (s), 123.3 (d), 129.7 (s), 130.8 (d), 133.6 (d), 155.3 (s), 198.6 (s).

Anal. Calcd. for $C_{10}H_8NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.44; H, 5.33; N, 7.83.

2-(2-Formylphenoxy)propanoic Acid **1j**.

A mixture of 2-hydroxybenzaldehyde (3.0 g, 22.0 mmoles), ethyl 2-bromopropanoate (8.9 g, 49.2 mmoles), tripotassium phosphate (7.8 g, 36.7 mmoles) and acetone (40 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 an ester of **1j**. It was dissolved in ethanol (50 ml) and hydrolyzed by adding a 2M aqueous potassium hydroxide solution (50 ml). The solution was acidified with 6M hydrochloric acid and the resulting precipitate was extracted with ether. The extract was washed, dried, and evaporated. The residue was recrystallized from ether to give **1j** (2.2 g, 46%) as colorless crystals, mp 61-63°; ir (potassium bromide): 1730 (CO₂H), 1660 cm⁻¹ (Ar-CO); ¹H nmr (deuterioacetone): δ 1.70 (d, J = 7.0 Hz, 3H, OCHCH₃), 5.09 (q, J = 7.0 Hz, 1H, OCHCH₃), 6.98-7.16 (m, 2H, Ar-H₂), 7.49-7.69 (m, 1H, Ar-H), 7.77 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 8.03 (broad s, 1H, CO₂H), 10.55 (d, J = 0.9 Hz, 1H, CHO); ¹³C nmr (deuterioacetone): δ 18.6 (q), 73.8 (d), 115.0 (d), 122.2 (d), 126.4 (s), 128.6 (d), 136.5 (d), 161.1 (s), 172.8 (s), 190.0 (d).

Anal. Calcd. for C₁₀H₁₀O₄: C, 61.85; H, 5.19. Found: C, 61.59; H, 5.42.

2-(2-Formylphenoxy)butanoic Acid **1k**.

Compound **1k** (43%) was obtained as colorless crystals from ether in a manner similar to the synthesis of **1j**, mp 95-97°; ir (potassium bromide): 1735 (CO₂H), 1650 cm⁻¹ (Ar-CO); ¹H nmr (deuterioacetone): δ 1.13 (t, J = 7.0 Hz, 3H, CH₂CH₃), 1.95-2.29 (m, 2H, CH₂CH₃), 4.97 (t, J = 5.7 Hz, 1H, OCH), 6.98-7.14 (m, 2H, Ar-H₂), 7.49-7.68 (m, 1H, Ar-H), 7.78 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 10.08 (broad s, 1H, CO₂H), 10.59 (d, J = 0.6 Hz, 1H, CHO); ¹³C nmr (deuterioacetone): δ 9.6 (q), 26.4 (t), 78.3 (d), 114.8 (d), 122.2 (d), 126.5 (s), 128.7 (d), 136.5 (d), 161.2 (s), 172.1 (s), 189.8 (d).

Anal. Calcd. for C₁₁H₁₂O₄: C, 63.45; H, 5.81. Found: C, 63.23; H, 6.04.

2-(2-Formylphenoxy)-3-methylbutanoic Acid **1l**.

Compound **1l** (47%) was obtained as colorless crystals from ether-hexane in a manner similar to the synthesis of **1j**, mp 75-76°; ir (potassium bromide): 1750, 1710 (CO₂H), 1680 cm⁻¹ (Ar-CO); ¹H nmr (deuterioacetone): δ 1.15 (d, J = 6.7 Hz, 6H, CH(CH₃)₂), 2.16-2.59 (m, 1H, OCHCH), 4.81 (d, J = 4.4 Hz, 1H, OCHCH), 6.97-7.14 (m, 2H, Ar-H₂), 7.47-7.67 (m, 1H, Ar-H), 7.79 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 8.14 (broad s, 1H, CO₂H), 10.61 (d, J = 0.6 Hz, 1H, CHO); ¹³C nmr (deuterioacetone): δ 17.5 (q), 19.0 (q), 32.0 (d), 81.8 (d), 114.5 (d), 122.0 (d), 126.4 (s), 128.6 (d), 136.5 (d), 161.3 (s), 171.8 (s), 190.0 (d).

Anal. Calcd. for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 64.62; H, 6.21.

2-Acetylphenoxyacetic Acid **2i**.

Compound **2i** (84%) was obtained as colorless crystals from ether in a manner similar to the synthesis of **1j**, mp 113-115° (lit [13] mp 114-114.5°); ir (potassium bromide): 1740, 1710 (CO₂H), 1660 cm⁻¹ (Ar-CO); ¹H nmr (deuterioacetone): δ 2.66 (s, 3H, COCH₃), 4.88 (s, 2H, OCH₂), 6.94-7.13 (m, 2H, Ar-H₂), 7.40-7.59 (m, 1H, Ar-H), 7.69 (dd, J = 1.5 and 6.0 Hz, 1H, Ar-H), 9.97 (broad s, 1H, CO₂H); ¹³C nmr (deuterioacetone): δ 31.8 (q), 65.8 (t), 113.8 (d), 122.0 (d), 129.4 (s), 130.8 (d), 134.3 (d), 158.0 (s), 169.8

(s), 199.6 (s).

Anal. Calcd. for C₁₀H₁₀O₄: C, 61.85; H, 5.19. Found: C, 61.64; H, 5.38.

Ethyl 2-Acetylphenoxyacetate **2g**.

A mixture of **2i** (3.0 g, 15.4 mmoles), concentrated sulfuric acid (0.3 ml) and ethanol (50 ml) was refluxed for 4 hours. The solution was extracted with ether. The extract was washed with a 0.5M aqueous potassium carbonate solution, then with water, dried and evaporated. The residue was chromatographed and eluted with benzene (95)-ether (5) to give **2g**. It formed colorless crystals (2.6 g, 76%) from benzene-hexane, mp 49-50° (lit [13] mp 40-50.5°); ir (neat): 1760 (CO₂CH₂CH₃), 1670 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.29 (t, J = 7.0 Hz, 3H, OCH₂CH₃), 2.71 (s, 3H, COCH₃), 4.26 (q, J = 7.0 Hz, 2H, OCH₂CH₃), 4.71 (s, 2H, OCH₂CO), 6.78-7.09 (m, 2H, Ar-H₂), 7.28-7.46 (m, 1H, Ar-H), 7.74 (dd, J = 2.0 and 7.7 Hz, 1H, Ar-H); ¹³C nmr (deuteriochloroform): δ 14.1 (q), 31.9 (q), 61.4 (t), 65.6 (t), 112.4 (d), 121.6 (d), 129.0 (s), 130.6 (d), 133.4 (d), 157.0 (s), 168.1 (s), 199.4 (s).

Anal. Calcd. for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 64.73; H, 6.54.

2-(2-Acetylphenoxy)propanoic Acid **2j**.

Compound **2j** (65%) was obtained as colorless crystals from ether in a manner similar to the synthesis of **1j**, mp 86-88° (lit [14] mp 92°); ir (potassium bromide): 1740 (CO₂H), 1650 cm⁻¹ (Ar-CO); ¹H nmr (deuterioacetone): δ 1.69 (d, J = 6.7 Hz, 3H, CHCH₃), 2.65 (s, 3H, COCH₃), 5.09 (q, J = 6.7 Hz, 1H, CHCH₃), 6.92-7.09 (m, 2H, Ar-H₂), 7.37-7.56 (m, 1H, Ar-H), 7.68 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 10.40 (broad s, 1H, CO₂H); ¹³C nmr (deuterioacetone): δ 18.6 (q), 31.6 (q), 73.3 (d), 114.0 (d), 121.9 (d), 129.5 (s), 130.8 (d), 134.2 (d), 157.6 (s), 172.8 (s), 199.8 (s).

Anal. Calcd. for C₁₁H₁₂O₄: C, 63.45; H, 5.81. Found: C, 63.71; H, 6.02.

2-(2-Acetylphenoxy)butanoic Acid **2k**.

Compound **2k** (79%) was obtained as colorless crystals from ether in a manner similar to the synthesis of **1j**, mp 124-125°; ir (potassium bromide): 1740 (CO₂H), 1640 cm⁻¹ (Ar-CO); ¹H nmr (deuterioacetone): δ 1.12 (t, J = 7.3 Hz, 3H, CH₂CH₃), 1.95-2.24 (m, 2H, CH₂CH₃), 2.66 (s, 3H, COCH₃), 4.97 (t, J = 5.9 Hz, 1H, OCHCO₂), 6.93-7.10 (m, 2H, Ar-H₂), 7.37-7.57 (m, 1H, Ar-H), 7.67 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 9.57 (broad s, 1H, CO₂H); ¹³C nmr (deuterioacetone): δ 9.9 (q), 26.5 (t), 31.8 (q), 78.1 (d), 114.0 (d), 121.8 (d), 129.8 (s), 130.9 (d), 134.2 (d), 157.9 (s), 172.1 (s), 199.5 (s).

Anal. Calcd. for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 64.78; H, 6.16.

2-(2-Acetylphenoxy)-3-methylbutanoic Acid **2l**.

Compound **2l** (28%) was obtained as colorless crystals from ether-hexane in a manner similar to the synthesis of **1j**, mp 86-87°; ir (potassium bromide): 1750 (CO₂H), 1660 cm⁻¹ (Ar-CO); ¹H nmr (deuterioacetone): δ 1.14 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 2.25-2.54 (m, 1H, CH(CH₃)₂), 4.84 (d, J = 5.0 Hz, 1H, OCHCO₂), 6.92-7.09 (m, 2H, Ar-H₂), 7.37-7.57 (m, 1H, Ar-H), 7.66 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 8.56 (broad s, 1H, CO₂H); ¹³C nmr (deuterioacetone): δ 18.0 (q), 19.0 (q), 31.9 (d), 32.0 (q), 81.8 (d), 113.9 (d), 121.8 (d), 129.9 (s), 130.9 (d), 134.1 (d), 158.0 (s), 171.6 (s), 199.7 (s).

Anal. Calcd. for C₁₃H₁₆O₄: C, 66.09; H, 6.83. Found: C, 66.25; H, 6.80.

(2-Acetylphenoxy)phenylacetic Acid **2m**.

Compound **2m** (48%) was obtained as colorless crystals from ether in a manner similar to the synthesis of **1j**, mp 115-117°; ir (potassium bromide): 1735 (CO₂H), 1640 cm⁻¹ (Ar-CO); ¹H nmr (deuteriodimethyl sulfoxide): δ 2.71 (s, 3H, COCH₃), 6.13 (s, 1H, OCHCO₂), 6.92-7.18 (m, 2H, Ar-H₂), 7.34-7.70 (m, 7H, Ar-H₂ and Ph-H₅); ¹³C nmr (deuteriodimethyl sulfoxide): δ 31.6 (q), 77.8 (d), 113.7 (d), 121.1 (d), 127.4 (d), 128.7 (s), 128.7 (d), 129.7 (d), 133.3 (d), 135.7 (s), 155.9 (s), 170.4 (s), 199.0 (s).

Anal. Calcd. for C₁₆H₁₄O₄: C, 71.10; H, 5.22. Found: C, 70.84; H, 5.24.

4-Acetylphenoxyacetic Acid **1l**.

Compound **1l** (53%) was obtained as colorless crystals from ether in a manner similar to the synthesis of **1j**, mp 171-172° (lit [15] mp 172.5-174.5°); ir (potassium bromide): 1760 (CO₂H), 1640 cm⁻¹ (Ar-CO); ¹H nmr (deuterioacetone): δ 2.53 (s, 3H, COCH₃), 3.93 (s, 2H, OCH₂), 6.92-7.08 (m, 2H, Ar-H₂), 7.84-8.00 (m, 2H, Ar-H₂); ¹³C nmr (deuterioacetone): δ 26.4 (q), 65.5 (t), 115.2 (d), 131.2 (d), 131.9 (s), 162.9 (s), 169.9 (s), 196.7 (s).

Anal. Calcd. for C₁₀H₁₀O₄: C, 61.85; H, 5.19. Found: C, 61.86; H, 5.36.

2-(2-Acetylphenoxy)-2-methylpropanoic Acid **13**.

Compound **13** (24%) was obtained as colorless crystals from ether-hexane in a manner similar to the synthesis of **1j**, mp 116.5-117.5°; ir (potassium bromide): 1740 (CO₂H), 1660 cm⁻¹ (Ar-CO); ¹H nmr (deuteriochloroform): δ 1.70 (s, 6H, C(CH₃)₂), 2.65 (s, 3H, COCH₃), 6.91-7.15 (m, 2H, Ar-H₂), 7.28-7.46 (m, 1H, Ar-H), 7.75 (dd, J = 2.0 and 8.0 Hz, 1H, Ar-H), 8.51 (broad s, 1H, CO₂H); ¹³C nmr (deuteriochloroform): δ 25.1 (q), 30.7 (q), 118.7 (d), 122.3 (d), 130.2 (s), 131.3 (d), 133.6 (d), 154.4 (s), 176.8 (s), 201.1 (s).

Anal. Calcd. for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 64.60; H, 6.50.

General Procedure for Photocyclization Reactions of Ethers **1a-f**, **2a-h** and Acids **1i-l**, **2i-m**.

Freshly prepared compounds were used in photoreactions. Irradiation of compounds containing impurity afforded considerable decomposition products. An acetonitrile solution (500 ml) of a starting material (2.00 mmoles) was deoxygenated by bubbling nitrogen gas for 1 hour and irradiated under monitoring by high performance liquid chromatography (hplc). In the case of ethers **1a-f**, **2a-h** irradiation was stopped when the starting material almost disappeared. In contrast, using acids **1i-l**, **2i-m** irradiation was continued until ether compounds which were produced by decarboxylation almost disappeared. After the photoreaction the acetonitrile was evaporated under reduced pressure below 40°. The residue was chromatographed and eluted with benzene-ether to give a variety of products.

2,3-Dihydro-3-benzofuranol **3a**.

Compound **3a** was obtained as a colorless oil (lit [16] bp 122° at 15 Torr); ir (neat): 3370 cm⁻¹ (OH); ¹H nmr (deuteriochloroform): δ 2.72 (broad s, 1H, OH), 4.29 (dd, J = 3.3 and 10.7 Hz, 1H, C₂-H), 4.45 (dd, J = 5.7 and 10.7 Hz, 1H, C₂-H), 5.18 (broad s, 1H, C₃-H), 6.78-7.40 (m, 4H, Ar-H₄); ¹³C nmr (deuteriochloroform): δ 72.0 (d), 79.0 (t), 110.5 (d), 120.9 (d), 125.5 (d), 128.3 (s), 130.6 (d), 160.2 (s).

Anal. Calcd. for C₈H₈O₂: C, 70.58; H, 5.92. Found: C, 70.60; H, 6.10.

trans-2-Methyl-2,3-dihydro-3-benzofuranol *trans*-**3b**.

Compound *trans*-**3b** was obtained as a colorless oil; ir (neat): 3400 cm⁻¹ (OH); ¹H nmr (deuteriobenzene): δ 1.06 (d, J = 6.4 Hz, 3H, CH₃), 3.92 (broad s, 1H, OH), 4.42 (dq, J = 3.6 and 6.4 Hz, 1H, C₂-H), 4.52 (broad s, 1H, C₃-H), 6.62-7.30 (m, 4H, Ar-H); ¹³C nmr (deuteriobenzene): δ 19.0 (q), 78.5 (d), 87.3 (d), 110.7 (d), 120.9 (d), 126.1 (d), 128.7 (s), 130.6 (d), 160.1 (s).

Anal. Calcd. for C₉H₁₀O₂: C, 71.98; H, 6.71. Found: C, 71.78; H, 6.87.

cis-2-Methyl-2,3-dihydro-3-benzofuranol *cis*-**3b**.

Compound *cis*-**3b** was obtained as a mixture with *trans*-**3b** and difficult to isolate; ¹H nmr (deuteriobenzene): δ 1.32 (d, J = 6.6 Hz, 3H, CH₃), 3.40 (broad s, 1H, OH), 4.20-4.60 (m, 2H, C₂-H and C₃-H), 6.64-7.26 (m, 4H, Ar-H₄); ¹³C nmr (deuteriobenzene): δ 13.6 (q), 72.9 (d), 83.4 (d), 110.6 (d), 120.8 (d), 126.1 (d), 128.9 (s), 130.0 (d), 160.3 (s).

trans-2-Ethyl-2,3-dihydro-3-benzofuranol *trans*-**3c**.

Compound *trans*-**3c** was obtained as a colorless oil; ir (neat): 3400 cm⁻¹ (OH); ¹H nmr (deuteriobenzene): δ 0.87 (t, J = 7.0 Hz, 3H, CH₂CH₃), 1.26-1.54 (m, 2H, CH₂CH₃), 3.18 (broad s, 1H, OH), 4.31 (dt, J = 3.7 and 6.6 Hz, 1H, C₂-H), 4.62 (broad s, 1H, C₃-H), 6.64-7.33 (m, 4H, Ar-H₄); ¹³C nmr (deuteriobenzene): δ 9.5 (q), 26.8 (t), 77.0 (d), 92.4 (d), 110.6 (d), 120.8 (d), 126.0 (d), 129.1 (s), 130.6 (d), 160.5 (s).

Anal. Calcd. for C₁₀H₁₂O₂: C, 73.15; H, 7.37. Found: C, 72.90; H, 7.40.

trans-2-Isopropyl-2,3-dihydro-3-benzofuranol *trans*-**3d**.

Compound *trans*-**3d** was obtained as a colorless oil; ir (neat): 3380 cm⁻¹ (OH); ¹H nmr (deuteriochloroform): δ 0.87 (d, J = 6.6 Hz, 3H, CH(CH₃)₂), 0.90 (d, J = 6.6 Hz, 3H, CH(CH₃)₂), 1.42-1.86 (m, 1H, CH(CH₃)₂), 3.52 (broad s, 1H, OH), 4.15 (dd, J = 4.2 and 6.6 Hz, 1H, C₂-H), 4.82 (d, J = 4.2 Hz, 1H, C₃-H), 6.64-7.30 (m, 4H, Ar-H₄); ¹³C nmr (deuteriochloroform): δ 17.8 (q), 17.9 (q), 31.7 (d), 75.3 (d), 95.9 (d), 110.3 (d), 120.7 (d), 125.8 (d), 129.3 (s), 130.5 (d), 160.6 (s).

Anal. Calcd. for C₁₁H₁₄O₂: C, 74.13; H, 7.92. Found: C, 73.90; H, 8.04.

cis-2-Phenyl-2,3-dihydro-3-benzofuranol *cis*-**3e**.

Compound *cis*-**3e** was obtained as colorless crystals from benzene-hexane, mp 123-125° (lit [4a] mp 126-127°); ir (potassium bromide): 3410 cm⁻¹ (OH); ¹H nmr (deuteriochloroform): δ 1.54 (broad s, 1H, OH), 5.18 (d, J = 5.9 Hz, 1H, C₃-H), 5.53 (d, J = 5.9 Hz, 1H, C₂-H), 6.86-7.04 (m, 2H, Ar-H₂), 7.20-7.47 (m, 7H, Ar-H₂ and Ph-H₅).

Anal. Calcd. for C₁₄H₁₂O₂: C, 79.23; H, 5.70. Found: C, 79.15; H, 5.77.

trans-2-Phenyl-2,3-dihydro-3-benzofuranol *trans*-**3e**.

Compound *trans*-**3e** was obtained as a colorless oil [4a]; ir (neat): 3430 cm⁻¹ (OH); ¹H nmr (deuteriochloroform): δ 2.80 (broad s, 1H, OH), 5.08 (broad s, 1H, C₃-H), 5.41 (d, J = 3.7 Hz, 1H, C₂-H), 6.78-6.96 (m, 2H, Ar-H₂), 7.14-7.32 (m, 7H, Ar-H₂ and Ph-H₅).

Anal. Calcd. for C₁₄H₁₂O₂: C, 79.23; H, 5.70. Found: C, 79.36; H, 5.82.

3-Methyl-2,3-dihydro-3-benzofuranol **5a**.

Compound **5a** was obtained as a colorless oil [17]; ir (neat):

3400 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 1.31 (s, 3H, CH_3), 3.70 (broad s, 1H, OH), 3.91 (d, $J = 9.9$ Hz, 1H, $\text{C}_2\text{-H}$), 4.21 (d, $J = 9.9$ Hz, 1H, $\text{C}_2\text{-H}$), 6.67-7.19 (m, 4H, Ar- H_4); ^{13}C nmr (deuteriobenzene): δ 25.3 (q), 77.6 (s), 83.9 (t), 110.6 (d), 121.0 (d), 123.4 (d), 130.1 (d), 132.7 (s), 160.2 (s).

Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{O}_2$: C, 71.98; H, 6.71. Found: C, 71.85; H, 6.91.

cis-2,3-Dimethyl-2,3-dihydro-3-benzofuranol *cis*-5b.

Compound *cis*-5b was obtained as colorless crystals from benzene-hexane, mp 84-85°; ir (potassium bromide): 3360 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 1.29 (d, $J = 6.4$ Hz, 1H, $\text{C}_2\text{-CH}_3$), 1.29 (s, 3H, $\text{C}_3\text{-CH}_3$), 2.44 (broad s, 1H, OH), 4.05 (q, $J = 6.4$ Hz, 1H, $\text{C}_2\text{-H}$), 6.63-7.19 (m, 4H, Ar- H_4); ^{13}C nmr (deuteriobenzene): δ 13.2 (q), 24.2 (q), 77.2 (s), 88.0 (d), 110.6 (d), 120.8 (d), 123.8 (d), 130.1 (d), 133.6 (s), 159.7 (s).

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 73.15; H, 7.37. Found: C, 73.02; H, 7.49.

trans-2,3-Dimethyl-2,3-dihydro-3-benzofuranol *trans*-5b.

Compound *trans*-5b was obtained as colorless crystals from benzene-hexane, mp 77-78°; ir (potassium bromide): 3300 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 1.06 (d, $J = 6.6$ Hz, 3H, $\text{C}_2\text{-CH}_3$), 1.21 (s, 3H, $\text{C}_3\text{-CH}_3$), 2.42 (broad s, 1H, OH), 4.40 (q, $J = 6.6$ Hz, 1H, $\text{C}_2\text{-H}$), 6.66-7.18 (m, 4H, Ar- H_4); ^{13}C nmr (deuteriobenzene): δ 15.6 (q), 22.1 (q), 79.8 (s), 89.7 (d), 110.7 (d), 120.9 (d), 123.6 (d), 130.1 (d), 133.7 (s), 159.2 (s).

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 73.15; H, 7.37. Found: C, 73.32; H, 7.14.

cis-2-Ethyl-3-methyl-2,3-dihydro-3-benzofuranol *cis*-5c.

Compound *cis*-5c was obtained as a colorless oil; ir (neat): 3450 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 1.09 (t, $J = 7.0$ Hz, 3H, CH_2CH_3), 1.35 (s, 3H, $\text{C}_3\text{-CH}_3$), 1.52-1.90 (m, 2H, CH_2CH_3), 2.32 (broad s, 1H, OH), 3.87 (dd, $J = 5.5$ and 8.1 Hz, 1H, $\text{C}_2\text{-H}$), 6.64-7.17 (m, 4H, Ar- H_4); ^{13}C nmr (deuteriobenzene): δ 11.0 (q), 21.9 (t), 25.0 (q), 77.2 (s), 93.5 (d), 110.6 (d), 120.8 (d), 123.6 (d), 130.1 (d), 133.7 (s), 159.6 (s).

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 74.38; H, 7.73.

trans-2-Ethyl-3-methyl-2,3-dihydro-3-benzofuranol *trans*-5c.

Compound *trans*-5c was obtained as a colorless oil; ir (neat): 3430 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 1.03 (t, $J = 6.6$ Hz, 3H, CH_2CH_3), 1.26 (s, 3H, $\text{C}_3\text{-CH}_3$), 1.26-1.50 (m, 2H, CH_2CH_3), 2.76 (broad s, 1H, OH), 4.19 (dd, $J = 5.1$ and 8.6 Hz, 1H, $\text{C}_2\text{-H}$), 6.64-7.21 (m, 4H, Ar- H_4); ^{13}C nmr (deuteriobenzene): δ 11.1 (q), 22.4 (q), 23.6 (t), 79.7 (s), 94.9 (d), 110.7 (d), 120.9 (d), 123.5 (d), 130.0 (d), 134.2 (s), 159.1 (s).

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 73.95; H, 7.97.

cis-2-Isopropyl-3-methyl-2,3-dihydro-3-benzofuranol *cis*-5d.

Compound *cis*-5d was obtained as colorless crystals from hexane, mp 69-70.5°; ir (potassium bromide): 3350 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 1.00 (d, $J = 6.6$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, $J = 6.6$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.42 (s, 3H, $\text{C}_3\text{-CH}_3$), 1.68 (s, 1H, OH), 1.88-2.28 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.61 (d, $J = 9.5$ Hz, 1H, $\text{C}_2\text{-H}$), 6.62-7.11 (m, 4H, Ar- H_4); ^{13}C nmr (deuteriobenzene): δ 19.2 (q), 20.5 (q), 26.5 (q), 28.8 (d), 77.5 (s), 96.6 (d), 110.5 (d), 120.7 (d), 123.4 (d), 130.2 (d), 134.0 (s), 159.3 (s).

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 74.85; H, 8.27.

trans-2-Isopropyl-3-methyl-2,3-dihydro-3-benzofuranol *trans*-5d.

Compound *trans*-5d was obtained as colorless crystals from benzene-hexane, mp 72-74°; ir (neat): 3420 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 0.97 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.05 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.30 (s, 3H, $\text{C}_3\text{-CH}_3$), 1.64-2.12 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.80 (d, $J = 8.4$ Hz, 1H, $\text{C}_2\text{-H}$), 6.64-7.18 (m, 4H, Ar- H_4); ^{13}C nmr (deuteriochloroform): δ 19.6 (q), 22.8 (q), 29.0 (d), 79.9 (s), 97.7 (d), 110.4 (d), 121.1 (d), 122.9 (d), 129.8 (d), 135.5 (s), 159.0 (s).

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 74.76; H, 8.47.

cis-3-Methyl-2-phenyl-2,3-dihydro-3-benzofuranol *cis*-5e.

Compound *cis*-5e was obtained as colorless crystals from benzene-hexane, mp 72-73.5° [4j]; ir (potassium bromide): 3520, 3430 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 1.33 (s, 3H, CH_3), 1.42 (broad s, 1H, OH), 4.98 (s, 1H, $\text{C}_2\text{-H}$), 6.70-7.25 (m, 9H, Ar- H_4 and Ph- H_5); ^{13}C nmr (deuteriobenzene): δ 25.1 (q), 78.1 (s), 93.1 (d), 110.7 (d), 121.3 (d), 124.1 (d), 127.5 (d), 128.3 (d), 128.5 (d), 130.2 (d), 132.8 (s), 135.7 (s), 159.8 (s).

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_2$: C, 79.62; H, 6.24. Found: C, 79.48; H, 6.34.

trans-3-Methyl-2-phenyl-2,3-dihydro-3-benzofuranol *trans*-5e.

Compound *trans*-5e [4j] was obtained as a mixture with 3-methyl-2-phenylbenzofuran because of facile dehydration of *trans*-5e; ir (neat): 3430 cm^{-1} (OH); ^1H nmr (deuteriobenzene): δ 1.02 (s, 3H, CH_3), 2.36 (broad s, 1H, OH), 5.44 (s, 1H, $\text{C}_2\text{-H}$), 6.79-7.29 (m, 9H, Ar- H_4 and Ph- H_5).

3-Methyl-2-phenylbenzofuran was obtained as a colorless oil by complete dehydration of *trans*-5e, bp 122° at 0.7 Torr (lit [18] bp 117-118° at 0.3 Torr); ^1H nmr (deuteriochloroform): δ 2.39 (s, 3H, $\text{C}_3\text{-CH}_3$), 7.15-7.82 (m, 9H, Ar- H_4 and Ph- H_5); ^{13}C nmr (deuteriochloroform): δ 9.4 (q), 110.9 (d), 111.2 (s), 119.2 (d), 122.3 (d), 124.2 (d), 126.7 (d), 127.8 (d), 128.5 (d), 131.2 (s), 131.4 (s), 150.7 (s), 153.8 (s).

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}$: C, 86.51; H, 5.81. Found: C, 86.32; H, 6.08.

2,2,3-Trimethyl-2,3-dihydro-3-benzofuranol 5f.

Compound 5f was obtained as a colorless oil; ir (neat): 3430 cm^{-1} (OH); ^1H nmr (deuteriochloroform): δ 1.25 (s, 3H, $\text{C}_3\text{-CH}_3$), 1.48 (s, 3H, $\text{C}_2\text{-CH}_3$), 1.52 (s, 3H, $\text{C}_2\text{-CH}_3$), 6.72-7.30 (m, 4H, Ar- H_4).

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 74.29; H, 8.02.

Ethyl *cis*-3-Hydroxy-3-methyl-2,3-dihydro-2-benzofuranocarboxylate *cis*-5g.

Compound *cis*-5g was obtained as colorless crystals from benzene-hexane, mp 73-74°; ir (potassium bromide): 3450 (OH), 1745 cm^{-1} ($\text{CO}_2\text{CH}_2\text{CH}_3$); ^1H nmr (deuteriobenzene): δ 0.98 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 1.58 (s, 3H, $\text{C}_3\text{-CH}_3$), 2.86 (broad s, 1H, OH), 3.98 (q, $J = 7.0$ Hz, 1H, OCH_2CH_3), 4.00 (q, $J = 7.0$ Hz, 1H, OCH_2CH_3), 4.63 (s, 1H, $\text{C}_2\text{-H}$), 6.64-7.14 (m, 4H, Ar- H_4); ^{13}C nmr (deuteriobenzene): δ 14.1 (q), 25.7 (q), 61.2 (t), 79.4 (s), 89.5 (d), 111.0 (d), 121.6 (d), 123.7 (d), 130.6 (d), 131.4 (s), 159.4 (s), 167.8 (s).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.56; H, 6.54.

Ethyl *trans*-3-Hydroxy-3-methyl-2,3-dihydro-2-benzofurancarboxylate *trans*-**5g**.

Compound *trans*-**5g** was obtained as a colorless oil; ir (neat): 3500 (OH), 1740 cm^{-1} ($CO_2CH_2CH_3$); 1H nmr (deuteriobenzene): δ 0.88 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.53 (s, 3H, C_3-CH_3), 3.52 (broad s, 1H, OH), 3.88 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 5.07 (s, 1H, C_2-H), 6.66-7.18 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriobenzene): δ 14.0 (q), 23.6 (q), 61.1 (t), 80.9 (s), 91.0 (d), 110.9 (d), 121.7 (d), 123.7 (d), 130.5 (d), 131.8 (s), 159.4 (s), 169.0 (s).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.73; H, 6.47.

2-Cyano-3-methyl-2,3-dihydro-3-benzofuranol *cis*-**5h** or *trans*-**5h**.

Compound *cis*-**5h** or *trans*-**5h** was obtained as a colorless oil; ir (neat): 3420 (OH), 2250 cm^{-1} (CN); 1H nmr (deuteriobenzene): δ 1.52 (s, 3H, CH_3), 3.12 (broad s, 1H, OH), 4.73 (s, 1H, C_2-H), 6.63-7.02 (m, 4H, Ar-H₄); ^{13}C nmr (deuteriochloroform): δ 24.1 (q), 80.6 (s), 80.7 (d), 111.3 (d), 115.9 (s), 122.9 (d), 123.5 (d), 130.1 (s), 131.1 (d), 157.8 (s).

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.41; H, 5.37; N, 7.83.

cis- and *trans*-3-Methyl-1,3-dihydro-1-isobenzofuranol *cis*-**4b** and *trans*-**4b**.

Compounds *cis*-**4b** and *trans*-**4b** were obtained as a mixture (colorless oil).

The major component had ir (neat): 3400 cm^{-1} (OH); 1H nmr (deuteriobenzene): δ 1.27 (d, J = 6.5 Hz, 3H, CH_3), 5.06 (broad s, 1H, OH), 5.32 (dq, J = 1.8 and 6.4 Hz, 1H, C_3-H), 6.40 (broad s, 1H, C_1-H), 6.68-7.28 (m, 4H, Ar-H₄).

The minor component had ir (neat): 3400 cm^{-1} (OH); 1H nmr (deuteriobenzene): δ 1.41 (d, J = 6.5 Hz, 3H, CH_3), 4.96 (q, J = 6.5 Hz, 1H, C_3-H), 5.06 (broad s, 1H, OH), 6.40 (broad s, 1H, C_1-H), 6.68-7.28 (m, 4H, Ar-H₄).

cis- and *trans*-3-Ethyl-1,3-dihydro-1-isobenzofuranol *cis*-**4c** and *trans*-**4c**.

Compounds *cis*-**4c** and *trans*-**4c** were obtained as a mixture (colorless oil).

The major component had ir (neat): 3400 cm^{-1} (OH); 1H nmr (deuteriobenzene): δ 0.88 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.40-1.80 (m, 2H, CH_2CH_3), 3.38 (broad s, 1H, OH), 5.22 (broad s, 1H, C_3-H), 6.40 (broad s, 1H, C_1-H), 6.72-7.26 (m, 4H, Ar-H₄).

The minor component had ir (neat): 3400 cm^{-1} (OH); 1H nmr (deuteriobenzene): δ 0.96 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.40-1.80 (m, 2H, CH_2CH_3), 3.88 (broad s, 1H, OH), 4.89 (t, J = 6.8 Hz, 1H, C_3-H), 6.40 (broad s, 1H, C_1-H), 6.72-7.26 (m, 4H, Ar-H₄).

3,3-Dimethyl-1,3-dihydro-1-isobenzofuranol **4f**.

Compound **4f** was obtained as colorless crystals from benzene-hexane, mp 103-105°; ir (potassium bromide): 3230 cm^{-1} (OH); 1H nmr (deuterioacetone): δ 1.43 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 5.49 (d, J = 7.5 Hz, 1H, OH), 6.35 (d, J = 7.5 Hz, 1H, C_1-H), 7.10-7.32 (m, 4H, Ar-H₄); ^{13}C nmr (deuterioacetone): δ 29.5 (q), 31.0 (q), 85.3 (s), 100.3 (d), 121.3 (d), 123.7 (d), 128.2 (d), 129.6 (d), 140.7 (s), 148.9 (s).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.12; H, 7.32.

cis- and *trans*-1,3-Dimethyl-1,3-dihydro-1-isobenzofuranol *cis*-**6b** and *trans*-**6b**.

Compounds *cis*-**6b** and *trans*-**6b** were obtained as a mixture (colorless oil).

The major component had ir (neat): 3400 cm^{-1} (OH); 1H nmr (deuteriobenzene): δ 1.27 (d, J = 6.4 Hz, 3H, C_3-CH_3), 1.78 (s, 3H, C_1-CH_3), 4.06 (broad s, 1H, OH), 5.27 (q, J = 6.4 Hz, 1H, C_3-H), 6.70-7.20 (m, 4H, Ar-H₄).

The minor component had ir (neat): 3400 cm^{-1} (OH); 1H nmr (deuteriobenzene): δ 1.39 (t, J = 6.4 Hz, 3H, C_3-CH_3), 1.70 (s, 3H, C_1-CH_3), 4.06 (broad s, 1H, OH), 4.96 (q, J = 6.4 Hz, 1H, C_3-H), 6.70-7.20 (m, 4H, Ar-H₄).

cis- and *trans*-3-Ethyl-1-methyl-1,3-dihydro-1-isobenzofuranol *cis*-**6c** and *trans*-**6c**.

Compounds *cis*-**6c** and *trans*-**6c** were obtained as a mixture (colorless oil).

The major component had ir (neat): 3400 cm^{-1} (OH); 1H nmr (deuteriobenzene): δ 0.89 (t, J = 7.0 Hz, 3H, CH_2CH_3), 1.40-2.08 (m, 2H, CH_2CH_3), 1.78 (s, 3H, C_1-CH_3), 3.48 (broad s, 1H, OH), 5.14 (dd, J = 5.4 and 6.4 Hz, 1H, C_3-H), 6.74-7.18 (m, 4H, Ar-H₄).

The minor component had ir (neat): 3400 cm^{-1} (OH); 1H nmr (deuteriobenzene): δ 0.97 (t, J = 7.0 Hz, 3H, CH_2CH_3), 1.40-2.08 (m, 2H, CH_2CH_3), 1.72 (s, 3H, C_1-CH_3), 3.48 (broad s, 1H, OH), 4.88 (t, J = 6.4 Hz, 1H, C_3-H), 6.74-7.18 (m, 4H, Ar-H₄).

1,3,3-Trimethyl-1,3-dihydro-1-isobenzofuranol **6f**.

Compound **6f** was obtained as colorless crystals from benzene-hexane, mp 96-98°; ir (potassium bromide): 3390 cm^{-1} (OH); 1H nmr (deuterioacetone): δ 1.42 (s, 3H, C_3-CH_3), 1.52 (s, 3H, C_3-CH_3), 1.65 (s, 3H, C_1-CH_3), 4.94 (s, 1H, OH), 7.10-7.42 (m, 4H, Ar-H₄); ^{13}C nmr (deuterioacetone): δ 29.0 (q), 29.7 (q), 30.7 (q), 84.1 (s), 106.2 (s), 121.3 (d), 122.8 (d), 128.2 (d), 129.3 (d), 143.5 (s), 148.2 (s).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.25; H, 8.01.

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