Photocyclization Reactions. Part 6 [1]. Solvent and Substituent Effects in the Synthesis of Dihydrobenzofuranols Using Photocyclization of 2-Alkoxybenzophenones and Ethyl 2-Benzoylphenoxyacetates

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Photocyclization reactions were carried out on 2-alkoxybenzophenones **1a-h** and ethyl 2-benzoylphenoxyacetates **5a-e** in three solvents of different polarity (benzene, acetonitrile and methanol) to examine solvent and substituent effects on the cyclization of 1,5-biradical intermediates to dihydrobenzofuranols. Irradiation of **1a-f** in benzene gave dihydrobenzofuranols **4a-f** in 80-94% yields. The ratios of *cis*- and *trans*-isomers of **4b-f** were 12:1 to 1:0, showing stereoselective formation of *cis*-isomers. On the other hand, irradiation of **1a-f** in acetonitrile and methanol gave **4a-f** in 68-81% and 7-75% yields, respectively. However, the ratios of *cis*- and *trans*-isomers of **4b-f** were 3.5:1 to 1.3:1 in acetonitrile and 2.0:1 to 1:1.7 in methanol, showing decreased stereoselectivity. The decrease in stereoselectivity was attributed to intermolecular hydrogen bonding between the hydroxyl group of 1,5-biradicals and solvents (acetonitrile and methanol). Similarly, irradiation of **5a-e** in benzene afforded *cis*-dihydrobenzofuranols *cis*-**11a-e** stereoselectively. In contrast, irradiation of **5a-e** in acetonitrile and methanol gave a mixture of *cis*- and *trans*-isomers of **11a-e** because of intermolecular hydrogen bonding between the hydroxyl group of 1,5-biradicals and solvents. The *cis* and *trans* ratios of **11a-e** varied from 1.5:1 to 17.8:1 in acetonitrile and from 2.6:1 to 1:4.5 in methanol. Solvent and substituent effects on the cyclization of 1,5-biradicals and reaction pathways are discussed.

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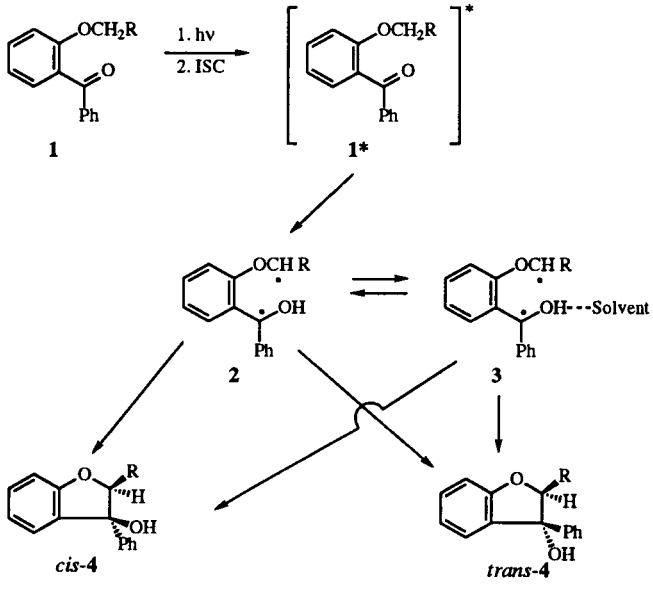
Introduction.

It is well-known that photocyclization reactions of *o*-substituted aromatic carbonyl compounds are useful in the synthesis of benzofuran derivatives. Carbonyl compounds consist of benzaldehydes [2], acetophenones [2b-c,3], benzophenones [3a,3c-d,4], cyclic ketones [1a-b,5], α-dicarbonyl compounds [6] or benzoquinones [7]. Among the compounds benzophenones have been extensively studied from a view-point of reaction mechanisms and synthetic applications [3a,3c-d,4a-h]. In general, photocyclization reactions of carbonyl compounds **1** proceed *via* 1,5-biradical intermediates **2** formed through δ-hydrogen abstraction by the excited carbonyl group as shown in Scheme 1 [3a,3c,4a-c,4e]. Intramolecular cyclization of **2** gives *cis*- and *trans*-dihydrobenzofuranols **4**. The isomer ratios vary according to the solvents used in the reaction and the kind of substituents R. Polar solvents such as acetonitrile and methanol would hydrogen bond with the hydroxyl group of 1,5-biradicals and play an important role on cyclization [8]. Substituents R would show a steric effect on cyclization of 1,5-biradicals. In literatures, there are few examples which discuss in detail solvent and substituent effects on cyclization of 1,5-biradicals [3c,6a,6c].

In fact, Wagner *et al.* reported that photocyclization of 2-benzyloxybenzophenone and 2-benzyloxyacetophenone derivatives in nonpolar benzene revealed high stereoselectivity of *cis*-isomer [3c-d]. However, in the presence of Lewis base solvents stereoselectivity decreased markedly [3a,3c].

Scheme 1

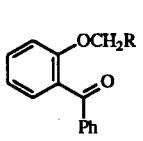


In this paper, we report solvent and substituent effects on cyclization of 1,5-biradical intermediates using photocyclization of 2-alkoxybenzophenones **1a-h** and 2-benzoylphenoxyacetates **5a-e** in benzene (nonpolar solvent), acetonitrile (polar aprotic solvent) and methanol (polar protic solvent).

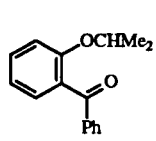
Results and Discussion.

2-Alkoxybenzophenones **1a-h** and ethyl 2-benzoylphenoxyacetates **5a-e** for photocyclization were easily

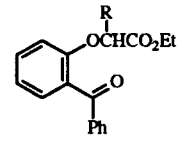
Figure 1



1



1h



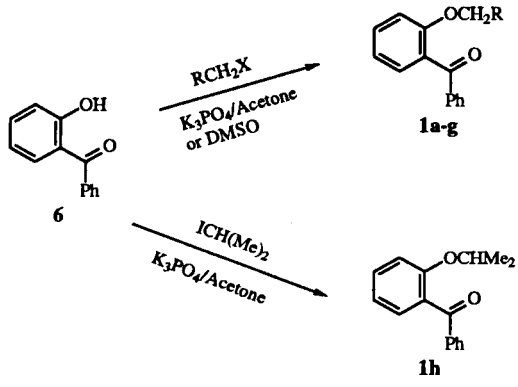
5

1a, R = H
1b, R = Me
1c, R = Et
1d, R = *i*-Pr
1e, R = Ph
1f, R = CH=CH$_2$
1g, R = CN

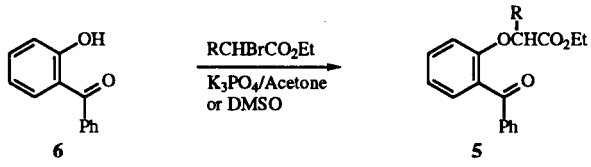
5a, R = H
5b, R = Me
5c, R = Et
5d, R = *i*-Pr
5e, R = Ph

prepared in good yields by the reactions of 2-hydroxybenzophenone **6** with the corresponding alkyl halides or ethyl α-bromoacetates as shown in Scheme 2 and Scheme 3 [1c].

Scheme 2



Scheme 3



At first, photocyclization reactions on ether compounds **1a-h** were conducted with a 400-W high-pressure mercury lamp (Pyrex filter) in three solvents of different polarity (benzene, acetonitrile and methanol) under nitrogen atmosphere. The results are given in Scheme 4 and Table 1.

When 2-methoxybenzophenone **1a** (R = H) was irradiated in a deoxygenated benzene or acetonitrile solution, 3-phenyl-2,3-dihydro-3-benzofuranol **4a** was obtained as a sole product in 80% and 68% yields, respectively (Scheme 4 and Table 1). Carrying out the same experiment in a methanol solution afforded **4a** (7%), 1-(2-methoxyphenyl)-1-phenylmethanol **7a** (12%) as a reduction product, methanol-incorporated product (dihydroxy product) **8a** (33%) and a diastereomeric mixture of *meso*- and *dl*-pinacols **9a** (30%). The isomer ratio of **9a** was 1:1 as detected from ^{1}H nmr spectrum. The yield of dihydrobenzofuranol **4a** in methanol was poor because by-products such as alcohol **7a**, dihydroxy product **8a** and pinacol **9a** were produced. Compounds **7a**, **8a**, **9a** would be produced through hydrogen abstraction from methanol by the excited carbonyl group of **1*** as shown in Scheme 5. The results show that an alchoholic solvent reveals a dramatic effect on product distribution and reaction pathways. In the photoreactions of **1a**, rearranged products *via* spirocyclization reactions [3a] were not observed as in the photoreactions of 2-alkoxybenzaldehydes and 2'-alkoxyacetophenones [2b].

Interestingly, when 2-isopropoxybenzophenone **1h** was irradiated in benzene, acetonitrile or methanol, only 2,2-dimethyl-3-phenyl-2,3-dihydro-3-benzofuranol **4h** was isolated in each case. The yields of **4h** were 74%, 69% and 80%, respectively. A large difference in product distribution between photoreactions of **1a** and **1h** in methanol may be attributed to two factors. In methanol, intramolecular δ-hydrogen abstraction competes with intermolecular hydrogen abstraction from methanol by the excited carbonyl group [9] as shown in Scheme 5. Compound **1a**

Scheme 4

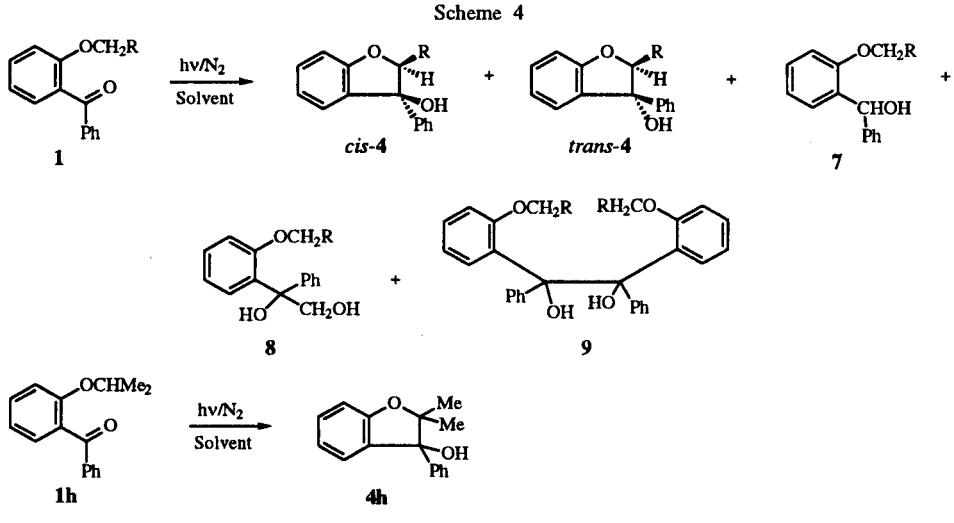


Table 1

Photocyclization Reactions of 2-Alkoxybenzophenones **1a-h** [a]

Starting material	R	Conversion	Solvent	Irradiation time (minutes)	Product yields [b] (%) **4** (*cis:trans*) [c]	**7**	**8**	**9** (isomer ratio)
1a	H	100	C_6H_6	30	80	0	-	0
1a	H	100	CH_3CN	40	68	0	-	0
1a	H	93	CH_3OH	30	7	12	33	30 (1:1)
1b	Me	100	C_6H_6	15	94 (12:1)	0	-	0
1b	Me	100	CH_3CN	20	81 (2.4:1)	0	-	0
1b	Me	93	CH_3OH	20	40 (1:1.1)	8	0	9 (1:1.4)
1c	Et	100	C_6H_6	20	84 (1:0)	0	-	0
1c	Et	100	CH_3CN	30	77 (3.5:1)	0	-	0
1c	Et	60	CH_3OH	13	33 (1:1.1)	5	0	0
1d	i-Pr	100	C_6H_6	20	82 (15:1)	0	-	0
1d	i-Pr	100	CH_3CN	30	71 (2.6:1)	0	-	0
1d	i-Pr	50	CH_3OH	10	35 (1:1.7)	0	0	0
1e	Ph	100	C_6H_6	25	84 (14:1)	0	-	0
1e	Ph	100	CH_3CN	25	81 (1.7:1)	0	-	0
1e	Ph	96	CH_3OH	15	75 (1:1.3)	0	0	0
1f	$CH=CH_2$	100	C_6H_6	30	90 (1:0)	0	-	0
1f	$CH=CH_2$	100	CH_3CN	20	70 (1.3:1)	0	-	0
1f	$CH=CH_2$	100	CH_3OH	36	69 (2.0:1)	0	0	0
1g	CN	81	C_6H_6	10	97 (1.2:1)	0	-	0
1g	CN	100	CH_3CN	60	84 (1:1.6)	0	-	0
1g	CN	84	CH_3OH	15	28 (1:3.0)	0	0	0
1h [d]	-	100	C_6H_6	25	74	0	-	0
1h [d]	-	100	CH_3CN	30	69	0	-	0
1h [d]	-	94	CH_3OH	24	80	0	0	0

[a] A benzene, acetonitrile or methanol solution (500 ml) of **1a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] Yields based on reacted starting materials. Product yields and isomer ratios in acetonitrile were cited from reference **1c**. [c] *Cis*- and *trans*-isomers with regard to the R and hydroxyl groups. The stereochemistry of the dihydrobenzofuranols was determined from the chemical shift values of R and C_2-H in the ^1H nmr spectra. [d] 2-Isopropoxybenzophenone.

gives unstable primary radical such as **2** (R = H) at the carbon atom adjacent to phenoxy group. In contrast, **1h** affords the corresponding stable tertiary radical. Formation of the stable tertiary radical from **1h** make intramolecular δ-hydrogen abstraction favorable compared with hydrogen abstraction from methanol. Moreover, in the case of **1h**, abstraction of hydrogen atom from methanol by the carbonyl group of 2-isopropoxybenzophenone would be suppressed by steric hindrance of bulky isopropyl group because methanol molecules can not approach easily to the carbonyl group. This is why photocyclization of **1h** gave dihydrobenzofuranol **4h** preferentially.

Irradiation of 2-ethoxybenzophenone **1b** (R = Me) in a benzene solution under the same conditions gave *cis*-isomer (with regard to R and hydroxyl group) of 2-methyl-3-phenyl-2,3-dihydro-3-benzofuranol **4b** selectively. In the experiment a small amount of *trans*-isomer **4b** was also isolated. The total yield was 94% and *cis* and *trans* ratio was 12:1. On the other hand, photoreaction of **1b** in an acetonitrile solution furnished a mixture of *cis*- and *trans*-2-methyl-3-phenyl-2,3-dihydrobenzofuranols **4b** in 81% yield (*cis* and *trans* ratio = 2.4:1), showing a decrease in stereoselectivity. In the case of methanol, a mixture of *cis*- and *trans*-**4b** (*cis* and *trans* ratio = 1:1.1) was obtained in 40% yield along with a small amount of reduction product **7b** (8%) and pinacol **9b** (9%, isomer ratio = 1:1.4). Stereoselectivity of *cis*- and *trans*-dihydrobenzofuranols was not good in an acetonitrile or methanol solution. Stereochemistry of *cis*- and *trans*-isomers of **4b** was determined by considering an anisotropic effect of C_3-phenyl group for C_2-R or C_2-H in the ^1H nmr spectra [3c,6a]. Generally, in dihydrobenzofuranols C_3-phenyl group shields C_2-R or C_2-H at the *cis* position, that is, C_2-R or C_2-H chemical shift appears at a higher magnetic field than that of *trans* position.

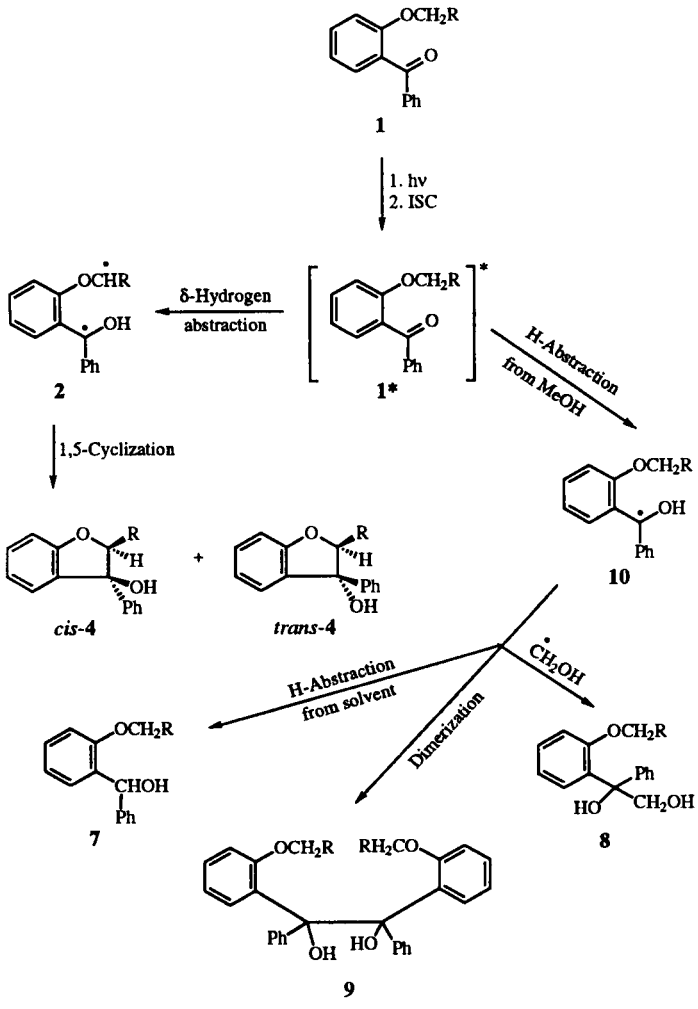
Irradiation of 2-propoxybenzophenone **1c** (R = Et) in benzene gave *cis*-2-ethyl-3-phenyl-2,3-dihydro-3-benzofuranol **4c** as a single isomer (84% yield), showing excellent stereoselectivity. In the case of the reaction in acetonitrile, a mixture of *cis*- and *trans*-dihydrobenzofuranols **4c** was obtained in 77% yield. *Cis* and *trans* ratio was 3.5:1 which reflected low stereoselectivity. In more polar methanol, a mixture of *cis*- and *trans*-isomers of **4c** (33%, *cis* and *trans* ratio = 1:1.1) was obtained along with 1-(2-propoxyphenyl)-1-phenylmethanol **7c** (5%). The total yield (38%) in methanol was not good due to partial decomposition of starting material **1c** during irradiation. When compounds **1d-f** (R = *i*-Pr, Ph, $CH=CH_2$) were

irradiated in benzene, *cis*-dihydrobenzofuranols **4d-f** were isolated selectively in each case. In contrast, irradiation of **1d-f** in acetonitrile or methanol gave a mixture of *cis*- and *trans*-isomers of **4d-f** (2.6:1 to 1.3:1 in acetonitrile and 1:1.3 to 2.0:1 in methanol), showing decreased stereoselectivity. In the photocyclization of 2-benzoylphenoxyacetonitrile **1a**, loosing of *cis* and *trans* stereoselectivity of dihydrobenzofuranol **4g** occured not only in nonpolar benzene but also in polar acetonitrile or methanol. It may be attributed to a large decrease in steric hindrance on cyclization of 1,5-biradical intermediate because the cyano group has a small size.

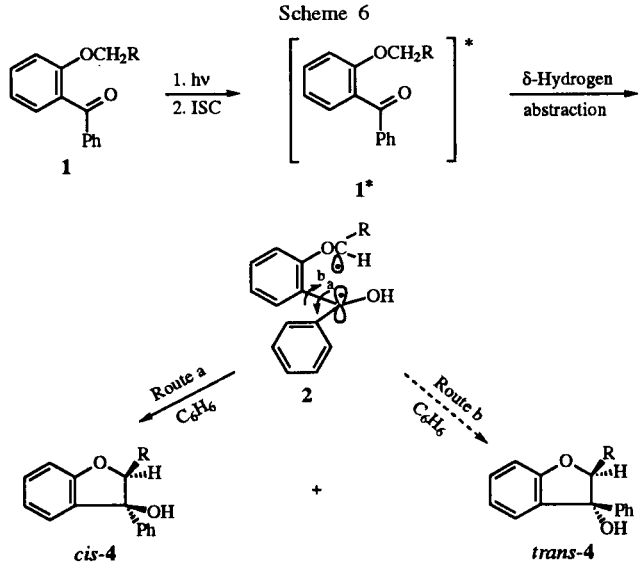
From the results mentioned above, the plausible reaction pathways of photocyclization of **1** are shown in Scheme 5. Irradiation of **1** produces (n, π^*) excited triplet state **1*** after intersystem crossing process (ISC). The carbonyl group of **1*** abstracts δ-hydrogen to give 1,5-biradicals **2** [3a,3c,4a-c]. Intramolecular cyclization of **2** affords *cis*- and *trans*-isomers of dihydrobenzofuranols **4**. When the photoreactions are carried out in methanol, the carbonyl group of **1*** abstracts hydrogen from methanol to give ketyl radicals **10** [9,10] and hydroxymethyl radical ($\bullet CH_2OH$). Dimerization of **10** or intermolecular coupling with hydroxymethyl radical gives pinacols **9** or dihydroxy products **8**, respectively. Production of alcohols **7** occurs through a second hydrogen abstraction from hydroxymethyl radical or methanol by the ketyl radicals **10** [10e,10g].

It is noteworthy to discuss the solvent and substituent effects on cyclization of 1,5-biradicals. The large difference in stereoselectivity among photocyclizations in benzene, acetonitrile and methanol would be explained by intermolecular hydrogen bonding between the hydroxyl group of 1,5-biradicals and solvent molecules [3a,3c,8] and steric bulkiness of substituents R. Explanations of photochemical reactions which are conducted in benzene are shown in Scheme 6 and those in acetonitrile and methanol in Scheme 7.

Scheme 5

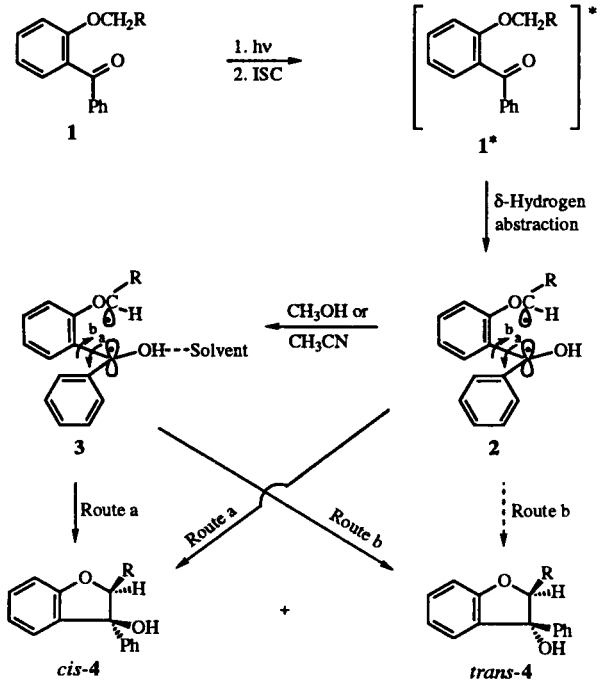


Scheme 6



Irradiation of **1** in a benzene solution produces 1,5-biradicals **2** through δ-hydrogen abstraction. Benzene is a nonpolar solvent and does not undergo hydrogen bonding with the hydroxyl group of 1,5-biradicals **2**. For benzofuranol formation *p*-orbital at the benzylic carbon of **2** is neccessary to rotate by 90° [3a] around the single bond between the alkoxyphenyl group and benzyl group (Scheme 6). In this case, counterclockwise rotation (Route a) and clockwise rotation (Route b) are possible. If rotation of Route a occurs, *cis*-isomer of **4** is formed as a more stable product because two larger groups (R and Ph) are arranged at the *trans* position. On the other hand, rotation of Route b affords less stable *trans*-**4**. Product distribution of *cis*- and *trans*-isomers would be controlled by steric bulkiness of the larger phenyl group and the alkyl group R. A large difference in steric bulkiness between phenyl and hydroxyl groups and between the alkyl group and hydrogen in 1,5-biradicals **2** would produce high stereoselectivity for *cis*-isomer, that is, a sterically favoured isomer is produced selectively.

Scheme 7



Irradiation of **1** in acetonitrile or methanol also produces 1,5-biradicals **2** through δ-hydrogen abstraction as shown in Scheme 7. However, acetonitrile and methanol are polar solvents and have the ability to hydrogen bond with the hydroxyl group of 1,5-biradicals **2**. Therefore, the most part of 1,5-biradicals **2** would be solvated by hydrogen bonding with solvent molecules like **3** [3a,3c,8]. The hydrogen bonding increases bulkiness of the hydroxyl group more than the free one [1c]. In this case, steric bulkiness of the solvated hydroxyl group is comparable to that of the phenyl group becoming bulkier, especially in a methanol solution. Small differences in steric bulkiness between the phenyl group and the hydrogen-bonded hydroxyl group would make both rotations (Route a and Route b) possible. Therefore, the hydrogen bonding decreases stereoselectivity of *cis*- and *trans*-isomers.

Next, photocyclization reactions of ethyl 2-benzoylphenoxyacetates **5a-e** were examined in benzene, acetonitrile and methanol under the same conditions. The results are summarized in Scheme 8 and Table 2.

Irradiation of ethyl 2-benzoylphenoxyacetate **5a** (R = H) in a benzene solution gave mainly *cis*-isomer of dihydrobenzofuranol **11a** (*cis* and *trans* ratio = 12:1, 74%). In contrast, irradiation of **5a** in an acetonitrile solution afforded a mixture of *cis*- and *trans*-isomers (isomer ratio = 1.5:1) of **11a**. Photoreaction of **5a** in a methanol solution resulted in complete decomposition of the starting material during irradiation. The stereochemistry of the *cis*- and *trans*-isomers was assigned on the basis of ^{1}H nmr spectra using an anisotropic effect of phenyl group mentioned above. The large difference in *cis* and *trans* ratios from reactions in benzene and acetonitrile is attributed to the solvent effect.

Photoreactions of **5b** (R = Me) in a benzene, acetonitrile or methanol solution gave a mixture of *cis*- and *trans*-dihydrobenzofuranols **11b** (93%, 72% and 68%, respectively) in each case. The *cis* and *trans* ratios were 30:1, 4.1:1 and 1:1.4 in benzene, acetonitrile and methanol, respectively. In a benzene solution stereoselectivity was high, however, it decreased in acetonitrile and methanol. Ethyl acrylate **13b** (6%) was also produced on irradiation of **5b** in acetonitrile. Similarly, irradiation of **5c** (R = Et) in a benzene, acetonitrile or methanol solution afforded a mixture of *cis*- and *trans*-dihydrobenzofuranols **11c** in 61-84% yields. In a benzene solution *cis* and *trans* ratio was 50:1, showing high streoselectivity for *cis*-isomer. The isomer ratios of **11c** were 5.2:1 and 1:4.5 in acetonitrile and methanol, respectively. Dihydroxy product **12c** and ethyl acrylate **13c** were also produced. In contrast, photoreactions of **5d-e** (R = *i*-Pr, Ph) in a benzene solution afforded only *cis*-isomers of **11d-e** in 70% and 74% yields, respectively. In contrast, irradiation of **5a-e** in an acetonitrile or methanol solution produced a mixture of *cis*- and *trans*-isomers of **11a-e**. *Cis* and *trans* ratios of **11d-e** were 5.8:1 and 17.8:1 in acetonitrile and 1:4.0 and 2.6:1 in methanol.

Scheme 8

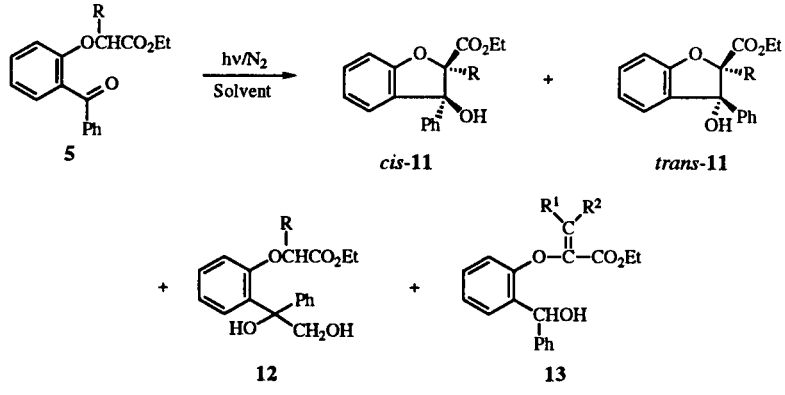


Table 2

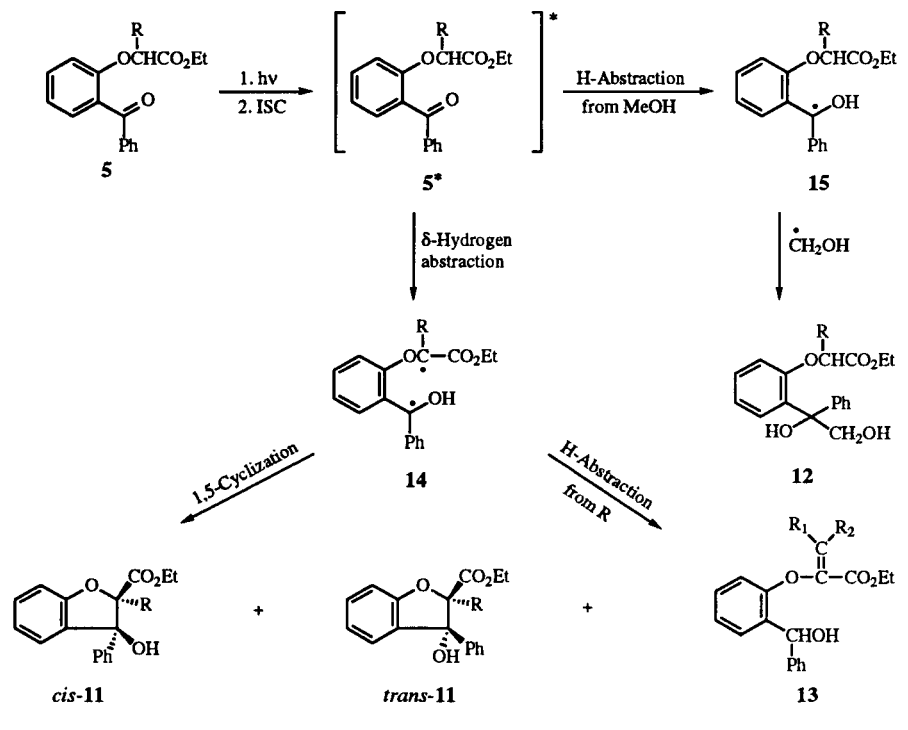
Photocyclization Reactions of Ethyl 2-Benzoylphenoxyacetates **5a-e** [a].

Starting material	R	Conversion	Solvent	Irradiation time (minutes)	Product yields (%) [b] **11** *(cis:trans)* [c]	**12** (isomer ratio)	**13** [d] (*E*:*Z*)
2a	H	100	C_6H_6	35	74 (15:1)	–	–
2a	H	100	CH_3CN	30	75 (1.5:1)	–	–
2a [e]	H	100	CH_3OH	11	0	0	–
2b	Me	100	C_6H_6	30	93 (30:1)	–	0
2b	Me	100	CH_3CN	15	72 (4.1:1)	–	6
2b	Me	70	CH_3OH	20	68 (1:1.4)	0	0
2c	Et	100	C_6H_6	30	84 (50:1)	–	0
2c	Et	100	CH_3CN	20	74 (5.2:1)	–	8 (1:4)
2c	Et	100	CH_3OH	14	61 (1:4.5)	21 (1:1)	6 (1.2:1)
2d	i-Pr	100	C_6H_6	30	70 (1:0)	–	0
2d	i-Pr	100	CH_3CN	20	75 (5.8:1)	–	0
2d	i-Pr	100	CH_3OH	25	48 (1:4.0)	0	0
2e	Ph	100	C_6H_6	30	74 (1:0)	–	–
2e	Ph	100	CH_3CN	25	75 (17.8:1)	–	–
2e	Ph	100	CH_3OH	35	72 (2.6:1)	18 (1:1.3)	–

[a] A benzene, acetonitrile or methanol solution (500 ml) of **5a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] Yields based on reacted starting materials. Product yields and isomer ratios in acetonitrile were cited from reference **1c**. [c] *Cis*- and *trans*-isomers with regard to the ethoxycarbonyl and hydroxyl groups. The stereochemistry of the dihydrobenzofuranols was determined from the chemical shift values of R and CO_2Et in the ^1H nmr spectra. [d] **13b**, $R^1 = R^2 = H$; **13c**, $R^1 = H$, $R^2 = CH_3$ or $R^1 = CH_3$, $R^2 = H$. [e] Starting material was decomposed after 11 minutes.

The reaction pathways for formation of **11**, **12** and **13** are similar to those of 2-alkoxybenzophenones as shown in Scheme 9. Irradiation of esters **5a-e** produces (n,π*) excited triplet state **5*** after intersystem crossing process. The carbonyl group abstracts δ-hydrogen to give 1,5-biradicals **14** which afford a variety of products [3a,3c,4a-c,4e]. For example, intramolecular cyclization of **14** affords *cis*- and *trans*-benzofuranols **11**. On the other hand, if the ketyl radical of **14** abstracts hydrogen of the alkyl groups, ethyl acrylates **13** would be obtained. The carbonyl group of **5*** abstracts hydrogen from methanol to give ketyl radicals **15** [9,10]. Intermolecular coupling of **15** with hydroxymethyl radical gives methanol-incorporated products **12**.

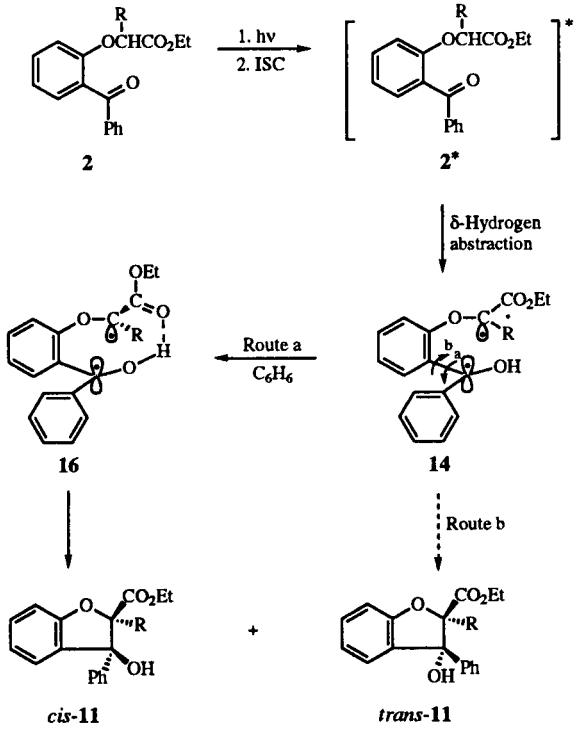
Scheme 9



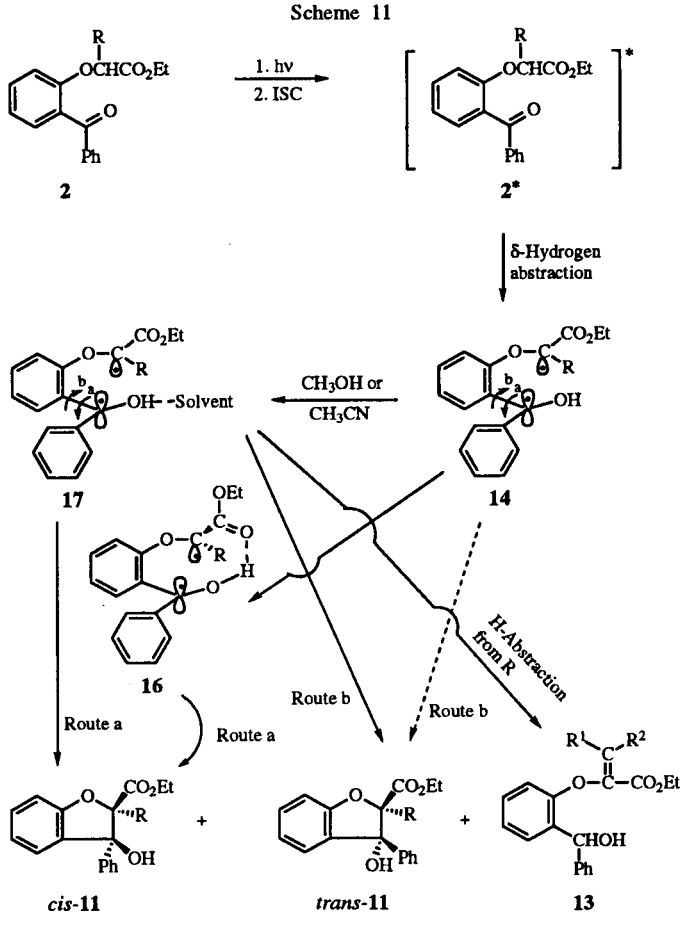
From the above results, *cis*-isomers were always obtained selectively from the photoreactions of **5a-e** in a benzene solution in spite of steric bulkiness of R (H, Me, Et, *i*-Pr, Ph). The facts suggest that benzylic *p*-orbital of 1,5-biradicals **14** rotates counterclockwise (Route a) to give *cis*-isomer of **11** *via* intramolecular hydrogen bonding like **16** between the hydroxyl and ethoxycarbonyl groups as shown in Scheme 10. However, in polar solvents such as acetonitrile and methanol, the hydroxyl group of 1,5-biradicals **14** would be partly or mostly solvated using intermolecular hydrogen bonding with a solvent like **17** in Scheme 11 [1c]. The intermolecular hydrogen bonding interrupts intramolecular hydrogen bonding and prevents preferential counterclockwise rotation (Route a) to give *cis*-isomers. The hydrogen-bonded hydroxyl group of **17** became bulkier than the free one and was comparable to the phenyl group in steric effect. Therefore, both the counterclockwise and clockwise rotations (Route a and Route b) are possible to give *cis*- and *trans*-isomers of **11**, showing a decrease in stereoselectivity. Ethyl acrylates **13** seems to come from the solvated 1,5-biradicals **17** because **13** is not obtained in a nonpolar benzene solution. The *E* and *Z* ratio of **13c** were determined from ^{1}H nmr spectra of the mixture in which the ethoxycarbonyl group deshielded the hydrogen at the *cis* position. Methanol-incorporated compounds **12** were obtained from the photoreactions of **2c** and **2e** in a methanol solution.

In summary, photocyclization reactions of benzophenones in nonpolar benzene proceed in a stereoselective manner. In contrast, photocyclizations in polar solvents such as acetonitrile or methanol proceed in a nonstereoselective way. Polarity of solvents play an important role in changing *cis* and *trans* ratios and reaction pathways. Photocyclization reactions are useful to prepare dihydrobenzofuranols.

Scheme 10



Scheme 11



EXPERIMENTAL

The melting points are uncorrected. Column choromatography was performed on silica gel (Wakogel C-200). Ether refers to diethyl ether. Dry benzene for photoreactions was prepared by distillating over calcium hydride. Acetonitrile was dried by distillating over phosphorus pentoxide, then over potassium carbonate. Methanol was used after distillation. Photoreactions were carried out with 400-W high-pressure mercury lamp (Riko UVL-400 HA) with Pyrex filter. The ir spectra were determined on a Hitachi Model 270-30 IR spectrometer. The ^{1}H and ^{13}C nmr spectra were determined at 90 MHz and 22.49 MHz on a JEOL-FX 90Q FT NMR spectrometer or at 200 MHz and 50 MHz on a Varian Gemini 200 FT NMR spectrometer, using tetramethylsilane as the internal standard.

Synthesis of Ethers **1a-h** and Esters **5a-e**.

Starting ether compounds **1a-h** and ester compounds **5a-e** were prepared according to procedures reported in the previous paper [1c].

General Procedure for Photocyclization Reactions of Ethers **1a-h** and Esters **5a-e**.

In benzene, acetonitrile or methanol solvent (500 ml), 2.00 mmoles of the starting materials **1a-h**, **5a-e** were dissolved. The solution 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 starting materials almost disappeared. After irradiation the solvent was evaporated under reduced pressure below 40°. The residue was chromatographed and eluted with benzene-ether to give a variety of products. The products of benzofuranols **4a-h**, **11a-e** and ethyl acrylates **13b-c** were identical with authentic samples [1c] in the ^{1}H nmr (90 MHz) and ir spectra.

1-(2-Methoxyphenyl)-1-phenylmethanol **7a**.

Compound **7a** (12%) was obtained as a colorless oil [11, 176-178° at 8 torr] after irradiation of **1a** in methanol; ir (neat): 3410 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 200 MHz): δ 3.09 (d, J = 5 Hz, 1H, CHO*H*), 3.78 (s, 3H, OCH_3), 6.04 (d, J = 5 Hz, 1H, C*H*OH), 6.87 (d, J = 8 Hz, 1H, Ar-H), 6.93 (dd, J = 8 and 8 Hz, 1H, Ar-H), 7.17-7.43 (m, 7H, Ph-H_5 and Ar-H_2); ^{13}C nmr (deuteriochloroform, 200 MHz): δ 55.4 (q), 72.2 (d), 110.7 (d), 120.8 (d), 126.5 (d), 127.1 (d), 127.8 (d), 128.1 (d), 128.7 (d), 131.9 (s), 143.2 (s), 156.7 (s).

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.29; H, 6.48.

1-(2-Methoxyphenyl)-1-phenyl-1,2-ethanediol **8a**.

Compound **8a** (33%) was obtained as colorless crystals from benzene-hexane after irradiation of **1a** in methanol, mp 71-72°; ir (potassium bromide): 3500 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 200 MHz): δ 2.74 (broad s, 1H, OH), 3.56 (s, 3H, OCH_3), 3.90 (d, J = 12 Hz, 1H, CH_2OH), 4.16 (dd, J = 7 and 12 Hz, 1H, CH_2OH), 4.88 (s, 1H, OH), 6.87 (d, J = 8 Hz, 1H, Ar-H), 7.03 (dd, J = 8 and 8 Hz, 1H, Ar-H), 7.13-7.38 (m, 6H, Ar-H and Ph-H_5), 7.53 (d, J = 8 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 200 MHz): δ 55.5 (q), 68.8 (t), 79.2 (s), 112.2 (d), 121.0 (d), 125.7 (d), 126.9 (d), 127.8 (d), 128.4 (d), 128.9 (d), 131.2 (s), 144.9 (s), 157.3 (s).

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.66; H, 6.57.

dl- and *meso*-1,2-Bis(2-methoxyphenyl)-1,2-diphenyl-1,2-ethanediols **9a**.

These diastereoisomers of 9a (30%) were obtained as a 1:1 mixture (crystals) after irradiation of **1a** in methanol. It was difficult to isolate each isomer in a pure state.

The mixture had ir (potassium bromide): 3500 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 200 MHz): δ 3.21 (s, 6H, OCH_3 and OCH_3), 3.35 (s, 6H, OCH_3 and OCH_3), 5.45 (s, 2H, OH and OH), 6.09 (s, 2H, OH and OH), 6.64-6.90 (m, 12H, Ar- and Ph-H_{12}), 6.95-7.25 (m, 16H, Ar- and Ph-H_{16}), 7.35-7.53 (m, 6H, Ar- and Ph-H_6), 8.05 (dd, J = 2 and 8 Hz, 2H, Ar-H and Ar-H).

1-(2-Ethoxyphenyl)-1-phenylmethanol **7b**.

Compound **7b** (8%) was obtained as colorless crystals from benzene-hexane, mp 75-76° [11, mp 77-79°] after irradiation of **1b** in methanol; ir (potassium bromide): 3310 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 200 MHz): δ 1.33 (t, J = 7 Hz, 3H, OCH_2CH_3), 3.16 (d, J = 5 Hz, 1H, CHO*H*), 3.90-4.12 (m, 2H, OCH_2CH_3), 6.02 (d, J = 5 Hz, 1H, C*H*OH), 6.85 (d, J = 8 Hz, 1H, Ar-H), 6.92 (dd, J = 8 and 8 Hz, 1H, Ar-H), 7.16-7.45 (m, 7H, Ph-H_5 and Ar-H_2); ^{13}C nmr (deuteriochloroform, 200 MHz): δ 14.8 (q), 63.7 (t), 72.7 (d), 111.6 (d), 120.6 (d), 126.5 (d), 127.1 (d), 127.8 (d), 128.1 (d), 128.6 (d), 132.1 (s), 143.4 (s), 156.1 (s).

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.84; H, 6.96.

dl- and *meso*-1,2-Bis(2-ethoxyphenyl)-1,2-diphenyl-1,2-ethanediols **9b**.

These diastereoisomers of **9b** (9%) were obtained as a 1:1.4 mixture (crystals) after irradiation of **1b** in methanol. It was difficult to isolate each isomer in a pure state.

The mixture had ir (potassium bromide): 3500 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 200 MHz): δ 0.86 (t, J = 7 Hz, 6H, OCH_2CH_3 and OCH_2CH_3), 0.90 (t, J = 7 Hz, 6H, OCH_2CH_3 and OCH_2CH_3), 3.15-3.40 (m, 2H, OCH_2CH_3), 3.48 (q, J = 7 Hz, 4H, OCH_2CH_3 and OCH_2CH_3), 3.77-4.00 (m, 2H, OCH_2CH_3), 5.49 (s, 2H, OH and OH), 6.22 (s, 2H, OH and OH), 6.62-6.93 (m, 12H, Ar- and Ph-H_{12}), 6.95-7.23 (m, 16H, Ar- and Ph-H_{16}), 7.35-7.72 (m, 6H, Ar- and Ph-H_6). 8.07 (dd, J = 2 and 8 Hz, 2H, Ar-H and Ar-H).

1-(2-Propoxyphenyl)-1-phenylmethanol **7c**.

Compound **7c** (5%) was obtained as colorless crystals from benzene-hexane, mp 67-69° [11, mp 69-71°] after irradiation of **1b** in methanol; ir (potassium bromide): 3320 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 200 MHz): δ 0.93 (t, J = 7 Hz, 3H, $OCH_2CH_2CH_3$), 1.73 (tq, J = 7 and 7 Hz, 2H, $OCH_2CH_2CH_3$), 3.15 (d, J = 5 Hz, 1H, CHO*H*), 3.78-4.00 (m, 2H, $OCH_2CH_2CH_3$), 6.02 (d, J = 5 Hz, 1H, C*H*OH), 6.84 (d, J = 8 Hz, 1H, Ar-H), 6.92 (d, J = 8 Hz, 1H, Ar-H), 7.15-7.42 (m, 7H, Ph-H_5 and Ar-H_2); ^{13}C nmr (deuteriochloroform, 200 MHz): δ 10.6 (q), 22.5 (t), 69.6 (t), 72.6 (d), 111.4 (d), 120.5 (d), 126.5 (d), 127.0 (d), 127.8 (d), 128.1 (d), 128.6 (d), 131.9 (s), 143.4 (s), 156.1 (s).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.25; H, 7.55.

Ethyl 2-[2-(1,2-Dihydroxy-1-phenylethyl)pheoxy]butyrate **12c**.

These diastereoisomers of **12c** (21%) were obtained as a 1:1 mixture (oil) after irradiation of **5c** in methanol. It was difficult to isolate each isomer in a pure state.

The mixture had ir (neat): 3480 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 90 MHz): δ 0.44 (t, J = 7 Hz, 3H, $OCHCH_2CH_3$), 0.94 (t, J = 7 Hz, 3H, $OCHCH_2CH_3$), 1.16 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.24 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.62 (dq, J = 7 and 7 Hz, 2H, $OCHCH_2CH_3$), 1.85 (dq, J = 7 and 7 Hz, 2H, $OCHCH_2CH_3$), 2.68 (broad s, 1H, OH), 3.14 (broad s, 1H, OH), 3.68-4.08 (m, 4H, CH_2OH and CH_2OH), 4.19 (q, J = 7 Hz, 4H, $CO_2CH_2CH_3$ and $CO_2CH_2CH_3$), 4.52 (broad s, 1H, OH), 4.62 (t, J = 7 Hz, 1H, $OCHCH_2CH_3$), 4.65 (t, J = 7 Hz, 1H, $OCHCH_2CH_3$), 5.44 (s, 1H, OH), 6.70 (d, J = 8 Hz, 2H, Ar-H and Ar-H), 6.84-7.46 (m, 14H, Ar-H_2, Ar-H_2, Ph-H_5 and Ph-H_5), 7.52-7.72 (m, 2H, Ar-H and Ar-H).

Ethyl 2-[2-(1,2-Dihydroxy-1-phenylethyl)pheoxy]-2-phenylacetate **12e**.

These diastereoisomers of **12e** (18%) were obtained as a 1:1.3 mixture (oil) after irradiation of **5e** in methanol. It was difficult to isolate each isomer in a pure state.

The mixture had ir (neat): 3520 cm^{-1} (OH); ^{1}H nmr (deuteriochloroform, 90 MHz): δ 1.11 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$),

1.21 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$) 2.82 (broad s, 2H, OH and OH), 3.73-4.52 (m, 8H, CH_2OH, CH_2OH, $CO_2CH_2CH_3$ and $CO_2CH_2CH_3$), 4.85 (broad s, 1H, OH), 5.43 (s, 1H, OCHPh), 5.62 (s, 1H, OCHPh), 5.84 (s, 1H, OH), 6.53-6.80 (m, 2H, Ar-H and Ar-H), 6.84-7.48 (m, 24H, $Ar\text{-}H_2$, $Ar\text{-}H_2$, $Ph\text{-}H_5$, $Ph\text{-}H_5$, $Ph\text{-}H_5$ and $Ph\text{-}H_5$) 7.50-7.72 (m, 2H, Ar-H and Ar-H).

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