Photocyclization Reactions. Part 7 [1]. Solvent and Substituent Effects in the Synthesis of Dihydrobenzofuranols Using Photocyclization of α-(2-Acylphenoxy)toluenes and Ethyl 2-Acylphenoxyacetates

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Photocyclization reactions were carried out on α-(2-acylphenoxy)toluenes **1a-e** and 2-acylphenoxyacetates **2a-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-e** in benzene gave *cis*-dihydrobenzofuranols *cis*-**4b-e** selectively in 14-84% yields along with rearranged products, 2-acylbenzophenones **5b-d** (23-39% yields). Photocyclization of **1a-e** in acetonitrile or methanol gave a mixture of *cis*- and *trans*-dihydrobenzofuranols **4a-e** in 28-81% yields and small amount of 2-acylbenzophenones **5b-c** in 6-12% yields. In polar acetonitrile or methanol, the *cis* and *trans* stereoselectivity of dihydrobenzofuranols decreased. The decrease in stereoselectivity was attributed to intermolecular hydrogen bonding between the hydroxyl group of 1,5-biradicals and solvents. On the other hand, irradiation of esters **2a-e** in benzene afforded *cis*-dihydrobenzofuranols *cis*-**13a-e** selectively in 48-74% yields. Similarly, photocyclization of **2a-e** in acetonitrile or methanol produced dihydrobenzofuranols **13a-e** in a fair to good yields. In the photocyclization of **2b-d**, not only in nonpolar benzene but also in polar acetonitrile or methanol, increasing the size of alkyl group from methyl (R = Me) to ethyl or isopropyl group (R = Et or *i*-Pr) gave *cis*-dihydrobenzofuranols *cis*-**13b-d** predominantly. Conformational, solvent and substituent effects on the cyclization of 1,5-biradicals and reaction pathways are discussed.

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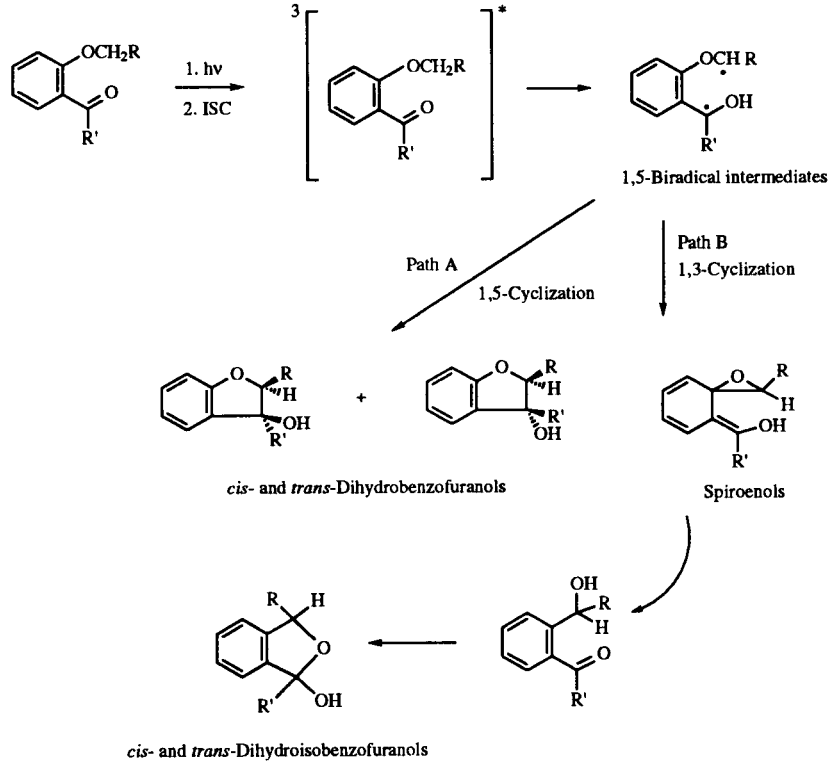
Introduction.

Photocyclization reactions of *o*-substituted aromatic carbonyl compounds are useful in the synthesis of benzofuran derivatives. The first example of photocyclization to prepare benzofuran was reported by Pappas *et al.* They prepared *cis*- and *trans*-benzofuranols by irradiation of 2-benzyloxybenzaldehyde in acetonitrile [2a]. Carbonyl compounds consist of benzaldehydes [2], acetophenones [2b-c,3], benzophe-

Scheme 1



nones [3a,3c-d,4], cyclic ketones [1a-b,5], α-dicarbonyl compounds [6] or benzoquinones [7].

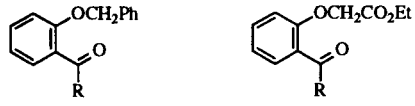
In general, photocyclization reactions of carbonyl compounds proceed *via* 1,5-biradical intermediates formed through δ-hydrogen abstraction by the excited carbonyl group as shown in Scheme 1 [3a,3c,4a-c,4e]. The 1,5-biradicals can undergo 1,5-cyclization to dihydrobenzofuranols (path A) or 1,3-cyclization to spiroenols (path B) [2b,3a,3c] which rearrange to the corresponding 2-acylalcohols or their hemiacetals. Preference for path A or path B depends on the type of substituents R and R'. For example, when benzophenones (R' = Ph) are used as starting materials, 1,5-cyclization occurs to give dihydrobenzofuranols [3a,3c]. However, when benzaldehydes (R' = H) and acetophenones (R' = Me) are employed, 1,3-cyclization competes with 1,5-cyclization to afford rearranged products [2b]. Changing R from alkyl group to electron-withdrawing ethoxycarbonyl or cyano group, 1,5-cyclization occurs predominantly [2b].

The *cis* and *trans* ratios of dihydrobenzofuranols vary according to polarity of solvent used in the reaction and kind of substituents R and R' [1d,3a,8]. Wagner *et al.* reported that photocyclization of 2-benzyloxybenzophenone and 2'-benzyloxyacetophenone derivatives in nonpolar benzene revealed high stereoselectivity of the *cis*-isomer [3c-d]. However, in the presence of Lewis base solvents stereoselectivity decreased markedly [3a,8]. In this paper, we report synthesis of dihydrobenzofuranols using photocyclization of α-(2-acylphenoxy)toluenes (acyl ethers) **1a-e** and 2-acylphenoxyacetates (acyl esters) **2a-e**, and conformational, solvent and substituent effects on the cyclization of 1,5-biradical intermediates.

Results and Discussion.

Starting ethers **1a-b, e** (R = H, Me, Ph) and esters **2a-b, e** (R = H, Me, Ph) for photocyclization reactions were prepared from the reactions of **3a-b, e** (R = H, Me, Ph) and benzyl chloride or ethyl bromoacetate according to the procedures described in references [1c,2b-c]. Ethers **1c-d** and esters **2c-d** were synthesized by the reactions of benzyl chloride or ethyl bromoacetate with 2'-hydroxypropiophenone **3c** (R = Et) and 2'-hydroxyisobutyrophenone **3d** (R = *i*-Pr) in the presence of tripotassium phosphate as a base. The results are summarized in Scheme 2 and Table 1.

Figure 1



1 **2**

1a, R = H **2a**, R = H
1b, R = Me **2b**, R = Me
1c, R = Et **2c**, R = Et
1d, R = *i*-Pr **2d**, R = *i*-Pr
1e, R = Ph **2e**, R = Ph

Initially, photocyclization reactions on ether compounds **1a-e** were performed with 400-W high-pressure mercury lamp (Pyrex filter) in benzene, acetonitrile and methanol. The results are outlined in Scheme 3 and Table 2.

Irradiation of 2-benzyloxybenzaldehyde **1a** (R = H) in benzene resulted in low conversion (42%) and decomposition of starting material after 90 minutes irradiation. On the other hand, photoreaction of **1a** in acetonitrile furnished a mixture of *cis*- and *trans*-2-phenyl-2,3-dihydro-3-benzofuranols **4a** (*cis* and *trans* ratio = 1.7:1) in 40% yield and a diastereomeric mixture of *meso*- and *dl*-pinacols **7a** (isomer ratio = 1:1.1 or 1.1:1) in 12% yield. The stereoselectivity of *cis*- and *trans*-**4a** was not good in acetonitrile. Stereochemistry of *cis*- and *trans*-isomers of **4a** was determined by considering coupling constant between C_2-H and C_3-H ($Jcis > Jtrans$) [2a,9,10] and an

Scheme 2

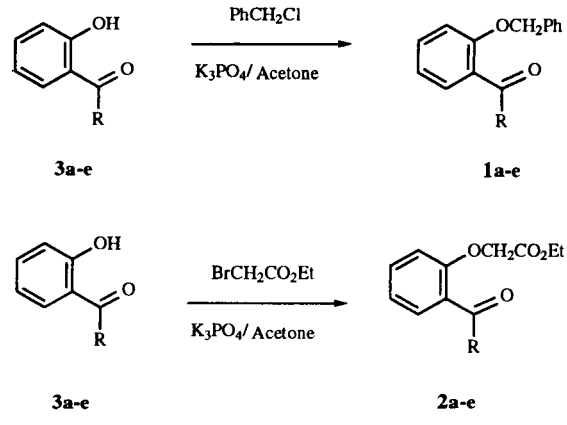


Table 1

Synthesis of α-(2-Acylphenoxy)toluenes **1a-e** and 2-Acylphenoxyacetates **2a-e**

Starting material	R	Reagent	Base	Solvent	Temperature (°C)	Time (hours)	Product	Yield (%)
3c	Et	$PhCH_2Cl$	K_3PO_4	Acetone	Reflux	7	**1c**	66 [a]
3d	*i*-Pr	$PhCH_2Cl$	K_3PO_4	Acetone	Reflux	7	**1d**	57 [a]
3c	Et	$BrCH_2CO_2Et$	K_3PO_4	Acetone	Reflux	5	**2c**	95
3d	*i*-Pr	$BrCH_2CO_2Et$	K_3PO_4	Acetone	Reflux	5	**2d**	95

[a] Yield based on reacted starting material. Starting materials of 18% and 16% were recovered for **1c** and **1d**, respectively.

Scheme 3

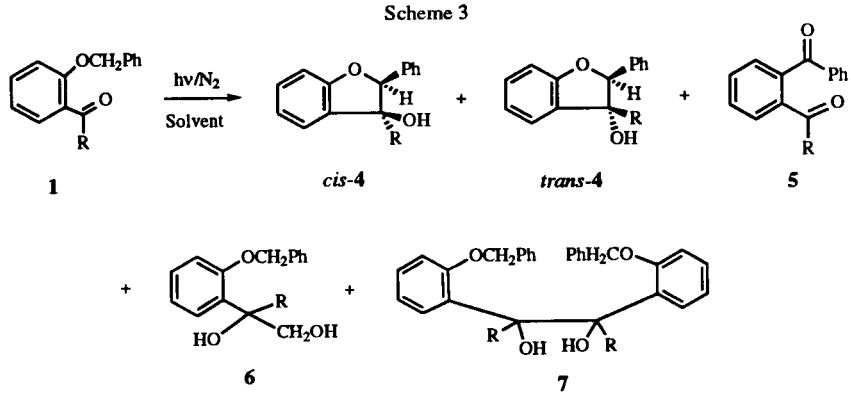


Table 2

Photoreactions of α-(2-Acylphenoxy)toluenes **1a-e** [a]

Starting material	R	Solvent	Irradiation time (minutes)	Conversion (%)	4 (*cis*:*trans*) [c]	Product 5	yields [b] (%) 6	7 (isomer ratio)
1a	H	C_6H_6	90	42	0	0	-	0
1a	H	CH_3CN	60	88	40(1.7:1)	0	-	12(1:1.1)
1a	H	CH_3OH	35	98	0	0	39	33(1:1.1)
1b	Me	C_6H_6	90	55	24(1:0)	23	-	0
1b	Me	CH_3CN	45	56	64(4.3:1)	12	-	0
1b	Me	CH_3OH	55	89	75(1.5:1)	10	0	0
1c	Et	C_6H_6	55	59	14(1:0)	26	-	0
1c	Et	CH_3CN	52	64	28(6.8:1)	6	-	0
1c	Et	CH_3OH	30	73	65(2.8:1)	8	0	0
1d	*i*-Pr	C_6H_6	35	70	17(1:0)	39	-	0
1d	*i*-Pr	CH_3CN	35	64	32(5.1:1)	0	-	0
1d	*i*-Pr	CH_3OH	35	65	47(2.2:1)	0	0	0
1e	Ph	C_6H_6	25	100	84(14:1)[d]	0	-	0
1e	Ph	CH_3CN	25	100	81(1.7:1)[d]	0	-	0
1e	Ph	CH_3OH	15	96	75(1:1.3)[d]	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. [c] *Cis*- and *trans*-isomers with regard to the Ph 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] Cited from reference [1d].

anisotropic effect [7f,10] of C_2-phenyl group for C_3-R (R = H) in the ^1H nmr spectra. In contrast, photoreaction of **1a** in methanol did not afford dihydrobenzofuranols **4a** at all, but it gave pinacols **7a** (33%, isomer ratio = 1:1.1) and methanol-incorporated product **6a** (39%).

When compounds **1b-d** (R = Me, Et, *i*-Pr) were irradiated in benzene, only *cis*-dihydrobenzofuranols *cis*-**4b-d** were isolated selectively in each case, showing excellent stereoselectivity. In contrast, irradiation of **1b-d** in acetonitrile or methanol gave a mixture of *cis*- and *trans*-isomers of **4b-d** (4.3:1 to 6.8:1 in acetonitrile and 1.5:1 to 2.8:1 in methanol), showing decreased steroselectivity. In the photoreactions of **1b-d** in benzene, acetonitrile and methanol, rearranged products, 2-acylbenzophenones **5b-d**, were isolated. The yields of **5b-d** were 23-39%, 0-12% and 0-10% in benzene, acetonitrile and methanol, respectively. Production of rearranged 2-acylbenzophenones **5b-d** caused decrease in the yield of dihydrobenzofuranols **4b-d**.

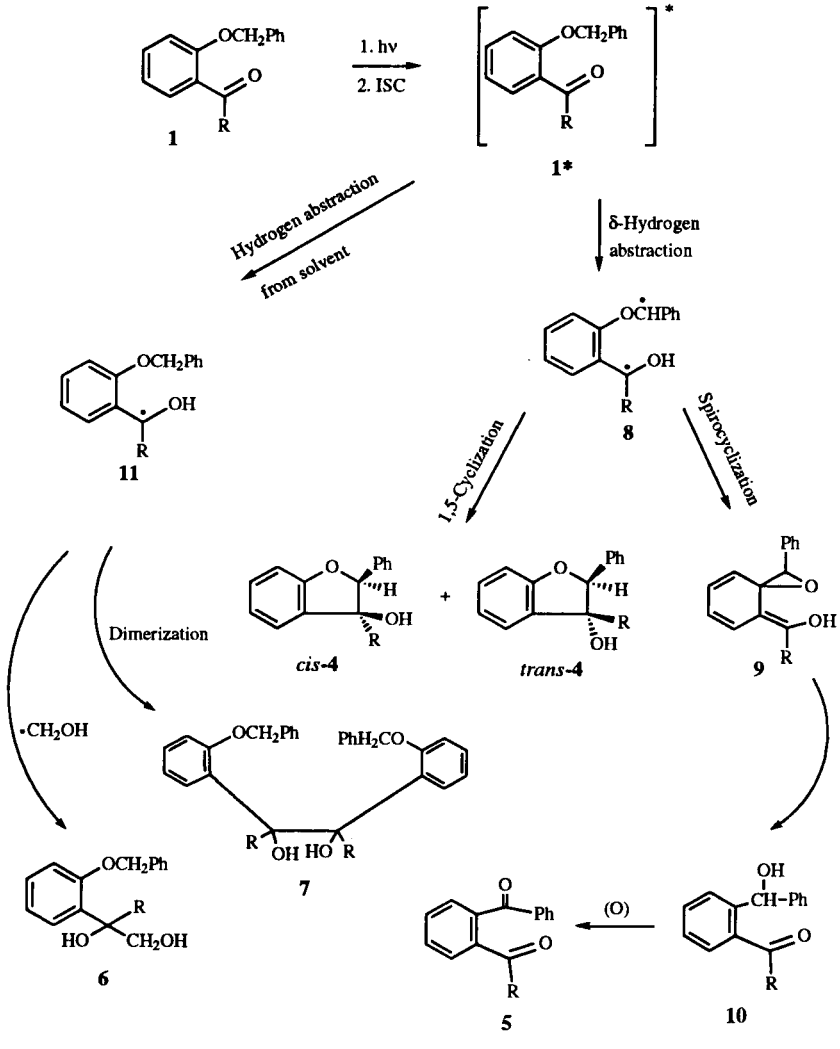
On the contrary to the photocyclization of **1b-d**, photoreaction of 2-benzyloxybenzophenone **1e** (R = Ph) in benzene, acetonitrile or methanol gave only dihydrobenzofuranols **4e** in 75-84% yields and did not afford rearranged product **5e** [1d]. In this case, polar acetonitrile and methanol decreased *cis* and *trans* stereoselectivity.

From the results mentioned above, the plausible reaction pathways of photocyclization of α-(2-acylphenoxy)toluenes **1** are outlined in Scheme 4. 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 **8** [3a,3c,4a-c,4e]. Intramolecular cyclization of **8** affords *cis*- and *trans*-dihydrobenzofuranols **4**. On the other hand, the 1,5-biradicals **8** can undergo competitive 1,3-spirocyclization [3a] to spiroenols **9** which rearrange to 2-acylbenzyl alcohols **10** and then oxidized with oxygen in solvents to give 2-acylbenzophenones **5**. When the photoreactions are carried out in acetonitrile or methanol, the carbonyl group of

1* abstracts hydrogen from solvent to give ketyl radicals **11** [11]. Dimerization of **11** or intermolecular coupling with hydroxymethyl radical ($\cdot CH_2OH$) derived from methanol gives pinacol **7** or dihydroxy product **6**, respectively [1d,11g,11i]. Hydrogen abstraction of **1*** from methanol molecule seems easier than that from acetonitrile molecule.

1'a (R = H) would be controlled by steric interactions between R or carbonyl group and benzyloxy group at the *ortho* position. In the case of 2-benzyloxybenzaldehyde (R = H), conformer **1'a** would show higher stability (high population) over conformer **1a** (low population). Conformer **1'a** can not abstract δ-hydrogen by the (n, π*) triplet state of the carbonyl group and instead the excited

Scheme 4

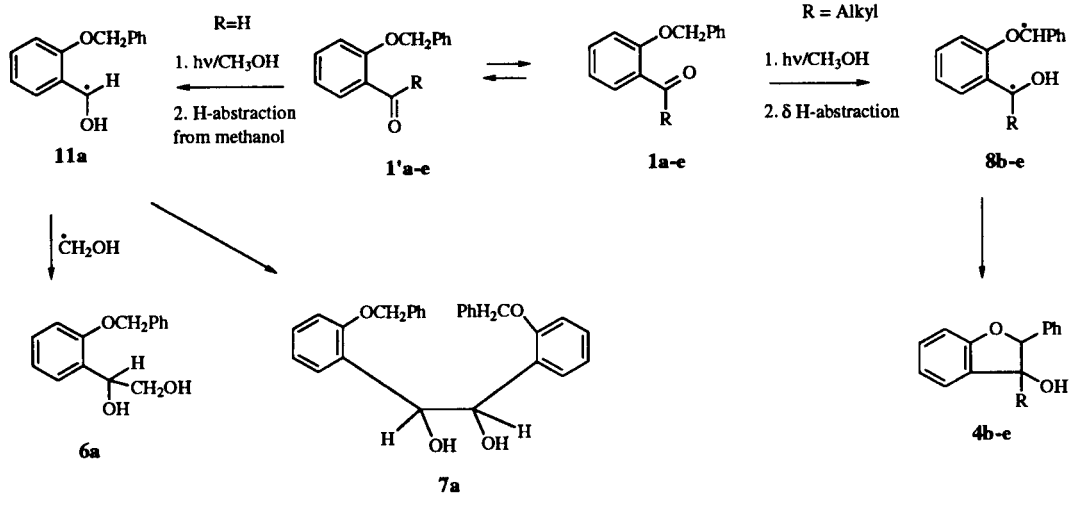


It is noteworthy to discuss the conformational, solvent and substituent effects on product distribution and reaction pathways. For example, on photocyclization of **1a** in acetonitrile and methanol, pinacols **7a** and dihydroxy product **6a** were isolated. In contrast, such products were not observed during the photoreactions of **1b-e** in acetonitrile and methanol. These result would be explained by conformational effect of the starting materials [12]. For effective δ-hydrogen abstraction, the δ-hydrogen must be in a suitable position with regard to the carbonyl group as shown in Scheme 5. This occurs only if conformation **1a** (R = H) is acheived. Preference for conformation **1a** or carbonyl group abstracts hydrogen from the solvent molecule, especially from methanol, to give pinacols **7a** and dihydroxy product **6a**.

On the other hand, replacement of the hydrogen atom of 2-benzyloxybenzaldehyde (R = H) by alkyl or phenyl group (R = Me, Et, *i*-Pr, Ph) favors conformation **1b-e** (sterically favorable) over **1'b-e** (sterically unfavorable). Conformation **1b-e** is desirable for δ-hydrogen abstraction and accordingly no pinacols **7** and dihydroxy product **6** were observed.

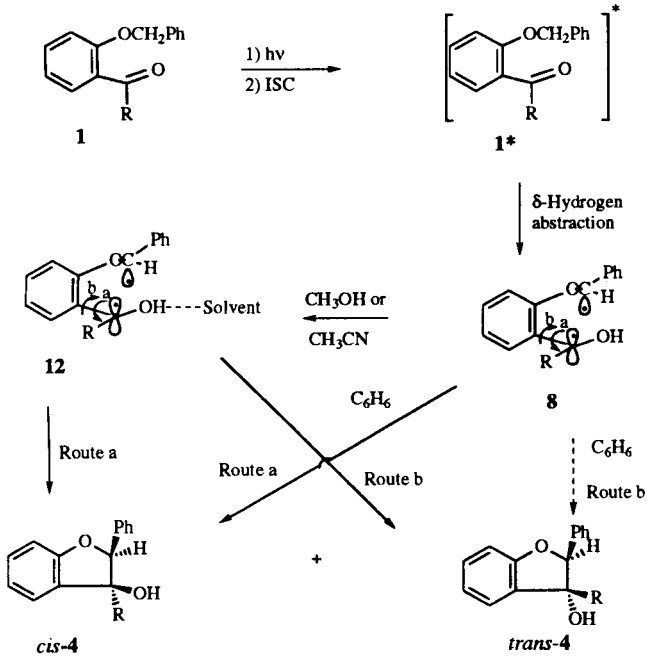
The large difference in the *cis* and *trans* stereoselectivity of dihydrobenzofuranols **4a-e** among photocycliza-

Scheme 5



tions 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 on photochemical reactions which are conducted in benzene, acetonitrile and methanol are shown in Scheme 6.

Scheme 6



Benzene is a nonpolar solvent and does not make effective hydrogen bonding with the hydroxyl group of 1,5-biradicals **8**. For benzofuranol formation *p*-orbital at the ketyl carbon of **8** is neccessary to rotate by 90° [3a] around the single bond between the benzyloxyphenyl group and ketyl group. 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 *trans* position. On the other hand, rotation of Route b affords less stable *trans*-**4**. A large difference in steric bulkiness between hydrogen and phenyl group and between alkyl group and hydroxyl groups in 1,5-biradicals **8** would produce high stereoselectivity for *cis*-isomer, that is, sterically favorable isomer is produced selectively.

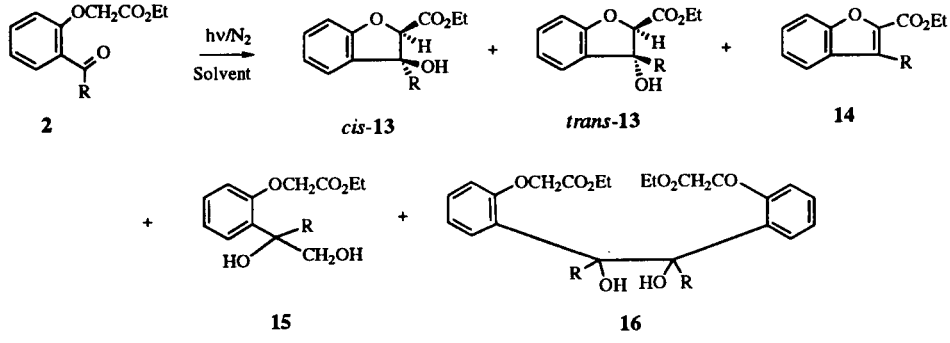
In contrast, acetonitrile and methanol are polar solvents and have ability of hydrogen bonding formation with the hydroxyl group of 1,5-biradicals **8**. Therefore, most part of the 1,5-biradicals **8** would be solvated by hydrogen bonding with solvent molecules like **12** [3a,3c,8]. The hydrogen bonding increases bulkiness of the hydroxyl group than free one [1c-d]. In this case, steric bulkiness of solvated hydroxyl group is comparable to that of alkyl group R, especially in methanol. Small difference in steric bulkiness between alkyl group and hydrogen-bonded hydroxyl group would make both rotations (Route a and Route b) possible to give a mixture of *cis*- and *trans*-isomers.

Irradiation of **1b-d** (R = alkyl group) gave rearranged products **5b-d** in considerable yields (23-39%) along with benzofuranols **4b-d**. However, irradiation of **1e** gave no rearranged products **5e** [1c-d]. The results suggest that 1,5-cyclization of 1,5-biradical is slow when R is alkyl group compared with the 1,5-biradical of R = Ph. For formation of benzofuranols **4b-d**, rotation by 90° of *p*-orbital at ketyl group is necessary. When R is alkyl group, the rotation looses benzylic conjugation energy. Therefore, 1,3-cyclization to spiroenols competes with 1,5-cyclization to benzofuranols when R is alkyl group [2b-c,3a]. However, when R is phenyl group, energy loss of deconjugation is compensated by conjugation with another phenyl group, therefore, 1,5-cyclization occurs selectively. Lower yields of 2-acylbenzophenones **5b-c** in

methanol or acetonitrile than in benzene would be attributed to steric hindrance during 1,3-cyclization between solvated hydroxyl group and benzyloxy radical at the *ortho* position of the 1,5-biradical intermediates **12**. In summary, conformational, solvent and substituent effects caused dramatic change in product distribution.

Next, photocyclization of ethyl 2-acylphenoxyacetates **2a-e** were examined in benzene, acetonitrile and methanol. The results are summarized in Scheme 7 and Table 3.

Scheme 7



2 *cis*-**13** *trans*-**13** **14** **15** **16**

Table 3

Photoreactions of Ethyl 2-Acylphenoxyacetates **2a-e** [a]

Starting material	R	Solvent	Irradiation time (minutes)	Conversion (%)	**13** (*cis*:*trans*) [c]	Product yields (%) [b] **14**	**15**	**16** (isomer ratio)
2a	H	C_6H_6	217	93	48(1:0)	0	-	0
2a	H	CH_3CN	120	97	46(1.5:1)	0	-	21(1:1)
2a	H	CH_3OH	49	98	0	0	46	28(1:1.1)
2b	Me	C_6H_6	105	94	76(1:0)	0	-	0
2b	Me	CH_3CN	120	96	86(3.0:1)	0	-	0
2b	Me	CH_3OH	30	92	63(2.0:1)	0	11	13(1:1.1)
2c	Et	C_6H_6	100	85	75(1:0)	0	-	0
2c	Et	CH_3CN	60	68	22(9.0:1)	43	-	0
2c	Et	CH_3OH	22	49	35(10:1)	14	0	0
2d	*i*-Pr	C_6H_6	32	62	61(1:0)	0	-	0
2d	*i*-Pr	CH_3CN	35	59	63(1:0)	0	-	0
2d	*i*-Pr	CH_3OH	60	58	26(1:0)	0	0	0
2e	Ph	C_6H_6	35	100	74(15:1)[e]	0	-	0
2e	Ph	CH_3CN	30	100	75(1.5:1)[e]	0	-	0
2e [d]	Ph	CH_3OH	11	100	0[e]	0	0	0

[a] A benzene, acetonitrile or methanol solution (500 ml) of **2a-e** (2.00 mmoles) was irradiated after deoxygenation by bubbling nitrogen gas for 1 hour. [b] Yields based on reacted starting materials. [c] *Cis*- and *trans*-isomers with regard to ethoxycarbonyl and hydroxyl groups. The stereochemistry of the dihydrobenzofuranols was determined from the chemical shift values of CO_2Et and C_3-R or NOE experiment in the ^1H nmr spectra. [d] Starting material was decomposed after 11 minutes. [e] Cited from reference [1d].

Photoreaction of ethyl 2-formylphenoxyacetate **2a** (R = H) in benzene afforded only ethyl *cis*-3-hydroxy-2,3-dihydro-2-benzofurancarboxylate *cis*-**13a** (48%), showing excellent stereoselectivity. Carrying out the same experiment in acetonitrile furnished a mixture of *cis*- and *trans*-isomers of **13a** (46%) along with a diastereomeric mixture of *meso*- and *dl*-pinacols **16a** (21%, isomer ratio = 1:1). The *cis* and *trans* ratio of dihydrobenzofuranols **13a** was 1.5:1, showing decreased stereoselectivity. The stereochemistry of dihydrobenzofuranol **13a** was assigned on the basis of ^1H nmr spectra using coupling constant between C_2-H and C_3-H (J *cis* > J *trans*) [9,10].

In contrast to the above results, photoreaction of **2a** in methanol did not give dihydrobenzofuranols **13a** at all but it afforded pinacols **16a** (28%, isomer ratio = 1:1.1) and methanol-incorporated product **15a** (46%). Such results are explained by conformation of the starting material **2a** as mentioned in Scheme 5.

Irradiation of **2b** (R = Me) in benzene, acetonitrile or methanol gave dihydrobenzofuranols **13b** in each case. The yields of **13b** were 76%, 86% and 63% in benzene, acetonitrile and methanol, respectively. In nonpolar benzene the *cis* and *trans* ratio was 1:0, showing excellent stereoselectivity. However, it decreased in polar acetonitrile (*cis* and *trans* ratio = 3.0:1) or methanol (*cis* and *trans* ratio = 2.0:1). Stereochemistry of **13b** was deter-

mined by considering an anisotropic effect of substituent R in the ^1H nmr spectra. Substituent R (Me) induces down field shift of C_2-H at *trans* position [10]. Pinacols **16b** (13%, isomer ratio = 1:1.1) and methanol-incorporated product **15b** (11%) were also produced on irradiation of **2b** in methanol. Formation of pinacols **16a-b** or methanol-incorporated products **15a-b** reduced yields of dihydrobenzofuranols **13a-b**.

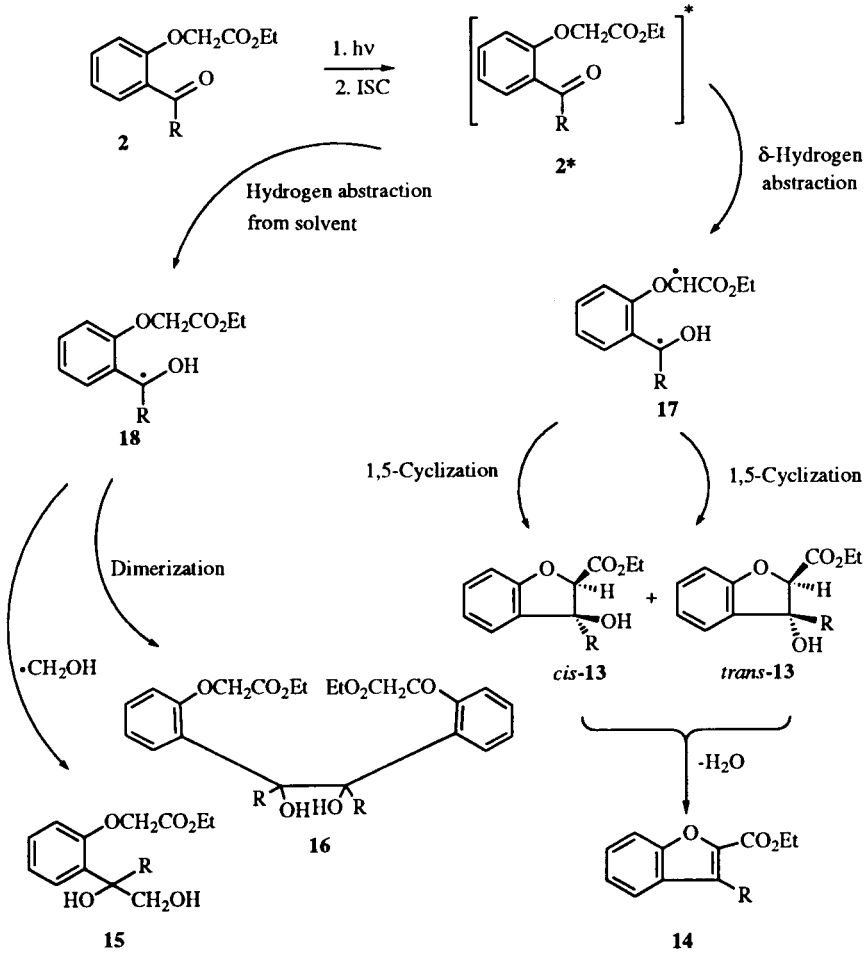
When compound **2c** was irradiated in benzene, *cis*-isomer of **13c** (75%) was obtained as a single isomer. On the other hand, when the photoreaction of **2c** was performed in acetonitrile or methanol, *cis*-dihydrobenzofuranol *cis*-**13c** were isolated predominantly along with dehydrated ethyl 3-ethylbenzofuran-2-carboxylate **14c**. The *cis* and *trans* ratios of **13c** were 9.0:1 and 10:1 in acetonitrile and methanol, respectively. Compound **14c** would be obtained during irradiation by elimination of water from **13c**.

The photocyclization of ethyl 2-isobutyrylphenoxyacetate **2d** in benzene, acetonitrile and methanol gave only *cis*-dihydrobenzofuranol *cis*-**13d** in each case. The yields of *cis*-**13d** were 61%, 63% and 26% in benzene, acetonitrile and methanol, respectively. Selective formation of *cis*-isomers **13c-d** in the photoreaction of **2c-d** showed no solvent effect. The stereochemistry of cis-**13d** was determined by measuring NOE effect in a deuteriochloroform solution. Irradiation of two methyl groups (doublet at 0.88 and doublet at 1.07 ppm were irradiated independently) induced 10% and 10% enhancement in integral of the methyne hydrogen (4.99 ppm) at C_2-carbon.

The reaction pathways for formation of **13**, **14**, **15** and **16** are similar to those of α-(2-acylphenoxy)toluenes **1** and shown in Scheme 8. In the photocyclization of ethyl 2-acylphenoxyacetates, rearranged products *via* spirocyclization reaction are not observed [2c]. This is because the ethoxycarbonyl group and the phenoxy oxygen stabilizes the 1,5-biradical intermediates **17** by push-pull resonance (capto-dative stabilization) [13]. Stabilized 1,5-biradical is not highly reactive and do not suffer from 1,3-cyclization with benzene ring.

From the above results, *cis*-isomers were always obtained selectively from the photoreactions of **2a-e** in benzene in spite of steric bulkiness of R (H, Me, Et, *i*-Pr, Ph). In fact, in the case of **2a** sterically unfavorable *cis*-isomer *cis*-**13a** was obtained selectively. This suggests

Scheme 8



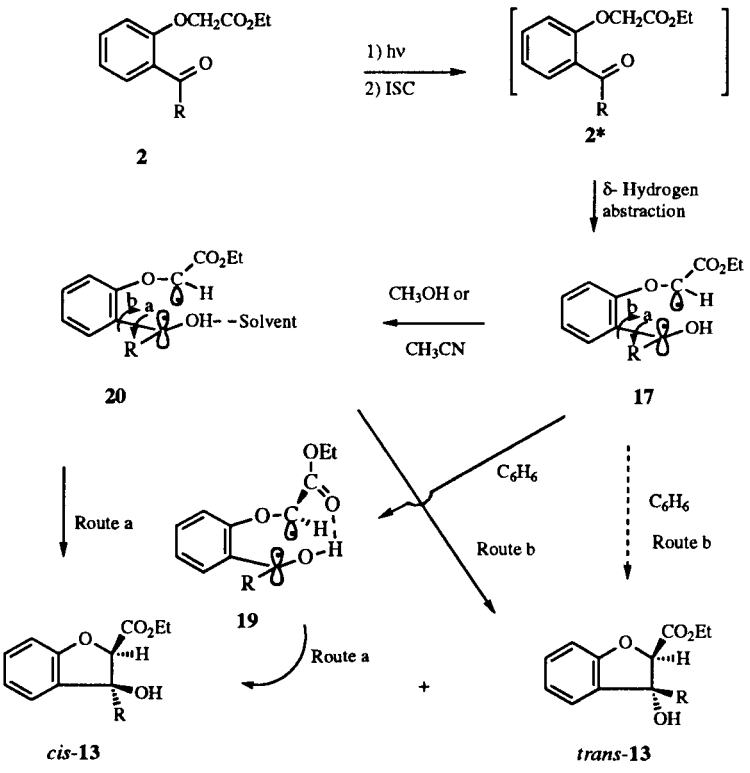
that the *p*-orbital at the ketyl group in 1,5-biradicals **17** rotates counterclockwise (Route a) to give *cis*-isomer of **13a** *via* intramolecular hydrogen bonding like **19** between the hydroxyl and ethoxycarbonyl groups as shown in Scheme 9. In benzene the intramolecular hydrogen bonding play an important role for stereoselectivity [1c-d].

However, in polar solvents such as acetonitrile and methanol, the hydroxyl group of 1,5-biradicals **17** would be partly or mostly solvated using intermolecular hydrogen bonding with solvent like **20** [3a,3c,8]. 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 **20** becomes bulkier than free one and comparable to R in steric effect. Therefore, both of counterclockwise and clockwise rotations (Route a and Route b) are possible to give *cis*- and *trans*-isomers of **13**, showing decreased stereoselectivity [1c-d].

In contrast to the above results, the photocyclization of **2e** (R = Ph) in acetonitrile afforded a mixture of *cis*- and *trans*-isomers of **13e** (ratio is 1.5:1) [1c-d]. In general, phenyl group is bulkier than isopropyl group, however, the result would be explained by perpendicular orientation to the plane of paper of planar phenyl group as in Scheme 10. Such conformation **17e** would reduce steric hindrance between the phenyl group and solvent molecules during solvation. In this case, intermolecular hydrogen bonding between hydroxyl group of 1,5-biradical **17e** and solvent occurs to give **20e**. Accordingly a mixture of *cis*- and *trans*-isomers of **13e** are obtained.

In summary, photocyclization reactions of α-(2-acylphenoxy)toluenes **1a-e** in benzene proceed in a stereoselective manner to give *cis*-dihydrobenzofuranols *cis*-**4b-e**. In contrast, photocyclization reactions in acetonitrile or methanol proceed in a non-stereoselective

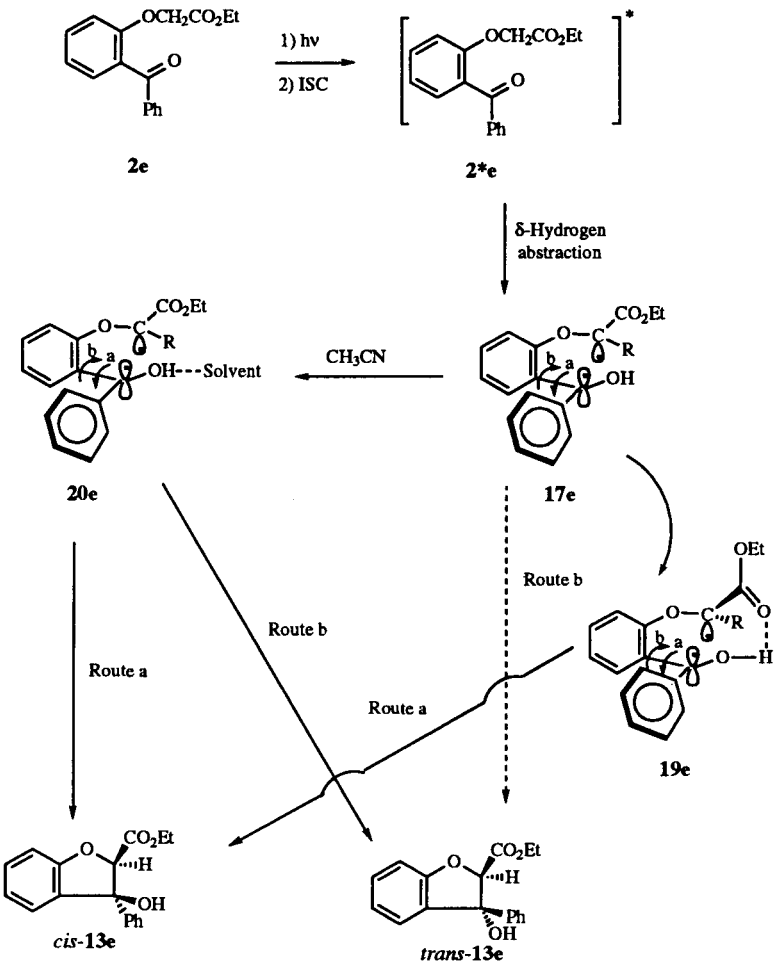
Scheme 9



In the photocyclization of **2c** (R = Et) and **2d** (R = *i*-Pr) in polar solvents (acetonitrile or methanol), solvation of hydroxyl group of 1,5-biradicals **17** would be completely or partly suppressed by steric hindrance of bulky ethyl or isopropyl group because solvent molecules can not approach easily to the hydroxyl group of **17**. This is why, by increasing the size of alkyl group from methyl to isopropyl group in the photocyclization of **2c-d**, *cis*-isomer *cis*-**13c-d** are isolated selectively.

manner to afford a mixture of *cis*- and *trans*-dihydrobenzofuranols as a result of intermolecular hydrogen bonding between the hydroxyl group of 1,5-biradicals and solvent. In spite of solvent polarity, the photocyclization of ethyl 2-acylphenoxyacetates **2c-d** gave *cis*-isomer selectively due to inhibition of solvation by steric effect of the alkyl group. The ethoxycarbonyl group suppresses spirocyclization reaction of the 1,5-biradical intermediates by captodative stabilization.

Scheme 10



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 ^1H 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.

2'-Benzyloxypropiophenone **1c**.

A mixture of 2'-hydroxypropiophenone (3.0 g, 12.5 mmoles), benzyl chloride (7.0 g, 55.3 mmoles), tripotassium phosphate (7.0 g, 33.0 mmoles) 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 to give **1c** (3.3 g, 66%) as a colorless oil; ir (neat): 1680 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform, 200 MHz): δ 1.11 (t, J = 7 Hz, 3H, CH_2CH_3), 2.98 (q, J = 7 Hz, 2H, CH_2CH_3), 5.13 (s, 2H, OCH_2 Ph), 6.94-7.04 (m, 2H, Ar-H_2), 7.28-7.46 (m, 6H, Ar-H and Ph-H_5), 7.68 (dd, J = 2 and 8 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 9.5 (q), 38.1 (t), 71.6 (t), 113.8 (d), 121.9 (d), 128.4 (d), 129.1 (d), 129.6 (d), 130.0 (s), 131.2 (d), 134.0 (d), 137.3 (s), 158.5 (s), 204.6 (s).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.86; H, 6.50.

2'-Benzyloxyisobutyrophenone **1d**.

Compound **1d** (57%) was obtained as a colorless oil from the reaction of 2'-hydroxyisobutyrophenone and benzyl chloride in a manner similar to the synthesis of **1b**; ir (neat): 1670 cm^{-1} (Ar-CO); ^1H nmr (deuteriochloroform, 200 MHz): δ 1.10 (d, J = 7 Hz, 6H, $CH(CH_3)_2$), 3.49 (septet, J = 7 Hz, 1H, $CH(CH_3)_2$), 5.13 (s, 2H, OCH_2 Ph), 6.94-7.05 (m, 2H, Ar-H_2), 7.29-7.46 (m, 6H, Ar-H and Ph-H_5), 7.51 (dd, J = 2 and 8 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 18.6 (q), 40.1 (d), 70.6 (t), 112.6 (d), 121.0 (d), 127.4 (d), 128.1 (d), 128.6 (d), 129.6 (s), 130.0 (d), 132.4 (d), 136.3 (s), 156.7 (s), 208.4 (s).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.37; H, 7.20.

Ethyl 2-Propionylphenoxyacetate **2c**.

Compound **2c** (95%) was obtained as colorless crystals from benzene-hexane by the reaction of 2'-hydroxypropiophenone and ethyl bromoacetate in a manner similar to the synthesis of **1c**, mp 35-36°; ir (potassium bromide): 1765 ($CO_2CH_2CH_3$), 1670 cm^{-1} (ArCO); ^1H nmr (deuteriochloroform, 90 MHz): δ 1.18 (t, J = 7 Hz, 3H, CH_2CH_3), 1.29 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 3.12 (q, J = 7 Hz, 2H, CH_2CH_3), 4.27 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.70 (s, 2H, OCH_2), 6.82 (d, J = 8 Hz, 1H, Ar-H), 7.02 (dd, J = 8 and 8 Hz, 1H, Ar-H), 7.34 (ddd, J = 2, 2 and 8 Hz, 1H, Ar-H), 7.70 (dd, J = 2 and 8 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 22.49 MHz): δ 8.5 (q), 14.1 (q), 37.1 (t), 61.4 (t), 65.7 (t), 112.4 (d), 121.7 (d), 129.2 (s), 130.5 (d), 133.0 (d), 156.6 (s), 168.1 (s), 203.0 (s).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.02; H, 6.98.

Ethyl 2-Isobutyrylphenoxyacetate **2d**.

Compound **2d** (95%) was obtained as a colorless oil from the reaction of 2'-hydroxyisobutyrophenone and ethyl bromoacetate in a manner similar to the synthesis of **1c**; ir (neat): 1745 ($CO_2CH_2CH_3$), 1670 cm^{-1} (ArCO); ^1H nmr (deuteriochloroform, 200 MHz): δ 1.17 (d, J = 7 Hz, 6H, $CH(CH_3)_2$), 1.30 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 3.66 (septet, J = 7 Hz, 1H, $CH(CH_3)_2$), 4.27 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.69 (s, 2H, OCH_2), 6.81 (d, J = 8 Hz, 1H, Ar-H), 7.05 (dd, J = 8 and 8 Hz, 1H, Ar-H), 7.40 (ddd, J = 2, 8 and 8 Hz, 1H, Ar-H), 7.54 (dd, J = 2 and 8 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 14.1 (q), 18.5 (q), 40.1 (d), 61.1 (t), 65.5 (t), 111.9 (d), 121.7 (d), 129.5 (s), 130.3 (d), 132.4 (d), 155.6 (s), 168.2 (s), 207.9 (s).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.99; H, 7.20.

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

In benzene, acetonitrile or methanol solvent (500 ml), 2.00 mmoles of the starting materials **1a-e**, **2a-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.

cis-2-Phenyl-2,3-dihydro-3-benzofuranol *cis*-**4a**.

Compound *cis*-**4a** was obtained as colorless crystals from benzene-hexane, mp 123-125° [2a, mp 126-127°], identical with an authentic sample [2b] in the ir and nmr spectra.

trans-2-Phenyl-2,3-dihydro-3-benzofuranol *trans*-**4a**.

Compound *trans*-**4a** was obtained as a colorless oil [2a], identical with an authentic sample [2b] in the ir and nmr spectra.

1-(2-Benzyloxyphenyl)-1,2-ethanediol **6a**.

Compound **6a** was obtained as a colorless oil after irradiation of **1a** in methanol; ir (neat): 3410 cm^{-1} (OH); ^1H nmr (deuteriochloroform, 200 MHz): δ 2.90 (br s, 1H, OH), 3.40 (broad s, 1H, OH), 3.61 (dd, J = 8 and 11 Hz, 1H, CH_2OH), 3.79 (dd, J = 3 and 11 Hz, 1H, CH_2OH), 5.04 (s, 2H, OCH_2Ph), 5.11 (dd, J = 3 and 8 Hz, 1H, ArCHOH), 6.84-7.00 (m, 2H, Ar-H_2), 7.14-7.45 (m, 7H, Ar-H_2 and Ph-H_5); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 66.5 (t), 70.0 (t), 70.6 (d), 111.6 (d), 121.0 (d), 127.2 (d), 127.2 (d), 128.0 (d), 128.6 (d), 128.6 (d), 128.8 (s), 136.6 (s), 155.4 (s).

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.62; H, 6.72.

dl- and *meso*-1,2-Bis(2-benzyloxyphenyl)-1,2-ethandiols **7a**.

These diastereoisomers of **7a** were obtained as a 1:1.1 or 1.1:1 mixture (crystals) after irradiation of **1a** in methanol and acetonitrile. It was difficult to isolate each isomer in a pure state.

The mixture had ir (potassium bromide): 3450 cm^{-1} (OH); ^1H nmr (deuteriochloroform, 200 MHz): δ 3.05 (s, 2H, OH and OH), 3.61 (s, 2H, OH and OH), 4.51 (d, J = 12 Hz, 2H, OCH_2Ph), 4.62 (d, J = 7 Hz, 2H, OCH_2Ph), 4.67 (d, J = 7 Hz, 2H, OCH_2Ph), 4.80 (d, J = 12 Hz, 2H, OCH_2Ph), 5.07 (d, J = 3 Hz, 2H, ArCHOH and ArCHOH), 5.35 (d, J = 3 Hz, 2H, ArCHOH and ArCHOH), 6.62-6.88 (m, 8H, Ar-H_4 and Ar-H_4), 7.05-7.18 (m, 8H, Ar-H_4 and Ar-H_4), 7.19-7.45 (m, 20H, Ph-H_{10} and Ph-H_{10}).

cis-3-Methyl-2-phenyl-2,3-dihydro-3-benzofuranol *cis*-**4b**.

Compound *cis*-**4b** was obtained as colorless crystals [3c] from benzene-hexane, mp 72-73.5°, identical with an authentic sample [2b] in the ir and nmr spectra.

trans-3-Methyl-2-phenyl-2,3-dihydro-3-benzofuranol *trans*-**4b**.

Compound *trans*-**4b** was obtained as a colorless oil [3c], identical with an authentic sample [2b] in the ir and nmr spectra.

2-Acetylbenzophenone **5b**.

Compound **5b** was obtained as a colorless oil [3c]; ir (neat): 1660 (ArCOPh), 1680 cm^{-1} ($ArCOCH_3$); ^1H nmr (deuteriochloroform, 200 MHz): δ 2.51 (s, 3H, CH_3), 7.32-7.68 (m, 6H, Ar-H_6), 7.71-7.79 (m, 2H, Ar-H_2), 7.85-7.92 (m, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 27.3 (q), 128.1 (d), 128.3 (d), 128.4 (d), 129.2 (d), 129.7 (d), 132.2 (d), 132.9 (d), 137.1 (s), 137.4 (s), 140.8 (s), 197.7 (s), 198.4 (s).

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.29; H, 5.44.

cis-3-Ethyl-2-phenyl-2,3-dihydro-3-benzofuranol *cis*-**4c**.

Compound *cis*-**4c** was obtained as a colorless oil; ir (neat): 3475 cm^{-1} (OH); ^1H nmr (deuteriochloroform, 200 MHz): δ 1.05 (t, J = 7 Hz, 3H, CH_3CH_2), 1.58 (broad s, 1H, OH), 1.90-2.20 (m, 2H, CH_3CH_2), 5.46 (s, 1H, C_2-H), 6.98 (dd, J = 8 and 8 Hz, 2H, Ar-H_2), 7.24-7.46 (m, 7H, Ar-H_2 and Ph-H_5); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 8.9 (q), 32.0 (t), 81.6 (s), 89.9 (d), 110.3 (d), 121.2 (d), 124.5 (d), 127.0 (d), 128.4 (d), 128.4 (d), 130.1 (d), 130.3 (s), 135.4 (s), 159.6 (s).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.00; H, 6.67.

trans-3-Ethyl-2-phenyl-2,3-dihydro-3-benzofuranol *trans*-**4c**.

Compound *trans*-**4c** contains small amount of *cis*-**4c** and it was difficult to isolate it in a pure state; ir (neat): 3475 cm^{-1} (OH); ^1H nmr (deuteriochloroform, 200 MHz): δ 0.75 (t, J = 7 Hz, 3H, CH_3CH_2), 1.18-1.58 (m, 2H, CH_3CH_2), 2.24 (s, 1H, OH), 5.50 (s, 1H, C_2-H), 6.98 (dd, J = 8 and 8 Hz, 2H, Ar-H_2), 7.24-7.48 (m, 7H, Ar-H_2 and Ph-H_5); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 7.1 (q), 29.7 (t), 83.4 (s), 94.6 (d), 110.5 (d), 120.9 (d), 126.1 (d), 127.9 (d), 128.0 (d), 128.1 (d), 139.8 (d), 131.7 (s), 136.5 (s), 158.9 (s).

2-Propionylbenzophenone **5c**.

Compound **5c** was obtained as a colorless oil; ir (neat): 1670 (ArCOPh), 1690 cm^{-1} (ArCOCH$_3$); ^1H nmr (deuteriochloroform, 200 MHz): δ 1.08 (t, J = 7 Hz, 3H, CH_3CH$_2$), 2.91 (q, J = 7 Hz, 2H, CH$_3$CH_2), 7.34-7.63 (m, 6H, Ar-H$_6$), 7.72-7.79 (m, 2H, Ar-H$_2$), 7.82-7.90 (m, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 8.0 (q), 33.0 (t), 128.3 (d), 128.3 (d), 128.4 (d), 129.3 (d), 129.7 (d), 131.7 (d), 132.9 (d), 137.1 (s), 137.9 (s), 140.6 (s), 197.7 (s), 201.6 (s).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.57; H, 5.97.

cis-3-Isopropyl-2-phenyl-2,3-dihydro-3-benzofuranol *cis*-**4d**.

Compound *cis*-**4d** was obtained as a colorless oil; ir (neat): 3530 cm^{-1} (OH); ^1H nmr (deuteriochloroform, 200 MHz): δ 0.98 (d, J = 7 Hz, 3H, CH(CH_3)$_2$), 1.08 (d, J = 7 Hz, 3H, CH(CH_3)$_2$), 1.46 (s, 1H, OH), 2.26 (septet, J = 7 Hz, 1H, CH(CH$_3$)$_2$), 5.57 (s, 1H, C$_2$-H), 6.88-7.00 (m, 2H, Ar-H$_2$), 7.21-7.42 (m, 7H, Ar-H$_2$ and Ph-H$_5$); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 16.8 (q), 17.4 (q), 37.4 (d), 84.6 (s), 87.9 (d), 109.8 (d), 121.1 (d), 124.9 (d), 127.0 (d), 128.3 (d), 128.5 (d), 129.9 (s), 130.1 (d), 136.4 (s), 159.6 (s).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.12; H, 6.92.

trans-3-Isopropyl-2-phenyl-2,3-dihydro-3-benzofuranol *trans*-**4d**.

Compound *trans*-**4d** contains a small amount of *cis*-**4d** and it was difficult to isolate it in a pure state; ir (neat): 3490 cm^{-1} (OH); ^1H nmr (deuteriochloroform, 200 MHz): δ 0.39 (d, J = 7 Hz, 3H, CH(CH_3)$_2$), 0.94 (d, J = 7 Hz, 3H, CH(CH_3)$_2$), 1.65 (broad s, 1H, OH), 1.79 (septet, J = 7 Hz, 1H, CH(CH$_3$)$_2$), 5.57 (s, 1H, C$_2$-H), 7.21-7.48 (m, 7H, Ar-H$_2$ and Ph-H$_5$), 7.54-7.65 (m, 2H, Ar-H$_2$); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 16.3 (q), 16.4 (q), 32.9 (d), 85.9 (s), 94.3 (d), 110.7 (d), 121.0 (d), 124.8 (d), 125.8 (d), 127.6 (d), 128.0 (d), 129.8 (d), 130.3 (s), 136.1 (s), 159.2 (s).

2-Isobutyrylbenzophenone **5d**.

Compound **5d** was obtained as a colorless oil; ir (neat): 1670 cm^{-1} (ArCO); ^1H nmr (deuteriochloroform, 200 MHz): δ 1.11 (d, J = 7 Hz, 6H, CH(CH_3)$_2$), 3.34 (septet, J = 7 Hz, 1H, CH(CH$_3$)$_2$), 7.36-7.64 (m, 6H, Ar-H$_6$), 7.71-7.84 (m, 3H, Ar-H$_3$); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 18.7 (q), 37.1 (d), 128.3 (d), 128.3 (d), 128.7 (d), 129.5 (d), 129.8 (d), 131.4 (d), 132.9 (d), 137.1 (s), 138.1 (s), 140.8 (s), 197.5 (s), 205.6 (s).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.85; H, 6.50.

Ethyl *cis*-3-Hydroxy-2,3-dihydro-2-benzofurancarboxylate *cis*-**13a**.

Compound *cis*-**13a** was obtained as colorless crystals from benzene-hexane, mp 80-82°, identical with an authentic sample [2c] in the ir and nmr spectra.

Ethyl *trans*-3-Hydroxy-2,3-dihydro-2-benzofurancarboxylate *trans*-**13a**.

Compound *trans*-**13a** was obtained as a colorless oil, identical with an authentic sample [2c] in the ir and nmr spectra.

Ethyl 2-[2-(1,2-Dihydroxyethyl)phenoxy]acetate **15a**.

Compound **15a** was obtained as colorless crystals from benzene-hexane after irradiation of **2a** in methanol, mp 48-49°; ir (potassium bromide): 3360 (OH), 3240 (OH), 1730 cm^{-1} ($CO_2CH_2CH_3$); ^1H nmr (deuteriochloroform, 90 MHz): δ 1.27 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 3.40 (s, 2H, OH and OH), 3.56-3.96 (m, 2H, CH_2OH), 4.23 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.64 (s, 2H, OC$H_2CO_2CH_2CH_3$), 5.09 (dd, J = 3 and 7 Hz, 1H, ArCHOH), 6.74 (d, J = 8 Hz, 1H, Ar-H), 6.84-7.30 (m, 2H, Ar-H$_2$), 7.38 (dd, J = 2 and 7 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 14.1 (q), 61.7 (t), 65.4 (t), 66.4 (t), 71.8 (d), 111.6 (d), 122.1 (d), 128.1 (d), 128.9 (d), 129.4 (s), 155.1 (s), 168.9 (s).

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 60.00; H, 6.71. Found: C, 59.92; H, 6.87.

dl- and *meso*-Pinacols **16a**.

A mixture of diastereoisomers (1:1.1 ratio) was produced by irradiation of **2a** in acetonitrile and methanol. One isomer was isolated as colorless crystals from benzene, mp 133-134° and another isomer was obtained as colorless crystals from benzene-hexane, mp 74-75°. The two compounds were identical with authentic samples [2c] in the ir and nmr spectra.

Ethyl *cis*-3-Hydroxy-3-methyl-2,3-dihydro-2-benzofurancarboxylate *cis*-**13b**.

Compound *cis*-**13b** was obtained as colorless crystals from benzene-hexane, mp 73-74°, identical with an authentic sample [2c] in the ir and nmr spectra.

Ethyl *trans*-3-Hydroxy-3-methyl-2,3-dihydro-2-benzofurancarboxylate *trans*-**13b**.

Compound *trans*-**13b** was obtained as a colorless oil, identical with an authentic sample [2c] in the ir and nmr spectra.

Ethyl 2-[2-(1,2-Dihydroxy-1-methylethyl)phenoxy]acetate **15b**.

Compound **15b** was obtained as a colorless oil after irradiation of **2b** in methanol; ir (neat): 3480 (OH), 1755 cm^{-1} ($CO_2CH_2CH_3$); ^1H nmr (deuteriochloroform, 90 MHz): δ 1.30 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.57 (s, 3H, CH$_3$), 3.10 (broad s, 2H, OH and OH), 3.68 (d, J = 11 Hz, 1H, CH_2OH), 4.12 (d, J = 11 Hz, 1H, CH_2OH), 4.27 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.69 (s, 2H, OC$H_2CO_2CH_2CH_3$), 6.77 (dd, J = 2 and 8 Hz, 1H, Ar-H), 6.88-7.33 (m, 2H, Ar-H$_2$), 7.49 (dd, J = 2 and 8 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform, 22.49 MHz): δ 14.1 (q), 24.5 (q), 61.7 (t), 65.3 (t), 69.5 (t), 75.2 (s), 111.9 (d), 122.1 (d), 128.1 (d), 128.6 (d), 133.2 (s), 155.0 (s), 168.7 (s).

Anal. Calcd. for $C_{13}H_{18}O_5$: C, 61.42; H, 7.09. Found: C, 61.49; H, 6.99.

dl- and *meso*-Pinacols **16b**.

These diastereoisomers of **16b** were obtained as a 1:1.1 or 1.1:1 mixture (crystals) after irradiation of **2b** in methanol. It was difficult to isolate each isomer in a pure state.

The mixture had ir (potassium bromide): 3505 (OH), 1745 cm^{-1} ($CO_2CH_2CH_3$); ^1H nmr (deuteriochloroform, 90 MHz): δ 1.32 (t, J = 7 Hz, 6H, $CO_2CH_2CH_3$ and $CO_2CH_2CH_3$), 1.33 (t, J = 7 Hz, 6H, $CO_2CH_2CH_3$ and $CO_2CH_2CH_3$), 1.69 (s, 6H, CH$_3$ and CH$_3$), 1.73 (s, 6H, CH$_3$ and CH$_3$), 3.70-4.40 (m, 16H, OCH$_2$, OCH$_2$ OCH$_2$, OCH$_2$, $CO_2CH_2CH_3$, $CO_2CH_2CH_3$, $CO_2CH_2CH_3$, $CO_2CH_2CH_3$), 5.58 (s, 4H, OH, OH and OH, OH), 6.30-6.58 (m, 4H, Ar-H$_2$ and Ar-H$_2$), 6.70-7.24 (m, 8H, Ar-H$_4$ and Ar-H$_4$), 7.44 (dd, J = 2 and 7 Hz, 4H, Ar-H$_2$ and Ar-H$_2$).

Ethyl *cis*-3-Hydroxy-3-ethyl-2,3-dihydro-2-benzofurancarboxylate *cis*-**13c**.

Compound *cis*-**13c** was obtained as colorless crystals from benzene-hexane, mp 60-61°; ir (potassium bromide): 3435 (OH), 1750 cm^{-1} ($CO_2CH_2CH_3$); ^1H nmr (deuteriochloroform, 90 MHz): δ 0.95 (t, J = 7 Hz, 3H, CH_2CH_3), 1.29 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 2.11 (q, J = 7 Hz, 2H, CH_3CH_2), 2.75 (s, 1H, OH), 4.26 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.90 (s, 1H, C_2-H), 6.78-7.02 (m, 2H, Ar-H_2), 7.09-7.33 (m, 2H, Ar-H_2); ^{13}C nmr (deuteriochloroform, 22.49 MHz): δ 8.7 (q), 14.1 (q), 32.0 (t), 61.4 (t), 82.9 (s), 86.5 (d), 110.7 (d), 121.5 (d), 123.9 (d), 129.2 (s), 130.5 (d), 159.3 (s), 168.4 (s).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.95; H, 6.71.

Ethyl *trans*-3-Hydroxy-3-ethyl-2,3-dihydro-2-benzofurancarboxylate *trans*-**13c**.

Compound *trans*-**13c** was obtained as a colorless oil; ir (neat): 3450 (OH), 1740 cm^{-1} ($CO_2CH_2CH_3$); ^1H nmr (deuteriochloroform, 90 MHz): δ 0.95 (t, J = 7 Hz, 3H, CH_2CH_3), 1.35 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.46-2.04 (m, 3H, CH_3CH_2 and OH), 4.33 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 5.02 (s, 1H, C_2-H), 6.82-7.04 (m, 2H, Ar-H_2), 7.10-7.38 (m, 2H, Ar-H_2).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.24; H, 6.96.

Ethyl 3-Ethyl-2-benzofurancarboxylate **14c**.

Compound **14c** was obtained as a colorless oil; ir (neat): 1710 cm^{-1} ($CO_2CH_2CH_3$); ^1H nmr (deuteriochloroform, 90 MHz): δ 1.30 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.43 (t, J = 7 Hz, 3H, CH_3CH_2), 3.10 (q, J = 7 Hz, 2H, CH_3CH_2), 4.45 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 7.10-7.68 (m, 4H, Ar-H_4); ^{13}C nmr (deuteriochloroform, 22.49 MHz): δ 14.4 (q), 14.4 (q), 17.7 (t), 61.0 (t), 112.4 (d), 121.1 (d), 123.1 (d), 127.6 (d), 128.4 (s), 131.7 (s), 140.6 (s), 154.7 (s), 160.3 (s).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.37; H, 6.58.

Ethyl *cis*-3-Hydroxy-3-isopropyl-2,3-dihydro-2-benzofurancarboxylate *cis*-**13d**.

Compound *cis*-**13d** was obtained as a colorless oil; ir (neat): 3480 (OH), 1740 cm^{-1} ($CO_2CH_2CH_3$); ^1H nmr (deuteriochloroform, 200 MHz): δ 0.88 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.07 (d, J = 7 Hz, 3H, $CH(CH_3)_2$), 1.29 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 2.32 (septet, J = 7 Hz, 1H, $CH(CH_3)_2$), 2.66 (s, 1H, OH), 4.24 (q, J = 7 Hz, 2H, $CO_2CH_2CH_3$), 4.99 (s, 1H, C_2-H), 6.86-7.00 (m, 2H, Ar-H_2), 7.20-7.32 (m, 2H, Ar-H_2); ^{13}C nmr (deuteriochloroform, 50 MHz): δ 14.2 (q), 16.5 (q), 17.6 (q), 36.9 (d), 61.5 (t), 84.5 (d), 85.8 (s), 110.5 (d), 121.5 (d), 124.0 (d), 128.7 (s), 130.6 (d), 159.5 (s), 169.1 (s).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.01; H, 7.23.

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REFERENCES AND NOTES

[1a] Part **3**, E. M. Sharshira, H. Iwanami, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic Chem.*, **33**, 17 (1996); [b] Part **4**, E. M. Sharshira, H. Iwanami, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic Chem.*, **33**, 137 (1996); [c] Part **5**, E. M. Sharshira, S. Shimada, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic Chem.*, **33**, 1797 (1996); [d] Part **6**, E. M. Sharshira, M. Okamura, E. Hasegawa and T. Horaguchi, *J. Heterocyclic Chem.*, **34**, 861 (1997).

[2a] S. P. Pappas and J. E. Blackwell, Jr., *Tetrahedron Letters*, 1171 (1966); [b] T. Horaguchi, C. Tsukada, E. Hasegawa, T. Shimizu, T. Suzuki and K. Tanemura, *J. Heterocyclic Chem.*, **28**, 1261 (1991); [c] T. Horaguchi, C. Tsukada, E. Hasegawa, T. Shimizu, T. Suzuki and K. Tanemura, *J. Heterocyclic Chem.*, **28**, 1273 (1991).

[3a] P. J. Wagner, M. A. Meador and J. C. Scaiano, *J. Am. Chem. Soc.*, **106**, 7988 (1984); [b] G. A. Kraus, P. J. Thomas and M. D. Schwinden, *Tetrahedron Letters*, **31**, 1819 (1990); [c] P. J. Wagner, M. A. Meador and B. -S. Park, *J. Am. Chem. Soc.*, **112**, 5199 (1990); [d] P. J. Wagner and J. S. Jang, *J. Am. Chem. Soc.*, **115**, 7914 (1993).

[4a] G. R. Lappin and J. S. Zannucci, *J. Chem. Soc.*, 1113 (1969); [b] G. R. Lappin and J. S. Zannucci, *J. Org. Chem.*, **36**, 1808 (1971); [c] M. A. Meador and P. J. Wagner, *J. Org. Chem.*, **50**, 419 (1985); [d] P. J. Wagner, M. A. Meador, B. P. Giri and J. C. Scaiano, *J. Am. Chem. Soc.*, **107**, 1087 (1985); [e] P. J. Wagner, *Acc. Chem. Res.*, **22**, 83 (1989); [f] T. Sumathi and Balasubramanian, *Tetrahedron Letters*, **31**, 3775 (1990); [g] P. J. Wagner and G. Laidig, *Tetrahedron Letters*, **32**, 895 (1991); [h] M. A. -Aziz, J. V. Auping and M. A. Meador, *J. Org. Chem.*, **60**, 1303 (1995).

[5] M. Yoshioka, H. Arai, K. Ichikawa and T. Hessegawa, *J. Chem. Soc., Chem. Commun.*, 848 (1988).

[6a] S. P. Pappas, B. C. Pappas and J. E. Blackwell, Jr., *J. Org. Chem.*, **32**, 3066 (1967); [b] S. P. Pappas, J. E. Alexander and R. D. Zehr, *J. Am. Chem. Soc.*, **92**, 6927 (1970); [c] S. P. Pappas and R. D. Zehr, *J. Am. Chem. Soc.*, **93**, 7112 (1971); [d] P. J. Wagner, P. Kelso, A. E. Kemppainen and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7500 (1972).

[7a] C. M. Orlando, Jr. and H. Mark, *Tetrahedron Letters*, 3003 (1966); [b] C. M. Orlando, Jr., H. Mark, A. K. Bose and M. S. Manhas, *J. Am. Chem. Soc.*, **89**, 6527 (1967); [c] C. M. Orlando, Jr., H. Mark, A. K. Bose and M. S. Manhas, *J. Org. Chem.*, **33**, 2512 (1968); [d] J. M. Bruce and D. Creed, *J. Chem. Soc.* **C**, 649 (1970); [e] J. M. Bruce, D. Creed and K. Dawes, *J. Chem. Soc.* **C**, 2244 (1971); [f] T. Kozuka, *Bull. Chem. Soc. Japan*, **25**, 2415 (1982); [g] K. Maruyama, H. Iwamoto, O. Soga and A. Takuwa, *Chem. Letters*, 1343 (1984); [h] K. Maruyama, H. Iwamoto, O. Soga, A. Takuwa and A. Osuka, *Chem. Letters*, 1675 (1985); [i] H. Iwamoto, *J. Org. Chem.*, **53**, 1507 (1988).

[8a] P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5898 (1967); [b] P. J. Wagner, I. E. Kochevar and A. E. Kemppainen, *J. Am. Chem. Soc.*, **94**, 7489 (1972).

[9a] D. P. Brust, D. S. Tarbell, S. M. Hecht, E. C. Hayward and L. D. Colebrook, *J. Org. Chem.*, **31**, 2192 (1966); [b] M.P. Mertes and L. J. Powers, *J. Chem. Soc., Chem. Commun.*, 620 (1970); [c] L. H. Zalkow, E. Keinan, S. Steindel, A. R. Kaylnaraman and J. A. Bertrand, *Tetrahedron Letters.*, 2837 (1972); [d] T. Okuyama, K. Kunugiza and T. Fueno, *Bull. Chem. Soc. Japan*, **47**, 1267 (1974).

[10a] E. C. Hayward, D. D. Tarbell and L. D. Colebrook, *J. Org. Chem.*, **33**, 399 (1968); [b] M. P. Mertes and L. J. Powers, *J. Org. Chem.*, **46**, 1805 (1971); [c] T. Kozuka, *Bull. Chem. Soc. Japan*, **55**, 2415 (1982); [d] T. Suzuki, *Bull. Chem. Soc. Japan*, **58**, 2821 (1985).

[11a] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959); [b] J. N. Pitts, Jr., H. W. Johnson, Jr. and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962); [c] G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959); [d] N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961); [e] W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); [f] G. S. Hammond, W. P. Baker and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961); [g] A. Beckett and G. Porter, *Trans. Farady Soc.*, **59**, 2051 (1963); [h] A. Padwa, *Tetrahedron Letters*, 3465 (1964); [i] S. G. Cohen and M. N. Siddigui, *J. Am. Chem. Soc.*, **86**, 5047 (1964); [j] C. Walling and M. J. Gibin, *J. Am. Chem. Soc.*, **87**, 3361 (1965); [k] J. S. Bradshaw, *J. Org. Chem.*, **31**, 237

(1966); [l] P. J. Wagner, R. J. Truman and J. C. Scaiano, *J. Am. Chem. Soc.*, **107**, 7093 (1985); [m] P. J. Wagner, R. J. Truman, A. E. Puchalski and R. Wake, *J. Am. Chem. Soc.*, **108**, 7727 (1986).

[12a] P. J. Wagner, B. P. Giri, J. C. Scaiano, D. L. Ward, E. Gabe and F. L. Lee, *J. Am. Chem. Soc.*, **107**, 5483 (1985).

[13a] L. Stella, Z. Janousek, R. Merenyi, H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **17**, 691 (1978); [b] H. G. Viehe, R. Merenyi, L. Stella, Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, **18**, 917 (1979); [c] R. W. Baldock, P. Hudson, A. R. Katritzky and F. Soti, *J. Chem. Soc., Perkin Trans. 1*, 1422 (1974).