Heteroatom Chemistry
Volume 16, Number 3, 2005

A Facile Synthesis of Dihydrobenzofuranols by Photocyclization of (2-Alkoxy-5-methylphenyl)(aryl) methanone and Ethyl 2-aroyl-4-methylphenyloxyacetates

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Received 17 November 2003; revised 27 September 2004

ABSTRACT: *Irradiation of 2-alkoxy substituted benzophenones* **2a–f** *and ethyl 2-aroyl-4-methylphenyloxyacetates* **2g–i** *in benzene and in acetonitrile underwent photocyclization to substituted dihydrobenzofuranols* **3a–i** *with* **3a–c** *in very less yield being racemate and* **3d–i** *in good yield being mixture of cis-trans isomers showing high stereoselectivity in benzene and decreased stereoselectivity in acetonitrile.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:212–217, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20111

INTRODUCTION

Photocyclization reactions of *o*-alkoxy aromatic carbonyl compounds have been used for synthesis of benzofuran derivatives [1–3]. Among the compounds, benzophenones have been extensively studied from a viewpoint of reaction mechanisms and synthetic applications [4–6]. Photocyclization reactions of ortho alkoxy benzophenones and its derivatives proceed via 1,5-biradical intermediates formed through δ-hydrogen abstraction by the excited carbonyl group. The isomer ratios vary according to the solvents used in the reaction [7,8]. In the literature, there are few examples that discuss in detail solvent and substituent effects on cyclization of 1,5-biradicals [9,10]. In fact, Wagner et al. have studied that photocyclization of 2-benzyloxybenzophenone and 2-benzyloxy acetophenone derivatives in nonpolar solvent like benzene, and revealed high stereoselectivity of cis isomer [5,6]. However, in the presence of Lewis base solvents stereoselectivity decreased markedly [4,6].

In this paper, we report the synthesis of substituted dihydrobenzofuranols (**3a–c)** (racemate, R = H) and **3d–i** (cis-trans isomers with regard to R and OH), using photocyclization of 2-alkoxy substituted benzophenones (**2a–f)** and ethyl-2-benzoyl phenyloxyacetates (**2g–i,** Scheme 1).

RESULTS AND DISCUSSION

Compounds **2a–i** were synthesized by the benzoylation of *p*-cresol with the corresponding acid chlorides followed by Fries rearrangement and etherification [11–13]. Their structural elucidation was confirmed by IR and ^{1}H NMR data.

Photocyclization reactions of compounds **2a–i** were conducted with a 400 W high-pressure mercury lamp (pyrex filter) in two solvents of different polarity (benzene and acetonitrile) under nitrogen atmosphere. From the results of irradiation of **2a–i,** the

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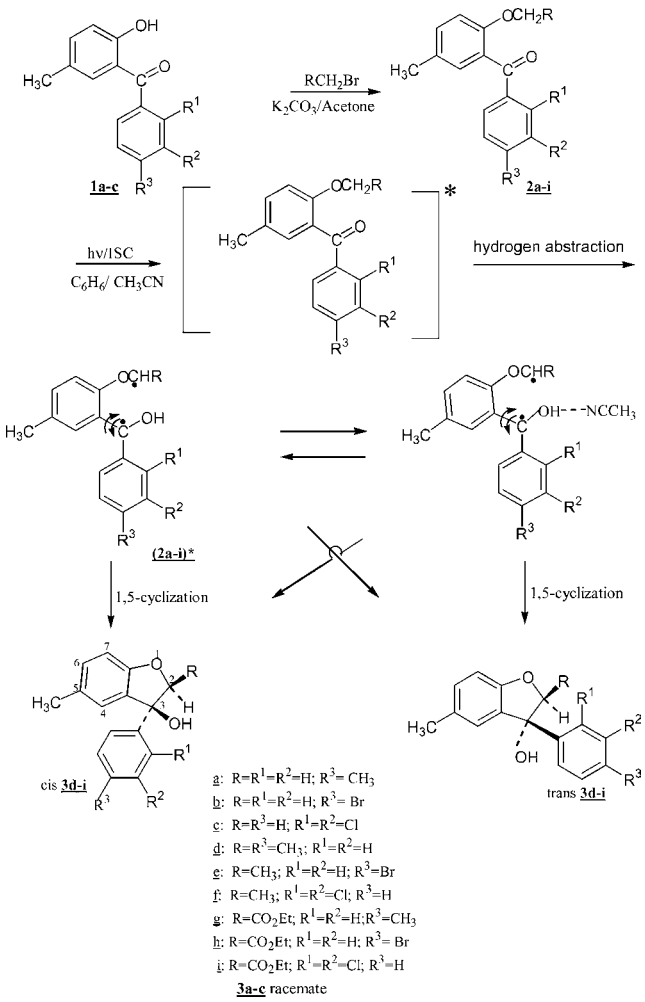

SCHEME 1

possible reaction pathway of photocyclization is as shown in Scheme 1 . During the process (n, π^*) excited triplet state is produced after intersystem crossing process (ISC) [4]. At this stage the carbonyl group abstracts δ-hydrogen to give 1,5-biradicals (**2a–i**)*. When 2-methoxy substituted benzophenones (R = H in Scheme 1) **2a–c** were irradiated in benzene as well as in acetonitrile solution, 3-aryl-2,3-dihydro-3-benzofuranols **3a–c** were obtained as a racemic mixture in 28–32% yield (Scheme 1 and Table 1).

Compounds **2a–c** generated less stable primary radical at the carbon atom adjacent to phenoxy group as in (**2a–c**)*. The products **3a–c** were formed only on long exposure of **2a–c** to UV light (13–20 h). After 10 h of exposure, only 15% of the product formed (observed by TLC). Irradiation was continued up to 20 h and gave only 28–32% of **3a–c**. In contrast, **2d–i** afforded the corresponding comparatively stable secondary radical as in (**2d–i**)* [14]. Formation of relatively stable secondary radical from **2d–i** made intramolecular δ-hydrogen abstraction favorable compared with the δ-hydrogen abstraction forming primary radical which was proved by irradiation period of **2d–i** (4–10 h), giving 76–90% of cis-trans **3d–i**. In addition to the stability of the radicals, the presence of CH_3 or bulkier group on alkoxy radical favors the stereoselective formation of cis isomer in benzene whereas in acetonitrile a mixture of cis-trans isomers was obtained.

Irradiation of 2-ethoxy substituted benzophenones **2d–f** (R = CH_3 in Scheme 1) and ethyl 2-aroyl-4-methylphenyloxyacetates **2g–i** (R = CO_2Et

TABLE 1 Time Required (h) and Yield (%) of All Compounds Prepared

							Product **3a–i**	
Starting Material	*R*	*R1*	*R2*	*R3*	*Solvent*	*Irradiation Time*	*(cis:trans)*	*Yield*
2a	H	H	H	CH_3	C_6H_6	13	**3a**	30
					CH_3CN	14		32
2b	H	H	H	Br	C_6H_6	18	**3b**	32
					CH_3CN	20		30
2c	H	Cl	Cl	H	C_6H_6	19	**3c**	28
					CH_3CN	18		31
2d	CH_3	H	H	CH_3	C_6H_6	4	**3d** (7.8:1)	88
					CH_3CN	4	(1.56:1)	82
2e	CH_3	H	H	Br	C_6H_6	8	**3e** (5.6:1)	80
					CH_3CN	9	1.71:1	76
2f	CH_3	Cl	Cl	H	C_6H_6	8	**3f** (8.5:1)	86
					CH_3CN	8	1.25:1	81
2g	CO_2Et	H	H	CH_3	C_6H_6	4	**3g** (14:1)	90
					CH_3CN	4	1.26:1	86
2h	CO_2Et	H	H	Br	C_6H_6	9	**3h** (16:1)	85
					CH_3CN	10	1.14:1	79
2i	CO_2Et	Cl	Cl	H	C_6H_6	9	**3i** (9.4:1)	83
					CH_3CN	10	1.5:1	80

in Scheme 1) in benzene solution under the same conditions gave cis isomer of benzofuranols **3d–i** as a predominant product selectively. In the experiment a small amount of trans-isomer **3d–i** was also isolated. The total yield was in the range 80–90%, and cis and trans ratio was varied from 5.6:1 to 16:1. The selectivity of cis product is attributed to little hydrogen bonding between the hydroxyl group of 1,5-biradical **(2d–i)*** and the nonpolar solvent benzene resulting in thermodynamically more stable product and hence cis ratio increases.

On the other hand, photo reactions of **2d–i** in acetonitrile solution furnished a mixture of cis and trans benzofuranols **3d–i** in 76–86% yield with cis-trans ratio ranging from 1.14:1 to 1.71:1 showing decrease in stereoselectivity. Since in polar solvent acetonitrile, intermolecular hydrogen bonding is established between hydroxyl group of 1,5-biradical and solvent molecule, which restricts the free rotation between hydroxyl group and *o*-alkoxy phenyl ring, thereby decreasing the stereoselectivity. Stereochemistry of cis and trans isomers of **3d–i** was determined by considering an anisotropic effect of C_3-phenyl group on C_2-H in the ^{1}H NMR spectra [5,9]. In substituted dihydrobenzofuranols, C_3-phenyl group shields C_2-H at the cis position, that is C_2-H chemical shift appears at a higher magnetic field than that of trans position. In a typical example, for compound **3d**, signals for C_2-H in cis isomer appeared at δ 3.9–4.2 and in trans isomer signals appeared at δ 4.3–4.5. Small difference in steric bulkiness between the substituted phenyl group and the hydrogen bonded hydroxyl group would make both counterclockwise and clockwise rotations possible resulting in decreased stereoselectivity in polar solvent acetonitrile. The large difference in cis and trans ratios from reaction in benzene and acetonitrile is attributed to the solvent effect.

Intramolecular cyclization of (**2a–i**)* afforded racemate-substituted dihydrobenzofuranols **3a–c** and cis-trans isomers of substituted dihydrobenzofuranols **3d–i**. But the presence of methyl group in 1,5-biradical (**2d–f**)*, which is electron releasing, stabilizes the 1,5-biradical intermediate and gives good yield of substituted dihydrobenzofuranols in a short time irradiation compare to irradiation period of **2a–c**. Irradiation period of **2a, 2d**, and **2g** is less than that of **2b–c, 2e–f** and **2h–i** respectively. This is due to the presence of CH_3 group on phenyl ring which is also electron releasing that favors the cyclization of 1,5-biradical. Under similar conditions, electron withdrawing group bromo in **2b, 2e, 2h** and also chloro group in **2c, 2f, 2i** destabilizes the 1,5-biradical there by decrease in the rate of cyclization.

EXPERIMENTAL

The melting points are uncorrected. Column chromatography was performed on silica gel (60–120 mesh). Unless otherwise stated anhydrous sodium sulfate was employed as a drying agent. Benzene for photoreactions was dried by distilling over sodium metal, and 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-400HA) with pyrex filter. The IR spectra in Nujol were determined on a Shimadzu 8300 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded on 300 and 75 MHz respectively, in deuterated chloroform ($CDCl_3$) using tetramethylsilane (TMS) as an internal standard.

The substituted benzophenone **1a–c** was prepared by Fries rearrangement according to the procedure described by Vogel [11] and Olah et al. [12]. These compounds have been thoroughly characterized by IR and ^{1}H NMR spectral data and were purified by column chromatography prior to use.

General Procedure for **2a–i**

A mixture of (2-hydroxy-5-methylphenyl)(aryl)-methanone **1** (10 mmol), alkyl bromide/ethyl bromo acetate (10 mmol), potassium carbonate (20 mmol), and acetone (25 mL) was refluxed for 4 h [13]. After the removal of insoluble material by filtration, water (25 mL) was added and extracted with ether (3 × 30 mL). Ether layer was washed with 5% sodium hydroxide (3 × 15 mL) and then with water (2 × 15 mL). Ether layer was dried with anhydrous sodium sulfate and evaporated. The residue was chromatographed and eluted with benzene-afforded product **2**.

2a: Yield 83% (1.99 g), mp 160–62°C; IR (Nujol): 1658 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 3H, Ar-CH_3), 2.32 (s, 3H, Ar-CH_3), 3.6 (s, 3H, OCH_3), 6.7–7.7 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 20.9 (q), 56.0 (q), 113.7 (d), 123.3 (s), 128.9 (d), 129.9 (s), 130 (d), 131.8 (d), 133.9 (d), 134.8 (s), 141.4 (s), 160.6 (s) 187.0 (s). Anal. Calcd for $C_{16}H_{16}O_2$(240):C, 80.0; H, 6.67%. Found: C, 80.12; H, 6.63%.

2b: Yield 75% (2.29 g), mp 55–58°C; IR (Nujol): 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 2.23 (s, 3H, Ar-CH_3), 3.55 (s, 3H, OCH_3), 6.65–7.5 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 20.9 (q), 56.0 (q), 113.7 (d), 123.3 (s), 126.8 (s), 129.7 (s), 131.5 (d), 131.8 (d), 132.3 (d), 133.9 (d), 136.8 (s), 160.6 (s), 187.0 (s). Anal. Calcd for $C_{15}H_{13}BrO_2$(305): C, 59.02; H, 4.26; Br, 26.23%. Found: C, 58.95; H, 4.25; Br, 26.21%.

2c: Yield 71% (2.09 g), mp 150–52°C; IR (Nujol): 1659 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 2.22 (s, 3H,

Ar-CH_3), 3.5 (s, 3H, OCH_3), 6.6–7.8 (bm, 6H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 20.9 (q), 56.0 (q), 113.7 (d), 123.3 (s), 127.7 (d), 129.6 (d), 129.7 (s), 131.8 (d), 133.9 (s), 133.9 (d), 134.0 (d), 135.8 (s), 139.6 (s), 160.6 (s), 187.0 (s). Anal. Calcd for $C_{15}H_{12}Cl_2O_2$ (295): C, 61.02; H, 4.07; Cl, 24.07%. Found: C, 60.89; H, 4.02; Cl, 24.05%.

2d: Yield 77% (1.96 g), liquid; IR (neat): 1650 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 1.3 (t, $J = 7$ Hz, 3H, CH_3), 2.2 (s, 3H, Ar-CH_3), 2.4 (s, 3H, Ar-CH_3), 4.1 (q, $J = 7$ Hz, 2H, OCH_2), 6.7–7.7 (bm, 7H, Ar-H) ;^{13}C NMR ($CDCl_3$): δ 14.3 (q), 20.9 (q), 65.1 (t), 113.8 (d), 123.4 (s), 128.9 (d), 129.0 (s), 130.0 (d), 131.4 (d), 133.5 (d), 134.8 (s), 141.4 (s), 157.7 (s), 187.0 (s). Anal. Calcd for $C_{17}H_{18}O_2$(254): C, 80.31; H, 7.09%. Found: C, 80.5; H, 7.1%.

2e: Yield 82% (2.62 g), pale yellow liquid; IR (neat): 1660 cm^{-1}(C=O); ^{1}H NMR ($CDCl_3$): δ 1.3 (t, $J = 7$ Hz, 3H, CH_3), 2.23 (s, 3H, Ar-CH_3), 4.1 (q, $J = 7$ Hz, 2H, OCH_2), 6.65–7.5 (bm, 7H, Ar-H);^{13}C NMR ($CDCl_3$): δ 14.3 (q), 20.9 (q), 65.1 (t), 113.8 (d), 123.4 (s), 126.8 (s), 129.0 (s), 131.4 (d), 131.5 (d), 132.3 (d), 133.5 (d), 136.8 (s), 157.4 (s), 187.0 (s). Anal. Calcd for $C_{16}H_{15}BrO_2$(319): C, 60.19; H, 4.70; Br, 24.6%. Found: C, 60.09; H, 4.65; Br, 24.4%.

2f: Yield 75% (2.42 g), pale yellow liquid; IR (neat): 1659 cm^{-1}(C=O); ^{1}H NMR ($CDCl_3$): δ 1.3 (t, $J = 7$ Hz, 3H, CH_3), 2.22 (s, 3H, Ar-CH_3), 4.1 (q, $J = 7$ Hz, 2H, OCH_2), 6.6–7.5 (bm, 6H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 14.3 (q), 20.9 (q), 61.1 (t), 113.8 (d), 123.4 (s), 127.7 (d), 129.0 (s), 129.6 (d), 131.4 (d), 133.5 (d) 133.9 (s), 134.0 (d), 135.8 (s), 139.6 (s), 157.4 (s), 187.0 (s). Anal. Calcd for $C_{16}H_{14}Cl_2O_2$(323): C, 62.14; H, 4.53; Cl, 22.72%. Found: C, 62.11; H, 4.51; Cl, 22.68%.

2g: Yield 90% (2.81 g), liquid; IR(neat): 1760 (ester, C=O); 1664 cm^{-1}(C=O); ^{1}H NMR ($CDCl_3$): δ 1.2 (t, $J = 7$ Hz, 3H, ester CH_3), 2.4 (s, 3H, Ar-CH_3), 2.45 (s, 3H, Ar-CH_3), 4.2 (q, $J = 7$ Hz, 2H, ester O-CH_2), 4.5 (s, 2H, OCH_2), 6.5–7.8 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.6 (q), 20.9 (q), 20.9 (q), 59.5 (t), 75.6 (t), 113.7 (d), 123.0 (d), 128.9 (d), 129.9 (s), 130.6 (d), 131.8 (d), 133.9 (d), 134.8 (s), 141.4 (s), 160.6 (s) 171.0 (s), 187.0 (s). Anal. Calcd for $C_{19}H_{20}O_4$(312): C, 73.08; H, 6.41%. Found: C, 7310; H, 6.38%.

2h: Yield 88% (3.32 g), brown liquid; IR (neat): 1763 (ester, C=O); 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 1.2 (t, $J = 7$ Hz, 3H, ester CH_3), 2.3 (s, 3H, Ar-CH_3), 4.2 (q, $J = 7$ Hz, 2H, ester O-CH_2), 4.5 (s, 2H, OCH_2), 6.5–7.8 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.6 (q), 20.9 (q), 59.5 (t), 75.6 (t), 113.7 (d), 123.3 (s), 126.8 (s), 129.7 (s), 131.5 (d), 131.8 (d), 132.3 (d), 133.9 (d), 136.8 (s), 160.6 (s), 171.0 (s), 187.0 (s). Anal. Calcd for $C_{18}H_{17}BrO_4$(377): C, 57.29; H, 4.51; Br, 21.22%. Found: C, 57.30; H, 4.50; Br, 21.28%.

2i: yield 74% (2.71 g), liquid; IR (neat): 1762 (ester, C=O); 1661 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ 1.2 (t, $J = 7$ Hz, 3H, ester CH_3), 2.2 (s, 3H, Ar-CH_3), 4.15 (q, $J = 7$ Hz, 2H, ester O-CH_2), 4.45 (s, 2H, OCH_2), 6.65–7.7 (bm, 6H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.6 (q), 20.9 (q), 59.5 (t), 75.6 (t), 113.7 (d), 123.3 (s), 127.7 (d), 129.6 (d), 129.7 (s), 131.8 (d), 133.9 (d), 134.0 (d), 139.6 (s), 160.6 (s), 171.0 (s), 187.0 (s). Anal. Calcd for $C_{18}H_{16}Cl_2O_4$(367): C, 58.86; H, 4.36; Cl, 19.35%. Found: C, 58.78; H, 4.32; Cl, 19.31%.

General Procedure for **3a–i**

In benzene or in acetonitrile solvent (50 mL), the starting material **2** (15 mmol) was dissolved and deoxygenated by bubbling nitrogen gas for 1 h and then irradiated for 4–20 h. After the completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure at 40°, the residue chromatographed and eluted with hexane : chloroform : acetone mixture (7:3:1) to give **3**.

3a: mp 156–157°C; IR (Nujol): 3410 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 2.4 (s, 3H, Ar-CH_3), 2.5 (s, 3H, Ar-CH_3), 3.9 (s, 1H, C_2-H), 4.3 (s, 1H, C_2-H), 6.0–6.2 (bs, 1H, OH), 7.2–8.0 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 20.9 (q), 21.2 (q), 80.5 (t), 88.3 (s), 114.6 (d), 127.3 (d), 128.3 (d), 128.6 (s), 129.7 (d), 129.8 (s), 135.2 (s), 140.0 (s), 155.7 (s). Anal. Calcd for $C_{16}H_{16}O_2$(240): C, 80.0; H, 6.67%. Found: C, 79.60; H, 6.62%.

3b: mp 155–157°C; IR (Nujol): 3420 cm^{-1}(OH); ^{1}H NMR ($CDCl_3$); δ 2.4 (s, 3H, Ar-CH_3), 3.8 (s, 1H, C_2-H), 4.4 (s, 1H, C_2-H), 6.0–6.2 (bs, 1H, OH), 7.2–8.0 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 21.2 (q), 80.5 (t), 88.3 (s), 114.6 (d), 120.6 (s), 127.3 (d), 128.3 (d), 128.6 (s), 129.7 (d), 129.8 (s), 155.7 (s). Anal. Calcd for $C_{15}H_{13}BrO_2$(305): C, 59.02; H, 4.26; Br, 26.23%. Found: C, 59.0; H, 4.21; Br 26.18%.

3c: mp 158–159°C; IR (Nujol): 3415 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$): 2.4 (s, 3H, Ar-CH_3), 3.9 (s, 1H, C_2-H), 4.4 (s, 1H, C_2-H), 6.0–6.3 (bs, 1H, OH), 7.2–8.0 (bm, 6H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 21.2 (q), 78.7 (s), 80.0 (t), 114.6 (d), 127.3 (d), 127.8 (d), 127.9 (d), 128.5 (d), 128.6 (s), 129.7 (d), 129.8 (s), 134.1 (s), 134.7 (s), 144.8 (s), 155.7 (s). Anal. Calcd for $C_{15}H_{12}Cl_2O_2$(295): C, 61.02; H, 4.07; Cl, 24.07%. Found: C, 61.0; H, 4.08; Cl, 23.04%.

Cis-3d: mp 158–159°C; IR (Nujol): 3410 cm^{-1}(OH); ^{1}H NMR ($CDCl_3$): δ 1.22 (d, $J = 7$ Hz, 3H, C_2-CH_3), 2.4 (s, 3H, Ar-CH_3), 2.6 (s, 3H, Ar-CH_3), 3.9–4.2 (q, $J = 7$ Hz ,1H, C_2-H), 6.1–6.2 (bs, 1H, OH), 7.3–8.1 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.8(q), 20.9 (q), 21.2 (q), 83.9 (d), 94.7 (s), 114.6 (d), 127.3 (d), 128.3 (d), 128.6 (s), 129.7 (d), 129.8

(s), 135.2 (s), 140.0 (s), 155.7 (s). Anal. Calcd for $C_{17}H_{18}O_2$(254): C, 80.31; H, 7.09%. Found: C, 80.11; H, 7.05%.

Trans-3d: mp 146–148°C; IR (Nujol): 3400 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 1.15–1.56 (d, $J = 7$ Hz, 3H, C_2-CH_3), 2.2 (s, 3H, Ar-CH_3), 2.4 (s, 3H, Ar-CH_3), 4.3–4.5 (q, $J = 7$ Hz, 1H, C_2-H), 6.0–6.2 (bs, 1H, OH), 7.2–7.8 (bm, 7H, Ar-H);^{13}C NMR ($CDCl_3$): δ 13.8 (q), 20.9 (q), 21.2 (q), 82.9 (d), 93.7 (s), 114.6 (d), 127.3 (d), 128.3 (d), 128.6 (s), 129.7 (d), 129.8 (s), 135.2 (s), 140.0 (s), 155.7 (s). Anal. Calcd for $C_{17}H_{18}O_2$(254): C, 80.31; H, 7.09%. Found: C, 80.10; H, 7.04%.

Cis-3e: mp 160–162°C; IR (Nujol): 3410 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 1.09–1.10 (d, $J = 7$ Hz, 3H, C_2-CH_3), 2.4 (s, 3H, Ar-CH_3), 3.7–4.0 (q, $J = 7$ Hz, 1H, C_2-H), 6.1–6.2 (bs, 1H, OH), 7.3–8.1 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.8 (q), 21.2 (q), 83.9 (d), 88.3 (s) 114.6 (d), 120.6 (s), 127.3(d), 128.6 (s), 129.7 (d), 129.8 (s), 130.6 (d), 132.3 (d), 142.0 (s), 155.7 (s). Anal. Calcd for $C_{16}H_{15}BrO_2$(319): C, 60.19; H, 4.70; Br, 24.6%. Found: C, 60.15; H, 4.71; Br, 24.4%.

Trans-3e: mp 118–119°C; IR (Nujol): 3400 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 1.15–1.6 (d, $J = 7$ Hz , 3H, C_2-CH_3), 2.2 (s, 3H, Ar-CH_3), 4.0–4.3 (q, $J = 7$ Hz , 1H, C_2-H), 6.0–6.2 (bs, 1H, OH), 7.2–7.8 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.8 (q), 21.2 (q), 82.9 (d), 87.3 (s), 114.6 (d), 120.6 (s), 127.3(d), 128.6 (s), 129.7 (d), 129.8 (s), 130.6 (d), 132.3 (d), 142.0 (s), 155.7 (s). Anal. Calcd for $C_{16}H_{15}BrO_2$(319): C, 60.19, H, 4.70, Br, 24.6%. Found: C, 60.15, H, 4.68, Br, 24.3%.

Cis-3f: mp 162–164°C; IR (Nujol): 3410 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 1.1–1.2 (d, $J = 7$ Hz , 3H, C_2-CH_3), 2.4 (s, 3H, Ar-CH_3), 3.8–4.0 (q, $J = 7$ Hz , 1H, C_2-H), 6.1–6.2 (bs, 1H, OH), 7.3–8.1 (bm, 6H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.8 (q), 21.2 (q), 83.9 (d), 94.7 (s), 114.6 (d), 127.3 (d), 127.8 (d), 128.5 (d), 128.6 (s), 129.7 (d), 129.8 (s), 129.9 (d), 134.1 (s), 144.8 (s), 155.7 (s). Anal. Calcd for $C_{16}H_{16}Cl_2O_2$(323): C, 62.14; H, 4.53; Cl, 22.98%. Found: C, 62.11; H, 4.48; Cl, 22.95%.

Trans-3f: mp 112–113°C; IR (Nujol): 3400 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$): δ 1.15–1.17 (d, $J = 7$ Hz , 3H, C_2-CH_3), 2.2 (s, 3H, Ar-CH_3), 4.1–4.4 (q, $J = 7$ Hz , 1H, C_2-H), 6.0–6.2 (bs, 1H, OH), 7.2–7.8 (bm, 6H, Ar-H);^{13}C NMR ($CDCl_3$): δ 13.8 (q), 21.2 (q), 82.9 (d), 93.7 (s), 114.6 (d), 127.3 (d), 127.8 (d), 128.5 (d), 128.6 (s), 129.7 (d), 129.8 (s), 129.9 (d), 134.1 (s), 144.8 (s), 155.7 (s). Anal. Calcd for $C_{16}H_{16}Cl_2O_2$(323): C, 62.14; H, 4.53; Cl, 22.98%. Found: C, 62.11; H, 4.51; Cl, 22.95%.

Cis-3g: mp 120–122°C; IR (Nujol): 3420–3480 (OH), 1745 cm^{-1} (ester C=O);^{1}H NMR ($CDCl_3$): δ 1.1–1.3 (t, $J = 7$ Hz, 3H, ester CH_3), 2.1 (s, 3H, Ar-CH_3), 2.3 (s, 3H, Ar-CH_3), 3.6–3.8 (q, $J = 7$ Hz , 2H, ester CH_2), 3.9 (s, 1H, C_2-H), 5.1–5.3 (bs, 1H, OH), 7.3–7.8 (bm, 7H, Ar-H);^{13}C NMR ($CDCl_3$): δ 13.6 (q), 20.9 (q), 21.2 (q), 59.8 (t), 87.6 (s), 93.6 (d), 114.6 (d), 127.3 (d), 128.3 (d), 128.6 (s), 129.7 (d), 129.8 (s), 135.2 (s), 140.0 (s), 155.7 (s), 172 (s). Anal. Calcd for $C_{19}H_{20}O_4$(312): C, 73.08; H, 6.41%. Found: C, 73.05; H, 6.38%.

Trans-3g: mp 90–95°C; IR (Nujol): 3420–3480 (OH), 1745 cm^{-1} (ester C=O); ^{1}H NMR ($CDCl_3$): δ 1.2–1.4 (t, $J = 7$ Hz, 3H, ester CH_3), 2.4 (s, 3H, Ar-CH_3), 2.6 (s, 3H, Ar-CH_3), 4.0–4.2 (q, $J = 7$ Hz, 2H, ester CH_2), 4.3 (s, 1H, C_2-H), 5.2–5.4 (bs, 1H, OH), 7.3-7.8 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.6 (q), 20.9 (q), 21.2 (q), 59.8 (t), 86.6 (s), 92.6 (d), 114.6 (d), 127.3 (d), 128.3 (d), 128.6 (s), 129.7 (d), 129.8 (s), 135.2 (s), 140.0 (s), 155.7 (s), 172 (s). Anal. Calcd for $C_{19}H_{20}O_4$(312): C, 73.08; H, 6.41%. Found: C, 73.06; H, 6.37%.

Cis-3h: mp 130–132°C; IR (Nujol): 3340–3380 (OH), 1763 cm^{-1} (ester C=O); ^{1}H NMR ($CDCl_3$): δ 1.2–1.4 (t, $J = 7$ Hz, 3H, ester CH_3), 2.3 (s, 3H, Ar-CH_3), 3.4–3.7 (q, $J = 7$ Hz, 2H, ester CH_2), 4.0 (s, 1H, C_2-H), 5.2–5.4 (bs, 1H, OH), 6.5–7.8 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.6 (q), 21.2 (q), 59.8 (t), 87.6 (s), 93.6 (d), 114.6 (d), 120.6 (s), 127.3 (d), 128.6 (s), 129.7 (d), 130.6 (d), 132.3 (d), 142.0 (s), 155.7 (s), 172.0 (s). Anal. Calcd for $C_{18}H_{17}BrO_4$(377): C, 57.24; H, 4.51; Br, 21.22%. Found: C, 57.23; H, 4.50; Br, 21.20%.

Trans-3h: mp 85–88°C; IR (Nujol): 3460–3500 (OH), 1763 cm^{-1}(ester C=O); ^{1}H NMR ($CDCl_3$): δ 1.2–1.4 (t, $J = 7$ Hz, 3H, ester CH_3), 2.3 (s, 3H, Ar-CH_3), 4.2–4.4 (q, $J = 7$ Hz, 2H, ester CH_2), 4.45 (s, 1H, C_2-H), 5.2–5.3 (bs, 1H, OH), 7.1–7.8 (bm, 7H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.6 (q), 21.2 (q), 59.8 (t), 86.6 (s), 92.6 (d), 114.6 (d), 120.6 (s), 127.3 (d), 128.6 (s), 129.7 (d), 130.6 (d), 132.3 (d), 142.0 (s), 155.7 (s), 172.0 (s). Anal. Calcd for $C_{18}H_{17}O_4Br$ (377): C, 57.29; H, 4.51; Br, 21.22%. Found: C, 57.25; H, 4.49; Br, 21.21%.

Cis-3i: mp 128–130°C; IR (Nujol): 3460–3500 (OH), 1762 cm^{-1}(ester C=O);^{1}H NMR ($CDCl_3$): δ 1.2–1.4 (t, $J = 7$ Hz, 3H, ester CH_3), 2.2 (s, 3H, Ar-CH_3), 3.7–4.0 (q, $J = 7$ Hz, 2H, ester CH_2), 4.1 (s, 1H, C_2-H), 5.0–5.2 (bs, 1H, OH), 7.0–7.7 (bm, 6H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 13.6 (q), 21.2 (q), 78.0 (s), 93.1 (d), 114.6 (d), 127.3 (d), 127.6 (d), 127.9 (d), 128.5 (d), 128.6 (s), 129.7 (d), 129.8 (s), 134.1 (s), 134.7 (s), 144.8 (s), 155.7 (s), 172.0 (s). Anal. Calcd for $C_{18}H_{16}Cl_2O_4$(367): C, 58.86, H, 4.36, Cl, 19.35%. Found: C, 58.85; H, 4.4; Cl, 19.32%.

Trans-3i: mp 80–82°C; IR (Nujol): 3460–3500 (OH), 1762 cm^{-1}(ester C=O);^{1}H NMR ($CDCl_3$): δ 1.3–1.5 (t, $J = 7$ Hz, 3H, ester CH_3), 2.2 (s, 3H, Ar-CH_3), 4.15–4.4 (q, $J = 7$ Hz, 2H, ester CH_2), 4.5 (s, 1H, C_2-H), 4.6–4.9 (bs, 1H, OH), 6.65–7.7 (bm, 6H, Ar-H);

^{13}C NMR ($CDCl_3$): δ 13.6 (q), 21.2 (q), 77.0 (s), 92.1 (d), 114.6 (d), 127.3 (d), 127.6 (d), 127.9 (d), 128.5 (d), 128.6 (s), 129.7 (d), 129.8 (s), 134.1 (s), 134.7 (s), 144.8 (s), 155.7 (s), 172.0 (s). Anal. Calcd for $C_{18}H_{16}Cl_2O_4$(367): C, 58.86; H, 4.36; Cl, 19.35%. Found: C, 58.83; H, 4.33; Cl, 19.31%.

CONCLUSION

In conclusion, we have synthesized a new series of dihydrobenzofuranols using photocyclization reaction in two solvents of different polarity and studied the electronic effect of the substituents at ortho, meta, para positions on intramolecular cyclization of 1,5-biradicals. From the above results, photocyclization of 2-alkoxy substituted benzophenones and their derivatives was a useful method for preparation of substituted dihydrobenzofuranols. Effect of substituents on rate of cyclization was confirmed by irradiation period (Table 1).

AKNOWLEDGMENTS

The authors express their sincere gratitude to University of Mysore, Mysore., for the laboratory facility. Two of the authors (BSS and SAK) are indebted to the UGC for the award of teacher's fellowship.

REFERENCES

[1] Sharshira, E. M.; Iwanami, H.; Okamura, M.; Hasegawa, E.; Horaguchi, T. J Heterocycl Chem 1996, 33, 17.
[2] Sharshira, E. M.; Iwanami, H.; Okamura, M.; Hasegawa, E.; Horaguchi, T. J Heterocycl Chem 1996, 33, 137.
[3] Sharshira, E. M.; Shimada, S.; Okamura, M.; Hasegawa, E.; Horaguchi, T. J Heterocycl Chem 1996, 33, 1797.
[4] Wagner, P. J.; Meador, M. A.; Scaiano, J. C. J Am Chem Soc 1984, 106, 7988.
[5] Wagner, P. J.; Meador, M. A.; Park, B. S. J Am Chem Soc 1990, 112, 5199.
[6] Wagner, P. J.; Jang, J. S. J Am Chem Soc 1993, 115, 7914.
[7] Wagner, P. J. J Am Chem Soc 1967, 89, 5898.
[8] Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. J Am Chem Soc 1972, 94, 7489.
[9] Pappas, S. P.; Pappas, B. C.; Blackwell, J. E. J Org Chem 1967, 32, 3066.
[10] Pappas, S. P.; Zehr, R. D. J Am Chem Soc 1971, 93, 7112.
[11] Vogel, A. I. Text Book of Practical Organic Chemistry, 5th ed; ELBS Longman 1989; p. 982.
[12] Olah, G. A.; Arvanghi, M.; Krishnamurthy, V. V. J Org Chem 1983, 48, 3359.
[13] Chatterjea, J. N.; Mehrotra, V. N.; Roy, S. K. Chem Ber 1963, 96, 1156.
[14] March, J. Advanced Organic Chemistry, 3rd ed; Wiley Eastern: New Delhi, 1992; p. 162.