Solution-phase photochemical transformation of 2-aroylbenzofurans: addition–elimination mechanism

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Abstract An efficient conversion of 2-aroylbenzofurans into arylbenzofurylmethanols through photoreduction has been described. In these molecules, the photo transformation occurred through the initial addition of solvent followed by elimination involving γ -hydrogen abstraction. The photoproduct distribution markedly depends upon the substituent present on the benzofuran moiety.

Keywords 2-Aroylbenzofurans \cdot Photoreduction $\cdot \gamma$ -Hydrogen abstraction \cdot Addition–elimination

Introduction

Synthetic organic photochemistry—chemistry of the electronic excited states of a molecule—differs from ground state chemistry and affords a convenient approach to complex structures that are difficult to obtain by traditional synthetic methods. The photochemistry of O-heterocycles is a less developed area as compared to carbon aromatics [1–4], such as benzene, naphthalene, and anthracene derivatives. Numerous types of conjugated O-heterocyclic compounds [5, 6] play important roles in both natural and artificial systems due to their particular photochemical and photophysical properties. From synthetic and mechanistic perspectives, benzofuran derivatives [7, 8] showing very interesting photochemical and photophysical properties are among the most extensively investigated organic compounds. Benzofuran [9] and its derivatives are widely distributed in nature, particularly among the plant monarchy. The benzofuran derivatives hold importance in molecular biology such as in the treatment of osteoporosis [10, 11], as anesthetic agents [12, 13], inhibitors of platelets aggregations [14], inhibitors of xanthine

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oxidase [15], antiarrhythmics [16, 17], anti-HIV agents [12], agonists of benzodiazepines [18], and as inhibitors of ATPase [19]. Some of these derivatives have also found applications as sedatives [20], agrochemicals [21], cosmetics [22], and dyes [23, 24], and as the building blocks of optical brighteners [25]. In addition to the biological properties, benzofuran derivatives have fascinating photo-luminescent properties due to their conjugated π -system [26, 27]. Moreover, some benzofuran derivatives have been used as light collectors in photovoltaic cells [28, 29].

In the light of the enormous interest in terms of versatile photochemistry and other applications as above, in this paper, we endeavored to study the photochemistry of some benzoyl derivatives of benzofuran. The salient feature of these substrates is their extended conjugation, as in these compounds the benzofuran ring is substituted with the benzoyl group at the 2-position and with a CH_3 group at the 3-position on the benzofuran moiety. The main focus is to explore the photolytic behavior of these specially designed 2-aroylbenzofurans with the objectives: (1) to observe the intramolecular γ -H abstraction by C=O from the suitably positioned 3-CH₃ group on the benzofuran moiety, (2) to analyze the direct intermolecular hydrogen transfer for photoreduction from the solvent to the C=O group of the substrate, (3) to examine the other photochemical reactions like the addition of solvent, etc. to the substrates as these have the chromophores as double bonds, (4) to analyze the ring photochemistry of the photoreduction of the carbonyl chromophore, (5) to explore the ring photochemistry of benzofurans, and (6) to investigate the formation of dimeric products.

Experimental

General

The nuclear magnetic resonance ¹H NMR (300 MHz) and proton-decoupled ¹³C NMR (75.4 MHz) spectra were recorded on a Bruker spectrometer using TMS as internal standard. The infrared (IR) spectra were scanned in KBr pellets on a MB3000 FT-IR with Horizon MBTM FTIR software from ABB Bomen. The mass spectral data was obtained on a Waters Q-TOF Micromass (LC–MS) spectrometer. Melting points were determined in open capillaries and are uncorrected. The photoirradiation of the deaerated solution of substrates was carried out using a Pyrex filter under nitrogen atmosphere from a 125 W Hg lamp. The columns for chromatographic separation were packed in petroleum ether with silica gel and were eluted with petroleum ether and ethyl acetate mixture (99:1).

Synthesis of 2-aroylbenzofurans

Synthesis of 2-(4-bromobenzoyl)-3-methylbenzofuran **3a** A mixture of o-hydroxyacetophenone (1.36 g, 0.01 mol), α -bromoketone (2.62 g, 0.01 mol), Na₂CO₃ (2.12 g, 0.02 mol) and n-Bu₄N⁺I⁻ (0.01 mol) was mixed in a mortar with pestle. This mixture was transferred to a round-bottom flask containing 10.0 ml water and then refluxed on a heating mantle. After completion of the reaction (30 min, TLC), the reaction mixture was cooled at room temperature. The brown-colored solid thus obtained was filtered, dried, and purified by column chromatography on silica gel (100–200 mesh) using petroleum ether/ethyl acetate as eluent mixture (petroleum ether:EtOAc::99:1) to remove the coloured impurities that furnished the pure white product.

The other 2-aroylbenzofurans **3b–e** and **3a'–e'** were also synthesized following a similar procedure by condensing the respective *o*-hydroxyacetophenones with α -bromoketones.

2-(4-Bromobenzoyl)-3-methylbenzofuran **3a** Yield 2.35 g (75 %), white solid, mp 80–82 °C; v_{max} (cm⁻¹): 1643 (C=O); δ_{H} (CDCl₃): 8.03 (d, 2H, $J_o = 8.4$ Hz, H-2", 6"), 7.74–7.70 (m, 1H, H-7), 7.68–7.53 (m, 4H, H-4, 6, 3", 5"), 7.39–7.37 (m, 1H, H-5), 2.68 (s, 3H, 3-CH₃); δ_{C} (CDCl₃): 184.49 (C=O), 154.17, 147.89, 136.38, 132.12, 131.53, 130.33, 129.01, 128.39, 127.64, 123.37, 121.45, 112.14, 10.01. Mass (*m*/*z*) ES+: 316.7, 314.7 (M⁺), 184.9, 182.9, 159.1 (100), 156.9, 154.9; Anal. Calcd. for C₁₆H₁₁BrO₂: C, 60.98; H, 3.52. Found: C, 60.93; H, 3.47.

2-(4-Bromobenzoyl)-5-chloro-3,6-dimethylbenzofuran **3b** Yield 2.78 g (77 %), white solid, mp 141–142 °C; v_{max} (cm⁻¹): 1643 (C=O); δ_{H} (CDCl₃): 7.94 (d, 2H, $J_{o} = 8.1$ Hz, H-2″, 6″), 7.64 (d, 2H, $J_{o} = 8.1$ Hz, H-3″, 5″), 7.40 (s, 1H, H-4), 7.24 (s, 1H, H-7), 2.58 (s, 3H, 3-CH₃), 2.50 (s, 3H, 6-CH₃); δ_{C} (CDCl₃): 184.15 (C=O), 152.93, 147.58, 137.02, 136.37, 131.64, 131.27, 130.13, 128.37, 128.22, 126.84, 121.16, 113.78, 21.23, 10.03. Mass (*m*/*z*) ES+: 367.0, 365.0, 363.0 (M⁺), 209.0, 207.0 (100), 184.9, 182.9, 156.9, 154.9; Anal. Calcd. for C₁₇H₁₂BrClO₂: C, 56.15; H, 3.33. Found: C, 56.19; H, 3.36.

2-(4-Bromobenzoyl)-3,5-dimethylbenzofuran **3c** Yield 2.69 g (82 %), white solid, mp 96–98 °C; v_{max} (cm⁻¹): 1,636 (C=O); $\delta_{\rm H}$ (CDCl₃): 8.01 (d, 2H, $J_{\rm o}$ = 8.4 Hz, H-2", 6"), 7.68 (d, 2H, $J_{\rm o}$ = 8.4 Hz, H-3", 5"), 7.50 (d, 1H, $J_{\rm m}$ = 1.5 Hz, H-4), 7.43 (d, 1H, $J_{\rm o}$ = 8.4 Hz, H-7), 7.34 (dd, 1H, $J_{\rm o}$ = 8.4 Hz, $J_{\rm m}$ = 1.5 Hz, H-6), 2.66 (s, 3H, 3-CH₃), 2.52 (s, 3H, 5-CH₃); $\delta_{\rm C}$ (CDCl₃): 184.56 (C=O), 152.83, 148.23, 136.62, 133.07, 131.58, 131.31, 130.04, 129.20, 127.59, 127.33, 120.98, 111.74, 21.36, 10.03; Mass (*m*/*z*) ES+: 330.7, 328.7 (M⁺), 173.0 (100), 184.9, 182.9, 156.9, 154.9; Anal. Calcd. for C₁₇H₁₃BrO₂: C, 62.03; H, 3.98. Found: C, 62.08; H, 3.93.

5-Bromo-2-(4-bromobenzoyl)-3-methylbenzofuran **3d** Yield 3.14 g (80 %), white solid, mp 126–128 °C; v_{max} (cm⁻¹): 1,643 (C=O); $\delta_{\rm H}$ (CDCl₃): 7.99 (d, 2H, $J_{\rm o} = 8.4$ Hz, H-2", 6"), 7.86 (d, 1H, $J_{\rm m} = 1.8$ Hz, H-4), 7.69 (d, 2H, $J_{\rm o} = 8.4$ Hz, H-3", 5"), 7.61 (dd, 1H, $J_{\rm o} = 8.7$ Hz, $J_{\rm m} = 1.8$ Hz, H-6), 7.44 (d, 1H, $J_{\rm o} = 8.7$ Hz, H-7), 2.64 (s, 3H, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 184.37 (C=O), 152.87, 148.85, 136.18, 131.71, 131.35, 131.28, 131.05, 128.01, 126.43, 124.19, 116.62, 113.77, 9.91. Mass (*m*/*z*) ES+: 396.8, 394.8, 392.8 (M⁺), 238.9, 236.9 (100), 184.9, 182.9, 156.9, 154.9; Anal. Calcd. for C₁₆H₁₀Br₂O₂: C, 48.77; H, 2.56. Found: C, 48.72; H, 2.51.

2-(4-Bromobenzoyl)-5-chloro-3-methylbenzofuran **3e** Yield 2.72 g (78 %), white solid, mp 106–108 °C; v_{max} (cm⁻¹): 1,643 (C=O); δ_{H} (CDCl₃): 8.03 (d, 2H,

 $\begin{array}{l} J_{\rm o} = 8.4 ~{\rm Hz}, {\rm H-2''}, 6''), 7.69-7.68 ~{\rm (m, 3H, H-4, 3'', 5'')}, 7.48-7.47 ~{\rm (m, 2H, H-6, 7)}, \\ 2.64 ~{\rm (s, 3H, 3-CH_3)}; ~\delta_{\rm C} ~{\rm (CDCl_3)}; ~184.38 ~{\rm (C=O)}, ~152.51, ~149.04, ~136.19, ~131.70, \\ 131.28, ~130.44, ~129.27, ~128.72, ~128.00, ~126.60, ~121.02, ~113.36, ~9.92. ~{\rm Mass}~(m/z) \\ {\rm ES+:} ~353.2, ~351.2, ~349.2 ~{\rm (M^+)}, ~195.1, ~193.1 ~{\rm (100)}, ~184.9, ~182.9, ~156.9, ~154.9; \\ {\rm Anal.} ~{\rm Calcd.}~{\rm for}~{\rm C_{16}H_{10}BrClO_2}; ~{\rm C}, ~54.97; ~{\rm H}, ~2.88. ~{\rm Found}; ~{\rm C}, ~54.90; ~{\rm H}, ~2.81. \end{array}$

2-(4-Chlorobenzoyl)-3-methylbenzofuran 3a' Yield 1.89 g (70 %), white solid, mp 100–102 °C; v_{max} (cm⁻¹): 1,643 (C=O). δ_{H} (CDCl₃): 8.09 (d, 2H, $J_{o} = 8.4$ Hz, H-2", 6"), 7.74 (dd, 1H, $J_{o} = 7.8$ Hz, $J_{m} = 1.5$ Hz, H-7), 7.58–7.50 (m, 4H, H-4, 6, 3", 5"), 7.40–7.35 (m, 1H, H-5), 2.69 (s, 3H, 3-CH₃). δ_{C} (CDCl₃): 184.39 (C=O), 154.28, 148.06, 139.02, 136.10, 131.22, 129.13, 128.88, 128.41, 127.44, 123.44, 121.49, 112.21, 10.03; Mass (*m*/*z*) ES+: 273.2, 271.2 (M⁺), 159.1 (100), 141.1, 139.1, 113.1, 111.1; Anal. Calcd. for C₁₆H₁₁ClO₂: C, 70.99; H, 4.10. Found: C, 70.93; H, 4.02.

5-*Chloro-2-(4-chlorobenzoyl)-3,6-dimethylbenzofuran* **3b**' Yield 2.16 g (68 %), white solid, mp 140 °C; v_{max} (cm⁻¹): 1,643 (C=O); δ_{H} (CDCl₃): 8.06 (d, 2H, $J_{o} = 8.4$ Hz, H-2", 6"), 7.69 (s, 1H, H-4), 7.51 (d, 2H, $J_{o} = 8.4$ Hz, H-3", 5"), 7.43 (s, 1H, H-7), 2.63 (s, 3H, 3-CH₃), 2.54 (s, 3H, 6-CH₃); δ_{C} (CDCl₃): 184.13 (C=O), 152.91, 148.52, 139.13, 136.99, 135.92, 131.18, 130.11, 128.66, 128.36, 126.80, 121.15, 113.77, 21.24, 10.04; Mass (*m*/*z*) ES+: 322.2, 321.2, 319.2 (M⁺), 209.2, 207.2 (100), 141.1, 139.1, 113.1, 111.1; Anal. Calcd. for C₁₇H₁₂Cl₂O₂: C, 63.97; H, 3.79. Found: C, 63.93; H, 3.75.

2-(4-Chlorobenzoyl)-3,5-dimethylbenzofuran 3c' Yield 2.04 g (72 %), white solid, mp 116 °C; v_{max} (cm⁻¹): 1,636 (C=O). $\delta_{\rm H}$ (CDCl₃): 8.01 (d, 2H, $J_{\rm o}$ = 8.1 Hz, H-2", 6"), 7.53–7.50 (m, 3H, H-4, 3", 5"), 7.43 (d, 1H, $J_{\rm o}$ = 8.4 Hz, H-7), 7.34 (d, 1H, $J_{\rm o}$ = 8.4 Hz, H-6), 2.66 (s, 3H, 3-CH₃), 2.51 (s, 3H, 5-CH₃). $\delta_{\rm C}$ (CDCl₃): 184.37 (C=O), 152.82, 148.27, 138.91, 136.19, 133.06, 131.21, 130.01, 129.20, 128.59, 127.27, 120.97, 111.73, 21.35, 10.02; Mass (*m*/*z*) ES+: 287.3, 285.3 (M⁺), 173.0 (100), 141.1, 139.1, 113.1, 111.1; Anal. Calcd. for C₁₇H₁₃ClO₂: C, 71.71; H, 4.60. Found: C, 71.75; H, 4.63.

5-Bromo-2-(4-chlorobenzoyl)-3-methylbenzofuran **3d**' Yield 2.26 g (65 %), white solid, mp 98–100 °C; v_{max} (cm⁻¹): 1,643 (C=O); δ_{H} (CDCl₃): 8.07 (d, 2H, $J_{\text{o}} = 8.4 \text{ Hz}, \text{H-2''}, 6''$), 7.85 (d, 1H, $J_{\text{m}} = 1.8 \text{ Hz}, \text{H-4}$), 7.60 (dd, 1H, $J_{\text{o}} = 8.4 \text{ Hz}, J_{\text{m}} = 1.8 \text{ Hz}, \text{H-6}$), 7.52 (d, 2H, $J_{\text{o}} = 8.4 \text{ Hz}, \text{H-3''}, 5''$), 7.44 (d, 1H, $J_{\text{o}} = 8.4 \text{ Hz}, \text{H-7}$), 2.63 (s, 3H, 3-CH₃); δ_{C} (CDCl₃): 184.10 (C=O), 152.83, 148.87, 139.30, 135.72, 131.30, 131.19, 131.03, 128.71, 126.37, 124.16, 116.61, 113.75, 9.91; Mass (m/z) ES+: 353.2, 351.2, 349.2 (M⁺), 239.1, 237.1 (100), 141.1, 139.1, 113.1, 111.1; Anal. Calcd. for C₁₆H₁₀BrClO₂: C, 54.97; H, 2.88. Found: C, 54.94; H, 2.82.

5-*Chloro-2-(4-chlorobenzoyl)-3-methylbenzofuran* **3***e*' Yield 2.22 g (73 %), white solid, mp 118 °C; v_{max} (cm⁻¹): 1,643 (C=O); δ_{H} (CDCl₃): 8.07 (d, 2H, J_{o} = 8.1 Hz, H-2", 6"), 7.70 (s, 1H, H-4), 7.54–7.45 (m, 4H, H-6, 7, 3", 5"), 2.64 (s, 3H, 3-CH₃); δ_{C} (CDCl₃): 184.18 (C=O), 152.49, 149.07, 139.30, 135.75, 131.19, 130.44, 129.26,

128.71, 128.68, 126.54, 121.01, 113.34, 9.91; Mass (*m*/*z*) ES+: 308.2, 307.2, 305.2 (M⁺), 195.1, 193.1 (100), 141.1, 139.1, 113.1, 111.1; Anal. Calcd. for $C_{16}H_{10}Cl_2O_2$: C, 62.97; H, 3.30. Found: C, 62.92; H, 3.23.

Photolysis of 2-aroylbenzofurans

2-(4-bromobenzoyl)-3-methylbenzofuran 3a A 1.0 mM deoxygenated solution of 2-aroylbenzofuran 3a in dry methanol was irradiated in a Pyrex glass vessel under nitrogen atmosphere for 90 min with a 125 W Hg vapor lamp. Progress of the reaction was monitored by tlc. The photolysate was chromatographed over a column of silica gel (100–200 mesh) and the column was eluted with increasing proportion of ethylacetate in petroleum ether-ethylacetate system yielding a photoproduct 5a along with some starting compound 3a.

The other 2-aroylbenzofurans **3b–e** and **3a'–e'** were also photolysed by similar procedure yielding their respective photoproducts **5b–e**, 4a'-e' and 5a'-e' along with some starting compound.

Compound 5a Yield 0.11 g (35 %), white solid, mp 104–106 °C; v_{max} (cm⁻¹): 3,263 (OH); δ_{H} (CDCl₃): 7.52–7.23 (8H, m, H-4, 5, 6, 7, 2", 3", 5", 6"), 6.03 (1H, d, J = 5.4 Hz, H-1'), 2.57 (1H, d, J = 5.4 Hz, –OH), 2.28 (3H, s, 3-CH₃); δ_{C} (CDCl₃): 154.09, 151.38, 139.85, 131.62, 129.71, 128.07, 124.67, 122.52, 121.83, 119.56, 112.64, 111.25, 68.12, 7.89; Mass (*m*/*z*) ES+: 318.3, 316.3, 301.0, 299.0 (100); Anal. Calcd. for C₁₆H₁₃BrO₂: C, 60.59; H, 4.13. Found: C, 60.46; H, 4.20.

Compound **5b** Yield 0.12 g (32 %), white solid, mp 118–120 °C; v_{max} (cm⁻¹): 3256 (OH); $\delta_{\rm H}$ (CDCl₃): 7.52 (1H, s, H-4), 7.49 (2H, d, $J_{\rm o}$ = 8.4 Hz, H-2", 6"), 7.35 (2H, d, $J_{\rm o}$ = 8.4 Hz, H-3", 5"), 7.28 (1H, s, H-7), 5.99 (1H, d, J = 5.4 Hz, H-1'), 2.50 (1H, d, J = 5.4 Hz, -OH), 2.46 (3H, s, 6-CH₃), 2.22 (3H, s, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 152.51, 151.48, 139.93, 132.00, 131.59, 129.78, 128.06, 125.89, 121.78, 119.40, 112.41, 110.76, 68.11, 21.31, 7.88; Mass (*m*/*z*) ES+: 367.0, 365.0, 363.0, 351.0, 349.0, 347.0 (100); Anal. Calcd. for C₁₇H₁₄BrClO₂: C, 55.84; H, 3.86. Found: C, 55.73; H, 3.93.

Compound 5*c* Yield 0.07 g (23 %), white solid, mp 62–63 °C; v_{max} (cm⁻¹): 3,354 (OH); $\delta_{\rm H}$ (CDCl₃): 7.51 (2H, d, $J_{\rm o}$ = 8.4 Hz, H-2″, 6″), 7.36–7.28 (4H, m, H-3″, 5″, 4, 7), 7.12 (1H, dd, $J_{\rm o}$ = 8.4 Hz, $J_{\rm m}$ = 2.4 Hz H-6), 5.99 (1H, d, J = 4.5 Hz, H-1′), 2.59 (1H, d, J = 4.5 Hz, –OH), 2.47 (3H, s, 3-CH₃), 2.46 (3H, s, 5-CH₃); $\delta_{\rm C}$ (CDCl₃): 152.36, 151.43, 139.29, 133.55, 132.00, 129.66, 128.43, 127.65, 125.75, 119.23, 112.76, 110.36, 76.79, 68.55, 21.31, 7.85; Mass (*m*/*z*) ES+: 331.0, 329.0, 315.0, 313.0 (100); Anal. Calcd. for C₁₇H₁₅BrO₂: C, 61.65; H, 4.56. Found: C, 61.52; H, 4.44.

Compound 5*d* Yield 0.17 g (44 %), white solid, mp 88–90 °C; v_{max} (cm⁻¹): 3,328 (OH); δ_{H} (CDCl₃): 7.62 (1H, d, $J_m = 2.1$ Hz, H-4), 7.42–7.33 (5H, m, H-2", 3", 5", 6", 6), 7.26 (1H, d, $J_o = 8.7$ Hz, H-7), 6.01 (1H, d, J = 5.4 Hz, H-1'), 2.50 (1H, d, J = 5.4 Hz, –OH), 2.22 (3H, s, 3-CH₃); δ_{C} (CDCl₃): 152.83, 152.74, 138.93,

133.89, 131.76, 128.32, 128.49, 127.69, 127.53, 122.41, 115.64, 112.53, 112.20, 76.63, 68.02, 7.91; Mass (m/z) ES+: 395.1, 393.1, 379.1, 377.1 (100); Anal. Calcd. for C₁₆H₁₂Br₂O₂: C, 48.52; H, 3.05. Found: C, 48.60; H, 3.11.

Compound **5***e* Yield 0.18 g (51 %), creamish solid, mp 56–58 °C; v_{max} (cm⁻¹): 3,263 (OH); $\delta_{\rm H}$ (CDCl₃): 7.52 (1H, d, $J_{\rm m} = 2.1$ Hz, H-4), 7.49–7.28 (5H, m, H-2", 6", 3", 5", 7), 7.25 (1H, dd, $J_{\rm m} = 2.1$ Hz, $J_{\rm o} = 8.4$ Hz, H-6), 6.00 (1H, d, J = 4.5 Hz, H-1'), 2.65 (1H, d, J = 4.5 Hz, -OH), 2.24 (3H, s, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 153.03, 152.42, 138.92, 133.83, 131.03, 128.71, 128.13, 127.63, 124.72, 119.24, 112.31 112.12, 68.01, 29.58, 7.61; Mass (*m*/*z*) ES+: 353.0, 351.0, 349.0, 337.0, 335.0, 333.0 (100); Anal. Calcd. for C₁₆H₁₂BrClO₂: C, 54.65; H, 3.44. Found: C, 54.71; H, 3.28.

Compound 4*a*′ Yield 0.05 g (15 %), white solid, mp 88–90 °C; v_{max} (cm⁻¹): 1,690 (C=O); δ_{H} (CDCl₃): 8.25 (2H, d, J_{o} = 8.7 Hz, H-2″, 6″), 7.51 (2H, d, J_{o} = 8.7 Hz, H-3″, 5″), 7.24–7.20 (2H, m), 7.07–6.98 (2H, m), 3.66 (1H, q, J = 7.2 Hz, H-3), 3.33 (3H, s, –OCH₃), 1.01 (3H, d, J = 7.2 Hz, 3-CH₃); δ_{C} (CDCl₃): 193.04 (C=O), 156.18, 140.43, 133.06, 131.08, 130.98, 129.11, 128.53, 123.98, 122.07, 114.46, 110.78, 52.08, 47.47, 17.21; Mass (*m*/*z*) ES+: 274.1, 272.1 (M⁺-OCH₃); Anal. Calcd. for C₁₇H₁₅ClO₃: C, 67.44; H, 4.99. Found: C, 67.21; H, 4.64.

Compound 5*a*′ Yield 0.11 g (41 %), white solid, mp 74–76 °C; v_{max} (cm⁻¹): 3,263 (OH). $\delta_{\rm H}$ (CDCl₃): 7.53–7.23 (8H, m, H-4, 5, 6, 7, 2″, 3″, 5″, 6″), 6.04 (1H, d, J = 5.1 Hz, H-1′), 2.58 (1H, d, J = 5.1 Hz, –OH), 2.28 (3H, s, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 154.08, 151.43, 139.31, 133.70, 129.72, 128.67, 127.74, 124.68, 122.53, 119.58, 112.63, 111.27, 68.05, 7.91; Mass (*m*/*z*) ES+: 271.1, 269.1, 257.1, 255.1 (100); Anal. Calcd. for C₁₆H₁₃ClO₂: C, 76.46; H, 4.80. Found: C, 76.33; H, 4.69.

Compound 4b' Yield 0.47 g (12 %), yellow solid, mp 202–204 °C; v_{max} (cm⁻¹): 1,690 (C=O); $\delta_{\rm H}$ (CDCl₃): 8.22 (2H, d, $J_{\rm o}$ = 8.7 Hz, H-2", 6"), 8.02 (2H, d, $J_{\rm o}$ = 8.7 Hz, H-3", 5"), 7.40 (1H, s, H-4), 7.22 (1H, s, H-7), 3.64 (1H, q, J = 7.2 Hz, H-3), 3.33 (3H, s, –OCH₃), 2.30 (3H, s, 6-CH₃), 1.00 (3H, d, J = 7.5 Hz, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 192.45 (C=O), 156.27, 141.24, 133.81, 132.19, 131.34, 131.02, 129.21, 128.48, 124.23, 114.28, 111.82, 52.21, 47.36, 29.69, 17.05; Mass (*m*/*z*) ES+: 322.0, 320.0 (M⁺-OCH₃); Anal. Calcd. for C₁₈H₁₆Cl₂O₃: C, 61.55; H, 4.59. Found: C, 61.30; H, 4.29.

Compound **5***b*′ Yield 0.1 g (35 %), white solid, mp 78–80 °C; v_{max} (cm⁻¹): 3,356 (OH); $\delta_{\rm H}$ (CDCl₃): 7.47 (1H, s, H-4), 7.41 (2H, d, $J_{\rm o}$ = 8.4 Hz, H-2″, 6″), 7.35 (2H, d, $J_{\rm o}$ = 8.4 Hz, H-3″, 5″), 7.27 (1H, s, H-7), 6.00 (1H, d, J = 5.4 Hz, H-1′), 2.53 (1H, d, J = 5.4 Hz, -OH), 2.46 (3H, s, 6-CH₃), 2.23 (3H, s, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 152.78, 152.08, 139.11, 133.79, 132.54, 128.98, 128.81, 128.71, 127.69, 119.47, 112.97, 112.16, 68.02, 20.79, 7.90; Mass (*m*/*z*) ES+: 324.1, 322.1, 320.1, 307.1, 305.1, 303.1 (100); Anal. Calcd. for C₁₇H₁₄Cl₂O₂: C, 63.57; H, 4.39. Found: C, 63.38; H, 4.20.

Compound 4c' Yield 0.04 (10 %), yellow gummy mass; v_{max} (cm⁻¹): 1,690 (C=O); δ_{H} (CDCl₃): 8.25 (2H, d, $J_{\text{o}} = 8.7$ Hz, H-2", 6"), 7.50 (2H, d, $J_{\text{o}} = 8.7$ Hz, H-3", 5"), 7.05–6.98 (2H, m, H-4, 6), 6.94 (1H, d, $J_{\text{o}} = 7.8$ Hz, H-7), 3.61 (1H, q, J = 7.5 Hz, H-3), 3.32 (3H, s, –OCH₃), 2.34 (3H, s, 5-CH₃), 0.99 (3H, d, J = 7.5 Hz, 3-CH₃); δ_{C} (CDCl₃): 193.16 (C=O), 154.07, 140.38, 133.10, 132.11, 131.09, 130.95, 129.09, 128.92, 124.52, 114.53, 110.35, 68.17, 52.02, 47.55, 17.19; Mass (*m*/*z*) ES+: 287.1, 285.1 (M⁺-OCH₃); Anal. Calcd. for C₁₈H₁₇ClO₃: C, 68.25; H, 5.41. Found: C, 68.10; H, 5.21.

Compound 5*c*' Yield 0.08 g (28 %), white solid, mp 68–70 °C; v_{max} (cm⁻¹): 3,364 (OH); $\delta_{\rm H}$ (CDCl₃): 7.42 (2H, d, J = 8.4 Hz, H-2″, 6″), 7.35–7.30 (4H, m, H-3″, 5″, 4, 7), 7.11 (1H, dd, $J_{\rm o} = 8.4$ Hz, $J_{\rm m} = 1.2$ Hz, H-6), 6.02 (1H, d, J = 5.4 Hz, H-1′), 2.53 (1H, d, J = 5.4 Hz, –OH), 2.46 (3H, s, 3-CH₃), 2.25 (3H, s, 5-CH₃); $\delta_{\rm C}$ (CDCl₃): 152.48, 151.52, 139.38, 133.63, 132.00, 129.76, 128.64, 127.73, 125.88, 119.41, 112.40, 110.76, 68.02, 21.34, 7.92; Mass (*m*/z) ES+: 285.1, 283.1, 271.1, 269.1 (100); Anal. Calcd. for C₁₇H₁₅ClO₂: C, 71.20; H, 5.27. Found: C, 71.08; H, 5.14.

Compound 4d' Yield 0.08 (18 %), yellow gummy mass; v_{max} (cm⁻¹): 1690 (C=O); $\delta_{\rm H}$ (CDCl₃): 8.23 (2H, d, $J_{\rm o}$ = 8.7 Hz, H-2", 6"), 7.52 (2H, d, $J_{\rm o}$ = 8.7 Hz, H-3", 5"), 7.36–7.31 (2H, m, H-4, 6), 6.94 (1H, d, $J_{\rm o}$ = 8.1 Hz, H-7), 3.64 (1H, q, J = 7.2 Hz, H-3), 3.32 (3H, s, –OCH₃), 0.99 (3H, d, J = 7.2 Hz, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 192.40 (C=O), 155.35, 140.67, 133.45, 132.76, 131.40, 131.02, 129.22, 127.11, 114.90, 113.69, 112.44, 52.23, 47.36, 17.08; Mass (*m*/*z*) ES+: 354.0, 352.0, 350.0 (M⁺-OCH₃); Anal. Calcd. for C₁₇H₁₄BrClO₃: C, 53.50; H, 3.70. Found: C, 53.32; H, 3.41.

Compound 5*d*' Yield 0.16 g (49 %), white solid, mp 60–62 °C; v_{max} (cm⁻¹): 3325 (OH); δ_{H} (CDCl₃): 7.63 (1H, d, J_{m} = 1.8 Hz, H-4), 7.43–7.34 (5H, m, H-2", 3", 5", 6", 6), 7.28 (1H, d, J_{o} = 8.7 Hz, H-7), 6.02 (1H, d, J = 5.4 Hz, H-1'), 2.52 (1H, d, J = 5.4 Hz, -OH), 2.24 (3H, s, 3-CH₃). δ_{C} (CDCl₃): 152.83, 152.81, 138.93, 133.89, 131.76, 128.76, 128.49, 127.69, 122.41, 115.64, 112.74, 112.20, 68.02, 7.83; Mass (*m*/*z*) ES+: 353.0, 351.0, 349.0, 337.0, 335.0, 333.0 (100); Anal. Calcd. for C₁₆H₁₂BrClO₂: C, 54.65; H, 3.44. Found: C, 54.38; H, 3.24.

Compound 4e' Yield 0.08 (20 %), white solid, mp 108–110 °C; v_{max} (cm⁻¹): 1,690 (C=O); $\delta_{\rm H}$ (CDCl₃): 8.23 (2H, d, $J_{\rm o}$ = 8.7 Hz, H-2", 6"), 7.51 (2H, d, $J_{\rm o}$ = 8.7 Hz, H-3", 5"), 7.21 (1H, d, $J_{\rm m}$ = 2.1 Hz, H-4), 7.19–7.17 (1H, m, H-6), 6.97 (1H, d, $J_{\rm o}$ = 8.4 Hz, H-7), 3.63 (1H, q, J = 7.2 Hz, H-3), 3.32 (3H, s, –OCH₃), 1.00 (3H, d, J = 7.2 Hz, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 192.45 (C=O), 156.27, 141.24, 133.81, 131.02, 130.18, 129.21, 125.18, 128.48, 124.23, 115.02, 111.82, 52.21, 29.69, 17.05; Mass (*m*/*z*) ES+: 310.1, 308.1, 306.1 (M⁺-OCH₃); Anal. Calcd. for C₁₇H₁₄Cl₂O₃: C, 60.55; H, 4.18. Found: C, 60.28; H, 3.69.

Compound 5e' Yield 0.16 g (55 %), creamish solid, mp 62–64 °C; v_{max} (cm⁻¹): 3,263 (OH); $\delta_{\rm H}$ (CDCl₃): 7.47 (1H, d, $J_{\rm m} = 2.1$ Hz, H-4), 7.42–7.28 (5H, m, H-2", 6", 3", 5", 7), 7.24 (1H, dd, $J_{\rm o} = 8.7$ Hz, $J_{\rm m} = 2.1$ Hz, H-6), 6.01 (1H, d,

J = 4.5 Hz, H-1'), 2.58 (1H, d, J = 4.5 Hz, -OH), 2.42 (3H, s, 3-CH₃); $\delta_{\rm C}$ (CDCl₃): 153.04, 152.44, 138.99, 133.88, 131.17, 128.75, 128.21, 127.69, 124.82, 119.31, 112.30, 112.25, 68.07, 7.82; Mass (*m*/*z*) ES+: 305.1, 303.1, 301.1, 293.1, 291.1, 289.1 (100); Anal. Calcd. for C₁₆H₁₂Cl₂O₂: C, 62.56; H, 3.94. Found: C, 62.38; H, 3.64.

Results and discussion

The substrates, 2-aroylbenzofurans **3a–e** and **3a'–e'**, were synthesized by the phase transfer catalyzed Rap–Stoermer [30–36] type cyclocondensation between *o*-hydroxyacetophenones **1a–e** and α -bromoketones **2a** and **2b** using water as solvent, Na₂CO₃ as a mild base, and n-Bu₄N⁺I[–] (Scheme 1) by developing a green protocol. The choice of aqueous media for chemical reactions has gained much attention due to its environmentally friendly impact and low cost of chemical processes. Using water as the reaction medium offers a number of advantages such as being cheap, readily available, non-toxic, non-flammable, and safe for use. Water often increases the reactivity or selectivity [37, 38] of the reaction that could be unattainable in organic solvents. In aqueous media, the work-up procedure becomes simple and the product can be easily isolated. The structures of these photo-labile substrates **3a–e** and **3a'–e'** were found to be consistent with their spectral parameters (IR, ¹H NMR, ¹³C NMR, and Mass; see "Experimental").

The IR spectrum of compound **3a** (mp 80–82 °C) showed a strong absorption at 1,643 cm⁻¹ for the carbonyl group. The compound **3a** in its ¹H NMR (300 MHz, CDCl₃) showed the most downfield signal at δ 8.03(dd, $J_o = 8.4$ Hz, $J_m = 1.5$ Hz), which could be ascribed to H-2" and H-6" due to the deshielding effect of the C=O group. The proton H-7 produced a multiplet between δ 7.74 and 7.70. The four protons H-4, -6, -3", and -5" gave an unresolved multiplet between δ 7.68 and 7.53. The spectrum exhibited a multiplet in the region δ 7.38–7.33 for proton H-5. The 3-CH₃ group protons were found to be located at δ 2.68 as a singlet. The structure of **3a** was further confirmed by the ¹³C NMR spectrum. The molecular ion peak in the mass spectrum of **3a** was located at m/z 314.7/316.7, but the base peak appeared at 159.1 (100 %). The structures of other benzofuran derivatives, **3b–e** and **3a'–e'** were ascertained likewise.

The methanolic solution of the benzofuran derivatives 3a-e and 3a'-e' was photolysed with Pyrex-filtered UV-light from a 125 W Hg lamp under nitrogen atmosphere (Scheme 2) that resulted in the formation of photoproducts 5a-e, 5a'-e', and 4a'-e'.

The structures of photoproducts were established by their IR, ¹H NMR, ¹³C NMR, and mass spectra data (*vide experimental*). The photoproduct **5a** in its IR spectrum showed absorption at 3,263 cm⁻¹ which indicated the presence of the –OH group. In the ¹H NMR spectrum (300 MHz, CDCl₃) of **5a**, the eight protons H-4, -5, -6, -7, -2", -3", -5", and H-6" gave unresolved multiplet between δ 7.52 and 7.23. The proton H-1' appeared as a doublet at δ 6.03 (J = 5.4 Hz). The –OH proton gave a doublet at δ 2.57 (J = 5.4 Hz). A sharp singlet integrating for three protons at δ 2.28 was assigned to the 3-CH₃ group. The D₂O shake of the photoproduct **5a**



Scheme 1 Synthesis of 2-aroylbenzofuran derivatives

further confirmed the –OH group. The structure of photoproduct **5a** was further corroborated by its proton decoupled ¹³C NMR spectra and mass spectrum. In the mass spectrum, the molecular ion peak did not appear due to its low intensity, but the base peak appeared at 299.0/301.0 (100 %). The direct photo irradiation of the isolated intermediates 4a'-e' also furnished the alcohols 5a'-e'.

The nature of the substituents onto the benzofuran ring had a noticeable effect on the photoproduct formation from these aroylbenzofurans (Table 1). The benzofuran(s), having electron-withdrawing groupd (which decrease the electron density on the benzofuran ring), furnished the photoproduct in higher yields while the benzofuran(s) with electron-releasing groups (which increase the electron density) gave the photoproducts in lower yields. The only assignable reason for this observation may be the participation in product formation of π - π * excitation as its energy is lowered more than that of n- π * excitation [39, 40], a case of state switching.

Solvent also have an appreciable effect on photoproduct formation (Table 1) which was determined by photoirradiating these benzofuran derivatives in different solvents like methanol, ethanol, isopropyl alcohol, and toluene, separately. The polar protic solvents: methanol, ethanol, and isopropyl alcohol offered a favorable environment for the phototransformation of the target benzofurans **3a–e**. The yield of the all the photoproducts **5a–e** and **5a'–e'** was in the order isopropanol > ethanol > methanol. When these substrates were photoirradiated in toluene, no photoproduct was detected, which rules out the possibility of direct intermolecular H-transfer from the solvent to the carbonyl group for photoreduction.

The phototransformations of target aroylbenzofurans **3** to photoproducts **5** can be rationalized to occur through two familiar mechanistic routes: route 1 and route 2 (Scheme 3). Route 1 is the simple direct intermolecular H-transfer from the solvent to the carbonyl group to furnish the alcohols **5** just like the photoreduction of benzophenones. But, here, the formation of the additional products, i.e. 1,2-diols (the products of reductive coupling) and the tertiary alcohols as found in the photoreduction of benzophenones, were not observed. This rules out the existence of the above proposed mechanism, i.e. route 1 for the phototransformation of these substrates into alcohols **5**. The route 2 mechanism is the addition–elimination process. There is an initial addition of methanol, the solvent, to the double bond of



Scheme 2 Photolysis of 2-aroylbenzofurans

Table 1 Effect of substituents and solvent on the photoproducts formation on the photolysis of compounds 3a-e and 3a'-e'

| Photoproduct | Yield (%) | | | | | |
|--------------|--------------|----------------|----------|---------|-------------------|---------|
| | Substituents | | Solvent | | | |
| | R | \mathbf{R}^1 | Methanol | Ethanol | Isopropyl alcohol | Toluene |
| 5a | Н | Н | 35 | 38 | 42 | - |
| 5b | Cl | CH_3 | 32 | 36 | 39 | - |
| 5c | CH_3 | Н | 23 | 27 | 35 | - |
| 5d | Br | Н | 44 | 49 | 62 | - |
| 5e | Cl | Н | 51 | 54 | 60 | - |
| 5a' | Н | Н | 41 | 43 | 50 | - |
| 5b′ | Cl | CH_3 | 35 | 40 | 43 | - |
| 5c′ | CH_3 | Н | 28 | 33 | 41 | - |
| 5d′ | Br | Н | 49 | 55 | 64 | - |
| 5e′ | Cl | Н | 55 | 59 | 67 | - |
| 4 a′ | Н | Н | 15 | - | _ | - |
| 4b′ | Cl | CH_3 | 12 | - | _ | - |
| 4 c' | CH_3 | Н | 10 | - | _ | _ |
| 4d′ | Br | Н | 18 | _ | _ | _ |
| 4e' | Cl | Н | 20 | - | _ | _ |

the benzofuran ring leading to the formation of intermediate 4. Then, the carbonyl group of the aroyl moiety present in the additional product 4 gets excited upon photoirradiation and abstracts hydrogen from $-OCH_3$ through Norrish type-II γ -H abstraction, which results in formation of 1,4-biradical. The elimination of HCHO from the 1,4-biradical gives the enol that upon 1,3-hydrogen shift furnishes the final product 5 (Scheme 3). This mechanism gets support from the fact that the intermediates 4a'-e' produced by the addition of solvent on 3a'-e' have been isolated when the methanol was used as the solvent and also by the formation of 5a'-e' from the direct irradiation of isolated intermediate 4a'-e'. The intermediates like 4a'-e' could not be isolated in other alcohols, i.e. ethanol and isopropanol because of the rapid ease of H-abstraction from the $-O-CH_2-CH_3$ and $-O-CH(CH_3)_2$ groups of the addition product to give the 1,4-biradical intermediate of higher stability. This is further corroborated by the yield of the photoproduct



Scheme 3 Probable mechanism of product 5 formation from 2-aroylbenzofurans 3 by photolysis

which was found to be in the order: isopropanol > ethanol > methanol. Hence, the addition–elimination mechanism seems to be the most preferred and plausible reaction pathway for the formation of these photoproducts.

In conclusion, the 2-aroylbenzofurans gave the arylbenzofurylmethanols very efficiently through photoreduction. In the photolysis of **3**, no ring photochemistry was observed and, also, no photoproduct whatsoever corresponding to the intramolecular H-abstraction by C=O from the 3-methyl group on the benzofuran moiety was furnished. The variation in substituents at the benzofuran ring has a pronounced effect on the yields of the photoproducts.

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