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Solvent dependent photobehaviour of some 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones

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ABSTRACT

*Photoirradiation of deoxygenated solutions of some 2-aryl-2-bromo-1H-indene-1,3(2H)-diones (**2**) under* N_2 *atmosphere in anhydrous alcohol and acetone has been studied. The photoreaction is envisaged to occur through β-cleavage in which homolytic cleavage of* C_2*–Br bond occurs preferentially to furnish the corresponding resonance stabilized 2-aryl-1H-indene-1,3(2H)-dione free radicals (**3**) which lead to the formation of a mixture of photoproducts depending upon the solvent employed, i.e. 2-aryl-2-ethoxy-1H-indene-1,3(2H)-diones (**4**), 2,2'-diaryl-1H,1'H-2,2'-biindene-1,1',3,3'(2H,2'H)-tetrones (**5**) and (Z)-2-(aryl)-2-((aryl)(3-oxoisobenzofuran-1(3H)-ylidene)methyl)-1H-indene-1,3(2H)-diones (**6**) in anhydrous alcohol and 2-aryl-1H-indene-1,3(2H)-diones (**1**) and bromoacetone (**8**) in dry acetone. The structural confirmation of the synthesized products was carried out on the basis of spectral (ir,* ^{1}*H NMR and mass) as well as elemental analysis results.*

Keywords: Photolysis, 2-Aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones, *β*-cleavage, Norrish Type 1.

INTRODUCTION

One of the most thoroughly and extensively investigated area in photochemistry is of carbonyl compounds. The main reasons for interest in this area, which remains unabated, are the discovery of a myriad of photochemical transformations of carbonyl compounds which have displayed considerable sensitivity to subtle structural and conformational factors, coupled with a growing knowledge of the nature of excited state/s of the carbonyl compounds which has permitted a high degree of comprehension of the mechanistic complexities of the photochemical reactions of this class of compounds. Photochemical *α*- and *β*-cleavages in the carbonyl compounds have attracted the attention of organic chemists in the past and these photoprocesses have emerged as a promising synthetic tool for obtaining a variety of photoproducts. Although *β*-cleavage is not formally a Norrish Type 1 process, yet it has been observed on n–π^* excitation of certain ketones [1]. *α*-Cleavage and *β*-cleavage may often be competitive reactions, which pathway actually predominates depends upon the structure of the ketones and presence of substituents [2–4]. *β*-Cleavage has also been observed in ketones possessing such *α*-substituents which have a tendency for formation of radicals, *i.e.* epoxy [5,6], halogen [7,8], acetoxy [9], aryloxy [10], sulphonyloxy [11] and thiyl [12–16] substituents. Depending upon the nature of the starting material and nature of the n–π^* excited states (singlet or triplet) both ionic [17] and radical intermediates have been implicated in this process. Furthermore, the reaction pathway can be influenced by the presence of substituents other than *α*-position [18]. Recently, we have also reported the stereoselective synthesis of (*Z*)-3-alkylidene-3*H*-isobenzofuranones through photo-reorganization of the corresponding 2-alkoxy-2-aryl-1*H*-indene-1,3(2*H*)-diones [19], photochemical synthesis of isomeric (*E*/*Z*)-3-alkylidene-3*H*-isobenzofuranones from photoisomerization of 2-aroyl-2-benzyl/methyl-1*H*-indene-1,3(2*H*)-diones

[20] and phototransformation of some *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)aryl/heterylamides [21] in excellent yields. In continuation of these studies and in order to examine the effect of bromo as polar substituent present at C_2–position, herein, we report the photochemistry of some 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (**2**) that resulted in the formation of different photoproducts, *i.e.* 2-aryl-2-ethoxy-1*H*-indene-1,3(2*H*)-diones (**4**), 2,2'-diaryl-1*H*,1'*H*-2,2'-biindene-1,1',3,3'(2*H*,2'*H*)-tetrones (**5**) and (*Z*)-2-(aryl)-2-((aryl)(3-oxoisobenzofuran-1(3*H*)-ylidene)methyl)-1*H*-indene-1,3(2*H*)-diones (**6**) in anhydrous alcohol and 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1**) and bromoacetone (**8**) in dry acetone in varying yields.

EXPERIMENTAL SECTION

Melting points (^{o}C) were observed in open capillaries and are uncorrected. The purity of synthesized compounds was tested using precoated TLC plates (SIL G/UV254, ALUGRAM) and visualization was achieved via UV or by iodine adsorption. IR spectra were scanned in Nujol on Perkin–Elmer 842 IR spectrophotometer and absorption frequencies (v) are stated in cm^{-1}. ^{1}H NMR spectra were recorded in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard on 200 MHz Bruker AM-200 spectrometer and 90 MHz Perkin Elmer spectrometer. The chemical shift values (δ) are expressed in parts per million (ppm). Coupling constants (J) were measured in Hz. Mass spectra were recorded at 70 eV using a VG-70S instrument. The value given in the parentheses represents relative intensities corresponding to the base peak taken as 100. Elemental analysis results for C and H were found within ± 0.4% of the theoretical values. Silica gel (100–200 mesh) was used for column chromatography. The columns were packed with silica gel in hexane and left overnight before separation. Solvents were dried using standard literature procedures.

General procedure for the synthesis of 2-aryl-1*H*-indene-1,3(2*H*)-diones (1). The 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1**) needed for the purpose were prepared by condensation of phthalide with an appropriate 4-substituted benzaldehyde in the presence of sodium alkoxide and an ester in high yields according to the procedure as described in the literature [22].

General procedure for the synthesis of 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (2). The 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (**2**) were obtained by bromination of the corresponding 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1**) with $Br_2/CHCl_3$ according to the procedure described in literature [22].

General procedure for the photolysis of 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (2) in ethanol. A solution of 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-dione (**2,** 700 mg) in anhydrous ethanol (80 mL) was deoxygenated by bubbling oxygen-free dry nitrogen gas for 20 min. The solution was then irradiated with a 450 W Hanovia mercury vapor lamp in a pyrex reactor under nitrogen atmosphere. The reaction progress was monitored by tlc (benzene: ethylacetate (19:1, v/v) on aliquots withdrawn from the reaction mixture at different intervals of time. During the course of the irradiation (after ~3 h of irradiation), a light yellow solid started separating out of the photolysate. After 5 h of irradiation, tlc showed complete disappearance of the starting compound (**2**). At the end of the photolysis, the solid that deposited during the course of irradiation was filtered which upon crystallization from benzene-ethanol mixture yielded **6** as light yellow crystals. The solvent was distilled off from the mother liquor left after the removal of **6** and the resulting viscous photolysate was chromatographed over a column of silica gel (25 g, packed in hexane). The column was then eluted initially with hexane followed by benzene: hexane (1:1, v/v) which afforded firstly **4**, followed by subsequent elution with benzene provided **5** and **6** in varying yields.

2-Ethoxy-2-phenyl-1*H*-indene-1,3(2*H*)-dione (4a). This compound was obtained as light yellow oily liquid, 9.4% yield; IR (nujol): 1742 and 1712 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 1.17 (t, J = 7.0 Hz, 3H, ethoxy-CH_3), 3.55 (q, J = 7.0 Hz, 2H, ethoxy-CH_2), 7.10–7.40 (m, 5H, 2'-H, 3'-H, 4'-H, 5'-H and 6'-H), 7.80–8.10 (m, 4H, 4-H, 5-H, 6-H and 7-H); ms: (70 eV, electron impact) m/z 267 (M^+ +1, 10.8), 266 (M^+, 54.0), 238 (23.5), 221 (14.0), 210 (34.0), 209 (100), 162 (13.6), 77 (16.4), 76 (10.6). *Anal*. Calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.75; H, 5.19.

2-Ethoxy-2-*p*-tolyl-1*H*-indene-1,3(2*H*)-dione (4b). This compound was obtained as light yellow oily liquid, 34% yield; IR (nujol): 1740 and 1710 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 1.20 (t, J = 7.0 Hz, 3H, ethoxy-CH_3), 2.25 (s, 3H, 4'-CH_3), 3.55 (q, J = 7.0 Hz, 2H, ethoxy-CH_2), 7.00 (d, 2H, J = 8.0 Hz, 3'-H and 5'-H), 7.25 (d, 2H, J = 8.0 Hz, 2'-H and 6'-H), 7.60–8.00 (m, 4H, 4-H, 5-H, 6-H and 7-H); ms: (70 eV, electron impact) m/z 281 (M$^+$ +1, 13.2), 280 (M$^+$, 78.4), 252 (16.5), 236 (7.0), 224 (17.4), 223 (100), 236 (16.2), 92 (21.5), 77 (18.4), 76 (11.6). *Anal*. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.37; H, 5.41.

2-Ethoxy-2-(4-methoxyphenyl)-1*H*-indene-1,3(2*H*)-dione (4c). This compound was obtained as yellow crystalline solid, 63% yield, mp 97–98 ^{o}C (lit [19] mp 97–98 ^{o}C); IR (nujol): 1741 and 1709 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 1.18 (t, J = 7.0 Hz, 3H, ethoxy-CH_3), 3.55 (q, J = 7.0 Hz, 2H, ethoxy-CH_2), 3.66 (s, 3H, 4'-OCH_3), 6.77 (d, J = 8.5 Hz, 2H, 3'-H and 5'-H), 7.32 (d, 2H, J = 8.5 Hz, 2'-H and 6'-H), 7.71–8.06 (m, 4H, 4-H, 5-H, 6-H and 7-H);ms: (70 eV, electron impact) m/z 297 (M$^+$ +1, 18.4), 296 (M$^+$, 85.4), 268 (26.5), 240 (37.4), 239 (100), 181 (13.7), 168 (10.2), 152 (17.0), 135 (44.9), 107 (10.2), 104 (12.7), 92 (13.5), 77 (26.4), 76 (14.6).

2-(4-Chlorophenyl)-2-ethoxy-1*H*-indene-1,3(2*H*)-dione (4d). This compound was obtained as light yellow oily liquid, 7.2% yield; IR (nujol): 1745 and 1712 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 1.18 (t, J = 7.0 Hz, 3H, ethoxy-CH_3), 3.55 (q, J = 7.0 Hz, 2H, ethoxy-CH_2), 7.00 (d, 2H, J = 8.5 Hz, 3'-H and 5'-H), 7.35 (d, 2H, J = 8.5 Hz, 2'-H and 6'-H), 7.70–8.10 (m, 4H, 4-H, 5-H, 6-H and 7-H); ms: (70 eV, electron impact) m/z 302 (M$^+$ +2, 12.4), 301 (M$^+$ +1, 8.9), 300 (M$^+$, 38.9), 272 (10.2), 256 (14.2), 244 (100.0), 112 (24.9), 92 (21.5), 77 (18.4), 76 (11.6). *Anal*. Calcd. for $C_{17}H_{13}ClO_3$: C, 67.89; H, 4.36. Found: C, 67.37; H, 4.19.

2,2'-Diphenyl-1*H*,1'*H*-2,2'-biindene-1,1',3,3'(2*H*,2'*H*)-tetrone (5a). This compound was obtained as white crystalline solid, 9.2% yield, mp 208–210 ^{o}C (lit [23] mp 208–210 ^{o}C; lit [24] mp 213–214 ^{o}C); IR (nujol): 1740 and 1708 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 7.10–7.40 (m, 10H, 2"-H 3"-H, 4"-H, 5"-H, 6"-H, 2'"-H, 3'"-H, 4'"-H, 5'"-H and 6'"-H), 7.80–8.15 (m, 8H, 4-H, 5-H, 6-H, 7-H, 4'-H, 5'-H, 6'-H and 7'-H); ms: (70 eV, electron impact) m/z 443 (M$^+$ +1, 2.7), 442 (M$^+$, 6.4), 222 (M$^+$/2 +1, 100), 194 (10.0), 193 (11.2), 77 (12.6), 76 (17.2), 58 (9.4). *Anal*. Calcd. for $C_{30}H_{18}O_4$: C, 81.44; H, 4.10. Found: C, 81.91; H, 3.71.

2,2'-Di*p*-tolyl-1*H*,1'*H*-2,2'-biindene-1,1',3,3'(2*H*,2'*H*)-tetrone (5b). This compound was obtained as white crystalline solid, 9.6% yield, mp 245–247 ^{o}C; IR (nujol): 1738 and 1705 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 2.25 (s, 6H, 4"-CH_3 and 4'"-CH_3), 7.05 (s, 8H, 2"-H 3"-H, 5"-H, 6"-H, 2'"-H 3'"-H, 5'"-H and 6'"-H), 7.55–7.95 (m, 8H, 4-H, 5-H, 6-H, 7-H, 4'-H, 5'-H, 6'-H and 7'-H); ms: (70 eV, electron impact) m/z 471 (M$^+$ +1, 3.0), 470 (M$^+$, 6.9), 237 (21.9), 236 (M$^+$/2 +1, 100), 208 (10.0), 207 (11.9), 193 (15.7), 179 (14.1), 178 (16.2), 165 (32.8), 77 (11.8), 76 (17.7), 58 (10.7). *Anal*. Calcd. for $C_{32}H_{22}O_4$: C, 81.19; H, 4.71. Found: C, 81.44; H, 4.40.

2,2'-*Bis*(4-methoxyphenyl)-1*H*,1'*H*-2,2'-biindene-1,1',3,3'(2*H*,2'*H*)-tetrone (5c). This compound was obtained as white crystalline solid, 9.2% yield, mp 242–244 ^{o}C (lit [23] mp 246–247 ^{o}C; lit [25] mp 247–248 ^{o}C); IR (nujol): 1745 and 1720 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 3.70 (s, 6H, 4"-OCH_3 and 4'"-OCH_3), 6.70 (d, 4H, J = 8.5 Hz, 3"-H, 5"-H, 3'"-H and 5'"-H),7.05 (d, 4H, J = 8.5 Hz, 2"-H, 6"-H, 2'"-H and 6'"-H), 7.55–7.90 (m, 8H, 4-H, 5-H, 6-H, 7-H, 4'-H, 5'-H, 6'-H and 7'-H); ms: (70 eV, electron impact) m/z 503 (M$^+$ +1, 4.9), 502 (M$^+$, 5.2), 253 (23.1), 252 (M$^+$/2 +1, 100.0), 238 (21.6), 237 (60.5), 209 (13.2), 181 (23.6), 165 (16.0), 153 (15.2), 152 (31.2), 77 (14.4), 76 (34.2), 71 (17.7), 69 (10.7), 57 (16.7). *Anal*. Calcd. For $C_{32}H_{22}O_6$: C, 76.48; H, 4.41 Found: C, 76.73; H, 4.25.

2,2'-*Bis*(4-chlorophenyl)-1*H*,1'*H*-2,2'-biindene-1,1',3,3'(2*H*,2'*H*)-tetrone (5d). This compound was obtained as light yellow crystalline solid, 9.4% yield, mp 225–227 ^{o}C (lit [26] mp 226–228 ^{o}C); IR (nujol): 1740 and 1712 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 6.95–7.35 (m, 8H, 2"-H 3"-H, 5"-H, 6"-H, 2'"-H, 3'"-H, 5'"-H and 6'"-H), 7.60–8.00 (m, 8H, 4-H, 5-H, 6-H, 7-H, 4'-H, 5'-H, 6'-H and 7'-H); ms: (70 eV, electron impact) m/z 512 (M$^+$ +2, 7.4), 511 (M$^+$ +1, 5.8), 510 (M$^+$, 8.4), 257 (24.0), 256 (M$^+$/2 +1, 100.0), 243 (23.5), 221 (21.7), 193 (37.5), 165 (55.5), 149 (29.7), 139 (18.4), 105 (10.7), 104 (25.7), 97 (19.0), 89 (24.9), 76 (34.2), 71 (34.4), 69 (28.1), 57 (49.4), 55 (34.9). *Anal*. Calcd. for $C_{30}H_{16}Cl_2O_4$: C, 70.46; H, 3.15 Found: C, 70.78; H, 3.38.

(*Z*)-2-((3-oxoisobenzofuran-1(3*H*)-ylidene)(phenyl)methyl)-2-phenyl-1*H*-indene-1,3(2*H*)-dione (6a). This compound was obtained as light yellow crystalline solid, 77.2% yield, mp 269–271 ^{o}C (lit [25] mp 270–271 ^{o}C); IR (nujol): 1785 (>C=O stretch, five-membered lactone), 1742 and 1708 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione), and 1650 (>C=C< stretch) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 6.17 (dd, 1H, J = 8.0 Hz and 2.5 Hz, 7'-H), 6.98 (dd, 2H, J = 8.0 Hz and 2.5 Hz, 5'-H, 6'-H), 7.05–7.45 (m, 10H, 2"-H 3"-H, 4"-H, 5"-H, 6"-H, 2'"-H, 3'"-H, 4'"-H, 5'''-H and 6'''-H), 7.60–8.10 (m, 5H, 4-H, 5-H, 6-H, 7-H and 4'-H); ms: (70 eV, electron impact) m/z 444 (M^+ +2, 9.2), 442 (M^+, 100), 414 (10.4), 369 (10.7), 341 (10.2), 339 (17.5), 281 (10.3), 265 (17.3), 252 (16.8), 221 (27.4), 209 (10.0), 165 (16.1), 105 (9.9), 104 (22.7), 76 (20.9). *Anal*. Calcd. for $C_{30}H_{18}O_4$: C, 81.44; H, 4.10. Found: C, 81.12; H, 3.79.

(*Z*)-2-((3-oxoisobenzofuran-1(3*H*)-ylidene)(*p*-tolyl)methyl)-2-*p*-tolyl-1*H*-indene-1,3(2*H*)-dione (6b). This compound was obtained as light yellow crystalline solid, 44.5% yield, mp 284–285 °C; IR (nujol): 1785 (>C=O stretch, five-membered lactone), 1745 and 1710 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione), and 1642 (>C=C< stretch) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 2.05 (s, 3H, 4''-CH_3), 2.22 (s, 3H, 4'''-CH_3), 6.17 (dd, 1H, J = 8.0 Hz and 2.5 Hz, 7'-H), 6.77 (d, 2H, J = 8.0 Hz, 3''-H and 5''-H), 6.93 (d, 2H, J = 8.0 Hz, 3'''-H and 5'''-H), 7.05–7.35 (m, 6H, 5'-H, 6'-H, 2''-H, 6''-H, 2'''-H and 6'''-H), 7.60–8.05 (m, 5H, 4-H, 5-H, 6-H, 7-H and 4'-H); ms: (70 eV, electron impact) m/z 472 (M^+ +2, 10.4), 471 (M^+ +1, 41.5), 470 (M^+, 100), 442 (18.8), 426 (10.3), 411 (16.4), 280 (52.4), 252 (33.7), 235 (34.2), 224 (27.8), 223 (72.2), 149 (75.9), 119 (61.5), 104 (44.3), 91 (53.4), 85 (40.4), 77 (22.3), 76 (34.3), 71 (58.5), 67 (23.5), 65 (24.3), 57 (89.7). *Anal*. Calcd. for $C_{32}H_{22}O_4$: C, 81.69; H, 4.71. Found: C, 81.81; H, 4.38.

(*Z*)-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)(3-oxoisobenzofuran-1(3*H*)-ylidene)methyl)-1*H*-indene-1,3(2*H*)-dione (6c). This compound was obtained as light yellow crystalline solid, 17.2% yield, mp 265–268 °C (lit [25] mp 269 °C); IR (nujol): 1784 (>C=O stretch, five-membered lactone), 1742 and 1710 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione), and 1640 (>C=C< stretch) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 3.80 (s, 3H, 4''-OCH_3), 3.76 (s, 3H, 4'''-OCH_3), 6.18 (dd, 1H, J = 8.0 Hz and 2.5 Hz, 7'-H), 6.71 (d, 2H, J = 8.5 Hz, 3'''-H and 5'''-H), 6.96 (d, 2H, J = 8.5 Hz, 3''-H and 5''-H), 7.10–7.35 (m, 6H, 5'-H, 6'-H, 2''-H, 6''-H, 2'''-H and 6'''-H), 7.60–8.00 (m, 5H, 4-H, 5-H, 6-H, 7-H and 4'-H); ms: (70 eV, electron impact) m/z 504 (M^+ +2, 10.6), 503 (M^+ +1, 25.8), 502 (M^+, 100), 474 (20.1), 458 (12.6), 430 (11.5), 402 (17.9), 252 (31.4), 251 (20.4), 224 (21.7), 223 (62.4), 181 (25.9), 135 (35.9), 107 (14.9), 92 (15.6), 77 (29.3), 76 (14.5), 69 (23.9), 57 (59.1). *Anal*. Calcd. for $C_{32}H_{22}O_6$: C, 76.48; H, 4.41. Found: C, 76.69; H, 4.11.

(*Z*)-2-(4-chlorophenyl)-2-((4-chlorophenyl)(3-oxoisobenzofuran-1(3*H*)-ylidene)methyl)-1*H*-indene-1,3(2*H*)-dione (6d). This compound was obtained as shining light yellow crystalline solid, 75.0% yield, mp 322–324 °C; IR (nujol): 1787 (>C=O stretch, five-membered lactone), 1740 and 1712 (>C=O stretch, 1*H*-indene-1,3(2*H*)-dione), and 1647 (>C=C< stretch) cm^{-1}; ^{1}H NMR (deuteriochloroform): δ 6.20 (dd, 1H, J = 7.75 Hz and 2.5 Hz, 7'-H), 6.80–7.40 (m, 10H, 5'-H, 6'-H, 2''-H, 3''-H, 5''-H, 6''-H, 2'''-H, 3'''-H, 5'''-H and 6'''-H), 7.60–8.10 (m, 5H, 4-H, 5-H, 6-H, 7-H and 4'-H); ms: (70 eV, electron impact) m/z 514 (M^+ +4, 10.3), 513 (M^+ +3, 15.5), 512 (M^+ +2, 43.5), 511 (M^+ +1, 22.6), 510 (M^+, 59.8), 470 (38.2), 442 (11.9), 368 (14.7), 339 (17.9), 258 (39.9), 257 (32.5), 256 (100), 255 (40.0), 236 (11.8), 235 (10.2), 221 (22.8), 199 (17.3), 193 (36.0), 165 (52.6), 104 (51.4), 77 (19.8), 76 (56.3), 69 (26.0), 57 (39.6), 55 (35.7). *Anal*. Calcd. for $C_{30}H_{16}Cl_2O_4$: C, 70.46; H, 3.15. Found: C, 70.81; H, 2.93.

Photolysis of 2-aryl-2-bromo-2-1*H*-indene-1,3(2*H*)-diones (2) in acetone: General procedure
A solution of 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-dione (**2**) (1.00 g) in dry acetone (100 mL) was deoxygenated by bubbling oxygen-free dry nitrogen gas for 20 min. The solution was then irradiated with a 450 W Hanovia mercury vapor lamp in a pyrex reactor under nitrogen atmosphere for a total period of 20–25 min. Distillation of the solvent left a residue which upon crystallization from aqueous ethanol yielded 2-aryl-1*H*-indene-1,3(2*H*)-dione (**1**) as a white crystalline solid.

2-Phenyl-1*H*-indene-1,3(2*H*)-dione (1a). This compound was obtained by photoirradiating the solution of **2a** for a total period of 25 min as white crystalline solid in 88.0% yield, mp 145–146 °C (lit [22] mp 148–149 °C).

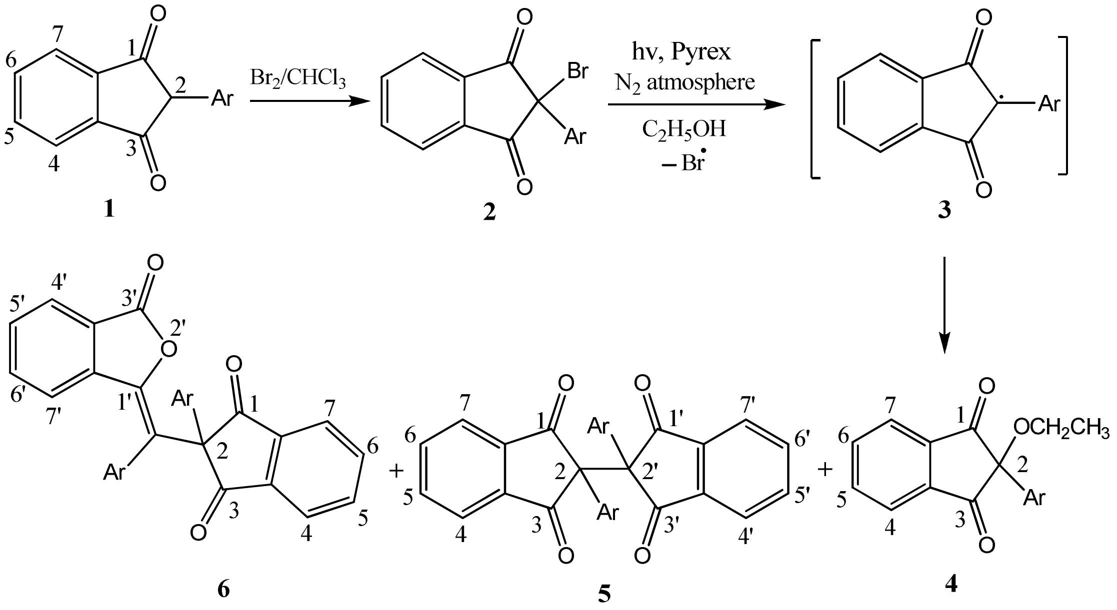
2-*p*-Tolyl-1*H*-indene-1,3(2*H*)-dione (1b). This compound was obtained by photoirradiating the solution of **2b** for a total period of 25 min as white crystalline solid in 90.0% yield, mp 145–147 °C (lit [22] mp 144–148 °C).

2-(4-Methoxyphenyl)-1*H*-indene-1,3(2*H*)-dione (1c). This compound was obtained by photoirradiating the solution of **2c** for a total period of 20 min as white crystalline solid in 92.0% yield, mp 152–153 °C (lit [22] mp 152–154 °C).

2-(4-Chlorophenyl)-1*H*-indene-1,3(2*H*)-dione (1d). This compound was obtained by photoirradiating the solution of **2d** for a total period of 20 min as white crystalline solid in 91.0% yield, mp 143–145 °C (lit [22] mp 142–145 °C).

RESULTS AND DISCUSSION

2-Aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (**2**) needed for the purpose were prepared by bromination of the corresponding 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1**) with $Br_2/CHCl_3$ according to the procedure as described in the literature [22]. Photoirradiation of a deoxygenated solution of **2** in anhydrous ethanol with a 450 W Hanovia mercury vapor lamp under nitrogen atmosphere in a pyrex reactor resulted in the formation of a mixture of photoproducts (**4–6**) which were separated by column chromatography (Scheme 1).



1a, **2a**, **3a**, **4a**, **5a**, **6a**; Ar = C_6H_5
1b, **2b**, **3b**, **4b**, **5b**, **6b**; Ar = C_6H_4-CH_3(*p*)
1c, **2c**, **3c**, **4c**, **5c**, **6c**; Ar = C_6H_4-OCH_3(*p*)
1d, **2d**, **3d**, **4d**, **5d**, **6d**; Ar = C_6H_4-Cl(*p*)

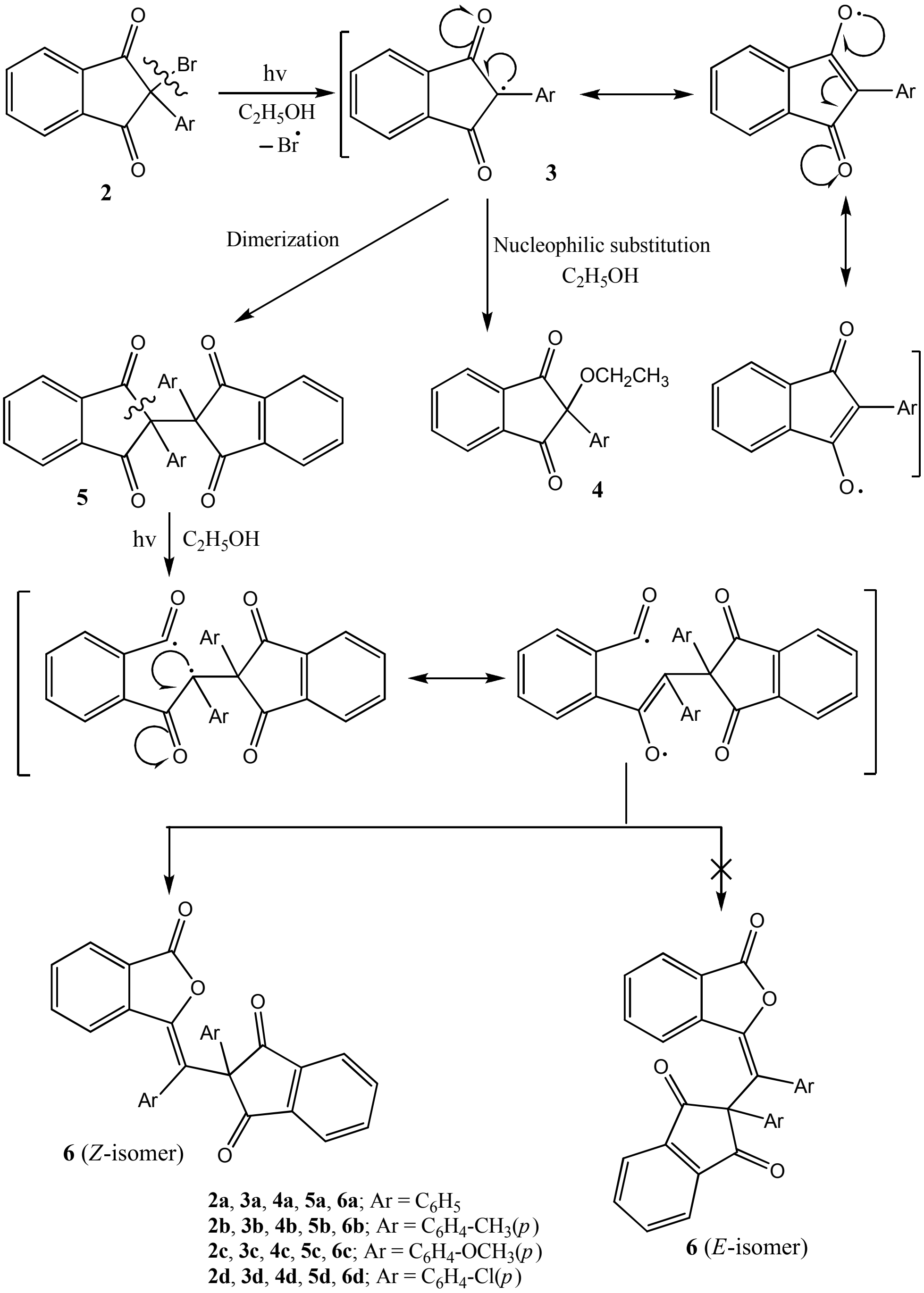
Scheme 1: Photolysis of 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (2) in ethanol.

The structures of all the photoproducts **4–6** were established on the basis of their physical and spectral data. The most characteristic feature of IR spectra of 2-aryl-2-ethoxy-2-1*H*-indene-1,3(2*H*)-diones (**4a**–**4d**) was that they displayed two strong absorption bands in the regions at 1745–1740 cm^{-1} and 1712–1708 cm^{-1} due respectively to asymmetrical and symmetrical coupling between the two in-plane carbonyl groups of 1*H*-indene-1,3(2*H*)-dione moiety [19–22, 27]. The ^1H NMR spectra of **4a**–**4d** displayed the characteristic pattern of an ethoxy group, *i.e.* a three-proton triplet (J = 7.0 Hz) in the region at δ 1.17–1.20 and a two-proton quartet (J = 7.0 Hz) centered at δ 3.55. The methyl protons of the *p*-tolyl and *p*-anisyl groups present in **4b** and **4c**, however, showed sharp singlets at δ 2.25 and δ 3.66, respectively. The aromatic region of the spectra of **4b**–**4d** exhibited two doublets (J = 8.0–8.5 Hz) each integrating for two protons in the regions at δ 6.77–7.00 and δ 7.25–7.35 attributed to $C_{3'}$-H & $C_{5'}$-H and $C_{2'}$-H & $C_{6'}$-H respectively. However, absorption due to the protons of phenyl group, *i.e.* $C_{2'}$-H, $C_{3'}$-H, $C_{4'}$-H, $C_{5'}$-H and $C_{6'}$-H appeared as a complex multiplet in the region at δ 7.10–7.40 in compound **4a**. The four aromatic protons due to 1*H*-indene-1,3(2*H*)-dione moiety present in **4a**–**4d** appeared, in each case, as a complex multiplet in the region at δ 7.60–8.10. Further, the ratio of aromatic to aliphatic protons was found satisfactory (*vide* experimental). However, Kapoor *et al* [19] have prepared **4c** by heating a solution of 2-bromo-2-(4-methoxyphenyl)-1*H*-indene-1,3(2*H*)-dione (**1c**) in dry ethanol at reflux.

The ir spectra of **5a**–**5d** displayed two strong absorption bands characteristic of carbonyl group of 1*H*-indene-1,3(2*H*)-dione moiety [19–22, 27] in the regions at 1745–1738 cm^{-1} and 1720–1705 cm^{-1}. The ^1H NMR spectra of **5b** and **5c** showed sharp singlets at δ 2.25 and δ 3.70 due to methyl protons of two *p*-tolyl and two *p*-anisyl groups present therein respectively. Likewise, the eight aromatic protons of the two *p*-tolyl groups in **5b** appeared as a singlet at δ 7.05. The eight aromatic protons of two *p*-anisyl groups in **5c** resonated as two doublets, each integrating for four protons, centered at δ 6.70 and δ 7.05 (J = 8.5 Hz) respectively. However, ten aromatic protons of the two phenyl groups in **5a** and eight aromatic protons of two 4-chlorophenyl groups in **5d**, in each case, resonated as a complex multiplet in the regions at δ 7.10–7.40 and at δ 6.95–7.35 respectively. The eight aromatic protons of the two 1*H*-indene-1,3(2*H*)-dione moieties present in **5a**–**5d** were appeared, in each case, as a complex multiplet in the region at δ 7.55–8.15. Further, the ratio of aromatic to aliphatic protons in **5** was found satisfactory. The mass spectra of **5a**–**5d** exhibited the highest peaks at m/z ($M^+/2+1$) which were also the base peaks of their spectra (*vide* experimental). All these spectral evidences presented above strongly support a C–C coupled dehydro symmetrical dimeric structure to **5**. It is worthy to mention here that Becker [23] has prepared **5a** and **5c** by DDQ assisted dimerization of 2-phenyl-1*H*-indene-1,3(2*H*)-dione and 2-(4-methoxyphenyl)-1*H*-indene-1,3(2*H*)-dione respectively whereas Karele *et al* [28] has prepared **5a** and **5c** by oxidation of the corresponding 2-aryl-1*H*-indene-1,3(2*H*)-diones in presence of $FeCl_3$ in aq. C_2H_5OH or $K_3Fe(CN)_6$ or $(NH_4)_2S_2O_8$ in aq. or aq.-alc. NaOH. However, Harnciar [26] has reported the synthesis of **5d** during substitution of phthalides and 1,3-indandiones by chlorine, bromine and thiocyanate.

The ir spectra of the compounds **6a**–**6d** exhibited, in each case, a strong absorption band in the region at 1787–1784 cm^{-1} due to five-membered lactone carbonyl [19–21] in addition to two strong carbonyl bands in the regions at 1745–1740 cm^{-1} and 1712–1708 cm^{-1} characteristic of 1*H*-indene-1,3(2*H*)-dione moiety [19–22, 27] and a band of medium intensity in the region at 1640–1650 cm^{-1} assignable to >C=C< stretch. The aliphatic region of the ^1H NMR spectrum of **6b** showed two singlets each integrating for three protons located at δ 2.05 and δ 2.22 due to *p*-tolyl groups. The former can easily be assigned to 4''–CH_3 protons and the latter to the 4'''–CH_3 protons. The shielding of the former protons relative to the latter presumably arises due to the orthogonal disposition of the *p*-tolyl group present on the double bond *w.r.t.* benzene ring of the phthalide part. However, the methyl protons of two *p*-anisyl groups in **6c** resonated as singlets in the region at δ 3.76–3.80 and could not be distinguished. The most characterstic feature of the ^1H NMR spectra of **6a**–**6d**, in each case, is that they displayed one-proton doublet of a doublet in the region at δ 6.17–6.20 (J = 8.0 Hz and 2.5 Hz) assignable to 7'–H in accordance with the results reported in the literature for the analogous compounds [19]. The chemical shift of this proton not only suggests the presence of 3-oxoisobenzofuran-1(3*H*)-ylidene moiety in **6** but also supports the view that the phenyl/4-substitutedphenyl group located on the double bond is held orthogonal to the benzene ring of the 3-oxoisobenzofuran-1(3*H*)-ylidene part thereby suggesting (*Z*)-configuration to it. Had the (*E*)-isomer been formed, the shielding of 7'-H would not have been observed rather it would have experienced deshielding due to interaction with the lone pairs of electrons present on oxygen atoms of 1*H*-indene-1,3(2*H*)-dione moiety. The other aromatic protons, however, appeared in the expected regions. It is worthy to mention here that Rigaudy et al [25] have synthesized **6a** and **6c** by oxidative photoisomerization of the corresponding 2-aryl-1*H*-indene-1,3(2*H*)-diones using ether as solvent. Further, the mass spectral data and analytical data of **4**, **5** and **6** were found in good agreement with their molecular formulae (*vide* experimental).

The mechanism may easily be rationalized in terms of initial β-cleavage in which homolytic cleavage of C_2–Br bond occurs preferentially to furnish resonance stabilized free radical (**3**) which leads to the formation of a dimerization product (**5**) that subsequently undergoes α-cleavage (Norrish Type 1 reaction) followed by reorganization of the biradical to give stereoselective photoproduct (**6**). The free radical (**3**) simultaneously also undergoes nucleophilic substitution by C_2H_5OH to give ethoxy derivative (**4**). The amount of the substitution product (**4**) obtained depends upon the nature of $C_{4'}$-substituent. With electron-donating substituents, *i.e.* CH_3 and OCH_3, sizeable amounts of the substitution products were obtained while with substituent such as chloro or absence of any substituent, only trace amounts of the substitution products were obtained (Scheme 2).

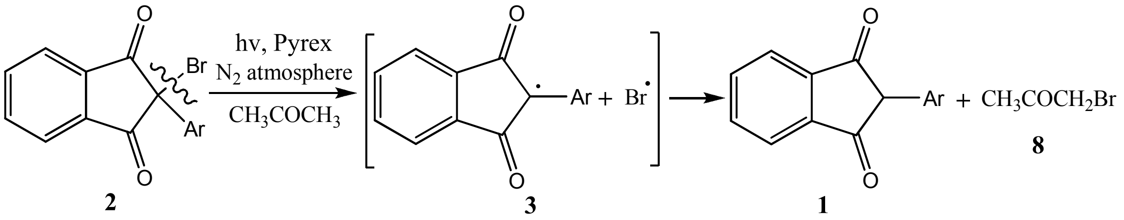


2a, **3a**, **4a**, **5a**, **6a**; Ar = C_6H_5
2b, **3b**, **4b**, **5b**, **6b**; Ar = C_6H_4-CH_3(*p*)
2c, **3c**, **4c**, **5c**, **6c**; Ar = C_6H_4-OCH_3(*p*)
2d, **3d**, **4d**, **5d**, **6d**; Ar = C_6H_4-Cl(*p*)

Scheme 2: Mechanistic pathway of photochemical synthesis of 4, 5 and 6 from 2 in ethanol

Further, with a view to examine the effect of the polarity of the solvent on the manner of the phototransformations of all the four 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (**2**), their photochemistry was also investigated in dry acetone under similar conditions as employed for anhydrous ethanol. The usual chromatographic work up of the photolysates yielded the corresponding 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1**) as white leaflets in excellent yields.

Mechanistically, the phototransformation **2**→**1** may be invisaged to occur through an initial homolytic cleavage of C_2–Br bond yielding the resonance stabilized radical (**3**) which then abstracts a hydrogen radical from acetone to give **1**. The acetone radical $CH_3COCH_2^{\cdot}$ (**7**) may then combine with the bromine radical to form bromoacetone (**8**). A support to this mechanism comes from the observation that during distillation of acetone from the photolysate, the formation of a lachrymatory substance presumably bromoacetone (**8**) was detected though not characterized (Scheme 3).



1a, **2a**, **3a**; Ar = C_6H_5: **1b**, **2b**, **3b**; Ar = C_6H_4-CH_3(*p*):
1c, **2c**, **3c**; Ar = C_6H_4-OCH_3(*p*): **1d**, **2d**, **3d**; Ar = C_6H_4-Cl(*p*)

Scheme 3: Photolysis of 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (2) in acetone

The structures of all the four 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1a–1d**) were corroborated by their undepressed mixed mp, co-tlc and superimposable ir and ^{1}H NMR spectra with those of authentic samples.

CONCLUSION

Based upon the above observations, it is concluded that the photobehaviour of 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (**2**) is solvent dependent. In acetone, only photodebromination occurs to afford the corresponding parent 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1**). However, in ethanol, the 2-aryl-1*H*-indene-1,3(2*H*)-dione radical (**3**) produced as a result of homolytic cleavage of the C_2–Br bond undergoes dimerization to give the 2,2'-diaryl-1*H*,1'*H*-2,2'-biindene-1,1',3,3'(2*H*,2'*H*)-tetrones (**5**) which subsequently undergo Norrish Type 1 reaction to afford the corresponding (*Z*)-2-(aryl)-2-((aryl)(3-oxoisobenzofuran-1(3*H*)-ylidene)methyl)-1*H*-indene-1,3(2*H*)-diones (**6**). Simultaneously, the radical **3** upon nucleophilic substitution by C_2H_5OH, furnishes 2-aryl-2-ethoxy-1*H*-indene-1,3(2*H*)-diones (**4**) in varying amounts depending upon the nature of $C_{4'}$-substituent.

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