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Stereoselective photochemical synthesis of some (*Z*)-3-(alkoxymethylene) isobenzofuran-1(3*H*)-ones

Satbir Mor* and Som Nath Dhawan#

**Dept. of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar-125001, Haryana, India, E-mail: satbir_mor@yahoo.co.in, +91-1662-263397, +91-1662-276240*
#Dept. of Chemistry, Kurukshetra University, Kurukshetra-132119, Haryana, India
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Abstract: In the present study, we have described stereoselective synthesis of some novel (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**) by photolysis of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl) benzamide/ 4-substituted benzamides (**6**) using acetone as solvent in high yields. The structures of all the photoproducts were elucidated by the application of spectral (IR, ^{1}H NMR and mass), and elemental analytical techniques.

Keywords: Photolysis; 1*H*-indene-1,3(2*H*)-diones; (*Z*)-isobenzofuran-1(3*H*)-ones.

1. Introduction

A large number of 3-alkyl and 3-alkylidene isobenzofuran-1(3*H*)-ones have been isolated from natural sources [1]. Typical examples are catalpalactone [2a], (-)-hydrastine [2b], vermistatin [2c], (+)-spirolaxine [2d], alcyopterosin E [2e], rubiginone-H [2f], typhaphthalide [2g], isopestacin [2h], cryphonectric acid [2i], fuscinarin [2j], etc. Some members of this family are known to possess interesting physiological activities and reported for attractive applications in medicinal chemistry by different investigators, being used as anti-bacterial, anti-spasmodic, anti-convulsant, anti-HIV, anti-asthmatic, anti-tumor, anti-platelet activities, anesthesia prolongation, PGF2a inhibitory, herbicidal, and insecticidal properties [3]. 3-Styryl phthalides are used as color formers for heat and pressure sensitive recording materials [4]. Also, isobenzofuran-1(3*H*)-ones are valuable intermediates in the synthesis of various polycyclic compounds [5] and intermediates [6] for the synthesis of a host of other naturally occurring biologically active compounds [7]. The importance and utility of these derivatives have led the chemists for development of numerous methods for their synthesis including the following categories: (i) a high temperature method originally

developed by Gabriel [8]; (ii) base catalyzed condensation of phthalides with aldehydes [9]; (iii) Wittig-Horner type condensation of aromatic aldehydes and phthalide phosphonates [10]; (iv) condensation of an *o*-halobenzoic acid with Cu(I) acetylides (Castro reaction) [11]; (v) cyclization reractions catalyzed by strong bases such as DBU, NaOH, KOH, $NaOCH_3$, $NaOC_2H_5$, $(C_2H_5)_2NH$ [12]. Strong acides such as CF_3COOH, CF_3SO_3H, montmorillonite K-10, Ac_2O, $ZrOCl_2.8H_2O$ [13] are also used in the synthesis of 3-alkyl phthalides. Preparation of these compounds have also been reported through iodolactonization of methyl 2-ynylbenzoates [14], palladium [15] and solid base [16] catalyzed reactions, photocatalyzed reaction by titanium dioxide [17] and comparative intramolecular dehydrative lactonization of 4-oxo carboxylic acids [18]. The synthesis of 3-alkylidene phthalides from photochemical rearrangements of substituted inden-1,3-diones and electrochemical reduction of phthaloyl chloride has also been reported [19]. In recent years, the use of solid acids as heterogeneous catalysts has received tremendous interest in different areas of organic synthesis that has also been applied for the synthesis of this class of compounds [20]. The synthetic methodologies and applications of this class of compounds studied recently have been reported by different researchers [21]. Photochemistry of carbonyl compounds constitutes an important area of research due to high degree of comprehension of mechanistic complexities of photochemical reactions of this category of compounds. Photochemical α- and β-cleavage processes in carbonyl compounds have drawn considerable attention of organic photochemists in the past. Which pathway actually predominates depends upon the structure of ketone and presence of substituents [22]. β-Cleavage route has been examined on n–π* excitation of certain ketones [23] and also in ketones holding α-substituents which have a propensity for formation of radicals, *i.e.* halogen [24,25], acetoxy [26], aryloxy [27], epoxy [28], sulphonyloxy [29], thiyl [30–34], etc. However, reaction pathway can be influenced by the presence of substituents other than α-position [35]. Moreover, both ionic [36] and radical intermediates have been involved in this course of action depending upon nature of the starting material and type of n–π* excited states, *i.e.* singlet or triplet involved. Photochemical behaviour of a few *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides/ heterylamides (**15**) has been studied earlier in our laboratory and it was observed that the presence of both hydroxyl and arylamido/ heterylamido functional groups in these cases at C_2 in 2,2-disubstituted-1*H*-indene-1,3(2*H*)-diones does not alter the course of the photochemical transformation and still the only course of the reaction remains to be Norrish Type 1 to give first a 1,5-biradical which subsequently reorganizes to afford the corresponding *N*-benzoyl/4-substituted benzoyl/ heteroyl-3-oxo-1,3-dihydroisobenzofuran-1-carboxamides [37] in excellent yields. With a view to investigate whether the hydrogen bonding between the 2-hydroxy substituent and one of the carbonyl groups of the 1*H*-indene-1,3(2*H*)-dione moiety plays any significant role in the photochemical transformations of *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl) benzamides/ heterylamides (**15**), we became interested in examining the effect of 2-alkoxy instead of a 2-hydroxy substituent on the manner of these photochemical reactions. Therefore, in continuation of our previous studies [37–40] on the photochemistry of 2,2-disubstituted-1*H*-indene-1,3(2*H*)-diones, in the current article, we report the synthesis of some 3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**) with complete *Z* selectivity by photolysis of the corresponding *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) in high yields.

2. Materials and methods

2.1 General: The chemicals used in the present investigation were procured from commercial sources and were used as such or after necessary purification following literature procedures. Melting points (°C) of the synthesized compounds were determined on an electrothermal apparatus in open head capillaries and are uncorrected. Purity of the synthesized compounds and progress of the reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates (chloroform-methanol) as stationary phase and different combinations of solvents as mobile phase. The developed TLC plates were examined using iodine staining for visualization of the spots. The synthesis of compounds was carried out by stirring on a magnetic stirrer and/ or heating at desired temperature on a water bath. Photochemical reactions were performed in a Pyrex photochemical reactor at room temperature under dry N_2 atmosphere using Hanovia mercury vapour lamp as a source of UV light. The structures of the synthesized compounds were corroborated by employing different spectral (IR, NMR, Mass) and elemental analytical techniques. IR spectra were scanned on a Perkin–Elmer 842 IR spectrophotometer in the range of 400-4000 cm^{-1} using Nujol mulls and absorption frequencies (ν) are stated in cm^{-1}. ^1H NMR spectra were recorded on 90 MHz Perkin-Elmer R-32 spectrometer using deuteriochloroform ($CDCl_3$) as solvent. The chemical shift values (δ) are reported in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; sext, sextet; sept, septet; m, multiplet; dd, doublet of doublets. Coupling constant (*J*) values are given in Hertz (Hz). Mass spectra were recorded at 70 eV using a VG-70S instrument. Elemental analysis data was recorded on Exeter analytical CE 440 and Perkin-Elmer 2400 instruments and analytical results for C and H were found within ±0.4% of the theoretical values.

2.2 General procedure for the synthesis of *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (3): A mixture of ninhydrin hydrate (**1**) (10.0 g, 0.05 mole) and benzamide/ 4-substituted benzamide (**2**) (0.05 mole) in benzene (100 mL) was heated on a water bath at reflux temperature till the completion of the reaction (1–1.5 hr). The water, formed during the reaction, was removed by azeotropic distillation using Dean and Stark apparatus. The solid separated after cooling of the reaction mixture was filtered and crystallized from ethanol-hexane mixture to give the desired product in high yield [41–43].

2.3 General procedure for the synthesis of *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (4): A mixture of *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl) benzamide/ 4-substituted benzamide (**3**) (0.07 mole) and thionyl chloride (12.20 mL, 0.14 mole) in dry dichloromethane (400 mL) was refluxed on a water bath till the completion of the reaction (2–2.5 hr). The solvent was removed under reduced pressure and the resulting residue triturated with benzene, filtered and crystallized from benzene to give **4** as colorless crystals [42,43].

2.4 General procedure for the synthesis of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (6): A solution of *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide/ 4-substituted benzamide (**4**) (0.0030 mole) in anhydrous alcohol (**5**) (100 mL) was heated at reflux on a water bath till the completion of the reaction (1–10 hr). Removal of the solvent under reduced pressure gave a residue that upon crystallization from a suitable solvent furnished the desired product (**6**) in high yields [42–44].

2.5 General procedure for photochemical synthesis of (*Z*)-3-(alkoxymethylene) isobenzofuran-1(3*H*)-ones (7): Solution of **6**

(1.0 g) in acetone (100 mL) was deoxygenated by bubbling oxygen-free dry nitrogen gas for 15 min. Thereafter, the solution was irradiated with light from a 450 Watts Hanovia mercury lamp in a Pyrex reactor under dry nitrogen atmosphere for a total period of 10–11 hr. The progress of the reactions was monitored by TLC on aliquots withdrawn from the reaction mixture at different intervals of time. After completion of the reaction, solvent was removed in vaccuo which left light yellow viscous oil that was chromatographed over a column of silica gel (30.0 g, column packed in hexane). Elution of the column first with hexane and then with hexane-benzene mixture (1:1, v/v) yielded (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**) as very dense colorless oil. Later elutions with benzene and then with benzene-acetone mixture (9:1, v/v) yielded white crystalline solid which was identified as benzamide/ 4-substituted benzamide (**2**) as shown by co-TLC, undepressed mixed mp and superimposable IR & ^{1}H NMR spectra with those of authentic sample whose physical data are given in Table 1

The characterization data of the compounds (**7a–7d**) are given as follows:

(*Z*)-3-(methoxymethylene)isobenzofuran-1(3*H*)-one (7a): The compound **7a** was obtained by photolysis of each of *N*-(2-methoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (**6a**), 4-chloro-*N*-(2-methoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (**6b**), 4-methoxy-*N*-(2-methoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (**6c**) and *N*-(2-methoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (**6d**) in acetone as solvent (Table 1). IR (Nujol): 1778 (C=O stretch (five-membered lactone)), 1640 (C=C stretch) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 3H, OCH_3), 5.89 (s, 1H, =C-H), 7.50–7.70 (m, 3H, H-4, H-5, H-6), 7.91 (dd, *J* = 8.0 Hz, *J* = 2.5 Hz, 1H, H-7); ms: (70 eV, electron impact) m/z 176 (M^+). *Anal*. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.54. Found: C, 68.31; H, 4.23.

(*Z*)-3-(ethoxymethylene)isobenzofuran-1(3*H*)-one (7b): The compound **7b** was obtained by photolysis of each of *N*-(2-

Table 1: Physical data of (*Z*)-isobenzofuran-1(3*H*)-ones (**7**) and 4-substituted benzamides (**2**).

Compound photolysed (**6**)	Time of irradiation (hr)	Isobenzo furan-1(3*H*)-one obtained (**7**)	Yield of **7** (%)	Benzamide/4-substituted benzamide obtained (**2**)	mp of **2** (°C)	Yield of **2** (%)
6a	10.0	**7a**	80	Benzamide (**2a**)	128–129	82
6b	10.5	**7a**	85	4-Chlorobenzamide (**2b**)	173–174	80
6c	11.0	**7a**	80	4-Methoxybenzamide (**2c**)	164–166	82
6d	10.0	**7a**	82	4-Methylbenzamide (**2d**)	161–162	81
6e	10.0	**7b**	81	Benzamide (**2a**)	128–129	84
6f	11.0	**7b**	79	4-Chlorobenzamide (**2b**)	173–174	82
6g	11.5	**7b**	81	4-Methoxybenzamide (**2c**)	164–166	80
6h	10.5	**7b**	82	4-Methylbenzamide (**2d**)	161–162	83
6i	10.0	**7c**	80	Benzamide (**2a**)	128–129	80
6j	11.0	**7c**	80	4-Chlorobenzamide (**2b**)	173–174	82
6k	10.5	**7c**	83	4-Methoxybenzamide (**2c**)	164–166	81
6l	11.0	**7c**	80	4-Methylbenzamide (**2d**)	161–162	85
6m	10.0	**7d**	80	Benzamide (**2a**)	128–129	81
6n	10.5	**7d**	78	4-Chlorobenzamide (**2b**)	173–174	82
6o	10.5	**7d**	81	4-Methoxybenzamide (**2c**)	164–166	84
6p	10.0	**7d**	80	4-Methylbenzamide (**2d**)	161–162	81

ethoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl) benzamide (**6e**), 4-chloro-*N*-(2-ethoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (**6f**), *N*-(2-ethoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methoxybenzamide (**6g**) and *N*-(2-ethoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (**6h**) in acetone as solvent (Table 1). IR (Nujol): 1773 (C=O stretch (five-membered lactone)), 1655 (C=C stretch) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.29 (t, *J* = 7.0 Hz, 3H, $OCH_2\underline{CH_3}$), 4.28 (q, *J* = 7.0 Hz, 2H, $O\underline{CH_2}CH_3$), 5.88 (s, 1H, =C-H), 7.50–7.80 (m, 3H, H-4, H-5, H-6), 7.91 (dd, *J* = 8.0 Hz, *J* = 2.5 Hz, 1H, H-7); ms: (70 eV, electron impact) m/z 190 (M^+). *Anal*. Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.26. Found: C, 69.73; H, 5.08.

(*Z*)-3-(propoxymethylene)isobenzofuran-1(3*H*)-one (7c): The compound **7c** was obtained by photolysis of each of *N*-(1,3-dioxo-2-propoxy-2,3-dihydro-1H-inden-2-yl)benzamide (**6i**), 4-chloro-*N*-(1,3-dioxo-2-propoxy-2,3-dihydro-1*H*-inden-2-yl) benzamide (**6j**), *N*-(1,3-dioxo-2-propoxy-2,3-dihydro-1*H*-inden-2-yl)-4-methoxybenzamide (**6k**) and *N*-(1,3-dioxo-2-propoxy-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (**6l**) in acetone as solvent (Table 1). IR (Nujol): 1778 (C=O stretch (five-membered lactone)), 1657 (C=C stretch) cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.92 (t, *J* = 7.0 Hz, 3H, $OCH_2CH_2\underline{CH_3}$), 1.70 (sext, *J* = 7.0 Hz, 2H, $OCH_2\underline{CH_2}CH_3$), 4.18 (t, *J* = 7.0 Hz, 2H, $O\underline{CH_2}CH_2CH_3$), 5.88 (s, 1H, =C-H), 7.45–7.75 (m, 3H, H-4, H-5, H-6), 7.91 (dd, *J* = 8.0 Hz, *J* = 2.5 Hz, 1H, H-7); ms: (70 eV, electron impact) m/z 204 (M^+). *Anal*. Calcd. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.88. Found: C, 70.91; H, 5.51.

(*Z*)-3-(isopropoxymethylene)isobenzofuran-1(3*H*)-one (7d): The compound **7d** was obtained by photolysis of each of *N*-(2-isopropoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (**6m**), 4-chloro-*N*-(2-isopropoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (**6n**), *N*-(2-isopropoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methoxybenzamide (**6o**) and *N*-(2-isopropoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (**6p**) in acetone as solvent (Table 1). IR (Nujol): 1780 (C=O stretch (five-membered lactone)), 1650 (C=C stretch) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.30 (d, *J* = 7.0 Hz, 6H, $OCH(\underline{CH_3})_2$), 5.12 (sept, *J* = 7.0 Hz, 1H, $O\underline{CH}(CH_3)_2$), 5.83 (s,1H, =C-H), 7.40–7.80 (m, 3H, H-4, H-5, H-6), 7.91 (dd, *J* = 8.0 Hz, *J* = 2.5 Hz, 1H, H-7); ms: (70 eV, electron impact) m/z 204 (M^+). *Anal*. Calcd. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.88. Found: C, 70.99; H, 6.02.

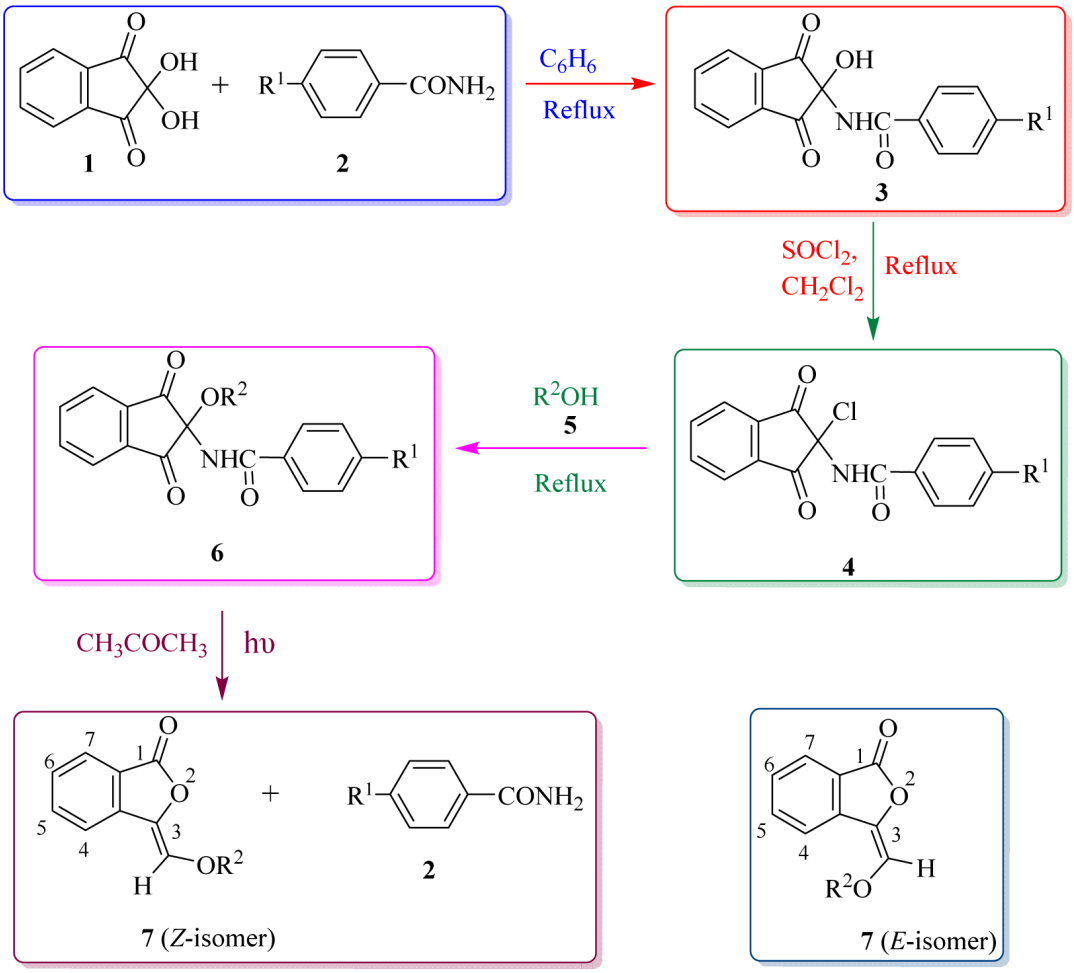
2.6 3-Oxo-1,3-dihydroisobenzofuran-1-carboxylic acid (phthalide-3-carboxylic acid) (8): (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7a**–**7d**), in each case, on standing at room temperature for about 6 months underwent oxidative hydrolysis to yield **8** as a colourless solid, yield 80–90%; mp 152–153 °C (Lit. [45] mp 153 °C); IR (Nujol): 2520–2760 (O–H stretch, carboxylic acid), 1785 (C=O stretch (five-membered lactone)), 1720 (C=O stretch, carboxylic acid) cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.83 (s, 1H, H-3), 7.40–7.85 (m, 4H, H-4, H-5, H-6), 10.50 (br s, 1H, exchangeable with D_2O, $COO\underline{H}$), 7.90 (dd, *J* = 8.0 Hz, *J* = 2.5 Hz, 1H, H-7); ms: (70 eV, electron impact) m/z 178 (M^+). *Anal*. Calcd. for $C_9H_6O_4$: C, 60.68; H, 3.40. Found: C, 60.83; H, 3.35.

3. Results and discussion

1.1. Chemistry

The protocol for the synthesis of (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**) is outlined in Scheme 1.

We obtained *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**3**) [41–43] upon reaction of ninhydrin (**1**) with corresponding benzamides (**2**) in benzene which upon subsequent treatment with $SOCl_2$ in CH_2Cl_2 afforded the corresponding *N*-(2-



Compounds	R^1	R^2	Compounds	R^1	R^2
2a	H	---	6c	OCH_3	CH_3
2b	Cl	---	6d	CH_3	CH_3
2c	OCH_3	---	6e	H	CH_2CH_3
2d	CH_3	---	6f	Cl	CH_2CH_3
3a	H	---	6g	OCH_3	CH_2CH_3
3b	Cl	---	6h	CH_3	CH_2CH_3
3c	OCH_3	---	6i	H	$CH_2CH_2CH_3$
3d	CH_3	---	6j	Cl	$CH_2CH_2CH_3$
4a	H	---	6k	OCH_3	$CH_2CH_2CH_3$
4b	Cl	---	6l	CH_3	$CH_2CH_2CH_3$
4c	OCH_3	---	6m	H	$CH(CH_3)_2$
4d	CH_3	---	6n	Cl	$CH(CH_3)_2$
5a	---	CH_3	6o	OCH_3	$CH(CH_3)_2$
5b	---	CH_2CH_3	6p	CH_3	$CH(CH_3)_2$
5c	---	$CH_2CH_2CH_3$	7a	---	CH_3
5d	---	$CH(CH_3)_2$	7b	---	CH_2CH_3
6a	H	CH_3	7c	---	$CH_2CH_2CH_3$
6b	Cl	CH_3	7d	---	$CH(CH_3)_2$

Scheme 1: Synthetic route of (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**)

chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl) benzamides (**4**) [42,43] in high yields. The *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) were prepared by refluxing the solution of *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4**) in corresponding anhydrous alcohols (**5**) in fairly good yields [42–44]. Photolysis of solution of **6** in acetone with light from a 450 Watts Hanovia mercury vapour lamp in a Pyrex reactor (10–11 hr) under N_2 atmosphere followed by usual chromatographic work up of the photolysates furnished 3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**) with complete *Z* selectivity as colorless dense oils and 4-substituted benzamides (**2**) as white crystalline solids in 79–85% and 80–85% yields, respectively (Table 1).

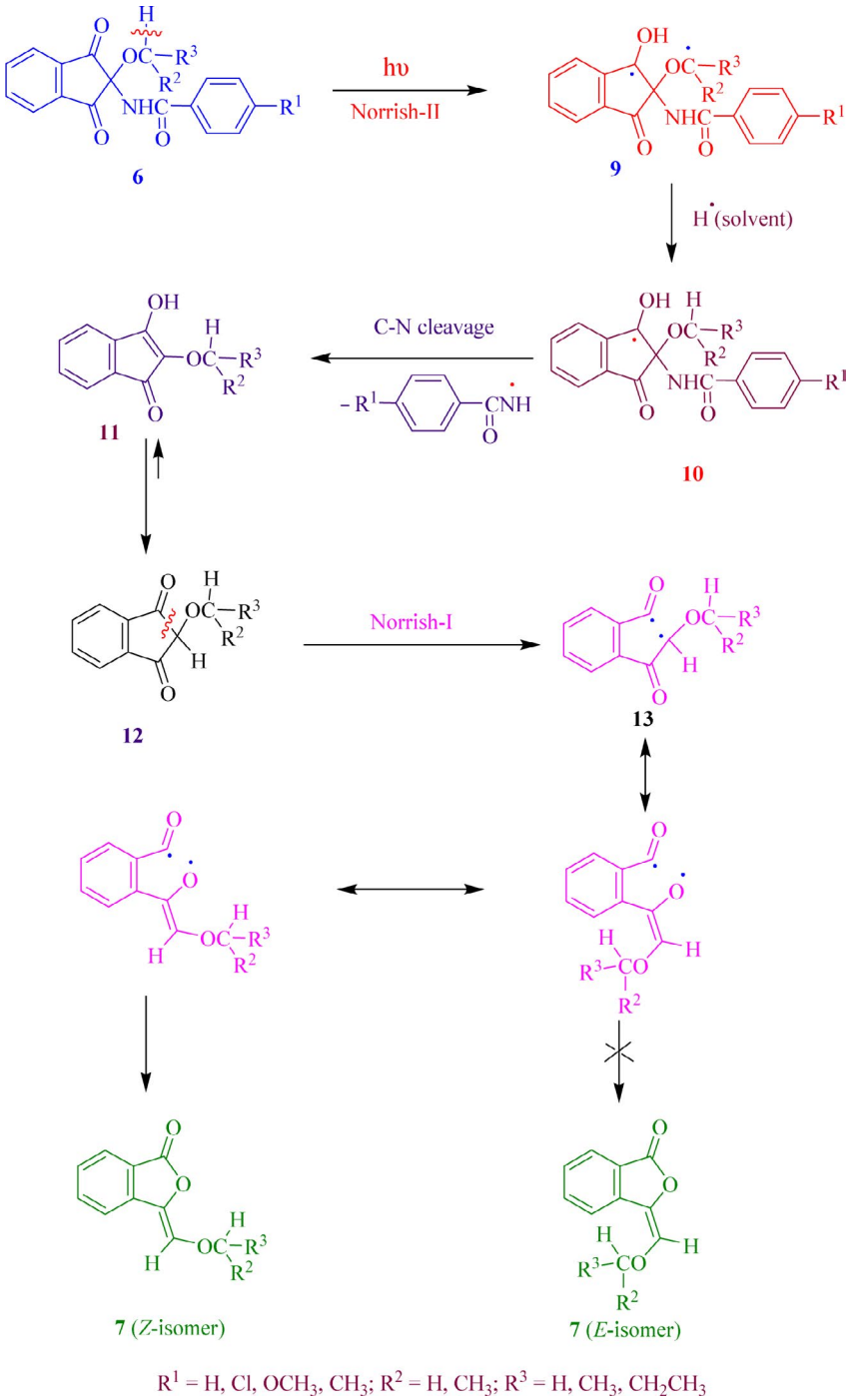
The structures of all the photoproducts **7** and **2** have been confirmed through analysis of their IR, ^{1}H NMR and mass spectra and analytical data (*vide experimental*). The IR spectra of **7a**–**7d**, in each case, displayed a strong absorption band (ν_{max}) in the region 1773–1780 cm^{-1} due to lactone (five-membered) carbonyl and a band of medium intensity in the region 1650–1660 cm^{-1} due to C=C stretching [38,39]. The most characteristic feature of ^{1}H NMR spectra of **7** was a one-proton singlet in the region at δ 5.83–5.89 which could safely be assigned to the olefinic proton (=C-H). The aromatic region of the spectra showed two distinct signals: a one-proton doublet of a doublet (*J* = 8.0 and 2.5 Hz) centered at δ 7.91 due to H-7 and a three-proton multiplet in the region at δ 7.40–7.80 attributable to H-4, H-5 and H-6. The deshielding of H-7 relative to other three aromatic protons is presumably due to the anisotropic effect of the adjacent lactone carbonyl group [6f,46]. The preference for (*Z*)- over (*E*)- isobenzofuran-1(3*H*)-ones (**7**) rests upon the results reported in literature [8f,11d,38,47] due to (i) in ^{1}H NMR, the H-4 aromatic proton resonated in the region at δ 7.40–7.80 with H-5 and H-6 which was not distinguished from them possibly due to absence of steric interactions between lone pair of electrons present on sp^3-hybridized oxygen atom of the olefinic alkoxy group and H-4 in the (*Z*)-isomer, and (ii) the olefinic proton chemical shift being somewhat at a higher field in the (*Z*)-isomer compared to (*E*)-isomer where the olefinic proton was deshielded due to lactone oxygen atom. Further, the mass spectral data and analytical data of **7** are in good agreement with their molecular formulae. The structures of the other photoproduct, *i.e.* 4-substituted benzamides (**2**) were established through their mp, mixed mp and superimposable IR and ^{1}H NMR spectra with their authentic samples.

An interesting point which warrants attention here is that all the (*Z*)-isobenzofuran-1(3*H*)-ones (**7a**–**7d**) have been isolated as colorless dense oils. All attempts aimed at their crystallization proved abortive.

The mechanistic details of the phototransformation, **6** → **7** & **2** discussed above have not been unraveled in the present investigation, however, it may be envisaged to occur through the mechanisms described as follows.

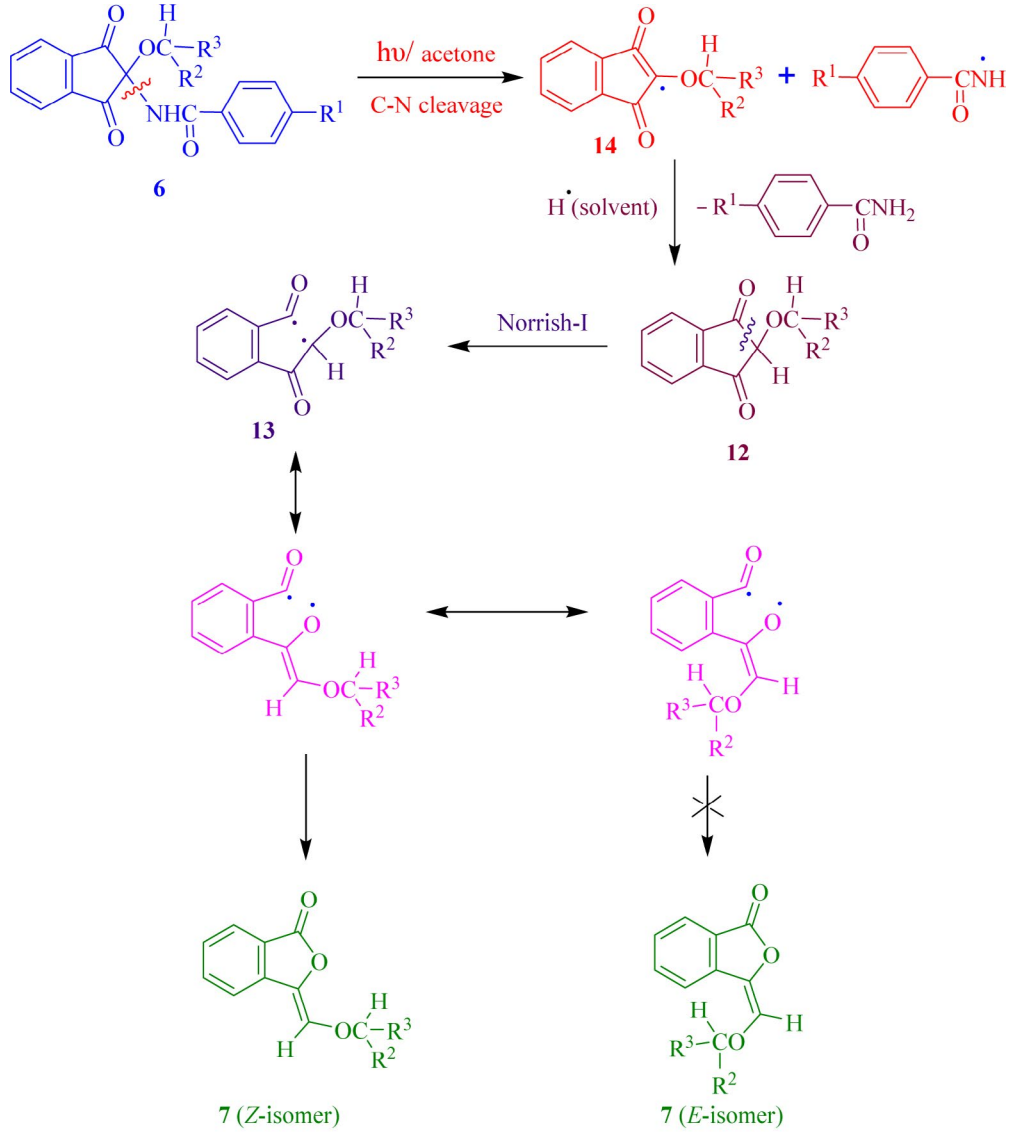
The *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) on irradiation first abstracts a γ-hydrogen (Norrish Type II reaction) leading to the formation of a 1,4-biradical (**9**) which subsequently abstracts a hydrogen radical from the solvent (acetone) or from the H_2O (moisture) which might have inadvertently crept in during the course of the photoreaction giving radical **10**. Since acetone is not known to be a good hydrogen donor, therefore, hydrogen must have come from moisture. The radical **10**, in turn, can either undergo C–O or C–N bond cleavage. Since the bond dissociation energy of a C–N bond is lower than that of a C–O bond [48], it preferentially undergoes C–N bond rupture yielding 2-alkoxy-1*H*-indene-1,3(2*H*)-dione (**12**) through keto-enol

tautomerism of the initially formed enol **11**. The 1*H*-indene-1,3(2*H*)-dione (**12**) furnished during the reaction then undergo Norrish Type I reaction followed by photoreorganization to give biradical **13** which subsequently recloses to afford (*Z*)-isobenzofuran-1(3*H*)-one (**7**). The benzamido/ 4-substituted benzamido radical may abstract a hydrogen radical from acetone or H_2O (moisture) to give benzamide/ 4-substituted benzamides (**2**) (Scheme 2).



Scheme 2: Plausible mechanism of formation of (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**) initiated through Norrish Type II reaction.

Alternatively, the possibility of direct *β*-cleavage of the C–N bond [23–25] upon irradiation of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) leading to the formation of radical **14** and benzamido/ 4-substituted benzamido radical cannot be ruled out. The radical **14** may, in turn, abstract a hydrogen radical from the solvent (acetone) or H_2O (moisture) or even benzamido radical to form 2-alkoxy-1*H*-indene-1,3(2*H*)-dione (**12**) which undergoes Norrish Type I reaction followed by photoreorganization to give biradical **13** that subsequently recloses to form (*Z*)-isobenzofuran-1(3*H*)-one (**7**) as depicted in Scheme 3. In a similar way benzamido/ 4-substituted benzamido radical may abstract a hydrogen radical from acetone or H_2O (moisture) to give benzamide/ 4-substituted benzamides (**2**).

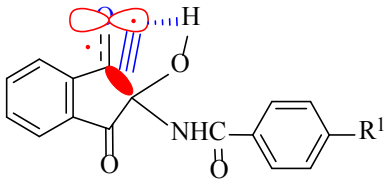


Scheme 3: Plausible mechanism of formation of (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**) initiated through direct *β*-cleavage of the C–N bond.

The 2-alkoxy-1*H*-indene-1,3(2*H*)-dione (**12**) formed during the photolysis of **6**, yielding biradical **13** through *α*-cleavage, can, in principle, furnish two stereoisomeric (*E*)- and (*Z*)- isobenzofuran-1(3*H*)-ones (**7**) but in all the sixteen cases studied during the present investigation, exclusive formation of the (*Z*)-isobenzofuran-1(3*H*)-ones (**7**) was observed.

Out of the two mechanistic pathways discussed above, the fragmentation process involving direct *β*-cleavage pathway is preferred in analogy with the results of photolysis of 2-alkoxy-2-(4-methoxyphenyl)-1*H*-indene-1,3(2*H*)-diones [38] already studied in our laboratory which did not yield Norrish Type II photoproducts even though they contain *γ*-hydrogens.

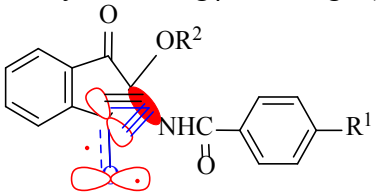
The irradiation of *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**15**) yield the *N*-benzoyl/ 4-substituted benzoyl-3-oxo-1,3-dihydroisobenzofuran-1-carboxamides [37] containing the benzamido group while the photolysis of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1H-inden-2-yl)benzamides (**6**) discussed in the present paper give the 3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**) bereft of the benzamido group. A plausible explanation for this photochemical behaviour of the indane-1,3-diones (**6**) may be offered in terms of *H*-bonding. In case of *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**15**), molecular models reveal that the singly occupied *n*-orbital of the *n*–*π** excited state of the indanedione carbonyl group lies close to the H-atom of the OH group in the same plane thus favouring *H*-bonding. Such a bonding may perceivably lock the *n*-orbital into a geometry which permits enhanced overlap between the *n*-orbital and the *σ*-orbital of the *α*-bond thereby facilitating *α*-cleavage (Fig. 1).



15

Fig. 1: *H*-bonding between *n*-orbital of the *n*–*π** excited state of the indanedione carbonyl group and H-atom of the OH group in **15**.

In contrast, in case of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**), the absence of *H*-bonding does not allow effective overlap between the *n*-orbital of the *n*–*π** excited state of the indanedione carbonyl group and *σ*-orbital of the *α*-bond thereby inhibiting *α*-cleavage. Instead, the *π**-orbital of the *n*–*π** excited state of the indanedione carbonyl group overlaps effectively with the *σ*-orbital of the *β*-bond thereby favouring *β*-cleavage (Fig. 2).

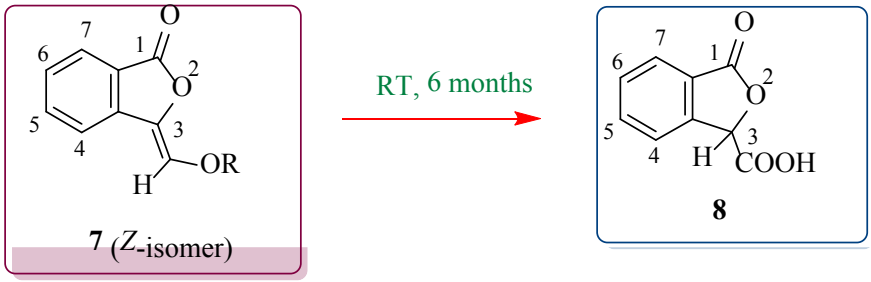


6

Fig. 2: Overlapping of *π**-orbital of the *n*–*π** excited state of the indanedione carbonyl group with *σ*-orbital of the *β*-bond thereby favouring *β*-cleavage in **6**.

Thus, it is inferred from the above results that *H*-bonding plays an important role in deciding the course of photochemical reactions in *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl) benzamides (**6**).

It is worthy to mention here that all the (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7a**–**7d**) upon keeping for about six months at ambient temperature, deposited a white crystalline solid, which has been characterized as 3-oxo-1,3-dihydroisobenzofuran-1-carboxylic acid (phthalide-3-carboxylic acid)



7a, R = CH_3; **7b**, R = CH_2CH_3; **7c**, R = $CH_2CH_2CH_3$; **7d**, R = $CH(CH_3)_2$

Scheme 4: Synthesis of 3-oxo-1,3-dihydroisobenzofuran-1-carboxylic acid (**8**) from (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**)

(**8**), mp 152–153 °C (Lit. [45] mp 153 °C) from its mass, IR and ^{1}H NMR spectra (Scheme 4).

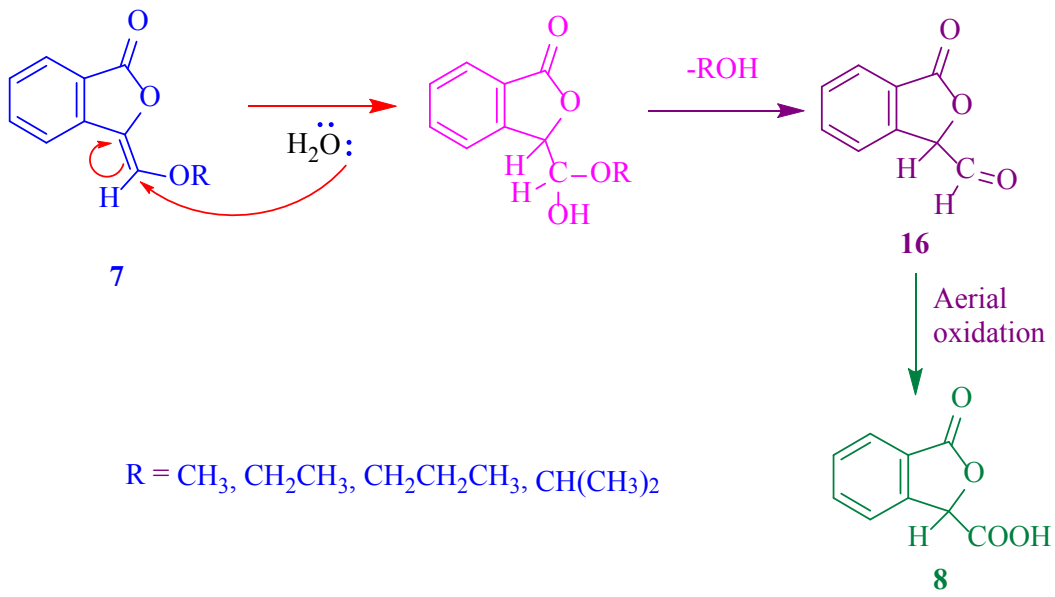
The acid (**8**), as expected, produced brisk effervescence due to evolution of CO_2 when treated with a saturated solution of $NaHCO_3$. The IR spectrum of the acid (**8**) showed two strong carbonyl bands at 1785 and 1720 cm^{-1} due respectively to lactone (five-membered) carbonyl and acid carbonyl groups in addition to multiplet weak peaks in the region 2520–2760 cm^{-1} due to hydrogen bonded OH group of the carboxylic acid. The ^{1}H NMR spectrum of **8** showed a one-proton singlet at δ 5.83 due to H-3 and a broad one-proton signal (exchangeable with D_2O) at δ 10.50 due the OH proton of the carboxylic acid. The aromatic region of the spectrum showed two distinct signals: a one-proton doublet of a doublet (J = 8.0 and 2.5 Hz) centered at δ 7.90 due to H-7 and a three-proton multiplet in the region at δ 7.40–7.85 attributable to H-4, H-5 and H-6. The deshielding of H-7 relative to other three aromatic protons is presumably due to the anisotropic effect of the adjacent lactone carbonyl group. Its mass spectrum showed the molecular ion peak albeit in very low abundance (2%) at m/z 178. The base peak of the spectrum was, however, located at m/z 133 due to the ion corresponding to the loss of •COOH radical. The other prominent peaks seen in the mass spectrum of the acid (**8**) were located at m/z 149 (10.2%), 134 (38.5%), 105 (50.1%), 77 (41.2%) and 58 (89.5%). Further, the analytical data of **8** are in good agreement with its molecular formula.

Mechanistically, the formation of 3-oxo-1,3-dihydroisobenzofuran-1-carboxylic acid (phthalide-3-carboxylic acid) (**8**) from the (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7a**–**7d**) may be envisaged to occur through an initial hydrolytic cleavage followed by aerial oxidation of the 3-oxo-1,3-dihydroisobenzofuran-1-carbaldehyde (phthalide-3-carboxaldehyde) (**16**) thus produced as shown in Scheme 5.

Conclusion

In conclusion, the incorporation of alkoxy and benzamido/ 4-substituted benzamido group at C_2 in1*H*-indene-1,3(2*H*)-dione moiety undergo phototransformation which involves an initial *β*-cleavage of C–N bond instead of *α*-cleavage of the 1*H*-indene-1,3(2*H*)-dione moiety followed by abstraction of hydrogen radical from the solvent which subsequently undergo Norrish Type I reaction (*α*-cleavage) followed by reorganization of the resulting 1,5-biradical to afford (*Z*)-isobenzofuran-1(3*H*)-ones (**7**) exclusively and corresponding benzamide/ 4-substituted benzamides (**2**) in high yields.

Acknowledgments



Scheme 5: Plausible mechanism of formation of 3-oxo-1,3-dihydroisobenzofuran-1-carboxylic acid (**8**) from (*Z*)-3-(alkoxymethylene)isobenzofuran-1(3*H*)-ones (**7**)

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References

1. (a) G. Lin, S. S.-K. Chan, H.-S. Chung, S. –L. Li, Chemistry and biological activities of naturally occurring phthalides. In *Studies in Natural Products Chemistry*; A. Rahman, Ed.; Elsevier: Amsterdam, **2005**, Vol 32, pp 611–669; (b) T. Noguchi, S. Fujita, M. Kawanami, J. Pharm. Soc. Jpn., **1937**, 57, 196; (c) H. J. Gold, C. W. Wilson III, J. Org. Chem., **1963**, 28, 985–987; (d) M. J. M. Gijbels, J. J. C. Scheffer, S. A. Banenheim, Planta Med., **1982**, 44, 207–211; (e) M. Puech-Baronnat, M. Kaouadji, A. M. Mariotte, Planta Med., **1984**, 46, 105–106; (f) P. M. Hon, C. M. Lee, T. F. Choang, K. Y. Chui, H. N. C. Wong, Phytochemistry, **1990**, 29, 1189–1191; (g) T. Naito, T. Katsuhara, L. Nitish, Y. Ikeya, M. Okada, H. Mitsuhashi, Phytochemistry, **1992**, 31, 639–642; (h) J. J. Beck, S. C. Chou, J. Nat. Prod., **2007**, 70, 891–900.
2. (a) M. D. Chordia, N. S. Narasimhan, J. Chem. Soc., Perkin Trans. 1, **1991**, 2, 371–376; (b) G. Blasko, D. J. Gula, M. Shamma, J. Nat. Prod., **1982**, 45, 105–122; (c) J. Fuska, D. Uhrin, B. Proksa, Z. Voticky, J. Ruppeldt, J. Antibiot., **1986**, 39, 1605–1608; (d) A. Arnone, G. Assante, G. Nasini, O. V. DePava, Phytochemistry, **1990**, 29, 613–616; (e) J. A. Palermo, M. V. R. Brasco, C. Spagnuolo, A. M. Seldes, J. Org. Chem., **2000**, 65, 4482–4486; (f) C. Puder, A. Zeeck, W. Beil, J. Antibiot., **2000**, 53, 329–336; (g) F. O. Shode, A. S. Mahomed, C. B. Rogers, Phytochemistry, **2002**, 61, 955–957; (h) G. Strobel, E. Ford, J. Worapong, J. K. Harper, A. M. Arif, D. M. Grant, P. C. W. Fung, R. M. W. Chau, Phytochemistry, **2002**, 60, 179–183; (i) A. Arnone, G. Assante, G. Nasini, S. Strada, A. Vercesi, J. Nat. Prod., **2002**, 65, 48–50; (j) K. Yoganathan, C. Rossant, S. Ng, Y. Huang, M. S. Butler, A.D. Buss, J. Nat. Prod., **2003**, 66, 1116–1117.
3. (a) F. M. Hauser, S. Prasanna, J. Am. Chem. Soc., **1981**, 103, 6378–6386; (b) F. M. Hauser, R. P. Rhee, J. Org. Chem., **1984**, 45, 3061–3068; (c) D. H. R. Barton, J. X. de Varies, J. Chem. Soc., **1963**, 1916–1919; (e) C. A. Boulet, G. A. Poulton, Heterocycles, **1989**, 28, 405–410; (f) H. Yang, G. Y. Hu, J. Chen, Y. Wang, Z. H. Wang, Bioorg. Med. Chem. Lett., **2007**, 17, 5210–5213.
4. M. V. Paradkar, S. Y. Gadre, T. A. Pujari, P. P. Khandekar, V. B. Kumbhar, Synth. Commun., **2005**, 35, 471–474.
5. E. W. Bousquet, M. D. Moran, J. Harmon, A. L. Johnson, J. C. Summers, J. Org. Chem., **1975**, 40, 2208–2211.
6. (a) R. K. Howe, B. R. Shelton, K. C. Liu, J. Org. Chem., **1985**, 50, 903–904; (b) I. S. Aidhein, N. S. Narasimhan, Tetrahedron Lett., **1989**, 30, 5323–5326; (c) V. G. Gore, M. D. Chordia, N. S. Narasimhan, Tetrahedron, **1990**, 46, 2483–2494; (d) A. Duchêne, J. Thibonnet, J. L. Parrain, E. Anselmi, M. Abarbri, Synthesis, **2007**, 4, 597–607; (e) E. Marchal, P. Uriac, B. Beatrice Legouin, L. Toupet, P. van de Weghe, Tetrahedron, **2007**, 63, 9979–9990.
7. (a) N. E. Cundasawmy, D. B. McLean, Can. J. Chem. **1972**, 50, 3028–3036; (b) V. Scartoni, R. Fiaschi, S. Catalano, I. Morelli, A. Marsili, J. Chem. Soc. Perkin Trans 1, **1979**,

1547–1551; (c) M. J. Broadhurst, C. H. Hassall, J. Chem. Soc. Perkin Trans 1, **1982**, 2227–2238; (d) R. H. Prager, J. M. Tipett, A. D. Ward, Aust. J. Chem., **1981**, 34, 1085–1093; (e) S. I. Clarke, B. Kusum, R. H. Prager, A. D. Ward, Aust. J. Chem., **1983**, 36, 2493–2498; (f) M. A. Bates, P. G. Sammes, G. A. Thomson, J. Chem. Soc. Perkin Trans 1, **1988**, 3037–3045.

8. (a) S. Gabriel, Ber. Dtsch. Chem. Ges., **1986**, 19, 838; (b) S. Gabriel, Ber. Dtsch. Chem. Ges., **1893**, 26, 952; (c) R. Weiss, Org. Synth., **1943**, 2, 61; (d) G. Berti, Gazz. Chim. Ital., **1956**, 86, 656; (e) Z. J. Vejdelek, O. Newmecek, V. Musil, A. Simek, Collect. Czech. Chem. Commun., **1964**, 29, 776; (f) J. Rigaudy, P. Derible, Bull. Soc. Chim. Fr., **1965**, 3047.
9. (a) R. L. Shriner, L. S. Keyser, J. Org. Chem., **1940**, 5, 200–203; (b) E. D. Bergmann, J. Org. Chem., **1956**, 21, 461–464; (c) S. L. Shapiro, K. Geiger, L. Freedman, J. Org. Chem., **1960**, 25, 1860–1865; (d) S. L. Shapiro, K. Geiger, J. Youlus, L. Freedman, J. Org. Chem., **1961**, 26, 3580–3582; (e) H. Zimmer, R. D. Barry, J. Org. Chem., **1962**, 27, 3710–3711.
10. (a) A. Yamaguchi, M. Okazaki, Nippon Kagaku Kaishi , **1973**, 110; (b) A. Yamaguchi, M. Okazaki, Chem. Abstr., **1973**, 78, 84494; (c) E. Napolitano, G. Spinelli, R. Fiaschi, A. Marsili, Synthesis, **1985**, 38–40.
11. (a) C. E. Castro, E. G. Gaughan, D. C. Owsley, J. Org. Chem., **1966**, 31, 4071–4078; (b) P. A. Chopard, R. F. Hudson, R. G. Searle, Tetrahedron Lett., **1965**, 2357–2360; (c) R. K. Howe, J. Org. Chem., **1973**, 38, 4164–4167; (d) C. F. Ingham, R. A. Massy-Westropp, G. D. Reynolds, W. D. Thorpe, Aust. J. Chem., **1975**, 28, 2499–2510; (e) R. S. Mali, S. R. Patil, B. K. Kulkarni, S. N. Yeola, Ind. J. Chem., Sec. B, **1990**, 29, 319; (f) R. S. Mali, S. R. Patil, Synth. Commun., **1990**, 20, 167–173; (g) R. S. Mali, P. G. Jagtap, J. Chem. Res. (s), **1993**, 184.
12. (a) P. Pahari, B. Senapati, D. Mal, Tetrahedron Lett., **2004**, 45, 5109–5112; (b) D. Mal, P. Pahari, S. C. De, Tetrahedron, **2007**, 63, 11781–11792; (c) D. C. G. A. Pinto, A. M. S. Silva, J. A. S. Jcavaleiro, J. Elguero, Eur. J. Org. Chem., **2003**, 2003(4), 747–755.
13. (a) M. V. Paradkar, S. Y. Gadre, T. A. Pujari, P. P. Khandekar, V. B. Kumbhar, Synth. Commun., **2005**, 35, 471–474; (b) R. Rendy, Y. Zhang, A. McElrea, A. Gomez, D. A. Klumpp, J. Org. Chem., **2004**, 69, 2340–2347; (c) S. M. Landge, M. Berryman, B. Torok, Tetrahedron Lett., **2008**, 49, 4505–4508; (d) J. Safari, H. Naeimi, A. K. Khakpour, R. Sharifi Jondani, S. Dehgan Khalili, J. Mol. Catal. A: Chem., **2007**, 270, 236–240; (e) J. N. Sangshetti, S. A. M. K. Ansar, D. B. Shinde, Chin. Chem. Lett., **2011**, 22, 163–166.
14. R. Rossi, A. Carpita, F. Bellina, P. Stabile, L. Mannia, Tetrahedron, **2003**, 59, 2067–2081.
15. F. Coelho, D.Veronese, C.H. Pavam, I.P.Vanderlei, R. Buffon, Tetrahedron, **2006**, 62, 4563–4572.
16. T. Seki, H. Tachikaw, T. Yamada, H. Hattori, J. Catal., **2003**, 217, 117–126.
17. M. Muneer, D. Bahnemann, M. Qamar, M.A. Tariq, M. Faisal, Appl. Catal. A: Gen. **2005**, 289, 224–230.
18. Taxus Research Laboratory, Vasvavi, P. U. 61, H-4440, T. Hungary, Arkivoc, **2006**, vi, 174–180.
19. (a) P. Hrnciar, A. Gaplovsky, V. Drgoncova, J. Donovalova, J. Chem. Pap., **1986**, 40, 649–654; (b) A. Guirado, F. Barba, M.B. Hursthouse, A. Martinez, A. Arcas, Tetrahedron Lett., **1986**, 27, 4063–4066.
20. (a) A. Emrani, A. Davoodnia, N. Tavakoli-Hoseini, Bull. Korean Chem. Soc., **2011**, 32, 2385–2390; (b) S. A. Pourmousavi, Z. Zinati, Turk. J. Chem., **2009**, 33, 385–392; (c) G. Thirunarayan, V. Renuka. J. Chil. Chem. Soc., **2014**, 59, 2574–2581; (d) S. Tekale, S. Kuthale, R. Pawar, J. Chil. Chem. Soc., **2013**, 58, 1619–1623; (e) A. Davoodnia, A. Khojastehnezhad, J. Chil. Chem. Soc., **2012**, 57, 1385–1387; (f) M. A. Zolfigol, P. Salehi, M. Shiri, T. Fall Rastegar, A. Ghaderi, J. Iran. Chem. Soc., **2008**, 5, 490–497; (g) R. S. Vrama, Green Chem., **1999**, 1, 43–55; (h) F. Khamooshi, B. Kekhaiyejhaleh, J. Chil. Chem. Soc., **2013**, 58, 1691–1694; (i) E. Rafiee, F. Rahimi, J. Chil. Chem. Soc., **2013**, 58, 1926–1929.
21. (a) F. Bellina, D. Ciucci, P. Vergamini, R. Rossi, Tetrahedron, **2000**, 56, 2533–2545; (b) R. Rossi, F. Bellina, M. Biagetti, A. Catanese, L. Mannina, Tetrahedron Lett,, **2000**, 41, 5281–5286; (c) R. Mukhopadhyay, N. G. Kundu, Tetrahedron, **2001**, 57, 9475–9480; (d) K. Y. Lee, J. M. Kim, J. N. Kim, Synlett, **2003**, 357–360; (e) R. Nannei, S. Dallavalle, L. Merlini, A. Bava, G. Nasini, J. Org. Chem., **2006**, 71, 6277–6280; (f) E. Genin, P. Y. Toullec, S. Antoniotti, C. Brancour, J.-P. Gen^et, V. Michelet, J. Am. Chem. Soc., **2006**, 128, 3112–3113; (g) H. Harkat, J.-M. Weibel, P. Pale, Tetrahedron Lett., **2006**, 47, 6273–6276; (h) E. Genin, P. Y. Toullec, P. Marie, S. Antoniotti, C. Brancour, J.-P. Gen^et, V. Michelet, Arkivoc, **2007**, 67–78; (i) D. J. Gonin, F. D. Toste, Nature, **2007**, 446, 395–403; (j) A. S. Hashmi, Chem. Rev., **2007**, 107, 3180–3211; (k) K. Kobayashi, K. Hashimoto, S. Fukamachi, H. Konishi, Synthesis, **2008**, 7, 1094–1098; (l) S. M. Landge, M. Berryman, B. Torok,Tetrahedron Lett., **2008**, 49, 4505–4508; (m) M.C. Jimenez, M. A. Mirinda, Photochemistry, **2009**, 37, 149–174; (n) M. R. Mohammadizadeh, M. Bahramzadeh, S. Z. Taghavi, Tetrahedron Lett., **2010**, 51, 5807–5809; (o) J. N. Sangshetti, S. A. M. K. Ansari, D. B. Shinde, Chinese Chemical Lett., **2011**, 22, 163–166; (p) **R. R. Teixeira, G. C. Bressan , W. L. Pereira, J. G. Ferreira, F. M. de Oliveira, D. C. Thomaz,** Molecules, **2013**, 18(2), 1881–1896; (q) R. Karmakar, P. Pahari, D. Mal, Chem. Rev., **2014**, 114, 6213–6284; (r) Z. Chunzhi, Z. Xingxing, Z. Dejian, J. Hongbin, Z. Jizhen, Chin. J. Org. Chem., **2014**, 34, 1881–1888; (s) B. Maleki, E. Koushki, M. Baghayeri, S. Sedigh Ashrafi, J. Chil. Chem. Soc., 60, **2015**, 2827–2831l; (t) S. Joardar, S. Chakravorty, S. P. Das,

Lett. Org. Chem., 13, **2016**, 127–134; (u) A. F. da Silva Maia, R. P. Siqueira, F. M. de Oliveira, J. G. Ferreira, S. F. da Silva, C. A. D. Caiuby, L. L. de Oliveira, S. O. de Paula, R. A. C. Souza, S. Guilardi, G. C. Bressan, R. R.Teixeira, Bioorg. Med. Chem. Lett., 26, **2016**, 2810–2816; (v) Y. Liu, Y. Yang, Y. Shi, X. Wang, L. Zhang, Y. Cheng, J. You, *Organometallics*, **2016**, 35(10), 1350–1353.

22. (a) W. G. Dauben, G. W. Shaffer, Tetrahedron Lett., **1967**, 8, 4415–4419; (b) W. G. Dauben, G. W. Shaffer, E. J. Deviny, J. Am. Chem. Soc., **1970**, 92, 6273–6281.
23. J. N. Pitts, I. Normann, J. Am. Chem. Soc., **1954**, 76, 4815–4819.
24. R. S. Givens, L. Sterkowski, R. Devonshire, J. Am. Chem. Soc., **1974**, 96, 1631–1633.
25. B. E. Kalpan, A. L. Hartwig, Tetrahedron Lett., **1970**, 11, 4855–4856.
26. J. C. Sheehan, R. M. Wilson, A. W. Oxford, J. Am. Chem. Soc., **1971**, 93, 7222–7228.
27. J. R. Collier, M. K. M. Dirania, J. Hill, J. Chem. Soc. C., **1970**, 1, 155–158.
28. H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, J. W. Wilson, J. Am. Chem. Soc., **1964**, 86, 947–948.
29. (a) K. Schaffner, Pure Appl. Chem., **1968**, 16, 75–86; (b) O. Jeger, K. Schaffner, Pure Appl. Chem., **1970**, 21, 247–262.
30. A. Padwa, A. Battisti, J. Am. Chem. Soc., **1972**, 94, 521–529.
31. P. Yates, Y. C. Toong, J. Chem. Soc. Chem. Commun., **1978**, 5, 205–206.
32. K. K. Maheshwari, G. A. Berchtold, J. Chem. Soc. D: Chem. Commun., **1969**, 1, 13a–13a.
33. P. H. McCabe, C. R. Nelson, Tetrahedron Lett., **1978**, 19, 2819–282.
34. W. C. Lumma Jr., G. A. Berchtold, J. Org. Chem., **1969**, 34, 1566–1572.
35. A. Gilbert, J. Baggot, In: Essentials of Molecular Photochemistry, Blackwell Scientific Publications: London, **1991**, p 301.
36. H. E. Zimmerman, G. A. Epling, J. Am. Chem. Soc., **1972**, 94, 7806–7811.
37. M. Kapoor, S. N. Dhawan, S. Mor, S. C. Gupta, J. Chem. Res., **2008**, 2008, 386–387.
38. M. Kapoor, S. N. Dhawan, S. Mor, S. C. Bhatia, S. C. Gupta, M. S. Hundal, Tetrahedron, **2003**, 59, 5027–5031.
39. S. Mor, S. N. Dhawan, M. Kapoor, D. Kumar, Tetrahedron, **2007**, 63, 594–597.
40. (a) S. Mor, S. N. Dhawan, J. Chem. Pharm. Res., **2015**, 7, 126–134; (b) S. Mor, S. N. Dhawan, Chemistry & Biology Interface, **2016**, 6, 143–156.
41. A. R. S. Babu, R. Raghunathan, G. Gayatri, G. N. Sastry, J. Heterocycl. Chem., **2009**, 43, 1467–1472.
42. D. Ben-Ishai, Z. Inbal, J. Org. Chem., **1973**, 38, 2251–2252.
43. D. Matthies, K. Hain, Synthesis, **1973**, 1973, 154–155.
44. J.-L. Parrain, J. Thibonnet, Science of Synthesis, 2005, 26, 745–868.
45. T. Matsuura, R. Sugae, R. Nakashima, K. Omura, Tetrahedron, **1968**, 24, 6149–6156.
46. H.-Y. Liao, C.-H. Cheng, J. Org. Chem., **1995**, 60, 3711–3716.
47. N. G. Kundu, M. Pal, B. Nandi, J. Chem. Soc. Perkin Trans 1, **1998**, 561–568.
48. Y. R. Luo, Comprehensive Handbook of Chemical Bond Energies, CRC Press, Boca, Raton, 2007.