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## Synthesis of some *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides by thermal and photochemical routes: A comparative study

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**Abstract:** Synthesis of some *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) from the corresponding *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4**) upon treatment with different anhydrous alcohols (**5**) via thermal and photochemical routes was carried out. The *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4**), in turn, were prepared by refluxing *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**3**) with SOCl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> in excellent yields. The study revealed that time required for completion of reaction for conversion of **4** to **6** is comparatively shorter in photochemical reaction (35–60 min) than thermal reaction (1–10 hr). The structures of all the products were elucidated by the application of spectral (FTIR, <sup>1</sup>H NMR and mass), and elemental analytical techniques.

**Keywords:** Thermal; Photochemical; *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides; *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides.

### 1. Introduction

Indane-1,3-dione and its derivatives constitute an important group of compounds and has become a focus for the attention that has drawn great attention of molecular architectures, organic chemists, biologists, medicinal chemists and researchers due to their distinctive features like (i) indane-1,3-diones have huge synthetic prospective due to 1,3-dicarbonyl nature which often serves as a synthon for various organic transformations [1–3]; (ii) they tender an ample scope for the study of physiochemical

properties *viz.* 1,3-indandione tautomerism, dual reactivity, electrochemical redox properties, unique property of polycrystalline films, and quantum mechanical calculations, and many more [4,5]; (iii) a wide-ranging bioactivities associated with them such as antitumor, antiviral, antimicrobial, anti-inflammatory, anticoagulant, antihepatitis, neurotropopic, antagonistic inhibitors, antiallergic, rodenticidal, herbicidal, insecticidal, etc. [6–17] make them an interesting moiety for medicinal chemistry. In addition, the indane (2,3-dihydro-1*H*-indene) ring system is an attractive scaffold

due to the combination of aromatic and aliphatic properties fused together in one rigid system and its occurrence in many natural products such as pterosins [18], indanomycin [19] and stawamycin [20]. Notably, this structural motif is also present in many marketed drugs used clinically to treat various diseases, *e.g.* indinavir [21] as an HIV-1 protease inhibitor; indantadol [22] as a potent MAO-inhibitor; indatraline [23] as amine uptake inhibitor; clidanac [24] as an anti-inflammatory; indecainide [25] as an antiarrhythmic agent; indocrinone [26] as diuretic and hedulin [27] as an anticoagulant. Given the big diversity of targets these drugs act on [28], one could argue that this ring system is a “privileged” substructure. Moreover, indenone-fused heterocycles and their derivatives are reported to show a wide array of pharmacological activities *viz.* indenopyridine skeleton is present in the 4-azafluorenone group of alkaloids; indenopyrazoles and indenopyridazines as CDK2 and CDK4 inhibitors; indenoquinolines as antitumor, acetylcholinesterase and steroid reductase inhibitors, and antimalarials; indenopyridones as anticancer agents targeting topoisomerase I, *etc.* [3]. Consequently, significant efforts have been made for the synthesis of compounds containing an indenone ring [29–32]. Majority of the synthetic routes involve thermal pathways, however, photochemical reactions are known as key steps in organic synthesis [33]. Photochemistry of carbonyl compounds is one of the most interesting areas of research. The main reasons for interest in this area are due to high degree of comprehension of the mechanistic complexities of the photochemical reactions of this category of compounds. Photochemical  $\alpha$ - and  $\beta$ -cleavage processes in the carbonyl compounds leading to the formation of a variety of photoproducts have attracted the attention of organic chemists significantly. Which pathway actually predominates depends upon the structure of the ketones and presence of substituents [34].  $\beta$ -Cleavage process has been

observed on  $n-\pi^*$  excitation of certain ketones [35] and in ketones possessing  $\alpha$ -substituents which have a tendency for formation of radicals, *i.e.* halogen [36,37], acetoxy [38], aryloxy [39], epoxy [40], sulphonyloxy [41] and thiyl [42–46] substituents. However, reaction pathway can be influenced by the presence of substituents other than  $\alpha$ -position [47]. Moreover, both ionic [48] and radical intermediates have been implicated in this process depending upon the nature of the starting material and nature of the  $n-\pi^*$  excited states, *i.e.* singlet or triplet. In continuation of our earlier studies [49–52] on the synthesis and photochemistry of 2,2-disubstituted-1*H*-inden-1,3(2*H*)-diones, in the current article, we present a comparative study for the synthesis of some *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) from the corresponding *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4**) upon treatment with different anhydrous alcohols (**5**) *via* thermal and photochemical routes in varying yields.

## 2. Materials and methods

### 2.1. General

The solvents were used as such or after necessary purification according to the standard literature procedures. Melting points (mp °C) of the synthesized compounds were determined on an electrothermal apparatus in open capillaries and are uncorrected. Purity of the synthesized compounds was checked by thin layer chromatography (TLC) using precoated silica gel plates (chloroform-methanol) as stationary phase and different combinations of solvents as mobile phase. The visualization of the spots was achieved by iodine adsorption. The progress of the reactions was also monitored by this method by withdrawal of aliquots of reaction mixture at different intervals of time. UV spectra were taken in diethyl ether or ethanol solution on U-2000 (Hitachi) UV spectrophotometer. IR spectra were scanned as Nujol mulls on a Perkin–Elmer 842 IR spectrophotometer and absorption

frequencies ( $\nu$ ) are stated in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded in deuteriochloroform ( $\text{CDCl}_3$ ) or deuteriochloroform ( $\text{CDCl}_3$ ) + dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) on 90 MHz Perkin-Elmer R-32 spectrometer. The chemical shifts are reported in parts per million ( $\delta$  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 constants ( $J$ ) are valued 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, H and N were found within  $\pm 0.4\%$  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 mol) and benzamide/ 4-substituted benzamide (2) (0.05 mol) in benzene (100 mL) was refluxed on a water bath 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 mixture was cooled and solid thus separated was filtered, recrystallized from ethanol-hexane mixture to give the desired product in high yield [5,53,54].

**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) (0.035 mole) and thionyl chloride (6.10 mL, 0.07 mole) in dry dichloromethane (200 mL) was refluxed on a water bath till the completion of the reaction (2–2.5 hr). Thereafter, 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. The characterization data of the compounds (**4a–d**) are given below.

***N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (4a):** Yield 93%, colorless crystals; mp 173–174 °C (lit. [53] mp 173–174 °C); UV (diethyl ether):  $\lambda_{\max}$  296 nm ( $\epsilon$  27,123); IR (nujol): 3428 (N–H stretch (amide)), 1776, 1728 (C=O stretch (indane-1,3-dione)), 1674 (C=O stretch (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.12–7.35 (m, 3H, H-3, H-4, H-5), 7.50 (br s, 1H, NH, deuterium oxide exchangeable), 7.63 (d,  $J$  = 8.25 Hz, 2H, H-2, H-6), 7.70–8.12 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact)  $m/z$  299 ( $M^+$ ). *Anal.* Calcd. for  $\text{C}_{16}\text{H}_{10}\text{ClNO}_3$ : C, 64.12; H, 3.36; N, 4.67. Found: C, 64.25; H, 3.29; N, 4.70.

**4-Chloro-*N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (4b):** Yield 94%, colorless crystals; mp 215–216 °C (lit. [54] mp 218–220 °C); UV (diethyl ether):  $\lambda_{\max}$  296 nm ( $\epsilon$  16,178); IR (nujol): 3320 (N–H stretch (amide)), 1755, 1728 (C=O stretch (indane-1,3-dione)), 1654 (C=O stretch (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.28 (d,  $J$  = 8.25 Hz, 2H, H-3, H-5), 7.50 (br s, 1H, NH, deuterium oxide exchangeable), 7.63 (d,  $J$  = 8.25 Hz, 2H, H-2, H-6), 7.75–8.12 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact)  $m/z$  336 ( $M^{+}+2$ ), 334 ( $M^+$ ). *Anal.* Calcd. for  $\text{C}_{16}\text{H}_9\text{Cl}_2\text{NO}_3$ : C, 57.48; H, 2.69; N, 4.19. Found: C, 57.85; H, 2.49; N, 4.00.

***N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methoxybenzamide (4c):** Yield 94%, colorless crystals; mp 215–217 °C; UV (diethyl ether):  $\lambda_{\max}$  253 nm ( $\epsilon$  27,678);  $\lambda_{\max}$  296 nm ( $\epsilon$  34,927); IR (nujol): 3350 (N–H stretch (amide)), 1750, 1725 (C=O (indane-1,3-dione)), 1642 (C=O stretch (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.75 (s, 3H, OCH<sub>3</sub>-4), 6.80 (d,  $J$  = 8.50 Hz, 2H, H-3, H-5), 7.70 (d,  $J$  = 8.50 Hz, 2H, H-2, H-6), 7.77–8.08 (m, 4H, H-4', H-5', H-6', H-7'), 8.60 (br s, 1H, NH, deuterium oxide

exchangeable); ms: (70 eV, electron impact) m/z 331.5 ( $M^++2$ ), 329.5 ( $M^+$ ). *Anal.* Calcd. for  $C_{17}H_{12}ClNO_4$ : C, 61.91; H, 3.64; N, 4.24. Found: C, 62.25; H, 3.49; N, 4.07.

**N-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (4d):** Yield 92%, colorless crystals; mp 221–223 °C; UV (diethyl ether):  $\lambda_{\text{max}}$  296 nm ( $\epsilon$  27,170); IR (nujol): 3327 (N–H stretch (amide)), 1748, 1725 (C=O stretch (indane-1,3-dione)), 1654 (C=O stretch (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3+\text{DMSO-d}_6$ ):  $\delta$  2.30 (s, 3H,  $\text{CH}_3$ -4), 7.10 (d,  $J$  = 8.00 Hz, 2H, H-3, H-5), 7.66 (d,  $J$  = 8.00 Hz, 2H, H-2, H-6), 7.75–8.02 (m, 4H, H-4', H-5', H-6', H-7'), 10.00 (br s, 1H, NH, deuterium oxide exchangeable); ms: (70 eV electron impact) m/z 315.5 ( $M^++2$ ), 313.5 ( $M^+$ ). *Anal.* Calcd. for  $C_{17}H_{12}ClNO_3$ : C, 65.07; H, 3.83; N, 4.46. Found: C, 65.35; H, 3.49; N, 4.00.

**2.4 General procedure for the synthesis of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (6); Method A (Thermal):** A solution of *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide/4-substituted benzamide (4) (0.0015 mole) in anhydrous alcohol (5) (60 mL) was refluxed 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.

**Method B (Photochemical):** A solution of *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide/4-substituted benzamide (4) (0.0015 mole) in anhydrous alcohol (5) (80 mL) was deoxygenated by bubbling oxygen-free nitrogen gas for about 15 min. Thereafter, the reaction mixture was irradiated with light from a 450 Watts Hanovia mercury lamp in a Pyrex reactor for 35–60 min under  $\text{N}_2$  atmosphere when TLC analysis of the reaction mixture showed complete disappearance of the starting

chloroamide (4). Distillation of the solvent on a water bath in vacuo gave a light yellow residue that upon crystallization from a suitable solvent afforded the corresponding *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (6) in high yields. The characterization data of the alkoxy derivatives (6a–6p) are given below.

**N-(2-methoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (6a); Method A:** The compound (6a) was obtained by refluxing a solution of 4a in anhydrous methanol (5a) for a period of 1 hr. Light yellow crystals (benzene-hexane), yield 67%; mp 166–167 °C (lit. [53] mp 166–167 °C); **Method B:** The compound (6a) was obtained by photoirradiating a solution of 4a in anhydrous methanol (5a) for a period of 35 min. Light yellow crystals (benzene-hexane), yield 83%; mp 166–167 °C (lit. [53] mp 166–167 °C); UV (ethanol):  $\lambda_{\text{max}}$  228.5 nm ( $\epsilon$  65,490); IR (nujol): 3320 (N–H stretch (amide)), 1759, 1721 (C=O stretch (indane-1,3-dione)), 1643 (C=O stretch (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.49 (s, 3H,  $\text{OCH}_3$ -2'), 7.22–7.46 (m, 3H, H-3, H-4, H-5), 7.58 (br s, 1H, NH, deuterium oxide exchangeable), 7.62 (dd,  $J$  = 8.0 Hz,  $J$  = 2.5 Hz, 2H, H-2, H-6), 7.80–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 295 ( $M^+$ ). *Anal.* Calcd. for  $C_{17}H_{13}NO_4$ : C, 69.15; H, 4.44; N, 4.74. Found: C, 68.89; H, 4.57; N, 4.98.

**4-Chloro-*N*-(2-methoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (6b); Method A:** The compound (6b) was obtained by refluxing a solution of 4b in anhydrous methanol (5a) for 6 hr. Light yellow crystals (benzene-hexane), yield 91%; mp 182–183 °C (lit. [54,55] mp 182–183 °C); **Method B:** The compound (6b) was obtained by photoirradiating a solution of 4b in anhydrous methanol (5a) for a period of 40 min. Light yellow crystals (benzene-hexane), yield 90%; mp 182–183 °C (lit. [54,55] mp 182–183 °C); UV (ethanol):  $\lambda_{\text{max}}$  227.5 nm ( $\epsilon$  83,198); IR (nujol): 3340 (N–H stretch

(amide)), 1754, 1722 (C=O stretch (indane-1,3-dione)), 1642 (C=O stretch (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.48 (s, 3H,  $\text{OCH}_3$ -2'), 7.25 (d,  $J$  = 8.25 Hz, 2H, H-3, H-5), 7.55 (br s, 1H, NH, deuterium oxide exchangeable), 7.61 (d,  $J$  = 8.25 Hz, 2H, H-2, H-6), 7.75–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 331.5 ( $M^{+}+2$ ), 329.5 ( $M^{+}$ ). *Anal.* Calcd. for  $\text{C}_{17}\text{H}_{12}\text{ClNO}_4$ : C, 61.91; H, 3.64; N, 4.24. Found: C, 62.29; H, 3.99; N, 4.67.

#### **4-Methoxy-N-(2-methoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (6c);**

**Method A:** The compound (6c) was obtained by refluxing a solution of **4c** in anhydrous methanol (**5a**) for 8 hr. Light yellow crystals (benzene-hexane), yield 89%; mp 185–186 °C; **Method B:** The compound (6c) was obtained by photoirradiating a solution of **4c** in anhydrous methanol (**5a**) for a period of 45 min. Light yellow crystals (benzene-hexane), yield 90%; mp 185–186 °C; UV (ethanol):  $\lambda_{\max}$  227 nm ( $\epsilon$  1,03,515); IR (nujol): 3360 (N–H stretch (amide)), 1752, 1724 (C=O (indane-1,3-dione)), 1640 (C=O (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.28 (s, 3H,  $\text{CH}_3$ -4), 3.49 (s, 3H,  $\text{OCH}_3$ -2'), 7.09 (d,  $J$  = 8.0 Hz, 2H, H-3, H-5), 7.34 (br s, 1H, NH, deuterium oxide exchangeable), 7.59 (d,  $J$  = 8.0 Hz, 2H, H-2, H-6), 7.72–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 309 ( $M^{+}$ ). *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{15}\text{NO}_4$ : C, 69.90; H, 4.85; N, 4.53. Found: C, 69.76; H, 4.71; N, 4.65.

81%; mp 198–199 °C; UV (ethanol):  $\lambda_{\max}$  227 nm ( $\epsilon$  1,03,515); IR (nujol): 3360 (N–H stretch (amide)), 1752, 1724 (C=O (indane-1,3-dione)), 1640 (C=O (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.28 (s, 3H,  $\text{CH}_3$ -4), 3.49 (s, 3H,  $\text{OCH}_3$ -2'), 7.09 (d,  $J$  = 8.0 Hz, 2H, H-3, H-5), 7.34 (br s, 1H, NH, deuterium oxide exchangeable), 7.59 (d,  $J$  = 8.0 Hz, 2H, H-2, H-6), 7.72–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 309 ( $M^{+}$ ). *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{15}\text{NO}_4$ : C, 69.90; H, 4.85; N, 4.53. Found: C, 69.76; H, 4.71; N, 4.65.

**N-(2-ethoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (6e); Method A:** The compound (6e) was obtained by refluxing a solution of **4a** in anhydrous ethanol (**5b**) for 3 hr. Light yellow crystals (benzene-hexane), yield 76%; mp 192–193 °C; **Method B:** The compound (6e) was obtained by photoirradiating a solution of **4a** in anhydrous ethanol (**5b**) for a period of 40 min. Light yellow crystals (benzene-hexane), yield 81%; mp 192–193 °C; UV (ethanol):  $\lambda_{\max}$  228 nm ( $\epsilon$  58,056); IR (nujol): 3240 (N–H stretch (amide)), 1756, 1725 (C=O stretch (indane-1,3-dione)), 1622 (C=O stretch (amide))  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.05 (t,  $J$  = 7.0 Hz, 3H,  $\text{OCH}_2\text{CH}_3$ -2'), 3.84 (q,  $J$  = 7.0 Hz, 2H,  $\text{OCH}_2\text{CH}_3$ -2'), 7.10–7.42 (m, 3H, H-3, H-4, H-5), 7.50 (br s, 1H, NH, deuterium oxide exchangeable), 7.65 (dd,  $J$  = 8.0 Hz,  $J$  = 2.5 Hz, 2H, H-2, H-6), 7.72–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 309 ( $M^{+}$ ). *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{15}\text{NO}_4$ : C, 69.90; H, 4.85; N, 4.53. Found: C, 70.05; H, 4.71; N, 4.61.

#### ***N*-(2-methoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (6d);**

**Method A:** The compound (6d) was obtained by refluxing a solution of **4d** in anhydrous methanol (**5a**) for 6 hr. Light yellow crystals (benzene-hexane), yield 79%; mp 198–199 °C; **Method B:** The compound (6d) was obtained by photoirradiating a solution of **4d** in anhydrous methanol (**5a**) for a period of 40 min. Light yellow crystals (benzene-hexane), yield

**4-Chloro-N-(2-ethoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (6f); Method A:** The compound (6f) was obtained by refluxing a solution of **4b** in anhydrous ethanol (**5b**) for 10 hr. Light yellow crystals (anhydrous ethanol), yield 75%; mp 190–191 °C; **Method B:** The compound (6f) was obtained by photoirradiating a solution of **4b** in

anhydrous ethanol (**5b**) for a period of 40 min. Light yellow crystals (anhydrous ethanol), yield 80%; mp 190–191 °C; UV (ethanol):  $\lambda_{\text{max}}$  227 nm ( $\epsilon$  73,852); IR (nujol): 3260 (N–H stretch (amide)), 1755, 1725 (C=O stretch (indane-1,3-dione)), 1628 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.10 (t,  $J$  = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>-2'), 3.84 (q,  $J$  = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>-2'), 7.26 (d,  $J$  = 8.25 Hz, 2H, H-3, H-5), 7.58 (br s, 1H, NH, deuterium oxide exchangeable), 7.61 (d,  $J$  = 8.25 Hz, 2H, H-2, H-6), 7.72–8.05 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 345.5 (M<sup>+</sup>+2), 343.5 (M<sup>+</sup>). *Anal.* Calcd. For C<sub>18</sub>H<sub>14</sub>ClNO<sub>4</sub>: C, 62.88; H, 4.08; N, 4.07. Found: C, 62.98; H, 4.00; N, 4.15.

**N-(2-ethoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methoxybenzamide (**6g**); Method A:** The compound (**6g**) was obtained by refluxing a solution of **4c** in anhydrous ethanol (**5b**) for 10 hr. Light yellow crystals (anhydrous ethanol), yield 86%; mp 196–197 °C; **Method B:** The compound (**6g**) was obtained by photoirradiating a solution of **4c** in anhydrous ethanol (**5b**) for a period of 40 min. Light yellow crystals (anhydrous ethanol), yield 85%; mp 196–197 °C; UV (ethanol):  $\lambda_{\text{max}}$  223 nm ( $\epsilon$  65,069);  $\lambda_{\text{max}}$  255 nm ( $\epsilon$  17,138); IR (nujol): 3200 (N–H stretch (amide)), 1755, 1725 (C=O stretch (indane-1,3-dione)), 1620 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.10 (t,  $J$  = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>-2'), 3.75 (s, 3H, OCH<sub>3</sub>-4), 3.80 (q,  $J$  = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>-2'), 6.79 (d,  $J$  = 8.5 Hz, 2H, H-3, H-5), 7.18 (br s, 1H, NH, deuterium oxide exchangeable), 7.65 (d,  $J$  = 8.5 Hz, 2H, H-2, H-6), 7.71–8.09 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 339 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>5</sub>: C, 67.25; H, 5.01; N, 4.13. Found: C, 67.61; H, 5.30; N, 4.41.

**N-(2-ethoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (**6h**); Method A:** The compound (**6h**) was obtained

by refluxing a solution of **4d** in anhydrous ethanol (**5b**) for 8 hr. Light yellow crystals (anhydrous ethanol), yield 81%; mp 213–214 °C; **Method B:** The compound (**6h**) was obtained by photoirradiating a solution of **4d** in anhydrous ethanol (**5b**) for a period of 50 min. Light yellow crystals (anhydrous ethanol), yield 85%, mp 213–214 °C; UV (ethanol):  $\lambda_{\text{max}}$  224 nm ( $\epsilon$  1,35,861); IR (nujol): 3218 (N–H stretch (amide)), 1757, 1725 (C=O stretch (indane-1,3-dione)), 1620 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.09 (t,  $J$  = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>-2'), 2.30 (s, 3H, CH<sub>3</sub>-4), 3.84 (q,  $J$  = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>-2'), 7.10 (d,  $J$  = 8.0 Hz, 2H, H-3, H-5), 7.24 (br s, 1H, NH, deuterium oxide exchangeable), 7.59 (d,  $J$  = 8.0 Hz, 2H, H-2, H-6), 7.72–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 323 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>4</sub>: C, 70.58; H, 5.26; N, 4.33. Found: C, 70.75; H, 5.36; N, 4.16.

**N-(1,3-dioxo-2-propoxy-2,3-dihydro-1*H*-inden-2-yl)benzamide (**6i**); Method A:** The compound (**6i**) was obtained by refluxing a solution of **4a** in anhydrous *n*-propanol (**5c**) for 5 hr. Light yellow crystals (benzene-hexane), yield 78%; mp 151–152 °C; **Method B:** The compound (**6i**) was obtained by photoirradiating a solution of **4a** in anhydrous *n*-propanol (**5c**) for a period of 40 min. Light yellow crystals (benzene-hexane), yield 85%; mp 151–152 °C; UV (ethanol):  $\lambda_{\text{max}}$  228 nm ( $\epsilon$  84,787); IR (nujol): 3320 (N–H stretch (amide)), 1755, 1718 (C=O stretch (indane-1,3-dione)), 1642 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.78 (t,  $J$  = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 1.48 (sext,  $J$  = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 3.70 (t,  $J$  = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 7.12–7.42 (m, 3H, H-3, H-4, H-5), 7.49 (br s, 1H, NH, deuterium oxide exchangeable), 7.65 (dd,  $J$  = 8.0 Hz,  $J$  = 2.5 Hz, 2H, H-2, H-6), 7.71–8.05 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 323 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>4</sub>: C, 70.58; H, 5.26; N, 4.33. Found: C, 70.25; H, 5.55; N, 4.16.

**4-Chloro-N-(1,3-dioxo-2-propoxy-2,3-dihydro-1*H*-inden-2-yl)benzamide (6j);**

**Method A:** The compound (**6j**) was obtained by refluxing a solution of **4b** in anhydrous *n*-propanol (**5c**) for 10 hr. Light yellow crystals (benzene-hexane), yield 85%; mp 204–205 °C;

**Method B:** The compound (**6j**) was obtained by photoirradiating a solution of **4b** in anhydrous *n*-propanol (**5c**) for a period of 50 min. Light yellow crystals (benzene-hexane), yield 82%; mp 204–205 °C; UV (ethanol):  $\lambda_{\text{max}}$  229 nm ( $\epsilon$  33,451); IR (nujol): 3270 (N–H stretch (amide)), 1755, 1722 (C=O stretch (indane-1,3-dione)), 1640 stretch (C=O (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.77 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 1.46 (sext, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 3.70 (t, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 7.26 (d, 2H, *J* = 8.25 Hz, H-3, H-5), 7.58 (br s, 1H, NH, deuterium oxide exchangeable), 7.61 (d, *J* = 8.25 Hz, 2H, H-2, H-6), 7.75–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 353 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>NO<sub>5</sub>: C, 67.98; H, 5.38; N, 3.96. Found: C, 67.59; H, 5.46; N, 4.09.

**N-(1,3-dioxo-2-propoxy-2,3-dihydro-1*H*-inden-2-yl)-4-methoxybenzamide (6k);**

**Method A:** The compound (**6k**) was obtained by refluxing a solution of **4c** in anhydrous *n*-propanol (**5c**) for 10 hr. Light yellow crystals (benzene-hexane), yield 85%; mp 196–97 °C;

**Method B:** The compound (**6k**) was obtained by photoirradiating a solution of **4c** in anhydrous *n*-propanol (**5c**) for a period of 50 min. Light yellow crystals (benzene-hexane), yield 86%; mp 196–197 °C; UV (ethanol):  $\lambda_{\text{max}}$  225 nm ( $\epsilon$  1,76,853);  $\lambda_{\text{max}}$  255 nm ( $\epsilon$  66,717); IR (nujol): 3310 (N–H stretch (amide)), 1752, 1723 (C=O stretch (indane-1,3-dione)), 1635 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.77 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 1.49 (sext, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 3.70 (t, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 3.73 (s, 3H, OCH<sub>3</sub>-

4), 6.81 (d, 2H, *J* = 8.5 Hz, H-3, H-5), 7.19 (br s, 1H, NH, deuterium oxide exchangeable), 7.67 (d, *J* = 8.5 Hz, 2H, H-2, H-6), 7.72–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 353 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>NO<sub>5</sub>: C, 67.98; H, 5.38; N, 3.96. Found: C, 67.59; H, 5.46; N, 4.09.

**N-(1,3-dioxo-2-propoxy-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (6l);**

**Method A:** The compound (**6l**) was obtained by refluxing a solution of **4d** in anhydrous *n*-propanol (**5c**) for 8 hr. Light yellow crystals (benzene-hexane), yield 87%; mp 176–177 °C;

**Method B:** The compound (**6l**) was obtained by photoirradiating a solution of **4d** in anhydrous *n*-propanol (**5c**) for a period of 50 min. Light yellow crystals (benzene-hexane), yield 82%; mp 176–177 °C; UV (ethanol):  $\lambda_{\text{max}}$  225 nm ( $\epsilon$  1,61,338); IR (nujol): 3280 (N–H stretch (amide)), 1755, 1718 (C=O stretch (indane-1,3-dione)), 1625 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.78 (t, *J* = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 1.50 (sext, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 2.28 (s, 3H, CH<sub>3</sub>-4), 3.70 (t, *J* = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>-2'), 7.10 (d, 2H, *J* = 8.0 Hz, H-3, H-5), 7.20 (br s, 1H, NH, deuterium oxide exchangeable), 7.59 (d, *J* = 8.0 Hz, 2H, H-2, H-6), 7.72–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 337 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>NO<sub>4</sub>: C, 71.21; H, 5.63; N, 4.15. Found: C, 71.59; H, 5.48; N, 4.23.

**N-(2-isopropoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (6m); Method A:**

The compound (**6m**) was obtained by refluxing a solution of **4a** in anhydrous *i*-propanol (**5d**) for 10 hr. Light yellow crystals (benzene-hexane), yield 80%; mp 182–183 °C; **Method B:**

The compound (**6m**) was obtained by photoirradiating a solution of **4a** in anhydrous *i*-propanol (**5d**) for a period of 55 min. Light yellow crystals (benzene-hexane), yield 81.5%; mp 182–183 °C; UV (ethanol):  $\lambda_{\text{max}}$  229 nm

( $\epsilon$  60,966); IR (nujol): 3260 (N–H stretch (amide)), 1758, 1722 (C=O stretch (indane-1,3-dione)), 1640 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.19 (d,  $J$  = 7.0 Hz, 6H, OCH(CH<sub>3</sub>)<sub>2</sub>-2'), 4.47 (sept,  $J$  = 7.0 Hz, 1H, OCH(CH<sub>3</sub>)<sub>2</sub>-2'), 6.92 (br s, 1H, NH, deuterium oxide exchangeable), 7.22–7.50 (m, 3H, H-3, H-4, H-5), 7.74 (dd,  $J$  = 8.0 Hz,  $J$  = 2.5 Hz, 2H, H-2, H-6), 7.80–8.13 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 323 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>4</sub>: C, 70.58; H, 5.26; N, 4.33. Found: C, 70.91; H, 5.58; N, 4.06.

#### **4-Chloro-N-(2-isopropoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamide (6n);**

**Method A:** The compound (6n) was obtained by refluxing a solution of **4b** in anhydrous *i*-propanol (**5d**) for 10 hr. Light yellow crystals (benzene-hexane), yield 84%; mp 169–170 °C; **Method B:** The compound (6n) was obtained by photoirradiating a solution of **4b** in anhydrous *i*-propanol (**5d**) for a period of 1 hr. Light yellow crystals (benzene-hexane), yield 85%; mp 169–170 °C; UV (ethanol):  $\lambda_{\text{max}}$  224.5 nm ( $\epsilon$  1,19,539); IR (nujol): 3300 (N–H stretch (amide)), 1755, 1725 (C=O stretch (indane-1,3-dione)), 1640 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.11 (d,  $J$  = 7.0 Hz, 6H, OCH(CH<sub>3</sub>)<sub>2</sub>-2'), 4.40 (sept,  $J$  = 7.0 Hz, 1H, OCH(CH<sub>3</sub>)<sub>2</sub>-2'), 7.15 (br s, 1H, NH, deuterium oxide exchangeable), 7.28 (d, 2H,  $J$  = 8.25 Hz, H-3, H-5), 7.61 (d,  $J$  = 8.25 Hz, 2H, H-2, H-6), 7.76–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 359.5 (M<sup>++</sup>2), 357.5 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>19</sub>H<sub>16</sub>ClNO<sub>4</sub>: C, 63.77; H, 4.47; N, 3.91. Found: C, 63.91; H, 4.36; N, 4.02.

#### **N-(2-isopropoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methoxybenzamide (6o);**

**Method A:** The compound (6o) was obtained by refluxing a solution of **4c** in anhydrous *i*-propanol (**5d**) for 10 hr. Light yellow crystals (benzene-hexane), yield 83%; mp 165–166 °C;

**Method B:** The compound (**6o**) was obtained by photoirradiating a solution of **4c** in anhydrous *i*-propanol (**5d**) for a period of 55 min. Light yellow crystals (benzene-hexane), yield 80%; mp 165–166 °C; UV (ethanol):  $\lambda_{\text{max}}$  223.5 nm ( $\epsilon$  12,284);  $\lambda_{\text{max}}$  255.5 nm ( $\epsilon$  31,946); IR (nujol): 3350 (N–H stretch (amide)), 1750, 1725 (C=O stretch (indane-1,3-dione)), 1640 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.13 (d,  $J$  = 7.0 Hz, 6H, OCH(CH<sub>3</sub>)<sub>2</sub>-2'), 3.78 (s, 3H, OCH<sub>3</sub>-4), 4.42 (sept,  $J$  = 7.0 Hz, 1H, OCH(CH<sub>3</sub>)<sub>2</sub>-2'), 6.80 (d, 2H,  $J$  = 8.5 Hz, H-3, H-5), 6.86 (br s, 1H, NH, deuterium oxide exchangeable), 7.65 (d,  $J$  = 8.5 Hz, 2H, H-2, H-6), 7.72–8.08 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 353 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>NO<sub>5</sub>: C, 67.98; H, 5.38; N, 3.96. Found: C, 68.10; H, 5.75; N, 4.09.

#### **N-(2-isopropoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-4-methylbenzamide (6p);**

**Method A:** The compound (**6p**) was obtained by refluxing a solution of **4d** in anhydrous *i*-propanol (**5d**) for 10 hr. Light yellow crystals (benzene-hexane), yield 79%; mp 188–189 °C; **Method B:** The compound (**6p**) was obtained by photoirradiating a solution of **4d** in anhydrous *i*-propanol (**5d**) for a period of 1 hr. Light yellow crystals (benzene-hexane) yield 80%; mp 188–189 °C; UV (ethanol):  $\lambda_{\text{max}}$  224 nm ( $\epsilon$  84,611); IR (nujol): 3310 (N–H stretch (amide)), 1755, 1721 (C=O stretch (indane-1,3-dione)), 1640 (C=O stretch (amide)) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.12 (d,  $J$  = 7.0 Hz, 6H, OCH(CH<sub>3</sub>)<sub>2</sub>-2'), 2.28 (s, 3H, CH<sub>3</sub>-4), 4.42 (sept,  $J$  = 7.0 Hz, 1H, OCH(CH<sub>3</sub>)<sub>2</sub>-2'), 6.85 (br s, 1H, NH, deuterium oxide exchangeable), 7.10 (d, 2H,  $J$  = 8.0 Hz, H-3, H-5), 7.59 (d,  $J$  = 8.5 Hz, 2H, H-2, H-6), 7.71–8.10 (m, 4H, H-4', H-5', H-6', H-7'); ms: (70 eV, electron impact) m/z 337 (M<sup>+</sup>). *Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>NO<sub>4</sub>: C, 71.21; H, 5.63; N, 4.15. Found: C, 71.94; H, 5.50; N, 4.51.

### 3. Results and discussion

### 3.1 Chemistry

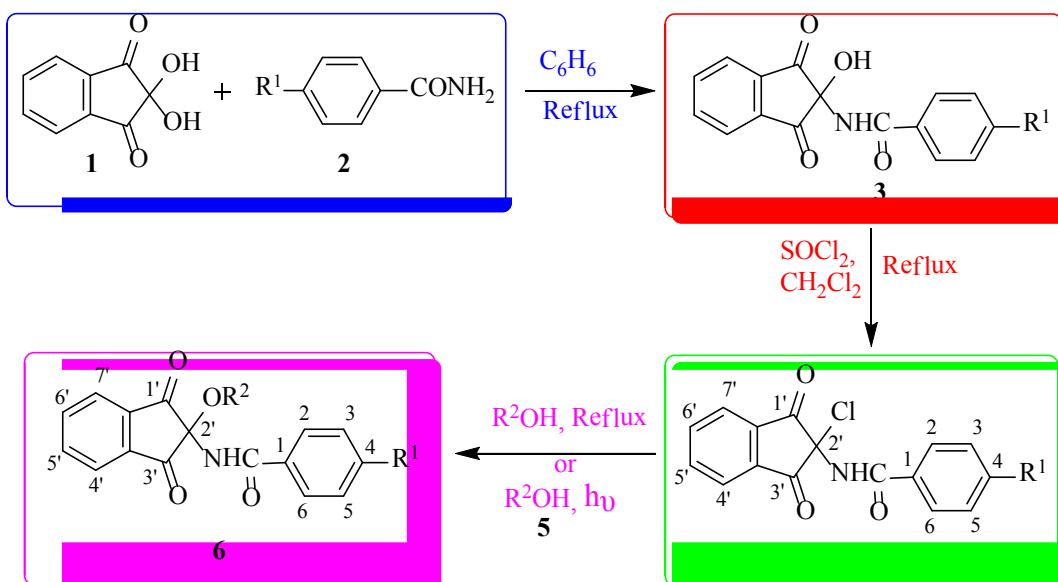
The protocol for the synthesis of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) is depicted in Scheme 1. Starting from ninhydrin (**1**), we obtained *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**3**) [51,53,54] upon reaction with corresponding benzamides (**2**) which upon subsequent treatment with  $\text{SOCl}_2$  in  $\text{CH}_2\text{Cl}_2$  afforded the corresponding *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4**) in high yields. The *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) were prepared either by refluxing the solution of *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4**) in different anhydrous alcohols (**5**) for 1–10 hr or photoirradiating the solutions of 1*H*-indene-1,3(2*H*)-diones (**4**) in different anhydrous alcohols (**5**) under  $\text{N}_2$  atmosphere with light from a 450 Watts Hanovia mercury vapour lamp in a Pyrex reactor for 35–60 min in fairly good yields.

The structures of all the *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4**) and *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) have been confirmed through analysis of their UV, IR,  $^1\text{H}$  NMR and mass spectra, and analytical data (*vide experimental*). UV spectra of **4a–4d** showed absorption maxima at wavelength ( $\lambda_{\max}$ ) 296 nm in all the derivatives. In their IR spectra, N–H stretching due to amide group was observed in the region at 3320–3428  $\text{cm}^{-1}$ . The most characteristic feature of IR spectra of **4** was the appearance of the two strong absorption bands ( $\nu_{\max}$ ) in the regions at 1748–1776  $\text{cm}^{-1}$  and 1725–1728  $\text{cm}^{-1}$  due respectively to the asymmetrical and symmetrical coupling between two in-plane carbonyl groups of the indane-1,3-dione moiety [49–52,56,57]. The  $>\text{C=O}$  stretching of the benzamido carbonyl [51,53–55], however, appeared in the region at 1642–1674  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra of **4**, in

each case, in the aromatic region, displayed a characteristic two-proton doublet ( $J = 8.00\text{--}8.50$  Hz) in the region at  $\delta$  7.63–7.70 due to H-2 & H-6 and a four-proton multiplet in the region at  $\delta$  7.70–8.12 attributable to H-4', H-5', H-6' and H-7'. The N–H proton, however, appeared as a broad singlet (deuterium oxide exchangeable) in the region at  $\delta$  7.50–10.00. Signals due to remaining protons were observed in the expected regions and the ratio of aromatic to aliphatic protons was found satisfactory (*vide experimental*).

The UV spectra of **6a–6p** exhibited absorption maxima at wavelength ( $\lambda_{\max}$ ) in the region at 223–229 nm, however, an additional absorption band was also displayed at wavelength ( $\lambda_{\max}$ ) in the region at 255–255.5 nm in the compounds **6a**, **6g** and **6o**. In their IR spectra, N–H stretching due to amide group was observed in the region at 3200–3360  $\text{cm}^{-1}$ . The salient feature of IR spectra of **6** was the appearance of the two strong absorption bands ( $\nu_{\max}$ ) in the regions at 1750–1759  $\text{cm}^{-1}$  and 1718–1725  $\text{cm}^{-1}$  due to carbonyl groups of the indane-1,3-dione moiety [49–52,56,57]. The  $>\text{C=O}$  stretching of the benzamido carbonyl [51,53–55], however, appeared in the region at 1620–1643  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra of **6a–6p**, in each case, in the aromatic region, displayed a characteristic two-proton doublet ( $J = 8.00\text{--}8.50$  Hz) in the region at  $\delta$  7.59–7.74 due to H-2 & H-6 and a four-proton multiplet in the region at  $\delta$  7.70–8.13 assignable to H-4', H-5', H-6' and H-7'. The N–H proton, however, appeared as a broad singlet (deuterium oxide exchangeable) in the region at  $\delta$  6.86–7.58. The signals due to remaining protons were observed in the expected regions and the ratio of aromatic to aliphatic protons was found satisfactory (*vide experimental*).

Further, the mass spectral data and elemental analytical data of **4** and **6** were found in good agreement with their molecular formulae. It deserves attention here that some of the



**2a, 3a, 4a**, R<sup>1</sup> = H; **2b, 3b, 4b**, R<sup>1</sup> = Cl; **2c, 3c, 4c**, R<sup>1</sup> = OCH<sub>3</sub>; **2d, 3d, 4d**, R<sup>1</sup> = CH<sub>3</sub>; **5a**, R<sup>2</sup> = CH<sub>3</sub>; **5b**, R<sup>2</sup> = CH<sub>2</sub>CH<sub>3</sub>; **5c**, R<sup>2</sup> = CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>; **5d**, R<sup>2</sup> = CH(CH<sub>3</sub>)<sub>2</sub>

Compounds	R <sup>1</sup>	R <sup>2</sup>	Compounds	R <sup>1</sup>	R <sup>2</sup>
<b>6a</b>	H	CH <sub>3</sub>	<b>6i</b>	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
<b>6b</b>	Cl	CH <sub>3</sub>	<b>6j</b>	Cl	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
<b>6c</b>	OCH <sub>3</sub>	CH <sub>3</sub>	<b>6k</b>	OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
<b>6d</b>	CH <sub>3</sub>	CH <sub>3</sub>	<b>6l</b>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
<b>6e</b>	H	CH <sub>2</sub> CH <sub>3</sub>	<b>6m</b>	H	CH(CH <sub>3</sub> ) <sub>2</sub>
<b>6f</b>	Cl	CH <sub>2</sub> CH <sub>3</sub>	<b>6n</b>	Cl	CH(CH <sub>3</sub> ) <sub>2</sub>
<b>6g</b>	OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	<b>6o</b>	OCH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
<b>6h</b>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	<b>6p</b>	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>

**Scheme 1.** The reaction sequence for the synthesis of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**).

derivatives *viz.* *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4a** and **4b**) and *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6a** and **6b**) have been reported in literature [53–55] synthesized by thermal reaction.

The physical data of the alkoxy derivatives (**6**) obtained from thermal and photochemical reactions for comparison are presented in the Table 1 given below.

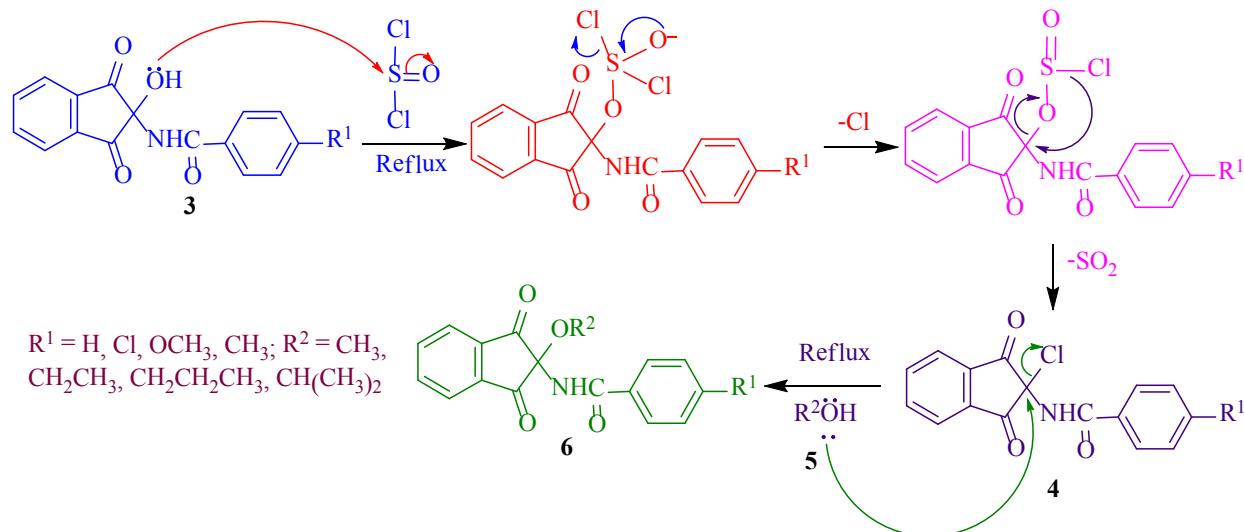
It is clearly revealed from the data presented in the Table 1 that similar product, *i.e.* **6** is formed

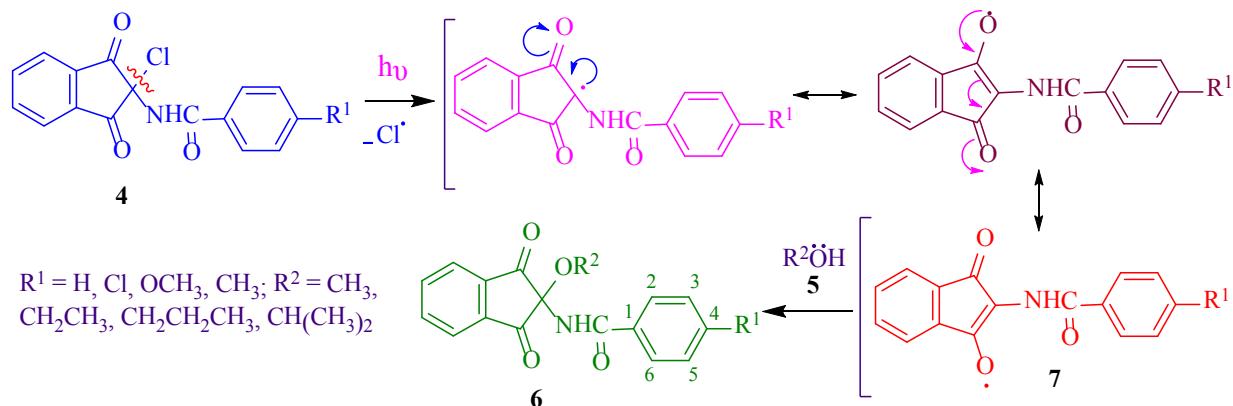
through both the routes; however, time required for completion of reaction for conversion of **4** to **6** is comparatively shorter in photochemical reaction (35–60 min) than thermal reaction (1–10 hr) and yields obtained range from 60–91% and 80–90%, respectively. On the basis of these results, it may be inferred that photochemical route is comparatively better than thermal route but to a little extent.

Mechanistically, the formation of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) from *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**3**)

**Table 1:** Physical data of *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6a–6p**).

Substrates used in the reaction	Products obtained( <b>6</b> )	Thermal reaction		Photochemical reaction	
		Time required for completion of reaction (hr)	Yield (%)	Time required for completion of reaction (min)	Yield (%)
<b>4a + 5a</b>	<b>6a</b>	1	60	35	83
<b>4b + 5a</b>	<b>6b</b>	6	91	40	90
<b>4c + 5a</b>	<b>6c</b>	8	89	45	90
<b>4d + 5a</b>	<b>6d</b>	6	79	40	81
<b>4a + 5b</b>	<b>6e</b>	3	76	40	80
<b>4b + 5b</b>	<b>6f</b>	10	75	40	80
<b>4c + 5b</b>	<b>6g</b>	10	86	40	85
<b>4d + 5b</b>	<b>6h</b>	8	81	50	85
<b>4a + 5c</b>	<b>6i</b>	5	78	40	85
<b>4b + 5c</b>	<b>6j</b>	10	85	50	82
<b>4c + 5c</b>	<b>6k</b>	10	85	50	86
<b>4d + 5c</b>	<b>6l</b>	8	87	50	82
<b>4a + 5d</b>	<b>6m</b>	10	80	55	81.5
<b>4b + 5d</b>	<b>6n</b>	10	84	60	85
<b>4c + 5d</b>	<b>6o</b>	10	83	55	80
<b>4d + 5d</b>	<b>6p</b>	10	79	60	80

**Scheme 2:** A plausible mechanism of formation of **6** via thermal route.

**Scheme 3:** A plausible mechanism for photoconversion of **4** to **6**.

may be envisaged to occur through an initial nucleophilic attack of 2'-OH of **3** on  $\text{SOCl}_2$  thereby generating the chloro derivatives (**4**) which upon subsequent treatment with anhydrous alcohols (**5**) under reflux conditions undergo nucleophilic substitution reaction to yield the corresponding alkoxy derivatives (**6**) as depicted in Scheme 2.

The mechanistic details of the phototransformation, **4**  $\rightarrow$  **6** have not been unravelled in the present investigation. However, a plausible mechanism is sketched in Scheme 3. The photoconversion may be envisaged to occur through an initial homolytic cleavage of C<sub>2</sub>-Cl bond of **4** leading to the formation of resonance stabilized free radical (**7**) followed by abstraction of alkoxy radical from the alcohol (**5**) to yield the alkoxy derivative (**6**).

The biological evaluation is underway and will be reported in due course of work.

## Conclusion

In conclusion, synthesis of a series of sixteen *N*-(2-alkoxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**6**) using ninhydrin (**1**) as starting compound *via* thermal and photochemical routes in fairly good yields has been carried out. It has been found that

time required for completion of reaction for conversion of key intermediate *N*-(2-chloro-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)benzamides (**4**) to **6** is comparatively shorter in photochemical reaction than thermal reaction. Hence, it may be inferred that photochemical route is comparatively better than thermal route.

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