

Studies on enamides. Part-7¹: a novel photochemical reaction pathway of *N*-aroyl-*N*-1-cyclohexenylanilines

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Dedicated to Professor (Mrs.) Asima Chatterjee on the occasion of her
85th birth anniversary

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Abstract

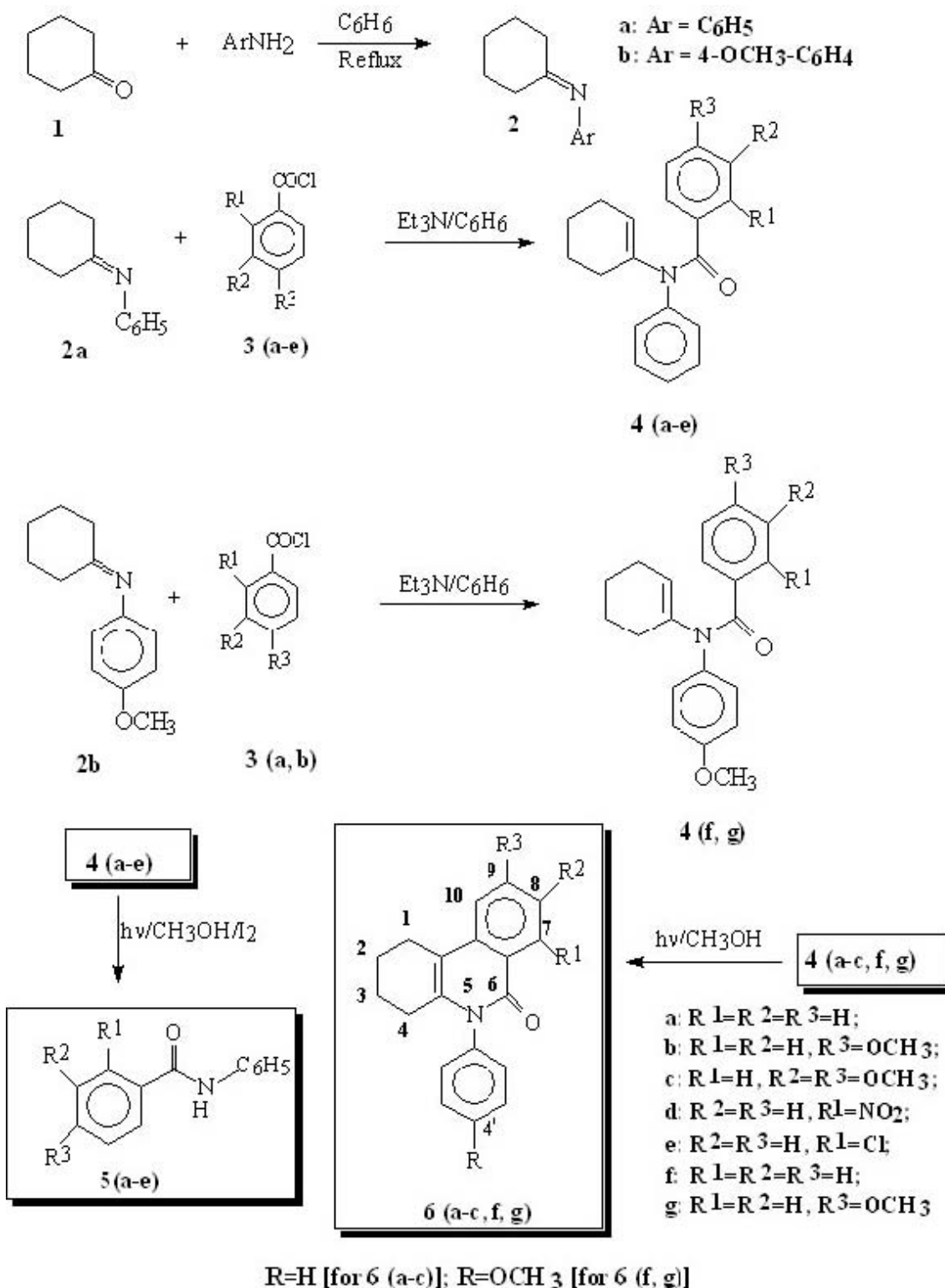
UV irradiation of *N*-aroyl-*N*-1-cyclohexenyl-anilines involves a cleavage of vinyl nitrogen bond under oxidative condition, whereas 6H-5-phenyl/aryl-1,2,3,4-tetrahydrophenanthridine-6-ones are obtained when the reaction is performed non-oxidatively.

Keywords: *N*-Aroyl-*N*-1-cyclohexenyl-anilines, vinyl nitrogen bond cleavage, oxidative UV irradiation, 6H-5-phenyl/aryl-1,2,3,4-tetrahydrophenanthridine-6-ones

Introduction

The photochemical reaction of enamides, apparently as first demonstrated by Eschenmoser *et al.*² has been extensively utilized for the synthesis³ of complex heterocycles, alkaloids and aza-steroids. In connection with our interest for the photochemical studies on enamides⁴⁻⁸ and other heterocyclic systems⁹, we envisaged to synthesize the hexahydrophenanthridones (**6**) – a potential molecule - by the oxidative irradiation of *N*-aroyl-*N*-1-cyclohexenyl-anilines [**4 (a-g)**]. But surprisingly, we found that the UV irradiation of the title compounds in the presence of iodine as oxidant (Scheme 1), led to a novel and unexpected cleavage of the vinyl nitrogen bond⁸ of the parent enamides (**4**); and the product was found to be anilides [**5 (a-e)**].

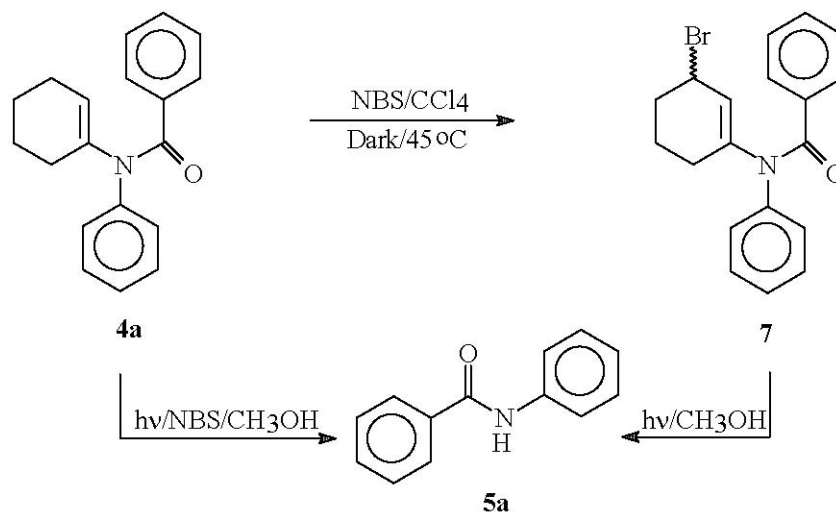
However, the same experiment, when carried out with **4a** in the absence of iodine for 25 h, afforded 6H-5-phenyl-1, 2,3,4-tetrahydrophenanthridin-6-one (**6a**) (19%), mp 153° C (acetone-light petroleum, 60-80° C), IR (KBr) ν_{max} 1655 cm⁻¹. Similarly, while the substrate [**4 (b-g)**] gave the phenanthridones [**6 (b-c), f, g**] (Table) during photo-irradiation, the compound (**4d**) appeared to be inert. under photochemical condition and **4e** produced some intractable oily material. The apparent lack of reactivity of **4d** and **4e** may be explained as follow:



Scheme 1

- i) the excited state of **4** is analogous to an azadiene system (**4p-electron**) and a dienophile unit (**2p-electron**) present in the cyclohexene moiety. The intramolecular photo-cyclisation of such type of compounds is a case of **reverse electron demand Diels-Alder reaction**. Thus, whenever an electron-withdrawing group such as nitro- (**4d**) or chloro- (**4e**) is present, the **HOMO** energy of the diene component increases and the **LUMO** energy of the dienophile unit also increases. This, therefore, causes the photocyclisation reactions very difficult, and as result of which the compounds **4d** and **4e** do not give any photocyclised products;
- ii) during photochemical cyclisation reaction of the parent enamide (**4**), the presence of *ortho*-substituent (*e.g.*, nitro and chloro in **4**) offers a considerable steric hindrance at the site of carbon-carbon bond formation in the transition state and the reaction, therefore, fails.

Incidentally, this is the first observation of **6-cleavage** for the proposed formation of anilides, and in order to substantiate the pathway for the formation of anilides, we have independently prepared the intermediate (**7**) as described in **Scheme 2**.



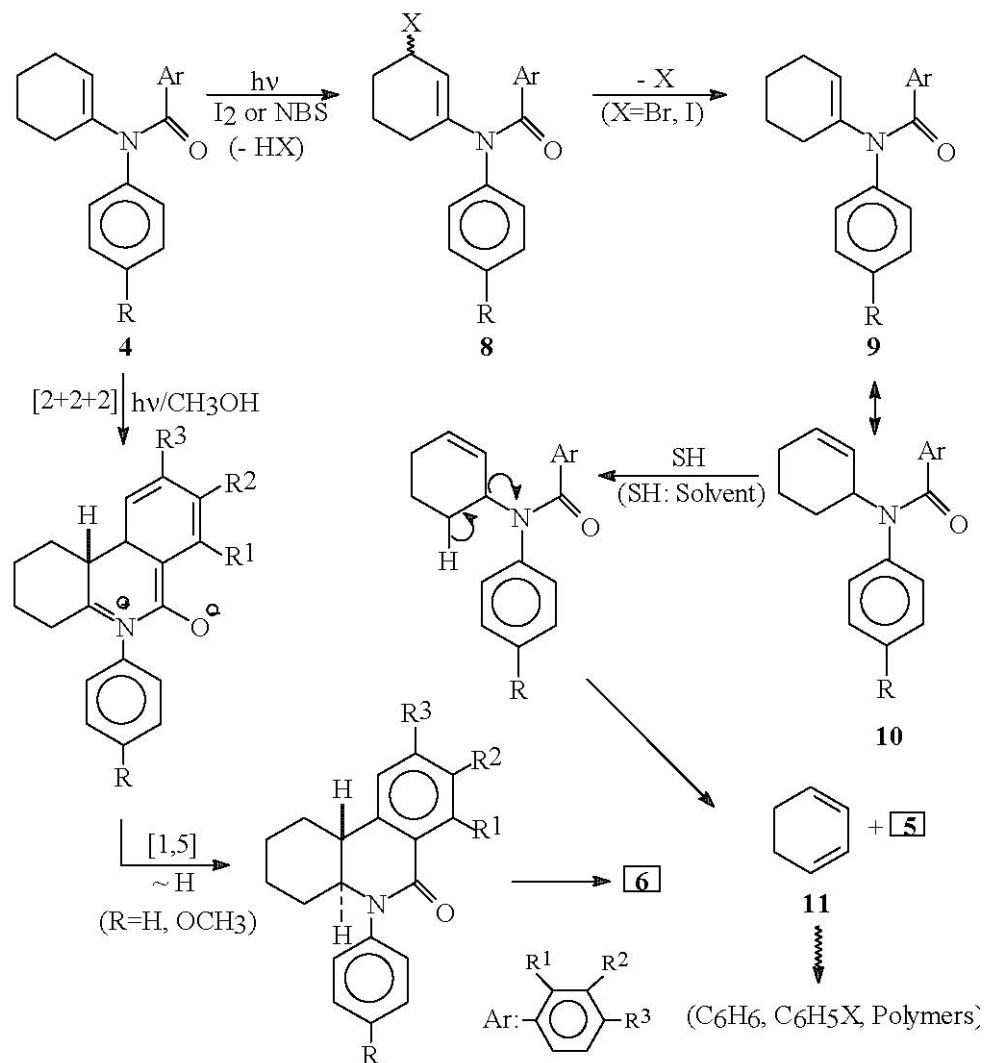
Scheme 2

As the anilides are only formed in the presence of iodine, we, therefore, reasoned the reaction probably involved an iodine radical induced isomerism of the double bond of the cyclohexane ring of **4**, followed by a fission of C–N bond to give the anilides **5**. This was established by irradiating **4a** in the presence of *N*-bromosuccinimide (NBS) in methanol, whence we could isolate **5a** in 53% yield. Furthermore, when 3-bromo-*N*-benzoyl-*N*-1-cyclohexenyl-*N*-phenylamine (**7**), prepared from **4a** by the reaction of NBS in dark, was irradiated in methanol only for 3 h., it afforded **5a** in 73% yield, showing the same to be a true intermediate in the reaction profile (Scheme 2).

The reaction thus proceeded through an allylic bromination or iodination to produce (**8**) and the loss of halogen radical during the reaction (Scheme 3) generated the radical (**9**). This further gave rise to a new radical (**10**) and thence to the anilides (**5**).

It is known¹⁰⁻¹² that for enamide photocyclisation reaction the involvement of the lone pair of the nitrogen atom is necessary. In the present instance, such participation of the lone pair of the nitrogen atom is difficult as the same is experiencing a conjugative effect of the phenyl group attached to the nitrogen atom. Thus, the phenyl group in **4** is acting as a sink for the lone pair of nitrogen atom and hence, behaves as an electron-withdrawing group (EWG). This EWG effect of the phenyl ring makes the lone pair relatively unavailable for a smooth [2+2+2]-cycloaddition reaction. However, when the phenyl ring is replaced by a 4-methoxyphenyl group, this mesomeric effect on the lone pair of the nitrogen atom is nullified and the photocyclisation becomes easier and higher yields of hexahydrophenanthridones (**6f** and **6g**) are obtained (Table). In the presence of only phenyl ring in the parent enamides (**4a-e**) as the lone pair is withdrawn, the photocyclisation becomes competitive with other alternate pathways leading to the anilides. In the absence of any radical initiator the enamide photocyclisation is the only available course of the reaction save Type I cleavage, to afford the highly conjugated hexahydrophenanthridones [**6 (a-c, f, g)**]. The isolation of hexahydrophenanthridones is well documented in the literature.¹³⁻¹⁵

It is also known in the literature the attachment of an **electron-releasing group** such as alkyl, allyl or benzyl to the nitrogen atom of an enamide enhances its reactivity towards the photochemical [2+2+2]-cycloaddition reaction (Reviews 2). On the other hand, when an **electron-withdrawing group** (carbonyl or an aromatic ring) is linked with the nitrogen atom as the third valent unit, a reluctance in the photocyclisation is the consequence and the photochemical rearrangement becomes the major pathway.^{2, 16, 17} However, the present study shows that even in the presence of an **EWG (phenyl or aryl)** on the nitrogen atom, a **photocyclisation** reaction occurs instead of a photo-rearrangement. This is notably a new observation and hence, a remarkable effect of the presence of EWG¹⁸ on the nitrogen atom of enamides on the course of their photochemical reactions is observed, and to synthesize the hexahydrophenanthridones from N-phenyl/aryl substituted enamides, a non-oxidative procedure should be employed.



Scheme 3

Table 1. Results of UV irradiation of *N*-aryl-*N*-(1-cyclohexenyl)anilines

Substrate (4)	Method A(time in h)	Yield of 5 mp in °C (solvent)	IR (ν_{max}) (cm ⁻¹)	Method B(time in h)	Yield of 6 mp in °C (solvent)	¹ H NMR (CDCl ₃) δ (ppm) [†]
a: 3.61 mmol	8	52 % 162° (A-H) (lit. 19 163°)	3350, 1660	25	19 % 153° (A-P)	8.46 (1H, d) J=8.7 Hz

b: 3.26 mmol	14.5	68 % 170° (A-P) (lit. ¹⁹ 168 _o)	3335, 1645	30	33 % 145-46° (E- H)	8.39 (1H, d) J=9.0 Hz
c: 2.97 mmol	20	83 % 152° (A-H) (lit. ¹⁹ 154 _o)	3310, 1640	21	37% 186-87° (A- H)	7.86 (1H, s)
d: 3.11 mmol	18	43 % 155° (A-H) (lit. ¹⁹ 155 _o)	3250, 1660	21	-	-
e: 3.21 mmol	20	42 % 118° (E-P') (lit. ¹⁹ 118 _o)	3220, 1640	19	-	-
f: 3.25 mmol	-	-	-	15	40 % 194° (A-H)	8.45 (1H, d) J=7.8 Hz
g: 2.96 mmol	-	-	-	27	55 % 163° (A-H)	8.38 (1H, d) J=8.8 Hz

† Only the characteristic proton signals for C₇-H of the hexaphydrophenanthridones are shown

Experimental Section

General Procedures. The melting points recorded in sulfuric acid bath, or boiling points are uncorrected. The IR spectra were obtained in a Perkin-Elmer 297 Infrared spectrophotometer, ¹H NMR spectra, unless otherwise stated, were recorded in a Bruker 300 MHz AM spectrophotometer in CDCl₃ with TMS as internal standard and the microanalyses were performed in a Perkin-Elmer 240 C Elemental analyzer. The photolysis experiments were carried out in a quartz vessel (immersion type) with a low-pressure mercury lamp (16 W, > 90% 254 nm, Model 3016) manufactured by Applied Photophysics Ltd., England. The solvent abbreviations are: A - Acetone, E - Diethyl ether, H - Hexane, MC - Methylene chloride, P - Light petroleum, 60-80° C. The yield denotes the combined amounts of crystallized or sublimed material obtained after chromatography (silica gel, 60-120 mesh, Glindia).

Preparation of Schiff Bases [2 (a, b)]

(a) Cyclohexanone (**1**) (14 g, 143 mmol) and aniline (13.3 g, 143 mmol) were refluxed in dry benzene (60 mL) for 4 h using a Dean-Stark apparatus. After the reaction, benzene was removed

in vacuum and the residue was distilled off to obtain 15.9 g (64%) of the Schiff base (**2a**), boiling at 110-12° C/ 2 mm Hg; IR (neat) ν_{max} 3030, 2930, 2860, 1660, 1605, 1495, 1450, 1345, 1225, 1130, 1030, 735, 700 cm^{-1} .

(b) Following the above procedure, the Schiff base (**2b**) was obtained from **1** (3.9 g, 40 mmol) and purified 4-methoxy aniline (6 g, 49 mmol) in 65% yield (5.3 g), bp 135-36° C/ 1 mm Hg, IR (neat) ν_{max} 3030, 2930, 2860, 2810, 1655, 1605, 1575, 1500, 1445, 1310, 1235, 1190, 1100, 1035, 840, 765, 745, 710 cm^{-1}

Preparation of *N*-aroyl-*N*-1-cyclohexenyl-anilines [4 (a-e)]. *N*-benzoyl-*N*-1-cyclohexenyl-aniline (4a).

A solution of benzoyl chloride (**3a**) (4.8 g, 34 mmol) in dry benzene (10 mL) was added dropwisely with stirring to an ice-cold solution of the anil (**2a**) (6.1 g, 35 mmol) and triethyl amine (5.3 g, 53 mmol) in dry benzene (10 mL) and kept overnight. It was then refluxed for 45 min, cooled and diluted with ice-cold water. Usual workup and removal of the solvent in vacuum gave a solid which was crystallized from acetone-light petroleum, 60-80° C to obtain 7.6 g (78%) of **4a** as shining white needle-shaped crystals, mp 128° C, IR (nujol): ν_{max} 3060, 1640, 1590, 1580, 1490, 1170, 1070, 1025, 920, 835, 780, 765, 700 cm^{-1} , ^1H NMR: δ 1.53 (2H, m), 1.68 (2H, m), 2.00 (2H, br. s), 2.18 (2H, br. s), 5.52 (1H, m), 7.17 (2H, dd. merged as t, $J=6.6, 1.2$ Hz), 7.31 (6H, m), 7.49 (2H, dd, $J=6.6, 1.2$ Hz).

Analysis: Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}$ (277.37) C, 82.28%, H, 6.90% and N, 5.05%; Found: C, 82.17%, H, 6.74% and N, 5.33%.

N-Aroyl-*N*-1-cyclohexenyl-anilines [4 (b-e)] were prepared by the above procedure using the anil (4 g, 23 mmol) and the acid chlorides [3 (b-e)] obtained from the equimolar proportions of the respective acids.

N-(4-Methoxybenzoyl)-*N*-1-cyclohexenyl-anilines (**4b**). Yield: 4.2 g (59%), shining white granular-shaped crystals, mp 105-106° C (MC-P), IR (nujol): ν_{max} 3050, 1645, 1605, 1595, 1485, 1375, 1250, 1165, 1030, 920, 840, 810, 780, 755, 715, 695 cm^{-1} , ^1H NMR: δ 1.54 (2H, ill-resolved t), 1.68 (2H, ill-resolved t), 2.03 (2H, br. s), 2.19 (2H, br. s), 3.79 (3H, s), 5.51 (1H, br. s), 6.77 (2H, d, $J=8.7$ Hz), 7.13 (2H, m), 7.32 (3H, m), 7.48 (2H, d, $J=8.7$ Hz).

Analysis: Calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ (307.39) C, 78.15%, H, 6.89% and N, 4.56%; Found: C, 77.72%, H, 7.02% and N, 4.19%.

N-(3,4-Dimethoxybenzoyl)-*N*-1-cyclohexenyl-anilines (**4c**). Yield: 5.4 g (69%), shining white needle-shaped crystals, mp 102-103° C (E-H), IR (nujol): ν_{max} 1635, 1600, 1585, 1510, 1490, 1375, 1330, 1260, 1235, 1145, 1025, 930, 860, 820, 795, 760, 725, 700 cm^{-1} , ^1H NMR: δ 1.67 (4H, m), 2.07 (2H, br. s), 2.22 (2H, br. s), 3.76 (3H, s), 3.87 (3H, s), 5.55 (1H, br. s), 6.73 (1H, d, $J=8.1$ Hz), 7.06 (1H, s), 7.14 (3H, m), 7.15 (1H, d, $J=8.1$ Hz), 7.30 (2H, d, $J=8.1$ Hz).

Analysis: Calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_3$ (337.42) C, 74.75%, H, 6.87% and N, 4.15%; Found: C, 74.65%, H, 6.75% and N, 4.23%.

N-(2-Nitrobenzoyl)-*N*-1-cyclohexenyl-anilines (**4d**). Yield: 4.1 g (55%), shining lemon yellow granular shaped crystals, mp 104-105° C (MC-H), IR (nujol): ν_{max} 3070, 1645, 1595, 1525, 1445, 1340, 850, 790, 755, 705 cm^{-1} , ^1H NMR (60 MHz): δ 1.30 (3H, m), 1.69 (4H, m), 2.24 (1H, m),

5.69 (1H, m), 7.30 (8H, m), 8.06 (1H, m). Analysis: Calcd. for $C_{19}H_{18}N_2O_3$ (322.36) C, 70.79%, H, 5.63% and N, 8.69%; Found: C, 71.27%, H, 5.51% and N, 8.52%.

***N*-(2-Chlorobenzoyl)-*N*-1-cyclohexenyl-anilines (4e).** Yield: 5.2 g (72%), shining white needle-shaped crystals, mp 112-13° C (A-P), IR (KBr): ν_{\max} 3060, 2940, 2860, 1650, 1590, 1545, 1335, 1290, 1250, 1100, 1025, 920, 815, 725, 700 cm^{-1} , 1H NMR: δ 1.43 (4H, m), 1.83 (4H, m), 5.80 (1H, br. s), 7.31 (9H, m).

Analysis: Calcd. for $C_{19}H_{18}NOCl$ (311.81) C, 73.19%, H, 5.82% and N, 4.49%; Found: C, 72.83%, H, 5.83% and N, 4.53%.

***N*-Benzoyl-*N*-1-cyclohexenyl- (4-methoxy)-aniline (4f).** Following the above procedure, the enamide (4f) was obtained in 53% yield (3.2 g), mp 92° C (E-P), IR (KBr): ν_{\max} 2920, 1715, 1645, 1600, 1500, 1440, 1335, 1290, 1250, 1100, 1025, 920, 815, 725, 700 cm^{-1} as shining white needles from the reaction of the Schiff base (2b) (4 g, 20 mmol) and benzoyl chloride (3a) (2.6 g, 19 mmol).

Analysis: Calcd. for $C_{20}H_{21}NO_2$ (307.39) C, 78.15%, H, 6.89% and N, 4.56%; Found: C, 77.91%, H, 6.72% and N, 4.67%.

***N*-(4-Methoxybenzoyl)-*N*-1-cyclohexenyl- (4-methoxy)-aniline (4g).** The Schiff base (2b) (4 g, 20 mmol) was reacted with 4-methoxybenzoyl chloride (3b), obtained from the equimolar quantity of the corresponding acid and 3.2 g (48%) of 4g was obtained as shining white granular crystals, mp 98° C (A-P), IR (nujol): ν_{\max} 1640, 1605, 1500, 1445, 1250, 1170, 1025, 920, 825, 750 cm^{-1} ; 1H NMR: δ 1.55 (2H, ill-resolved t), 1.69 (2H, ill-resolved t), 2.03 (2H, br. s), 2.19 (2H, br. s), 3.78 (3H, s), 3.79 (3H, s), 5.49 (1H, br. s), 6.77 (2H, d, J=8.7 Hz), 6.81 (2H, d, J=8.9 Hz), 7.07 (2H, d, J=8.7 Hz), 7.47 (2H, d, J=8.6 Hz).

Analysis: Calcd. for $C_{21}H_{23}NO_3$ (337.42) C, 74.75%, H, 6.87% and N, 4.15%; Found: C, 74.41%, H, 6.53% and N, 4.05%.

UV Irradiation of *N*-aroyl-*N*-1-cyclohexenyl-anilines [4 (a-g)]

Method A. A solution of 4a (1 g, 3.61 mmol) and iodine (0.92 g, 3.62 mmol) in dry methanol (350 mL) was irradiated for 8 h under nitrogen atmosphere at room temperature. The solvent was distilled off in vacuum and the crude product, after dilution with water (50 mL) was extracted with dichloromethane-ether mixture (3 x 30 ml). The combined organic layer was washed with saturated sodium thiosulphate solution (3 x 25 mL), alkali (5%, 2 x 20 mL), brine (4 x 25 mL) and dried (Na_2SO_4). The residue so obtained after evaporation of the solvent in vacuum, on chromatography gave benzanilide (5a), in hexane-ethyl acetate mixture (4:1, v/v mixture) as eluent.

Method B. A solution of 4a (1 g, 3.61 mmol) in dry methanol (350 mL) was irradiated for 25 h under nitrogen atmosphere and the crude product, obtained after the removal of the solvent in vacuum, on chromatography afforded 6H-5-phenyl-1, 2,3,4-tetrahydrophenanthridin-6-one (6a) in hexane-ethyl acetate mixture (9:1 v/v mixture) as eluent. IR (nujol): ν_{\max} 3060, 1660, 1620, 1590, 1380, 770, 700 cm^{-1} , 1H NMR: δ 1.73 (2H, m, C_3 -H₂), 1.83 (2H, m, C_2 -H₂), 2.16 (2H, t, J=6.3 Hz, C_4 -H₂), 2.80 (2H, t, J=6.3 Hz, C_1 -H₂), 7.24 (2H, dd, J=6.9, 1.5 Hz, C_8 -H+ C_4 -H), 7.45

(2H, dd, $J=7.5, 3.0$ Hz, C_{3'}-H+C_{5'}-H), 7.50 (2H, dd, $J=6.2, 1.9$ Hz, C_{2'}-H+C_{6'}-H), 7.66 (1H, d, $J=6.6$ Hz, C₉-H), 7.70 (1H, dd, $J=6.0, 1.5$ Hz, C₁₀-H), 8.46 (1H, d, $J=8.7$ Hz, C₇-H).

Analysis: Calcd. for C₁₉H₁₇NO (275.35) C, 82.88%, H, 6.22% and N, 5.09%; Found: C, 82.68%, H, 6.39% and N, 4.86%.

Table presents the experimental results of both the methods as applied to the substrates [**4 (a-g)**].

9-Methoxy-6H-5-phenyl-1, 2,3,4-tetrahydrophenanthridin-6-one (6b). IR (nujol): ν_{\max} 1645, 1610, 1545, 1375, 1260, 1020, 845, 835, 775, 745, 695 cm⁻¹, ¹H NMR: δ 1.73 (2H, m, C₃-H₂), 1.83 (2H, m, C₂-H₂), 2.13 (2H, m, C₄-H₂), 2.76 (2H, m, C₁-H₂), 3.95 (3H, s, C₉-OCH₃), 7.02 (1H, br. s, C₁₀-H), 7.07 (1H, d, $J=9.0$ Hz, C₈-H), 7.23 (2H, d, $J=7.9$ Hz, C_{2'}-H+C_{6'}-H), 7.48 (3H, m, C_{3'}-H+C_{4'}-H+C_{5'}-H), 8.39 (1H, d, $J=9.0$ Hz, C₇-H).

Analysis: Calcd. for C₂₀H₁₉NO₂ (305.38) C, 78.66%, H, 6.27% and N, 4.59%; Found: C, 78.32%, H, 6.39% and N, 4.41%.

8,9-Dimethoxy-6H-5-phenyl-1, 2,3,4-tetrahydrophenanthridin-6-one (6c). IR (nujol): ν_{\max} 1640, 1600, 1580, 1510, 1375, 1315, 1270, 1240, 1215, 1150, 1015, 870, 765, 745, 685 cm⁻¹, ¹H NMR: δ 1.73 (2H, m, C₃-H₂), 1.83 (2H, m, C₂-H₂), 2.15 (2H, ill-resolved t, C₄-H₂), 2.77 (2H, m, ill-resolved t, C₁-H₂), 3.98 (3H, s, C₈-OCH₃), 4.03 (3H, s, C₉-OCH₃), 6.99 (1H, s, C₁₀-H), 7.22 (2H, dd merged as t, $J=6.0$ Hz, C_{2'}-H+C_{6'}-H), 7.48 (3H, m, C_{3'}-H+C_{4'}-H+C_{5'}-H), 7.86 (1H, s, C₇-H).

Analysis: Calcd. for C₂₁H₂₁NO₃ (335.40) C, 75.20%, H, 6.31% and N, 4.18%; Found: C, 74.93%, H, 5.91% and N, 4.32%.

4'-Methoxy-6H-5-phenyl-1, 2,3,4-tetrahydrophenanthridin-6-one (6f). IR (nujol): ν_{\max} 3050, 1645, 1610, 1590, 1550, 1500, 1480, 1430, 1370, 1320, 1290, 1230, 1170, 1025, 820, 760, 700 cm⁻¹, ¹H NMR: δ 1.72 (2H, m, C₃-H₂), 1.82 (2H, m, C₂-H₂), 2.18 (2H, t, $J=5.9$ Hz, C₄-H₂), 2.79 (2H, t, $J=5.9$ Hz, C₁-H₂), 3.86 (3H, s, C_{4'}-OCH₃), 7.01 (2H, d, $J=9.1$ Hz, C_{3'}-H+C_{5'}-H), 7.13 (2H, d, $J=9.1$ Hz, C_{2'}-H+C_{6'}-H), 7.45 (1H, dd merged as t, $J=7.8$ Hz, C₁₀-H), 7.67 (2H, m, C₈-H+C₉-H), 8.45 (1H, d, $J=7.8$ Hz, C₇-H).

Analysis: Calcd. for C₂₀H₁₉NO₂ (305.38) C, 78.66%, H, 6.27% and N, 4.59%; found: C, 78.93%, H, 6.09% and N, 4.32%.

4',9-Dimethoxy-6H-5-phenyl-1, 2,3,4-tetrahydrophenanthridin-6-one (6g). IR (nujol): ν_{\max} 1665, 1615, 1595, 1510, 1485, 1375, 1300, 1250, 1170, 1030, 860, 770, 695 cm⁻¹, ¹H NMR: δ 1.73 (2H, m, C₃-H₂), 1.81 (2H, m, C₂-H₂), 2.17 (2H, t, $J=6.1$ Hz, C₄-H₂), 2.74 (2H, t, $J=6.1$ Hz, C₁-H₂), 3.86 (3H, s, C_{4'}-OCH₃), 3.94 (3H, s, C₉-OCH₃), 6.88 (1H, d, $J=2.3$ Hz, C₁₀-H), 6.93 (1H, dd, $J=7.8, 1.6$ Hz, C₈-H), 7.00 (2H, dd, $J=7.4, 2.0$ Hz, C_{3'}-H+C_{5'}-H), 7.13 (2H, dd, $J=6.7, 2.3$ Hz, C_{2'}-H+C_{6'}-H), 8.38 (1H, d, $J=8.8$ Hz, C₇-H).

Analysis: Calcd. for C₂₁H₂₁NO₃ (335.40) C, 75.20%, H, 6.31% and N, 4.18%; found: C, 75.06%, H, 6.12% and N, 4.11%.

Method C. A solution of **4a** (0.75 g, 2.7 mmol) and purified NBS (0.47 g, 2.7 mmol) in dry methanol (350 mL) was irradiated for 14 h as before. The crude product, obtained after stripping off the solvent in vacuum, was dissolved in ethyl acetate (30 mL) containing a few drops of methanol and washed successively with 1% NaOH (3 x 15 mL), dil. HCl (3 x 15 mL), brine (3 x 20 mL) and dried (Na₂SO₄). The residue obtained after removal of the solvent on

chromatography gave 680 mg (53%) of **5a**, mp 161° C (A-H) (lit.¹⁷ 163° C) in hexane-ethyl acetate mixture (8.5:1.5, v/v) as eluent.

Irradiation of 3-bromo-N-benzoyl-N-1-cyclohexenyl-N-phenylamine (7). A solution of **7** (0.5 g, mmol) was irradiated for 3 h in dry methanol (350 mL) under nitrogen atmosphere. Removal of the solvent gave a residue which on chromatography afforded **5a** (202 mg, 73%) in ethyl acetate-hexane mixture (15%, v/v) as eluent.

3-Bromo-N-benzoyl-N-1-cyclohexenyl-N-phenylamine (7). The enamide (**4a**) (1.5 g, 5.4 mmol) was taken in dry carbon tetrachloride (35 mL) and to it N-bromosuccinimide (0.964 g, 5.4 mmol) was added. The reaction mixture was heated at 45° C with stirring in dark, after which it was cooled and filtered to remove the succinimide. The residue was washed with dry carbon tetrachloride and the combined filtrate was further dried over sodium sulphate. The solvent was then removed in vacuum and a thick yellowish liquid was obtained, which on triturating with diethyl ether and light petroleum (40-60° C) in ice-bath gave the bromo-enamide (**7**), crystallized further from diethyl ether and light petroleum, 40-60° C into white granular shining crystals, mp. 94-95° C (E-P'), yield: 600 mg (32%), IR (KBr) ν_{\max} 1645, 1600, 1530, 1465, 790, 770, 710, 610 cm^{-1} , ¹H NMR (60 MHz): δ 1.63-2.33 (7H, m), 5.48 (1H, dd, J=6.0, 2.0 Hz), 7.03-7.42 (8H, m), 7.39-7.60 (2H, m).

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