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Photo-oxidation of 5-acetyl-3,4-dihydropyrimidin-2(*1H*)-ones

Hamid Reza Memarian*, Asadollah Farhadi, Hassan Sabzyan, Mousa Soleymani

Department of Chemistry, Faculty of Science, University of Isfahan, Hezar Jarib Ave., 81746-73441 Isfahan, I.R., Iran

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ABSTRACT

A variety of Biginelli 5-acetyl-3,4-dihydropyrimidin-2(*1H*)-ones are efficiently oxidized to their corresponding pyrimidin-2(*1H*)-one derivatives upon UV irradiation under argon atmosphere in chloroform solution. The nature of the additional substituent on the phenyl ring located on C-4 of the heterocyclic ring influences the rate of reaction. An electron-transfer induced photoreaction is proposed based on the formation of HCl and CH_2Cl_2.

1. Introduction

3,4-Dihydropyrimidin-2(*1H*)-ones (DHPMs) are one of important classes of heterocyclic compounds. Many of them are known as biological active natural products and drugs, such as blockers of calcium (Ca^{2+}) channel [1], inhibitors of the HIV virus [2], anti-cancer [3], antibacterial agents and also as anti-staphylococcal antibiotics [4]. All these effects are due to the existence of pyrimidine cores in these compounds. In addition, Itami et al. have reported that pyrimidine cores with extended π-systems exhibit interesting fluorescent properties [5]. However, in comparison to photochemical behavior of 1,4-dihydropyridines [6], surprisingly little is known about the light sensitivity of 3,4-dihydropyrimidin-2(*1H*)-ones. It is important to know that these compounds may easily lose their biological activities due to some molecular changes upon exposing to the UV light. Recently, we have studied the effect of the nature of the substituent on 4-position of the heterocyclic ring on the rate of oxidation of various ethyl 3,4-dihydropyrimidin-2(*1H*)-one-5-carboxylates by potassium peroxydisulfate under thermal conditions [7] or by applying the ultrasound irradiation [8]. In another work, we have further investigated this effect on the light sensitivity of these compounds by exposing them to the UV light [9].

The results of the computational studies of 3,4-dihydropyrimidin-2(*1H*)-ones indicate that the pyrimidine cores in these systems are not completely planar and the amount of deviation of C-4 of the ring from planarity depends on various factors such as: (i) the substituent located on C-4; (ii) the type of the group present on C-5 (being ester or keto groups); and (iii) the location of the additional substituent on the phenyl ring located on C-4. On the other hand, the type of the substituents located on the C-4 and C-5 atoms influence also the amount of the dihedral angle of both C-4 and C-5 substituents with respect to the ring atoms. All these observations are affected by the polar and steric effects of these substituents [10].

In our recent study, various 5-acetyl-3,4-dihydropyrimidin-2(*1H*)-ones were synthesized and the effect of the acetyl and the carboethoxy groups in position 5 of the dihydropyrimidinone ring on the rate of oxidation by potassium peroxydisulfate under microwave irradiation was investigated [11]. The results indicate that the ester derivatives are oxidized faster than the corresponding acetyl derivatives. In continuation of our work concerning the light sensitivity of dihydropyrimidinones especially to elucidate the comparative effects of the acetyl and carboethoxy groups on the rate of photo-oxidation, here the photochemical behavior of these compounds under oxygen and argon atmospheres are investigated.

2. Results and discussion

The important factor in photochemical behavior of organic compounds is the spin multiplicity (i.e. being singlet or triplet) of the excited state of the light absorbing compounds involved in the photoreaction. The lifetime of these species determine the rate of reaction especially in the triplet excited state, which can be affected by the triplet oxygen present in the reaction vessel either as the atmosphere or as a dissolved species during UV irradiation.

* Corresponding author. Tel.: +98 311 793 2707; fax: +98 311 668 9732.
E-mail address: memarian@sci.ui.ac.ir (H.R. Memarian).

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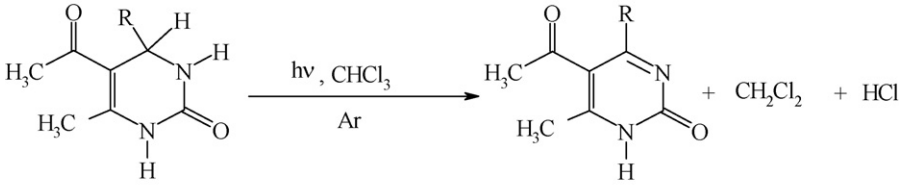


1a-1l **2a-2l**

R = **a**: C_6H_5, **b**: 4-$CH_3C_6H_4$, **c**: 4-$CH_3OC_6H_4$, **d**: 3-$CH_3OC_6H_4$, **e**: 2-$CH_3OC_6H_4$, **f**: 4-ClC_6H_4,

g: 3-ClC_6H_4, **h**: 2 -ClC_6H_4, **i**: 4 -BrC_6H_4, **j**: 2-BrC_6H_4, **k**: 4 -$NO_2C_6H_4$, **l**: 3-$NO_2C_6H_4$

Scheme 1.

Therefore, we first carried out irradiation of 4-phenyl substituted compound **1a**, as a model substrate, in the $CHCl_3$ solvent under oxygen and argon atmospheres. The results of the photoreactions indicate that irradiation of **1a** under oxygen atmosphere resulted in a complicated reaction because of the formation of the oxidation product **2a** as a major product besides various hitherto unidentified by-products. This is while, a clean reaction was observed by irradiation under argon atmosphere and a sole product **2a** has been obtained. In continuation, a 3 mM solution of each of the 3,4-dihydropyrimidinones (**1a**–**1l**) in chloroform was irradiated under argon atmosphere until total disappearance of **1a**–**1l** monitored by TLC (Scheme 1). The solvent was evaporated and the pure products were obtained by recrystallization from *n*-hexane/ethyl acetate solvent mixture. The results are summarized in Table 1.

The occurrence of the photo-dehydrogenation and characterization of the photoproducts was confirmed by comparison of the IR, UV, ^{1}H NMR, ^{13}C NMR and MS data of the photoproducts, pyrimidin-2(*1H*)-ones (**2a**–**2l**), with those of the starting materials, 3,4-dihydropyrimidin-2(*1H*)-ones (**1a**–**1l**). A comparative study of the UV data, presented in Table 2, shows bathochromic shift in the spectra of the products due to the formation of the imino-diene moiety in the heterocyclic ring system (formed after the elimination of the 3- and 4-hydrogens).

Comparison of the IR spectra of the products **2a**–**2l** with those of the corresponding starting materials **1a**–**1l**, presented in Table 3, shows a small shift of the CO stretching band of the acetyl group (5-$COCH_3$) to higher frequencies and shifts of the stretching modes of the 2-C=O and C_5=C_6 double bonds to lower frequencies due to the extended conjugation.

Table 1
Completion times and yields of the photo-oxidation of 5-acetyl-3,4-dihydropyrimidinones (**1a**–**1l**) under argon atmosphere.

1	R	2	Time (h)[a]	Yield (%)[b]
a	C_6H_5–	**a**	18	95
b	4-$CH_3C_6H_4$–	**b**	14	90
c	4-$CH_3OC_6H_4$–	**c**	8	90
d	3-$CH_3OC_6H_4$–	**d**	13	87
e	2-$CH_3OC_6H_4$–	**e**	7.15	92
f	4-ClC_6H_4–	**f**	9.5	90
g	3-ClC_6H_4–	**g**	13	85
h	2-ClC_6H_4–	**h**	8	95
i	4-BrC_6H_4–	**i**	13	83
j	2-BrC_6H_4–	**j**	10	90
k	4-$NO_2C_6H_4$–	**k**	12	90
l	3-$NO_2C_6H_4$–	**l**	13.5	85

[a] The times are given after total disappearance of DHPMs (100% conversion according to TLC observation).
[b] Isolated yields.

Table 2
Comparison of the UV-absorption [λ_{max} (nm)] peaks of **1a**–**1l** with those of **2a**–**2l** in acetonitrile solution.

1	λ_{max} (log ε)	2	λ_{max} (log ε)
a	290.5 (4.10)	**a**	307.5 (2.31), 249 (2.52)
b	288.8 (3.80), 241.4 (3.42)	**b**	320 (3.48, sh), 259.5 (3.70)
c	286.4 (3.82)	**c**	296.5 (4.06), 255 (4.06)
d	284.4 (3.88), 239.6 (3.43)	**d**	303.5 (3.75), 250 (3.88)
e	283.6 (4.42), 240.2 (3.90)	**e**	303 (4.15), 258 (4.15)
f	290.6 (4.04), 240 (3.77)	**f**	313 (3.35), 252 (3.56)
g	291.4 (3.08), 239.8 (2.68)	**g**	320 (sh, 3.99), 304 (4.03), 259 (4.18)
h	291 (3.99), 240.2 (3.62)	**h**	305 (3.34), 259 (3.45)
i	290.8 (4.04), 240.2 (3.85)	**i**	322 (sh, 2.36), 304 (sh, 3.48), 252 (3.76)
j	292.2 (3.98), 239.8 (3.70)	**j**	301.5 (3.89), 264 (3.86)
k	279.2 (4.07)	**k**	330 (sh, 3.71), 302 (sh, 3.86), 262.0 (4.07)
l	282.6 (3.98)	**l**	305.0 (3.57), 259.0 (3.85)

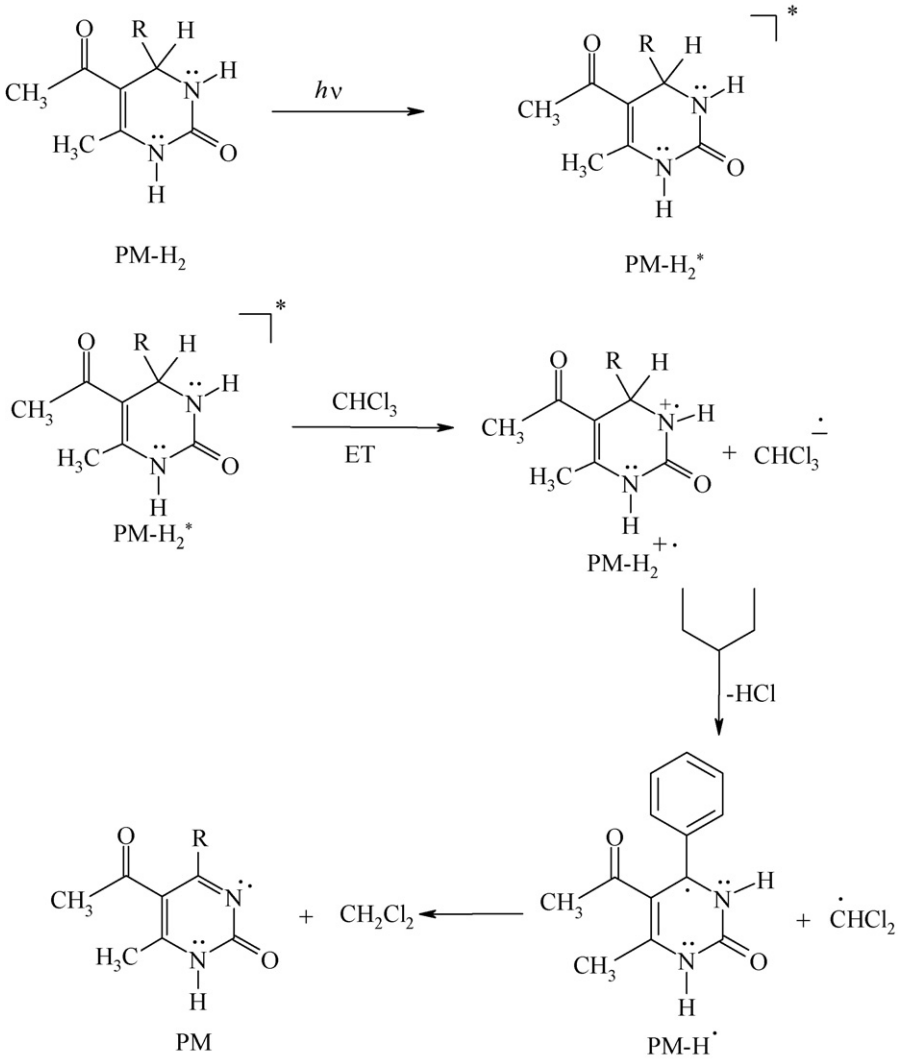
Table 3
Comparison of the IR spectra (ν/cm^{-1}) of **1a**–**1l** with those of **2a**–**2l**.

1	CH_3CO	2-CO	C=C	2	CH_3CO	2-CO	C=C
a	1700	1670	1600	**a**	1700	1670	1590
b	1640	1590	1505	**b**	1695	1590	1510
c	1650	1580	1430	**c**	1670	1680	1425
d	1670	1590	1425	**d**	1675	1595	1425
e	1670	1580	1430	**e**	1690	1590	1550
f	1690	1615	1420	**f**	1650	1580	1420
g	1700	1615	1525	**g**	1650	1580	1430
h	1690	1615	1420	**h**	1700	1620	1430
i	1650	1580	1420	**i**	1670	1620	1420
j	1700	1620	1420	**j**	1700	1615	1420
k	1650	1580	1520	**k**	1665	1600	1505
l	1650	1585	1420	**l**	1675	1590	1520

Analysis of the ^{1}H NMR spectra of the products shows a shift of the 1-NH line to lower fields, lack of 3-NH and 4-H lines due to being eliminated upon oxidation, and a shift of the 6-CH_3 resonance to higher fields as compared to those of the starting materials

Table 4
Structurally relevant ^{1}H NMR chemical shifts (δ values) of **1a**–**1l** compounds in comparison with those of **2a**–**2l**.

1	6-CH_3	1-NH	3-NH	4-H	Ref.	2	6-CH_3	1-NH
a	2.10	7.81	9.16	5.26	This work	**a**	1.84	12.33
b	2.07	7.76	9.13	5.20	–	**b**	1.85	12.26
c	2.06	7.80	9.16	5.20	[19]	**c**	1.87	12.18
d	2.07	7.80	9.11	5.22	[20]	**d**	1.85	
e	2.00	7.33	9.11	5.56	This work	**e**	1.87	12.12
f	2.10	7.80	9.20	5.20	[21]	**f**	1.90	12. 21
g	2.15	7.87	9.28	5.27	This work	**g**	1.90	9.27
h	2.05	7.72	9.27	5.66	–	**h**	1.90	12.26
i	2.12	7.88	9.23	5.23	–	**i**	1.91	12.30
j	2.04	7.69	9.28	5.62	–	**j**	1.85	12.36
k	2.18	7.98	9.34	5.39	[19]	**k**	1.95	12.48
l	2.19	7.99	9.34	5.45	This work	**l**	1.97	12.48

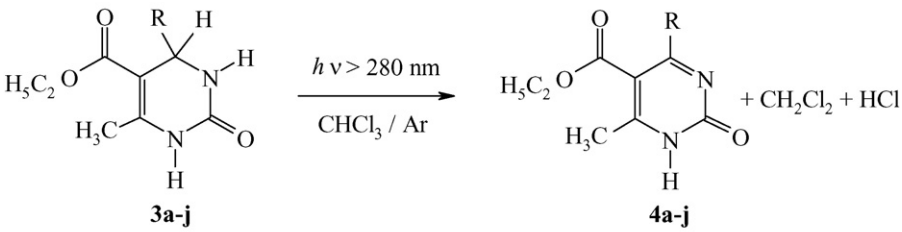


Scheme 2.

(Table 4). No significant changes have been observed for the protons of the acetyl group.

It can be seen from the data presented in Table 1 that the nature of the additional substituent on the phenyl ring located on C-4 position influences the rate of photo-oxidation of the 3,4-dihydropyrimidinone ring. As is expected, the efficient electron-donating substituents such as methoxy group or chlorine atom in 2- and 4-positions on the phenyl ring, as in **1e**, **1c**, **1h** and **1f**, decrease the time of reaction. This is due to the result of the dominant resonance effects of the methoxy group and chlorine atom over their inductive effects. On the contrary, the electron-withdrawing character of the nitro group (affecting as both the inductive and the resonance effects) in 4- and 3-positions (**1k**, **1l**) and the inductive effect of the methoxy group and chlorine atom in 3-position, i.e. the "wrong" position (**1d**, **1g**) increases the time of reaction.

According to the results summarized in Table 1 and the results obtained from our earlier study [9], our proposed mechanism is



R = **a**: C_6H_5, **b**: 4-$CH_3C_6H_4$, **c**: 4-$CH_3OC_6H_4$, **d**: 3-$CH_3OC_6H_4$, **e**:2-$CH_3OC_6H_4$

f: 3-ClC_6H_4, **g**: 2-ClC_6H_4, **h**: 2-BrC_6H_4, **i**: 3-$NO_2C_6H_4$, **j**: $PhCH_2CH_2$

Scheme 3.

Table 5
Photo-oxidation of 5-carboethoxy-3,4-dihydropyrimidin-2(*1H*)-ones (**3a–3j**) in $CHCl_3$ under argon atmosphere.

3	R	4	Time (h)[a]	Yield (%)[b]
a	C_6H_5–	**a**	26	93
b	4-$CH_3C_6H_4$–	**b**	7.5	95
c	4-$CH_3OC_6H_4$–	**c**	9.15	94
d	3-$CH_3OC_6H_4$–	**d**	12.5	92
e	2-$CH_3OC_6H_4$–	**e**	11.5	96
f	3-ClC_6H_4–	**f**	20	92
g	2-ClC_6H_4–	**g**	13.5	92
h	2-BrC_6H_4–	**h**	16	96
i	4-$NO_2C_6H_4$–	**i**	28.45	95
j	$PhCH_2CH_2$–	**j**	20.5	92

[a] The times are given after total disappearance of **3a–3j** (100% conversion according to TLC observation).
[b] Isolated yields after recrystallization.

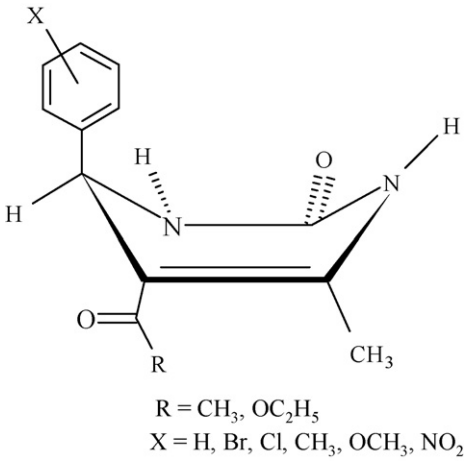


Fig. 1. Boat conformation of dihydropyrimidinone ring showing the *pseudoaxial* orientation of the C-4 aryl group.

confirmed, which is a *light-induced electron-transfer reaction* for the dehydrogenation of dihydropyrimidin-2(*1H*)-ones by irradiation in chloroform solution (Scheme 2). Since, the reaction is not occurred in the absence of light ($\lambda \geq 280$ nm), a comparison of the UV-absorption spectra of dihydropyrimidinones (**1a–1l**) and chloroform (solvent) indicate that only these compounds are selectively excited. Therefore, UV irradiation of dihydropyrimidinone (PM-H_2) leads to the generation of their excited state (PM-H_2^*), which donates an electron to chloroform to form PM-$H_2^{\bullet+}$ and $CHCl_3^{\bullet-}$ species. Elimination of HCl from both intermediates leads to the formation of a radical pair, namely the hydropyrimidinoyl (PM-H$^\bullet$), and the dichloromethyl ($^\bullet CHCl_2$) radicals. The final step of the reaction is the hydrogen abstraction by $^\bullet CHCl_2$ radical from hydropyrimidinoyl radical (PM-H$^\bullet$), which leads to the formation of the pyrimidinone compound (PM) and dichloromethane. This proposed mechanism is supported by the formation of dichloromethane during the reaction, which has been confirmed by GC-analysis of the reaction mixture and the acidity of the solution after irradiation. The proposed mechanism in the present work is also supported by a comparison of the oxidation potential of DHPMs considered in this study with the oxidation potential of $CHCl_3$. Electrochemical reduction of chloroform in acetonitrile has been studied [12]. The reported reduction potential at various metal electrodes in water–acetonitrile mixture *vs.* Fe/Fe^+ is between −2.58 and −2.88 V. We have measured the oxidation potential for some compounds considered in our study in acetonitrile *vs.* Fe/Fe^+. The obtained values **1a**, E_{ox} = 1.668 V; **1c**, E_{ox} = 1.665 V; **1h**, E_{ox} = 1.456 V and **1k**, E_{ox} = 1.660 V. Under our experimental condition for cyclic voltammetric studies, we did not observe any peak between 0 and 2 V for the oxidation of chloroform. This indicate that chloroform is not able to reduce the DHPMs. Other studies have also supported the electron-transfer induced mechanism by photo-oxidation of symmetrical 1,4-dihydropyridines in CCl_4 [13] and $CBrCl_3$ solvents [14,15], unsymmetrical 1,4-dihydropyridines [6] and 3,4-dihydropyrimidin-2(*1H*)-ones in $CHCl_3$ solvent [9].

A comparison of the rate of photo-oxidation of 5-carboethoxy-3,4-dihydropyrimidin-2(*1H*)-ones (**3a–3j**) (Scheme 3 and Table 5) [9] with those of 5-acetyl-3,4-dihydropyrimidin-2(*1H*)-ones (**1a–1l**) (Table 1) obtained in the present study explains that the reaction is faster in almost all the corresponding acetyl derivatives **1a–1l**.

Computational study on the geometries of some dihydropyrimidinones carried out at the B3LYP/6-31++G** level of theory indicates that the six-membered heterocyclic ring adopt a boat conformation, flatted at N1 towards an envelope conformation, with a *pseudoaxial* orientation of the C4-substituent, i.e. in all **1a–1l** the 4-substitution adopts the *up* orientation with respect to the heterocyclic ring boat plane (Figs. 1 and 2). This orientation corresponds to the antagonist activity of these compounds. The same structural trends had already been observed for the 1,4-dihydropyridines [16]. Therefore, similar activities are expected for dihydropyrmidinones and 1,4-dihydropyridines.

The natural bond order (NBO) atomic charges [17,18] for the N1, H1, N3, H3 atoms of 5-acetyl-3,4-dihydropyrimidin-2(*1H*)-ones (**1a–1l**) and 5-carboethoxy-3,4-dihydropyrimidin-2(*1H*)-ones (**3a–3j**) show that the electron density on N3 is greater than that on N1 in both series of compounds (Table 6). These data support our suggestion that N3 atom in the excited DHPM definitely donates an electron to $CHCl_3$ under the formation of PM-$H_2^{\bullet+}$ and $CHCl_3^{\bullet-}$ species.

The results of oxidation of various 5-acetyl-3,4-dihydropyrimidin-2(*1H*)-ones (**1a–1l**) and 5-carboethoxy-3,4-dihydropyrimidin-2(*1H*)-ones (**3a–3j**) by potassium peroxydisulfate (PPS)

Table 6
NBO atomic charges calculated for 5-acetyl-3,4-dihydropyrimidin-2(*1H*)-ones (**1a–1l**) and 5-carboethoxy-3,4-dihydropyrimidin-2(*1H*)-ones (**3a–3j**) using the B3LYP/6-31++G(p,d) method.

1	R	N1	N3	H5	3	R	N1	N3	H5
a	C_6H_5–	−0.655	−0.663	0.281	**a**	C_6H_5–	−0.654	−0.663	0.274
b	4-$CH_3C_6H_4$–	−0.656	−0.663	0.280	**b**	4-$CH_3C_6H_4$–	−0.655	−0.665	0.274
c	4-$CH_3OC_6H_4$–	−0.656	−0.663	0.278	**c**	4-$CH_3OC_6H_4$–	−0.250	−0.382	0.232
d	3-$CH_3OC_6H_4$–	−0.198	−0.380	0.255	**d**	3-$CH_3OC_6H_4$–	−0.225	−0.396	0.238
e	2-$CH_3OC_6H_4$–	−0.643	−0.663	0.274	**e**	2-$CH_3OC_6H_4$–	−0.653	−0.672	0.293
f	4-ClC_6H_4–	−0.655	−0.664	0.283	**f**	3-ClC_6H_4–	−0.655	−0.665	0.283
g	3-ClC_6H_4–	−0.655	−0.665	0.283	**g**	2-ClC_6H_4–	−0.322	−0.407	0.234
h	2-ClC_6H_4–	−0.285	−0.425	0.240	**h**	2-BrC_6H_4–	−0.323	−0.450	0.237
i	4-BrC_6H_4–	−0.655	−0.664	0.283	**j**	4-$NO_2C_6H_4$–	−0.273	−0.347	0.248
j	2-BrC_6H_4–	−0.647	−0.662	0.267					
k	4-$NO_2C_6H_4$–	−0.655	−0.666	0.286					
l	3-$NO_2C_6H_4$–	−0.655	−0.666	0278					

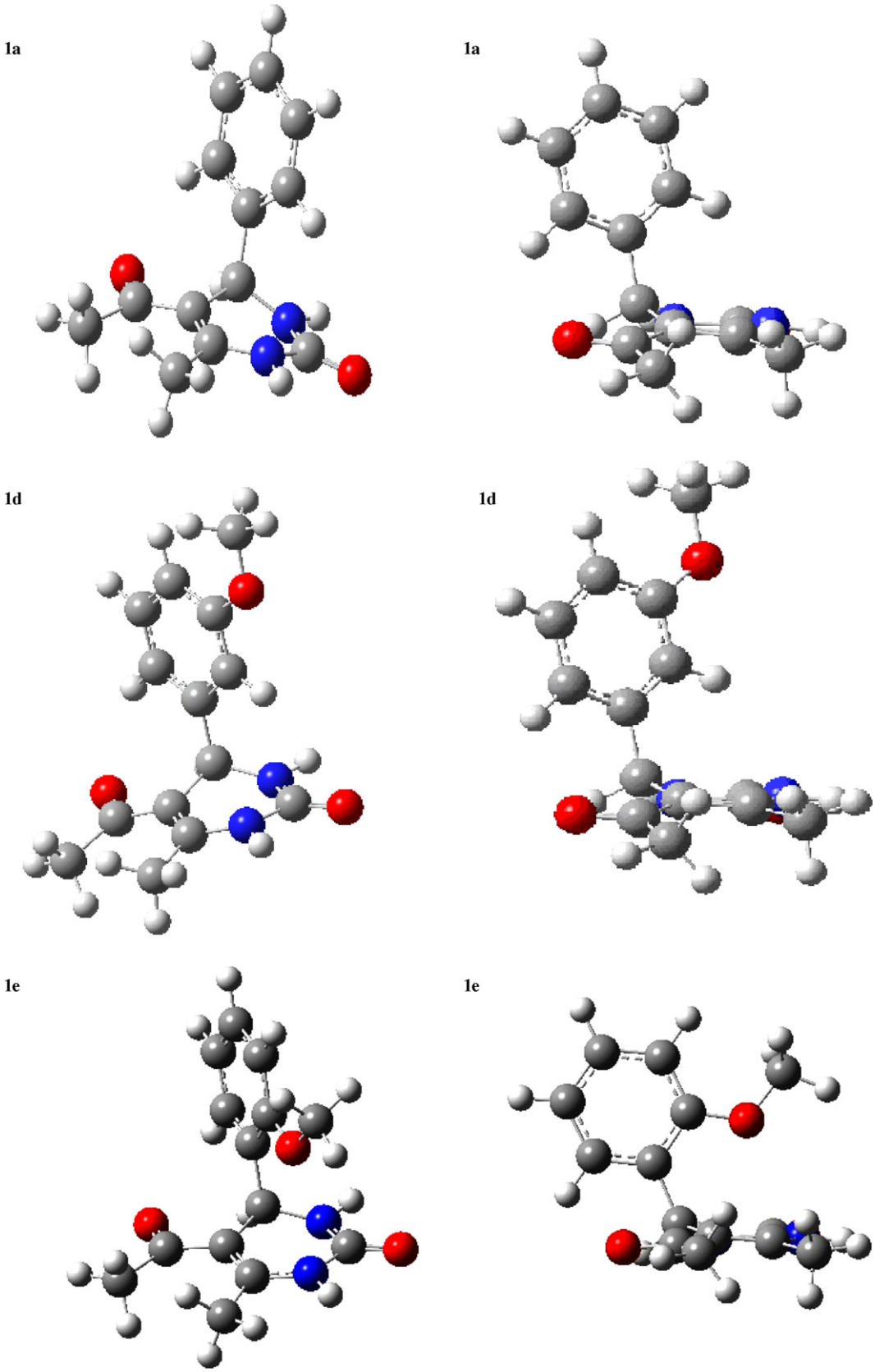


Fig. 2. Front side presentation (left) and boat conformation (right) of **1a**, **1d** and **1e**.

under microwave irradiation in water indicate that the ester derivatives (**3a**–**3j**) are oxidized faster than the corresponding acetyl derivatives (**1a**–**1l**) [11]. According to the proposed mechanism (presented as supplementary materials), thermal cleavage of the weakest O–O bond in PPS leads to the formation of potassium sulfate radicals, which abstract hydrogen from water to form hydroxyl radicals. Removal of 4-H by the hydroxyl radical in the rate determining step, followed by the elimination of the second hydrogen (3N–H), completes the reaction towards the formation of pyrimidinones. The results obtained from *ab initio* calculations at the B3LYP/6-31++G** level of theory for the optimized structures of these compounds can partially explain the observed comparative behavior of the two classes of compounds in oxidation reaction by PPS. Based on the results of these computations: (i) the dihydropyrimidinone ring adopts a boat conformation, flattened at N1 towards an envelope conformation, with a *pseudoaxial* orientation of the C4-substituent, (ii) the extent of deviation from planarity around C-4 depends on the orientation of the phenyl group attached to this atom, especially on the position of an additional substituent at the phenyl ring, and (iii) the dihedral angle of the ester carbonyl group or the acetyl moiety with respect to the $C_5{=}C_6$ bond depends on the type of the substituent on the C-4 atom. All these points explain that the electronic and steric factors influence the removal of 4-H by a hydroxyl radical in the rate determining step. The interesting result in the present work is the comparative behavior of the two classes of compounds after UV-light excitation. A comparison of the reaction times of photo-oxidation of corresponding 5-carboethoxy derivatives and 5-acetyl derivatives (with the same 4-aryl substituent) indicates that almost all 5-acetyl derivatives are photo-oxidized faster, which is in contrast to the results obtained by MW-reaction. These opposite trends explicitly show that the mechanisms for the thermal and photochemical reactions are totally different: "Free radical oxidation by *in situ* formed hydroxyl radical in the thermal reaction" *vs.* "light-induced electron-transfer oxidation". The faster photo-oxidation reaction observed for the acetyl compounds as compared to the photo-oxidation reaction of the corresponding ester compounds can be attributed to better light absorption of **1a**–**1l** compared to **3a**–**3j,** especially above 280 nm by comparison of their UV spectra (Table 2 and the supplementary data). Since the presence of the more excited DHPMs (PM^*-H_2 in Scheme 2) leads to an increase in the electron transfer to $CHCl_3$ under formation of $PM\text{-}H_2^{\bullet+}$ and $CHCl_3^{\bullet-}$ species, an increase of the rate of photo-oxidation of **1a**–**1l** is therefore expected.

3. Conclusion

In conclusion, this work describes electron-transfer induced photo-oxidation of various 5-acetyl-3,4-dihydropyrimidin-2(*1H*)-ones to their corresponding pyrimidinones in chloroform solution. The atmosphere of the reaction mixture (being oxygen or argon) plays an important role in the rate of reaction and also in the number, types, and mole ratios of the products. The nature of 4-substituent is a determining factor in the completion time of the reaction.

4. Experimental

The acetyl derivatives **1a**–**1l** were prepared by adoption of the known procedure [19]. Melting points were determined on a Stuart Scientific SMP2 apparatus and are uncorrected. IR spectra were recorded using KBr discs on a Shimadzu IR-435. ^{1}H NMR spectra were obtained with a Bruker 300 MHz instrument. They are reported as follows: chemical shifts [multiplicity, coupling constants *J* (Hz), number of protons, and assignment]. Mass spectra were obtained on Platform II Mass Spectrometer from Micromass; EI mode at 70 eV. UV spectra (in CH_3CN) were taken with Shimadzu UV-160 spectrometer.The cyclic voltammetric experiments were performed on Potentiostat Galvanostat (SAMA 500). The electrochemical studies were conducted by using acetonitrile solution containing tertbutylammonium perchlorate. A three electrode system with a silver electrode, a platinum foil and a platinum disk as the reference, counter and working electrodes, respectively, was used.

A solution of 3,4-dihydropyrimidinones (0.03 mmol) in 10 ml of distilled chloroform (c = 3 mM) was irradiated with a 400 W high pressure mercury lamp in a Pyrex tube while bubbling argon through the solution at ambient temperature. The reaction was followed by thin layer chromatography (TLC) until total disappearance of dihydropyrimidinones. The solvent was evaporated at room temperature under reduced pressure and the products were recrystallized from *n*-hexane/ethyl acetate solvent mixture. The photoproducts **2a**–**2l** were identified with the melting points, IR, ^{1}H NMR, MS and the UV spectra which are reported below.

4.1. 5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (*1a*)

White solid. Mp: 228–230 °C (Lit. [20] 233–236 °C). IR: ν 1700, 1670, 1600 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 290.5 nm (4.10). ^{1}H NMR (300 MHz, DMSO-d6): δ 2.10 (s, 3H, CH_3), 2.28 (s, 3H, CH_3CO), 5.26 (d, J = 3.32 Hz, 1H, 4-H), 7.29 (m_c, 5H, H-aromatic), 7.81 (s, 1H, 1-NH), 9.16 (s, 1H, 3-NH).

4.2. 5-Acetyl-6-methyl-4-(4′-methylphenyl)-3,4-dihydropyrimidin-2(1H)-one (*1b*)

White solid. Mp: 234–236 °C. IR: ν 1640, 1590, 1505 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 241.4 nm (3.41) and 288.8 (3.80). ^{1}H NMR (300 MHz, DMSO-d6): δ 2.07 (s, 3H, CH_3), 2.25 (s, 3H, CH_3CO), 2.27 (s, 3H, 4′-CH_3), 5.20 (s, 1H, 4-H), 7.12 (br, s, 4H, H-aromatic), 7.76 (s, 1H, 1-NH), 9.13 (s, 1H, 3-NH). EI-MS: m/z (%): 244 (M^+, 14), 243 (M^+-H, 25), 229 (M^+-CH_3, 49), 201 (M^+-CH_3CO, 32), 153 ($M^+-C_7H_7$, 100), 91 ($Ph-CH_2^+$, 30).

4.3. 5-Acetyl-4-(4′-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (*1c*)

White solid. Mp: 182–184 °C (Lit. [20] 168–170 °C). IR: ν 1650, 1580, 1430 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 286.4 nm (3.82).

4.4. 5-Acetyl-4-(3′-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (*1d*)

White solid. Mp: 226–228 °C (Lit. [21] 228–230 °C). IR: ν 1670, 1590, 1425 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 239.6 nm (3.43) and 284.4 (3.88).

4.5. 5-Acetyl-4-(2′-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (*1e*)

White solid. Mp: 250–252 °C. IR: ν 1670, 1580, 1430 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 240.2 nm (3.90) and 283.6 (4.42). ^{1}H NMR (300 MHz, DMSO-d6): δ 2.00 (s, 3H, CH_3), 2.28 (s, 3H, CH_3CO), 3.81 (s, 3H, CH_3O), 5.56 (s, 1H, 4-H), 7.06 (m_c, 4H, H-aromatic), 7.33 (s, 1H, 1-NH), 9.11 (s, 1H, 3-NH). EI-MS: m/z (%): 260 (s, M^+, 61), 259 (M^+-H, 80), 245 (M^+-CH_3, 51), 229 (M^+-CH_3O, 92), 217 (M^+-CH_3CO, 85), 153 ($M^+-2\text{-}CH_3COC_6H_4$, 100).

*4.6. 5-Acetyl-4-(4′-chlorophenyl)–6-methyl-3,4-dihydropyrimidin-2(1H)-one (**1f**)*

White solid. Mp: 249–251 °C (Lit. [22] 223–225 °C). IR: ν 1690, 1615, 1420 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 240.0 nm (3.77) and 290.6 (4.04).

*4.7. 5-Acetyl-4-(3′-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**1g**)*

White solid. Mp: 285–287 °C. IR: ν 1700, 1615, 1525 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 291.4 nm (3.08), 239.8 (2.68). ^1H NMR (300 MHz, DMSO-d6): δ 2.15 (s, 3H, CH_3), 2.30 (s, 3H, CH_3CO), 5.27 (d, J = 3.25 Hz, 1H, 4-H), 7.27 (m_c, 4H, H-aromatic), 7.87 (s, 1H, 1-NH), 9.28 (s, 1H, 3-NH). EI-MS: m/z (%): 266 ($M^{+37}Cl$, 49), 265 ($M^{+37}Cl$–H, 64), 264 ($M^{+35}Cl$, 32), 263 ($M^{+35}Cl$–H, 79), 249 ($M^{+35}Cl$–CH_3, 80), 229 ($M^{+35}Cl$–^{35}Cl, 42), 223 ($M^{+37}Cl$–CH_3CO, 28), 221 ($M^{+35}Cl$–CH_3CO, 74), 170 (2-$^{37}ClC_6H_4$–CH=NH^+, 3), 169 (2-$^{37}ClC_6H_4$–C=NH^+, 8), 168 (2-$^{35}ClC_6H_4$–CH=NH^+, 9), 167 (2-$^{35}ClC_6H_4$–C=NH^+, 9), 153 (M^+–2-ClC_6H_4, 100).

*4.8. 5-Acetyl-4-(2′-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**1h**)*

White solid. Mp: 262–264 °C. IR: ν 1690, 1615, 1420 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 291 nm (3.99), 240.2 (3.62). ^1H NMR (300 MHz, DMSO-d6): δ 2.05 (s, 3H, CH_3), 2.33 (s, 3H, CH_3CO), 5.66 (s, 1H, 4-H), 7.36 (m_c, 4H, H-aromatic), 7.72 (s, 1H, 1-NH), 9.27 (s, 1H, 3-NH). EI-MS: m/z (%): 266 ($M^{+37}Cl$, 4), 265 ($M^{+37}Cl$–H, 7), 264 ($M^{+35}Cl$, 10), 263 ($M^{+35}Cl$–H, 16), 249 ($M^{+35}Cl$–CH_3, 10), 231 ($M^{+37}Cl$–^{37}Cl, 6), 229 ($M^{+35}Cl$–^{35}Cl, 94), 223 ($M^{+37}Cl$–CH_3CO, 6), 221 ($M^{+35}Cl$–CH_3CO, 72), 170 (2-$^{37}ClC_6H_4$–CH=NH^+, 14), 169 (2-$^{37}ClC_6H_4$–C=NH^+, 18), 168 (2-$^{35}ClC_6H_4$–CH=NH^+, 17), 167 (2-$^{35}ClC_6H_4$–C=NH^+, 8), 153 (M^+–2-ClC_6H_4, 100).

*4.9. 5-Acetyl-4-(4′-bromophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**1i**)*

White solid. Mp: 232–233 °C. IR: ν 1650, 1580, 1420 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 290.8 nm (4.04), 240.2 (3.85). ^1H NMR (300 MHz, DMSO-d6): δ 2.12 (s, 3H, CH_3), 2.28 (s, 3H, CH_3CO), 5.23 (s, 1H, 4-H), 7.18 (d, J = 6.90 Hz, 2′- and 6′-H), 7.51 (d, J = 6.77 Hz, 3′- and 5′-H), 7.88 (s, 1H, 1-NH), 9.23 (s, 1H, 3-NH).

*4.10. 5-Acetyl-4-(2′-bromophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**1j**)*

White solid. Mp: 254–257 °C. IR: ν 1700, 1620, 1420 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 292.2 nm (3.98), 239.8 (3.70). ^1H NMR (300 MHz, DMSO-d6): δ 2.04 (s, 3H, CH_3), 2.33 (s, 3H, CH_3CO), 5.62 (d, J = 2.85 Hz, 1H, 4-H), 7.39 (m_c, 4H, H-aromatic), 7.69 (brd s, 1H, 1-NH), 9.28 (s, 1H, 3-NH). EI-MS: m/z (%): 267 ($M^{+81}Br$–CH_3CO, 10), 265 ($M^{+79}Br$–CH_3CO, 11), 231 ($M^{+81}Br$–^{81}Br, 2), 229 ($M^{+79}Br$–^{79}Br, 97), 214 ($M^{+79}Br$–^{79}Br, –CH_3, 13) 168 (2-BrC_6H_4–CH=NH^+, 5), 153 (M^+–2-BrC_6H_4, 100).

*4.11. 5-Acetyl-6-methyl-4-(4′-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (**1k**)*

Yellow solid. Mp: 229–230 °C (dec.) (Lit. [20] 230 °C (dec.). IR: ν 1650, 1580, 1520 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 279.2 nm (4.07).

*4.12. 5-Acetyl-6-methyl-4-(3′-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (**1l**)*

Yellow solid. Mp: 286–288 °C. IR: ν 1650, 1585, 1420 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 282.6 nm (3.98). ^1H NMR (300 MHz, DMSO-d6): δ 2.19 (s, 3H, CH_3), 2.32 (s, 3H, CH_3CO), 5.45 (d, J = 3.24 Hz, 1H, 4-H), 7.99 (brd s, 1H, 1-NH), 8.11 (m_c, 4H, H-aromatic), 9.34 (s, 1H, 3-NH). EI-MS: m/z (%): 259 (M^+–OH, 5), 258 (M^+–H_2O, 32), 232 (M^+–CH_3CO, 7), 228 (M^+–HNO_2, 27), 153 (3-$O_2NC_6H_4$–CH=NH^+, 100).

*4.13. 5-Acetyl-6-methyl-4-phenylpyrimidin-2(1H)-one (**2a**)*

Pale yellow solid. Mp: 162–163 °C. IR: ν 1700, 1670, 1590 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 307.5 nm (2.31), 249 (2.52). ^1H NMR (300 MHz, DMSO-d6): δ 1.84 (s, 3H, 6-CH_3), 2.30 (s, 3H, CH_3CO), 7.52 (m_c, 5H, H-aromatic), 12.33 (brd s, 1H, NH). ^{13}C NMR (75.48 MHz, DMSO-d6): δ = 18.82, 32.37, 118.33, 128.63, 129.25, 131.32, 155.89, 201.05. EI-MS: m/z (%): 228 (M^+, 42), 227 (M^+–H, 49), 213 (M^+–CH_3, 100), 185 (M^+–CH_3CO, 11), 104 (C_6H_5–C=NH^+, 61), 103 (C_6H_5–CN^+, 7), 77 ($C_6H_5^+$, 44).

*4.14. 5-Acetyl-6-methyl-4-(4'-methylphenyl)pyrimidine-2(1H)-one (**2b**)*

Pale yellow solid. Mp: 219–221 °C. IR: ν 1695, 1590, 1510 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 296.5 nm (4.06), 255 (4.06). ^1H NMR (300 MHz, DMSO-d6): δ 1.85 (s, 3H, CH_3), 2.29 (s, 3H, CH_3CO), 2.50 (s, 3H, 4′-CH_3), 7.31 (d, J = 7.83 Hz, 2H, 2-H′ and 6-H′), 7.37 (d, J = 8.52 Hz, 2H, 3-H′ and 5-H′), 12.26 (brd s, 1H, NH). ^{13}C NMR (75.48 MHz, DMSO-d6): δ = 19.05, 21.41, 32.42, 118.18, 128.67, 129.80, 135.06, 141.33, 156.26, 161.12, 201.29. EI-MS: m/z (%): 242 (M^+, 46), 241 (M^+–H, 32), 227 (M^+–CH_3, 100), 199 (M^+–CH_3CO, 11), 117 (4-$CH_3C_6H_4$–C=NH^+, 4), 116 (4-$CH_3C_6H_4$–CN^+, 8), 91 (–C_6H_4–CH_3, 37).

*4.15. 5-Acetyl-4-(4′-methoxyphenyl)-6-methylpyrimidin-2(1H)-one (**2c**)*

Pale yellow solid. Mp: 189–191 °C. IR: ν 1670, 1680, 1425 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 296.5 nm (4.06), 255 (4.06). ^1H NMR (300 MHz, DMSO-d6): δ 1.87 (s, 3H, 6-CH_3), 2.28 (s, 3H, CH_3CO), 3.82 (s, 3H, CH_3O), 7.06 (d, J = 8.55 Hz, 2H, 2-H′ and 6-H′), 7.45 (d, J = 8.52 Hz, 2H, 3-H′ and 5-H′), 12.18 (brd s, 1H, NH). ^{13}C NMR (75.48 MHz, DMSO-d6): δ = 18.83, 32.34, 55.84, 114.67, 117.91, 130.53, 155.97, 161.99, 155.97, 161.99, 201.35. EI-MS: m/z (%): 258 (M^+, 84), 257 (M^+–H, 40), 243 (M^+–CH_3, 100,), 227 (M^+–CH_3O, 10), 215 (M^+–CH_3CO, 11), 200 (M^+–CH_3CO, –CH_3, 18), 134 (4-$CH_3OC_6H_4$–CH=NH^+, 71), 133 (4-$CH_3OC_6H_4$–C=NH^+, 4), 132 (4-$CH_3OC_6H_4$–CN^+, 3).

*4.16. 5-Acetyl-4-(3′-methoxyphenyl)-6-methylpyrimidin-2(1H)-one (**2d**)*

Pale yellow solid. Mp: 163–164 °C. IR: ν 1675, 1595, 1425 cm^{-1}. UV (CH_3CN): λ_{max} ($\log\varepsilon$) 303.5 nm (3.75), 250 (3.88). ^1H NMR (300 MHz, DMSO-d6): δ 1.85 (s, 3H, 6-CH_3), 2.28 (s, 3H, CH_3CO), 3.80 (s, 3H, 4′-CH_3O), 6.98 (d, J = 7.33 Hz, 2H, 4′-H), 7.12 (d, J = 8.20 Hz, 2H, 6′-H), 7.03 (s, 1H, 2′-H), 7.41 (t, J = 6.67 Hz, J = 7.55 Hz, 1H). ^{13}C-NMR (75.48 MHz, DMSO-d6): δ = 30.87, 55.60, 111.79, 119.23, 121.19, 130.54, 132.43, 155.94, 156.40, 198.86. EI-MS: m/z (%): 258 (M^+, 3), 257 (M^+–H, 2), 243 (M^+–CH_3, 2), 200 (M^+–CH_3CO, –CH_3, 2), 134 (4-$CH_3OC_6H_4$–CH=NH^+, 14), 133 (4-$CH_3OC_6H_4$–C=NH^+, 7), 132 (4-$CH_3OC_6H_4$–CN^+, 8), 77 (100).

*4.17. 5-Acetyl-4-(2′-methoxyphenyl)-6-methylpyrimidin-2(1H)-one (**2e**)*

Pale yellow solid. Mp: 166–167 °C. IR: ν 1960, 1590, 1550 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 303 nm (4.15), 258 (4.15). ^1H NMR (300 MHz, DMSO-d6): δ 1.87 (s, 3H, CH_3), 2.32 (s, 3H, CH_3CO), 3.70 (s, 3H, CH_3O), 7.24 (m_c, 4H, H-aromatic), 12.12 (brd s, 1H, NH). ^{13}C NMR (75.48 MHz, DMSO-d6): δ = 30.85, 55.58, 111.78, 119.24, 121.18, 130.54, 132.44, 155.96, 198.82. EI-MS: *m*/*z* (%): 258 (M^+, 6), 257 (M^+-H, 4), 243 (M^+-CH_3, 13), 227 (M^+-CH_3O, 100), 215 (M^+-CH_3CO, 22), 134 (2-$CH_3OC_6H_4$–CH=NH^+, 38), 133 (2-$CH_3OC_6H_4$–C=NH^+, 10), 132 (2-$CH_3OC_6H_4$–CN^+, 6).

*4.18. 5-Acetyl-4-(4′-chlorophenyl)-6-methylpyrimidin-2(1H)-one (**2f**)*

Pale yellow solid. Mp: 235–237 °C. IR: ν 1650, 1580, 1420 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 313 nm (3.35), 252 (3.56). ^1H NMR (300 MHz, DMSO-d6): δ 1.90 (s, 3H, CH_3), 2.30 (s, 3H, CH_3CO), 7.49 (d, *J* 8.27 Hz, 2H, 3-H′ and 5-H′), 7.58 (d, *J* = 8.21 Hz, 2H, 2-H′ and 6-H′), 12.21 (brd s, 1H, NH).). ^{13}C NMR (75.48 MHz, DMSO-d6): δ = 18.97, 32.53, 118.30, 129.33, 130.51, 136.09, 137.02, 156.35, 161.11, 168.92, 200.99. EI-MS: *m*/*z* (%): 264 ($M^{+37}Cl$, 27), 263 ($M^{+37}Cl-H$, 32), 262 ($M^{+35}Cl$, 78), 261 ($M^{+35}Cl-H$, 59), 249 ($M^{+37}Cl-CH_3$, 69), 247 ($M^{+35}Cl-CH_3$, 99), 227 (M^+-Cl, 17), 221 ($M^{+37}Cl-CH_3CO$, 5), 219 ($M^{+35}Cl-CH_3CO$, 13), 140 (4-$^{37}ClC_6H_4C$=NH^+, 42), 139 (4-$^{37}ClC_6H_4CN^+$, 19), 138 (4-$^{35}ClC_6H_4C$=NH^+, 87), 137 (4-$^{35}ClC_6H_4CN^+$, 12).

*4.19. 5-Acetyl-4-(3′-chlorophenyl)-6-methylpyrimidin-2(1H)-one (**2g**)*

Pale yellow solid. Mp: 196–198 °C. IR: ν 1650, 1580, 1430 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 320 nm (sh, 3.99), 304 (4.03), 259 (4.18). ^1H NMR (300 MHz, DMSO-d6): δ 1.90 (s, 3H, CH_3), 2.30 (s, 3H, CH_3CO), 7.54 (m_c, 4H, H-aromatic), 9.27 (s, 1H, NH). ^{13}C-NMR (75.48 MHz, DMSO-d6): δ = 19.13, 32.55, 118.37, 127.31, 128.32, 130.89, 131.09, 133.93, 140.37, 156.73, 161.39, 168.58, 200.95. EI-MS: *m*/*z* (%): 264 ($M^{+37}Cl$, 21), 263 ($M^{+37}Cl-H$, 23), 262 ($M^{+35}Cl$, 58), 261 ($M^{+35}Cl-H$, 38), 249 ($M^{+37}Cl-CH_3$, 45), 247 ($M^{+35}Cl-CH_3$, 100), 227 (M^+-Cl, 14), 221 ($M^{+37}Cl-CH_3CO$, 5), 219 ($M^{+35}Cl-CH_3CO$, 9), 140 (3-$^{37}ClC_6H_4C$=NH^+, 36), 139 (3-$^{37}ClC_6H_4CN^+$, 18), 138 (3-$^{35}ClC_6H_4C$=NH^+, 78), 137 (3-$^{35}ClC_6H_4CN^+$, 9).

*4.20. 5-Acetyl-4-(2′-chlorophenyl)-6-methylpyrimidin-2(1H)-one (**2h**)*

Pale yellow solid. Mp: 175–176 °C. IR: ν 1700, 1620, 1430 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 305 nm (3.34), 259 (3.45). ^1H NMR (300 MHz, DMSO-d6): δ 1.90 (s, 3H, CH_3), 2.30 (s, 3H, CH_3CO), 7.47 (m_c, 4H, H-aromatic), 12.26 (brd s, 1H, NH). ^{13}C NMR (75.48 MHz, DMSO-d6): δ = 20.23, 31.50, 119.22, 127.88, 130.06, 130.54, 131.00, 131.61, 137.32, 156.67, 163.00, 198.89. EI-MS: *m*/*z* (%): 247 ($M^{+35}Cl-CH_3$, 5), 227 (M^+-Cl, 100), 219 ($M^{+35}Cl-CH_3CO$, 3), 140 (2-$^{37}ClC_6H_4C$=NH^+, 24), 139 (2-$^{37}ClC_6H_4CN^+$, 13) 138 (2-$^{35}ClC_6H_4C$=NH^+, 47), 137 (2-$^{35}ClC_6H_4CN^+$, 8).

*4.21. 5-Acetyl-4-(4′-bromophenyl)-6-methylpyrimidin-2(1H)-one (**2i**)*

Pale yellow solid. Mp: 239–240 °C. IR: ν 1670, 1620, 1420 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 322 nm (sh, 2.36), 304 (sh, 3.48), 252 (3.76). ^1H NMR (300 MHz, DMSO-d6): δ 1.91 (s, 3H, CH_3), 2.30 (s, 3H, CH_3CO), 7.41 (d, *J* = 8.18 Hz, 2H, 3-H′ and 5-H′), 7.72 (d, *J* = 8.12 Hz, 2H, 2-H′ and 6-H′), 12.30 (brd s, 1H, NH). ^{13}C NMR (75.48 MHz, DMSO-d6): δ = 19.02, 32.56, 118.30, 124.88, 130.70, 132.24, 137.40, 156.52, 161.20, 168.92, 201.01. EI-MS: *m*/*z* (%): 308 ($M^{+81}Br$, 38), 307 ($M^{+81}Br-H$, 32), 306 ($M^{+79}Br$, 37), 305 ($M^{+79}Br-H$, 26), 293 ($M^{+81}Br-CH_3$, 81), 291 ($M^{+79}Br-CH_3$, 83), 265 ($M^{+81}Br-CH_3CO$, 6), 263 ($M^{+79}Br-CH_3CO$, 7), 227 (M^+-Br, 24), 185 (4-$^{81}BrC_6H_4CH$=NH^+, 16), 183 (4-$^{79}BrC_6H_4CH$=NH^+, 61), 182 (4-$^{79}BrC_6H_4C$=NH^+, 16), 181 (4-$^{79}BrC_6H_4CN^+$, 45).

*4.22. 5-Acetyl-4-(2′-bromophenyl)-6-methylpyrimidin-2(1H)-one (**2j**)*

Pale yellow solid. Mp: 202–204 °C. IR: ν 1700, 1615, 1420 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 301.5 nm (3.89), 264 (3.86). ^1H NMR (300 MHz, DMSO-d6): δ 1.85 (s, 3H, CH_3), 2.37 (s, 3H, CH_3CO), 7.43 (m_c, 3H, H-aromatic), 7.73 (d, *J* = 7.82 Hz, 1H, 6-H′), 12.36 (brd s, 1H, NH). EI-MS: *m*/*z* (%): 227 (M^+-Br, 100), 185 (2-$^{81}BrC_6H_4CH$=NH^+, 10), 184 (2-$^{81}BrC_6H_4C$=NH^+, 26) 183 (4-$^{79}BrC_6H_4CH$=NH^+, 3), 182 (4-$^{79}BrC_6H_4C$=NH^+, 6).

*4.23. 5-Acetyl-6-methyl-4-(4'-nitrophenyl)pyrimidine-2(1H)-one (**2k**)*

Pale yellow solid. Mp: 265–267 °C. IR: ν 1665, 1600, 1505 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 330 nm (sh, 3.71), 302 (sh, 3.86), 262.0 (4.07). ^1H NMR (300 MHz, DMSO-d6): δ 1.95 (s, 3H, CH_3), 2.35 (s, 3H, CH_3CO), 7.73 (d, *J* = 8.52 Hz, 2H, 2-H′ and 6-H′), 8.33 (d, *J* = 8.49 Hz, 2H, 3-H′ and 5-H′), 9.27 (s, 1H, NH), 12.48 (brd s, 1H, NH). ^{13}C NMR (75.48 MHz, DMSO-d6): δ = 18.83, 124.33, 130.06, 144.44, 148.98. EI-MS: *m*/*z* (%): 273 (M^+, 20), 272 (M^+-H, 13), 258 (M^+-CH_3, 100), 256 (M^+-OH, 25), 226 (M^+-HNO_2, 12).

*4.24. 5-Acetyl-6-methyl-4-(3'-nitrophenyl)pyrimidine-2(1H)-one (**2l**)*

Pale yellow solid. Mp: 256-258 °C. IR: ν 1675, 159, 1520 cm^{-1}. UV (CH_3CN): λ_{max} (log ε) 305.0 nm (3.57), 259.0 (3.85). ^1H NMR (300 MHz, DMSO-d6): δ 1.97 (s, 3H, CH_3), 2.35 (s, 3H, CH_3CO), 7.80 (t, *J* = 8.80 Hz, 1H, 5-H′), 7.88 (d, *J* = 7.49 Hz, 1H, 6-H′), 8.29 (s, 1H, 2-H′), 8.39 (d, *J* = 7.96 Hz, 1H, 4-H′), 12.48 (brd s, 1H, NH). ^{13}C-NMR (75.48 MHz, DMSO-d6): δ = 32.68, 123.37, 125.69, 130.96, 134.92, 148.28. EI-MS: *m*/*z* (%): 273 (M^+, 15), 272 (M^+-H, 8), 258 (M^+-CH_3, 100), 256 (M^+-OH, 30), 226 (M^+-HNO_2, 16).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.10.012.

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