Light-induced Free Radical Oxidation of 2-Oxo-1,2,3,4-tetrahydropyrimidines

Hamid Reza Memarian[a], Leila Hejazi[a], and Asadallah Farhadi[b]

[a] Catalysis Division, Department of Chemistry, Faculty of Science, University of Isfahan, 81746-73441 Isfahan, I. R. Iran
[b] Faculty of Petroleum Engineering, Petroleum University of Technology of Ahwaz, Ahwaz, I. R. Iran

Reprint requests to Prof. Hamid R. Memarian. Fax: +98-311-6689732.
E-mail: memarian@sci.ui.ac.ir

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A variety of 4-substituted 5-acetyl- and 5-carboethoxy-2-oxo-1,2,3,4-tetrahydropyrimidines were oxidized under UV irradiation in the presence or absence of benzoyl peroxide. The nature of the substituents on the 4- and 5-positions of the heterocyclic ring affects the rate of photo-oxidation, and irradiation of these compounds in the presence of benzoyl peroxide decreases the time of reaction drastically. Removal of 4-H by a benzoyloxy radical under formation of a trihydropyrimidinoyl radical intermediate occurs in the rate-determining step. The stability of this benzylic and allylic radical intermediate is affected by the nature and the position of the additional substituent on the phenyl group located at C-4.

Key words: Benzoyl Peroxide, Dihydropyrimidinones, Photo-oxidation, Substituent Effects, Tetrahydropyrimidinones

Introduction

2-Oxo-1,2,3,4-tetrahydropyrimidine derivatives (THPMs), also known as 3,4-dihydropyrimidin-2(1*H*)-ones or Biginelli compounds, have received considerable interest in recent times because of their promising activities, as *e. g.* antihypertensive, antitumor, antibacterial, anti-inflammatory agents, and calcium channel blockers [1 – 6]. Moreover, 3-substituted 3H-pyrimidin-2(1*H*)-ones are pharmacophores present in many biologically active compounds [7]. There are a wide variety of methods to synthesize pyrimidinones [8], but the efficient synthesis of 1,2-dihydropyrimidinones by oxidation of 1,2,3,4-tetrahydropyrimidinones has rarely been explored [9 – 11]. In contrast to Hantzsch-type 1,4-dihydropyridines, whose aromatization to the corresponding pyridines, either thermally [12] or photochemically [13], is typically facile, the dehydrogenation of 1,2,3,4-tetrahydropyrimidinones is known to be non-trivial [9, 11]. Various powerful and mild oxidants such as chloranil, DDQ, $KMnO_4$/clay, MnO_2, PCC, $NaNO_2$/AcOH [9] or $RuCl_3/O_2$ in AcOH [14], $Co(NO_3)_2{\cdot}6H_2O/K_2S_2O_8$ [9], and also dehydrogenating agents such as Pd/C [8], Br_2 [15] and sulfur [16] have been used for this purpose, but none of these reagents is ideal, particularly due to their safety profile, lower yield and difficulty in product isolation.

Benzoyl peroxide (BPO) is known as radical initiator and oxidizing agent in many organic reactions [17 – 19]. This compound is very unstable and degrades to the benzyloxy radical in solution *via* a free radical mechanism by applying heat or UV irradiation [20]. This occurs because of the instability of the O–O bond (bond energy $\sim$ 120 kJ mol^{-1}) [21]. The decomposition rate of BPO is dependent on the nature of the solvent and also the presence of an oxygen atmosphere. It has been shown that decomposition of BPO in propan-2-ol is high among various alcohols and ethers [22], and the presence of oxygen decreases the rate of decomposition [23].

Numerous reports have been published on the application of ultraviolet radiation in the oxidation of organic compounds, but not for photo-oxidation of the title compounds. Recently we have reported the oxidation of various 4-arylsubstituted 5-acetyl- and 5-carboethoxy-2-oxo-1,2,3,4-tetrahydropyrimidines (THPMs) under thermal [24] and sonothermal conditions [25, 26], and microwave irradia-

tion [27] by potassium peroxydisulfate (PPS) in aqueous acetonitrile, and also by exposing them to UV light in chloroform solution [28, 29]. The results obtained by the reaction in the presence of PPS indicate that *in situ* formed hydroxyl radicals are responsible for the removal of the 4-hydrogen in the rate-determining step. Therefore due to steric and electronic effects, the oxidation of 5-carboethoxy derivatives is faster than that of the corresponding 5-acetyl compounds. In contrast to these results, oxidation of 5-acetyl derivatives under UV irradiation is faster than that of the corresponding 5-carboethoxy compounds. This finding is explained by better light absorption of the acetyl derivatives compared to the carboethoxy derivatives. Therefore, according to the proposed electron transfer-induced photo-oxidation in chloroform (electron transfer from excited THPMs to $CHCl_3$), shorter irradiation times are expected for the former compounds.

In continuation of these studies, we were interested to investigate the behavior of these compounds towards the benzoyloxy radical obtained by UV irradiation of BPO to elucidate

1. the effect of the nature of the acetyl group *versus* the carboethoxy group in 5-position on the rate of reaction;

2. the effect of the nature and position of the additional substituent on the phenyl group attached to C-4 of the heterocyclic ring;

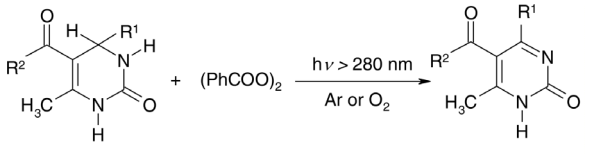
3. the possible competition between the hydrogen abstraction from 6-CH_3 (as allylic hydrogen) and 4-H (as both allylic and benzylic hydrogen); and finally

4. the effect of atmospheric oxygen and argon on the photo-oxidation of tetrahydropyrimidinones.

Results and Discussion

Optimization of the BPO/THPM ratio

The optimization of the BPO/THPM ratio was carried out by irradiation of compounds **1a** and **1i** in acetonitrile as an inert solvent to observe the maximum consumption of these compounds (Scheme 1).



1: $R^2 = OC_2H_5$
2: $R^2 = CH_3$

3: $R^2 = OC_2H_5$
4: $R^2 = CH_3$

Scheme 1. See Table 3 for R^1.

Table 1. The effect of the BPO / THPM ratio on the yield and irradiation time in Ar-saturated CH_3CN.

THPM	R^1	BPO / THPM	Irradiation time (h)	Conversion (%)
1a	C_6H_5	1 : 1	47	40
1a	C_6H_5	2 : 1	33	~ 100
1a	C_6H_5	3 : 1	31	~ 100
1a	C_6H_5	4 : 1	17	~ 100
1i	4-BrC_6H_4	4 : 1	16	100
1i	4-BrC_6H_4	5 : 1	8	100
1i	4-BrC_6H_4	6 : 1	5	100

Table 2. Solvent effect on the photooxidation of 5-acetyl-THPM (**2c**, R^1 = 4-$CH_3OC_6H_4$).

BPO : **2c**	Solvent	Irradiation time (h)	Conversion (%)
4 : 1	CH_3CN	4	100
4 : 1	propan-2-ol	4	60

The results presented in Table 1 indicated that by increasing the amount of BPO, as expected, the reaction time was shortened. Based on the light absorption by BPO and also THPMs under experimental conditions ($\lambda \geq 280$ nm), and a comparison of the molar extinction coefficients of THPMs and BPO at 310 nm (intensive emission line of mercury vapor), and also by avoiding the saturation of the reaction medium by BPO as a radical precursor, it was found that selective excitation of BPO was achieved by taking a ratio of 4 : 1 for BPO/THPMs. Since the light absorption by THPMs cannot be totally excluded even in the presence of four equivalents of BPO, photoreactions were carried out simultaneously in the presence or the absence of BPO under argon and oxygen atmosphere to determine also the extent of photo-oxidation of THPMs in the absence of BPO.

In order to study the effect of the solvent in the photo-oxidation of tetrahydropyrimidinones by BPO, especially the effect of a hydrogen-donating solvent, a mixture of 4 mM of BPO and 1 mM of compound **2c** as test substrate in propan-2-ol or acetonitrile were irradiated simultaneously with a 400 W high-pressure mercury lamp until maximum consumption of **2c**. The results presented in Table 2 show that the required irradiation time in acetonitrile is short, and the output is higher than in propan-2-ol. This retarding effect in propan-2-ol is probably due to the presence of an active secondary hydrogen atom in this molecule. The initially formed benzoyloxy radical (BOR) abstracts this easily accessible and active hydrogen atom and turns to benzoic acid rather than removing hydrogen from THPM to start oxidation. Therefore an increase of irradiation time and an incomplete reaction is expected

THPMs	R^1	R^2	Prod.	BPO/Ar or (Ar)[a]	BPO/O_2 or (O_2)[a]		
				Irrad. time (h)	Conv. (%)	Irrad. time (h)	Conv. (%).
1a	C_6H_5	C_2H_5O	**3a**	17 (50)	90 (60)	30 (50)	100 (40)
1b	4-$CH_3C_6H_4$	=	**3b**	18 (20)	100 (80)	20 (20)	60 (40)
1c	4-$CH_3OC_6H_4$	=	**3c**	17 (22)	100 (90)	22 (22)	90 (20)
1d	3-$CH_3OC_6H_4$	=	**3d**	24 (24)	100 (80)	24 (24)	80 (20)
1e	2-$CH_3OC_6H_4$	=	**3e**	20 (20)	100 (80)	22 (22)	80 (20)
1f	4-ClC_6H_4	=	**3f**	14 (18)	100 (60)	18 (18)	90 (40)
1g	3-ClC_6H_4	=	**3g**	20 (20)	100 (70)	20 (20)	90 (40)
1h	2-ClC_6H_4	=	**3h**	20 (20)	100 (60)	20 (20)	80 (30)
1i	4-BrC_6H_4	=	**3i**	16 (20)	100 (40)	20 (20)	80 (20)
1j	4-$NO_2C_6H_4$	=	**3j**	22 (22)	100 (60)	22 (22)	50 (10)
1k	$PhCH_2CH_2$	=	**3k**	11 (20)	100 (90)	13 (20)	100 (70)
1l	$CH_3(Ph)CH$	=	**3l**	13 (17)	100 (90)	16 (17)	100 (50)
1m	2-thienyl	=	**3m**	14 (16)	100 (60)	16 (16)	90 (40)
1n	4-$Me_2NC_6H_4$	=	**3n**	0.9 (3)	100 (100)	4 (7)	100 (100)
2a	C_6H_5	CH_3	**4a**	8 (22)	100 (90)	12 (22)	100 (60)
2b	4-$CH_3C_6H_4$	=	**4b**	12 (20)	100 (50)	20 (20)	80 (40)
2c	4-$CH_3OC_6H_4$	=	**4c**	4 (8)	100 (100)	11 (14)	90 (90)
2d	3-$CH_3OC_6H_4$	=	**4d**	9 (18)	100 (80)	14 (18)	100 (60)
2e	2-$CH_3OC_6H_4$	=	**4e**	6 (10)	100 (80)	8 (10)	90 (60)
2f	4-ClC_6H_4	=	**4f**	6 (13)	100 (90)	13 (13)	100 (80)
2g	3-ClC_6H_4	=	**4g**	8 (20)	100 (80)	16 (20)	90 (70)
2h	2-ClC_6H_4	=	**4h**	5 (12)	100 (100)	10 (16)	100 (100)
2i	4-BrC_6H_4	=	**4i**	7 (14)	100 (100)	12 (14)	100 (70)
2j	4-$NO_2C_6H_4$	=	**4j**	10 (18)	100 (80)	18 (18)	80 (50)
2k	3-$NO_2C_6H_4$	=	**4k**	16 (20)	100 (70)	20 (20)	80 (60)
2l	2-$NO_2C_6H_4$	=	**4l**	20 (20)	0 (0)	20 (20)	0 (0)
2m	$CH_3(Ph)CH$	=	**4m**	5 (11)	100 (100)	6 (11)	90 (70)
2n	2-thienyl	=	**4n**	6 (8)	100 (70)	6 (8)	80 (50)
2o	4-$Me_2NC_6H_4$	=	**4o**	0.5 (2)	100 (100)	1.3 (3)	100 (100)

Table 3. Photo-oxidation of 5-carboethoxy-THPMs (**1a** – **1n**) and 5-acetyl-THPMs (**2a** – **2o**) in dry acetonitrile in the presence or absence of BPO under argon and oxygen atmosphere.

[a] The times and yields presented in parentheses refer to the photoreactions in the absence of BPO.

by carrying out the reaction in propan-2-ol. It should be noted that due to the low solubility of THPMs in many solvents and avoiding either the possible electron transfer from excited THPMs to electron-accepting solvents (CCl_4 or $CHCl_3$) or hydrogen abstraction from the solvent (propan-2-ol) by benzoyloxy radical, as explained, the reaction is carried out in acetonitrile.

Under optimized reaction conditions (BPO : THPM = 4 : 1), simultaneous irradiation of acetonitrile solutions of each THPM (**1a** – **1n** and **2a** – **2o**) in the presence or the absence of BPO under argon and oxygen atmosphere was carried out until maximum progression of the reaction (Scheme 2). The results are summarized in Table 3.

The results presented in Table 3 indicate that the irradiation of THPMs (**1a** – **1n** and **2a** – **2o**) in acetonitrile either in the presence or in the absence of BPO leads to the removal of 3- and 4-hydrogens under formation of the same oxidation products, namely 2-oxo-1,2-dihydropyrimidines (**3a** – **3n** and **4a** – **4o**). IR, ^{1}H NMR and MS spectral data confirm the formation of the latter compounds. No hydrogen abstraction from 6-CH_3 as an allylic hydrogen by the benzoyloxy radical (BOR) was observed in our study.

For a better discussion of the output of this study, the results presented in Table 3 should be divided in two categories: i) irradiation in the absence of BPO (photo-oxidation), and ii) irradiation in the presence of BPO (free radical-induced photo-oxidation).

Photo-oxidation

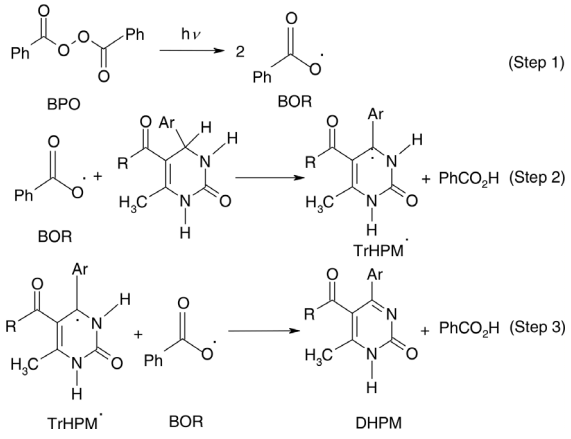
The results show that the photochemical oxidation of THPMs is faster in the presence of an argon as compared to an oxygen atmosphere. The increase of the required irradiation time in the presence of oxygen and also a failure of total quenching under oxygen are supporting the argument that both excited singlet and triplet states of THPMs are involved in the reaction as we also observed by irradiation in $CHCl_3$ solution [29, 30]. The removal of 3- and 4-hydrogens in this study, namely photo-oxidation of THPMs in acetonitrile solution, is probably a result of homolytic cleavage of both C–H and N–H bonds. The results show that the nature and the position of the additional substituent

on the phenyl ring in 4-position of the heterocyclic ring affect the rate of the reaction; therefore the homolytic cleavage of the C–H bond is expected to happen at the beginning of the reaction.

Free radical-induced photo-oxidation

A comparison of the results obtained by the reactions in the absence and in the presence of BPO reveals that photo-oxidation is faster using BPO. This indicates the involvement of the initially formed benzoyloxy radical (BOR) by photo-cleavage of BPO as an active species for the removal of the less polar C(4)–H bond rather than the more polar N(3)–H bond. The latter observation is supporting again the effect of the nature of the aryl group in the 4-position on the required time of irradiation. Whereas complete oxidation is observed using BPO under an argon atmosphere, a longer irradiation time is necessary, and incomplete oxidation is observed in many cases under an oxygen atmosphere. Again a comparison of the time of free radical photo-oxidation demonstrates that in contrast to the effect of the electron-withdrawing substituent the electron-donating substituents decrease the required irradiation time. According to these results the following mechanism is proposed for the free radical-induced photo-oxidation (Scheme 2).

Selective excitation of BPO leads to the formation of two benzoyloxy radicals (BOR) in the first step. These reactive species abstract an easily removable 4-hydrogen from the heterocyclic ring (4-H) under formation of a trihydropyrimidinoyl radical intermediate (TrHPM·) and benzoic acid. Removal of the second hydrogen atom in the last step completes the reaction under formation of 2-oxo-1,2-dihydropyrimidine



Scheme 2.

(DHPM). The observed effect of the nature of the substituent in the 4-position of the heterocyclic ring on the rate of reaction supports the argument that the removal of a hydrogen atom from the less polar C–H bond compared with the more polar N–H bond is more facile. Therefore, step 2 should be the rate-determining step. In fact, the stability of a trihydropyrimidinoyl radical intermediate (TrHPM·), which is both a benzylic and an allylic radical, should lower the activation energy for its formation. This influences the rate of step 2 as the rate-determining step. This observation is possibly the reason why the concurrent removal of a hydrogen atom from the allylic position (6-CH_3) is not observed in the present study. It should also be noted that the removal of a benzylic or secondary alkyl substituent on the 4-position of the heterocyclic ring has not been observed as it was found in the case of 1,4-dihydropyridines [12, 13].

Conclusion

In the present study, we have investigated the free radical-induced photodehydrogenation of 2-oxo-1,2,3,4-tetrahydropyrimidines to the corresponding 2-oxo-1,2-dihydropyrimidines using benzoyl peroxide in acetonitrile under argon and oxygen atmospheres. The reaction is faster under argon than under oxygen and is influenced by the nature of the substituent on the 4- and 5-positions of the THPM ring. The results of this study, especially the direct photo-oxidation of THPMs, show the photosensitivity of tetrahydropyrimidines. Due to their pharmaceutical activities, this is important for drug designers and manufacturers.

Experimental Section

The title compounds were prepared through a three components condensation using $Co(HSO_4)_2$ [30]. 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 DRX-300 Avance instrument. They are reported as follows: chemical shifts δ in ppm (multiplicity, coupling constants J in Hz, number of protons, and assignment). Mass spectra were obtained on a Platform II Mass Spectrometer from Micromass; EI mode at 70 eV. UV spectra (in CH_3CN) were taken with a Shimadzu UV-160 spectrometer.

A solution of a 2-oxo-1,2,3,4-tetrahydropyrimidine in dry acetonitrile ($c = 10^{-3}$ M) and a solution of a 2-oxo-1,2,3,4-tetrahydropyrimidine and dibenzoyl peroxide with a molar ratio of 1 : 4 in dry acetonitrile were prepared. Then two equal volumes of each solution in a Pyrex tube were irradiated simultaneously with a 400 W high-pressure mer-

cury lamp while bubbling argon or oxygen through the solutions during irradiation. The reaction was followed by thin-layer chromatography (TLC) until maximum consumption of THPMs. The products were purified with column and plate chromatography. The products were characterized by comparison of their physical and spectroscopic data with those of authentic samples.

*Ethyl 6-methyl-2-oxo-4-(1-phenylethyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**1k**)*

M. p.: 146 – 153 °C. – IR: ν = 3250 (NH), 1720 (COC_2H_5), 1700 (2-CO) cm^{-1}. – ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 1.15 (m$_c$, 6H, CHCH_3, CH$_2$CH_3), 2.15 (s, 3H, 6-CH_3), 2.84 (m$_c$, 1H, CHCH$_3$), 3.76 – 3.94 (two m, 2H, CH_2CH$_3$), 4.20 (m, 1H, 4-H), 7.20 (m$_c$, 6H, aromatic-H, 1-NH), 9. 59 (s, 1H, 3-NH). – MS (EI, 70 eV): m/z (%) = 243 (17) [M–C_2H_5O]$^+$, 183 (100) [M–PhCHCH$_3$]$^+$, 155 (85) [M–PhCHCH$_3$–C_2H_4]$^+$, 137 (84) [M–PhCHCH$_3$–C_2H_5OH]$^+$, 110 (64) [M–PhCHCH$_3$–$CO_2C_2H_5$]$^+$, 105 (85) [PhCHCH$_3$]$^+$, 77 (82) [C_6H_5]$^+$. – UV/Vis (CH$_3$CN): $\lambda_{max}(\log\varepsilon)$ = 277.2 (4), 241.6 (sh, 3.51), 209.6 nm (4.03).

*5-Acetyl-6-methyl-4-(1-phenylethyl)-1,2,3,4-tetrahydropyrimidin-2(1H)-one (**2m**)*

M. p.: 183 – 185 °C. – IR: ν = 3250 (NH), 1710 (CH_3CO), 1690 (2-CO) cm^{-1}. – ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 1.18 (m, 3H, PhCHCH_3), 1.96 (s, 3H, 6-CH_3), 2.16 (s, 3H, CH_3CO), 2.79 (m, 1H, PhCHCH$_3$), 4.25 (m, 1H, 4-H), 7.19 (m$_c$, 6H, aromatic-H, 1-NH), 8.95 (s, 1H, 3-NH). – MS (EI, 70 eV): m/z (%) = 153 (100) [M–MeCHPh]$^+$, 110 (17) [M–MeCHPh–$COCH_3$]$^+$, 105 (30) [MeCHPh]$^+$. – UV/Vis (CH$_3$CN): $\lambda_{max}(\log\varepsilon)$ = 291.6 (4.08), 211.2 nm (4.06).

*Ethyl 6-methyl-4-(1-phenylethyl)-2-oxo-1,2-dihydropyrimidine-5-carboxylate (**3k**)*

M. p.: 204 – 209 °C. – IR: ν = 3300 (NH), 1710 ($CO_2C_2H_5$), 1665 (2-CO), 1590 (C_5=C_6), 1420 (C=C), 1280 (C–O) cm^{-1}. – ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 1.15 (t, 3H, J = 7.06 Hz, CH$_2$CH_3), 1.42 – 1.44 (d, 3H, J = 6.52 Hz, CHCH_3), 2.23 (s, 3H, 6-CH_3), 4.09 (q, 2H, J = 6.56 Hz, CH_2CH$_3$), 4.45 – 4.47 (q, 1H, J = 6.81 Hz, CHCH$_3$), 7.22 (m$_c$, 5H, aromatic-H), 12.18 (brd s, 1H, NH). – MS (EI, 70 eV): m/z (%) = 286 (2) [M]$^+$, 137 (100) [M–MeCHPh–C_2H_5O]$^+$, 105 (52) [MeCHPh]$^+$, 77 (29) [C_6H_5]$^+$. – UV/Vis (CH$_3$CN): $\lambda_{max}(\log\varepsilon)$ = 306 (3.70), 245 nm (4.14).

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