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Photosensitized Oxidation of Unsymmetrical 1,4-Dihydropyridines

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Photosensitized oxidation of unsymmetrically substituted 1,4-dihydropyridines using dye sensitizers methylene blue, rose bengal and tetraphenylporphyrin by taking visible light source resulted in the aromatization of dihydropyridine ring and formation of the corresponding pyridine derivatives. Comparison of the results obtained under photosensitized reaction with those obtained by direct photo-oxidation indicated a very fast and smooth reaction of these compounds and formation of pyridine derivatives using theses dyestuffs.

Keywords: 1,4-Dihydropyridines, Photochemistry, Photooxidation, Photosensitized oxidation, Singlet oxygen

INTRODUCTION

1,4-Dihydropyridines (1,4-DHPs) are of considerable interest and well-known compounds because of their pharmaceutical properties. Many of these compounds act as calcium channel antagonist and they display a well-known cardiovascular activity due to the inhibition of L-type Ca^{2+} channels, which results in a reduced calcium influx with impaired electromechanical coupling both in vascular smooth muscle cell and in the heart [1-4]. It has been observed that, in the human body, these compounds are generally oxidized to their corresponding pyridine derivatives, which become biologically inactive [5,6]. Hence, a convenient method for the conversion of 1,4-dihydropyridines to pyridine derivatives is important for the identification of its metabolites.

Oxygen is an abundant element with multiple forms of activity. The most common and important form is molecular species (O_2), which is necessary for all aerobic cell metabolism. As a diradical species (in its ground state), oxygen molecule acts as inhibitor in many radical reactions. When the ground state oxygen is excited to a higher energy state, the main activated species of oxygen, namely singlet oxygen $^1O_2$ ($^1\Delta_g$) is formed. This form of oxygen is responsible for the oxidation and oxygenation of various compounds. Several alternative methods for the generation of singlet oxygen have been developed including reaction of sodium hypochlorite with hydrogen peroxide [7] and thermal decomposition of the ozonides of triphenyl phosphate [8], 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane [9] and 2,8,9-trioxa-1-phosphaadamantane [10]. Although many sources of singlet oxygen are now available, the photosensitized formation of singlet oxygen using various dyestuffs remains the best method of choice for most synthetic and mechanistic application. Therefore, many dye sensitizers are found to be able to generate singlet oxygen. Singlet oxygen is formed through energy transfer from excited color dyes such as methylene blue [11,12], clay-bound methylene blue [13,14], rose bengal [15-19], polymer-bound rose bengal [20,21], tetraarylporphyrin [22,23] and Zn-tetraphenyl-porphyrin complex [24,25] to molecular oxygen.

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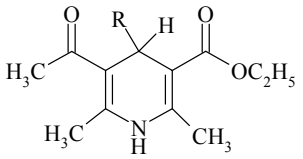
Chiral 1,4-dihydropyridines [26-28] have been employed as synthetic intermediates for a wide variety of compounds such as natural products [29], calcium channel blockers [30], and NADH models [31]. Because of the importance of C-4 chirality with respect to the pharmacological activity of 4-aryl-1,4-dihydropyridines, various studies have been devoted to the preparation of unsymmetrical 1,4-dihydropyidine-3,5-diesters, such as nitrendipine [32], felodipine [33,34], and also to the preparation of unsymmetrical 1,4-dihydropyridines, in which an alkoxycarbonyl (ester) group and an alkanoyl (keto) group are located on the 3- and 5- positions, respectively [35-38].

In the course of our studies on the chemistry of 1,4-dihydropyridine-3,5-diesters, known also as *Hantzsch* esters [39] and 3,5-diacetyl-1,4-dihydropyridines, we were especially interested to investigate the effect of the nature of the substituent on the 4-position and also the effect of the presence of acetyl groups instead of carboethoxy groups in positions 3 and 5 of 1,4-dihydropyridine ring on the rate and type of reaction in photooxidation of these compounds [40-43].

The interesting chemistry and pharmaceutical activity of unsymmetrically substituted 1,4-dihydropyridines led us to synthesize some novel and also some known ethyl 5-acetyl-1,4-dihydropyridine-3-carboxylates, with the general structure **1** [44], and to investigate their photochemical behavior under oxygen and argon atmospheres [45]. The aim of the present work is to elucidate the effect of the nature of the 4-substituents and also the presence and absence of oxygen atmosphere on the rate of photooxidation.



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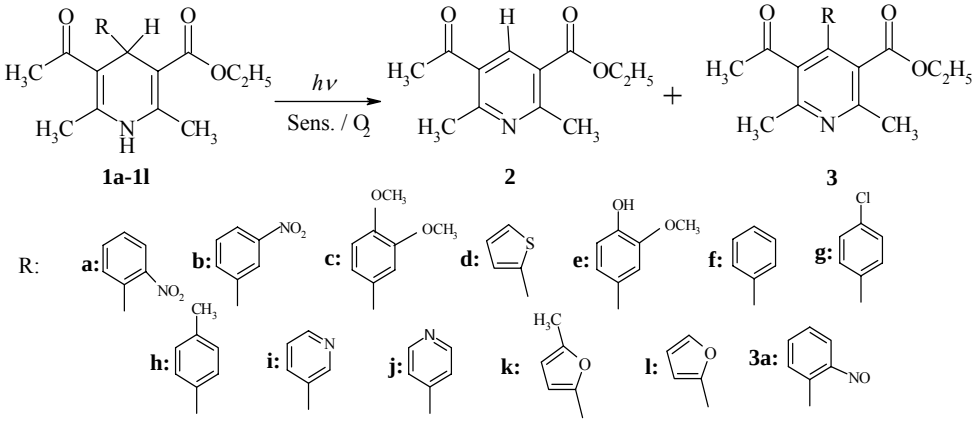
Owing to the formation of unsymmetrical pyridine derivatives by photoinduced aromatization of the corresponding 1,4-dihydropyridines, we would like to report the reactivity of unsymmetrical 1,4-dihydropyridines towards singlet oxygen by using dye sensitizers, methylene blue, rose bengal and tetraphenylporphyrin for the generation of singlet oxygen.

RESULTS AND DISCUSSION

In an optimized reaction condition, a mixture of dihydropyridines (DHPs) **1a-1l** and each of sensitizers (Sens.) methylene blue (MB, in chloroform solution), rose bengal (RB, in methanol solution) and tetraphenylporphyrin (TPP, in chloroform solution) with a DHP:Sens. mole ratio of 10:1 was irradiated with the emission of a 400 W VIAOX lamp from Osram ($\lambda \geq 450$ nm) by bubbling of oxygen through the solution under irradiation until total disappearance of DHPs (Scheme 1). The results are summarized in Table 1.

Owing to the similarity of the products obtained under



Scheme 1

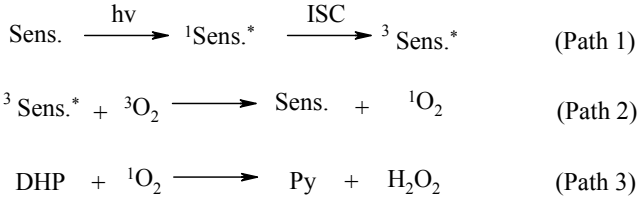
Table 1. Comparison of Photosensitized Oxidation of **1a-l** in the Presence of rose bengal (RB), Methylene blue (MB), Tetraphenylporphyrin (TPP), and Oxygen with the Direct Photooxidation of them under Oxygen and Argon Atmospheres [45]

1	RB in CH_3OH		MB in CH_3Cl		TPP in CH_3Cl		Direct oxidation			
							O_2		Ar	
	Product[a]	Time (h)[c]	Product[a]	Time (h)[c]	Product[a]	Time (h)[c]	Product (%)[b]	Time (h)[c]	Product (%)[b]	Time (h)[c]
a	**3a**	0.2	**3a**	0.2	**3a**	0.1	**3a** (60)	0.66	**3a**	0.33
b	**3b**	3.5	**3b**	5.5	**2** (27%) **3b** (45%)	3.75	**3b** (71)	5.5	**3b**	36
c	**3c**	3.5	**3c**	2.5	**3c**	2.75	**3c** (72)	9	**3c**	3.75
d	**3d**	1.75	**3d**	3	**3d**	1.5	**3d** (40)	6	**3d**	5.5
e	**3e**	2.5	**3e**	2.5	**3e**	2	**2** (20) **3e** (50)	9	**2** (18) **3e** (49)	22
f	**3f**	3.75	**3f**	1	**3f**	3.5	**3f** (84)	12.5	**3f**	8
g	**3g**	0.75	**3g**	0.75	**3g** (38%)	1	**3g** (73)	5.5	**3g**	3
h	**3h**	0.75	**3h**	2.25	**3h**	0.75	**3h** (67)	6	**3h**	4
i	**3i**	3.0	**3i**	1	**3i**	1.25	**3i** (65)	7.5	**3i**	8.5
j	**3j**	3.5	**3j**	1.5	**3j**	2.25	**3j** (80)	6	**3j**	15
k	**2**	0.1	**2**	1.5	**2**	0.33	**2** (63)	1.5	**2**	5
l	**2**	0.66	**2**	0.25	**2**	0.1	**2** (74)	2.25	**2**	5

[a]The products have not been isolated and compared with the TLC of authentic samples. [b]Isolated yield. [c]The times period are given after total disappearance of starting material **1a-1l**.

both photosensitized and direct oxidations, the products have not been isolated under photosensitized oxidation except for the cases of **3b** and **3g** by reaction in the presence of TPP, due to the formation of two different products. The data given in Table 1 indicate that a very fast reaction has been occured by photosensitized oxidation in comparison with photooxidation either under oxygen or argon atmosphere. The mechanism of the oxidation of dihydropyridines to the pyridine derivatives (Py) by singlet oxygen is shown in Scheme 2.

According to this mechanism, irradiation (at $\lambda \geq 450$ nm) of the mixture of each of sensitizers and each of dihydropyridines leads to selective excitation of the former, followed by intersystem crossing (ISC) and formation of triplet excited sensitizers (path 1). Then, singlet oxygen is generated by triplet-triplet annihilation according to path 2. Dehydrogenation of dihydropyridine ring by $^1O_2$ completed the reaction under formation of pyridine compound and H_2O_2.



Scheme 2

The ground state of molecular oxygen is a $^3\Sigma_g^-$ state. The corresponding singlet state $^1\Sigma_g^+$ is higher in energy by 35 kcal mol^{-1}, which is known as singlet diradical. There is a degenerate $^1\Delta_g$ state 22 kcal mol^{-1} above the $^3\Sigma_g^-$ ground state between these two Σ states [46]. Owing to very short life time of $^1\Sigma_g^+$ state, it has been proposed that most reactions occur by the involvement of singlet oxygen $^1\Delta_g$, since a ratio of O_2 ($^1\Delta_g$) /O_2 ($^1\Sigma_g^+$) >> 10^6 has been calculated for the presence of

Table 2. Triplet Energies of the Sensitizers (E_T), the Quantum Yield (Δ_Φ) and Life Time (τ_Δ) of the Singlet Oxygen ($^1\Delta_g$)

Sens.	E_T (kcal mol^{-1})	Δ_Φ	τ_Δ (μs)
Rose bengal	~41-44 [48]	0.76 (CH_3OH) [51]	7 (CH_3OH) [54]
Methylene blue	~33-34 [49]	0.52 (C_2H_5OH) [52]	
Tetraphenylporphyrin	33 [50]	0.50 ($CHCl_3$) [53]	60 ($CHCl_3$) [54]

$^1\Delta_g$ state [47]. Three important factors, (i) triplet energy of the sensitizers, (ii) the value of quantum yield for singlet oxygen generation and (iii) the life time of this species depending on the type of solvent should be considered for effective generation of singlet oxygen. These data for the sensitizers used in this work are summarized in Table 2.

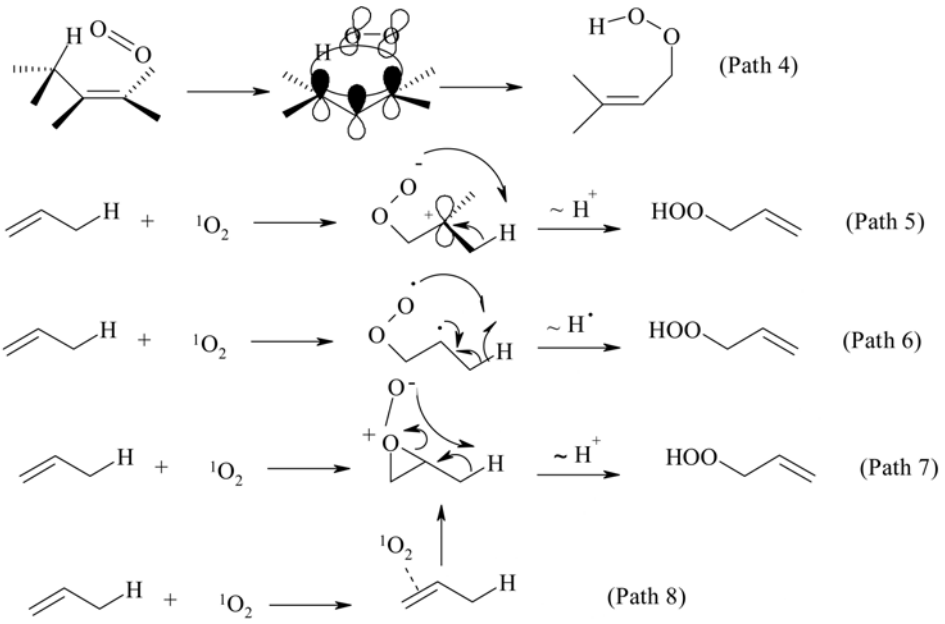
The important point in this work is the different behavior of sensitizers in increasing the rate of oxidation. The energy transfer process (path 2) requires that the triplet energy of sensitizer must be above the triplet energy of acceptor. From the comparison of the data shown in Table 2, especially the dependence of the quantum yields of the singlet oxygen generation on the type of sensitizer, we expect the ability of sensitizers used for this process to follow the order RB > MB > TPP. Because of polar nature of rose bengal, its reactions were carried out in methanol solution. Based on the reported data for the life time of the singlet oxygen, we should expect better results in chloroform solution than in methanol or ethanol solutions. The average irradiation times for the compounds considered in this study (Table 1) are 1.6 h for TPP, 1.83 h for MB, and 1.99 h for RB. These data match very well with the data presented in Table 2. It should be noted that, besides these factors, the most stable conformation of DHP ring for the removal of 1- and 4- hydrogens by $^1O_2$, and the mechanism of reaction should also be taken into account for analyzing this oxidative reaction.

Dehydrogenation of 1,4-dihydropyridine by singlet oxygen is actually a type of *Singlet Oxygen Ene Reaction* [55] – a reaction between singlet oxygen with compounds containing allylic hydrogens under formation of hydroperoxy compounds. Dehydrogenation of 1,4-dihydropyridines proceeds in two steps: (i) the formation of hydroperoxy compounds and (ii) the elimination of hydrogen peroxide and formation of dehydrogenated compounds, namely pyridine derivatives. For the first step of this reaction, two different mechanisms, concerted (path 4) and stepwise mechanisms (path 5-8) have been suggested [56]. The stepwise pathways have invoked zwitterionic (path 5), biradical (path 6), perepoxide (path 7), and exciplex (path 8) intermediates (Scheme 3).

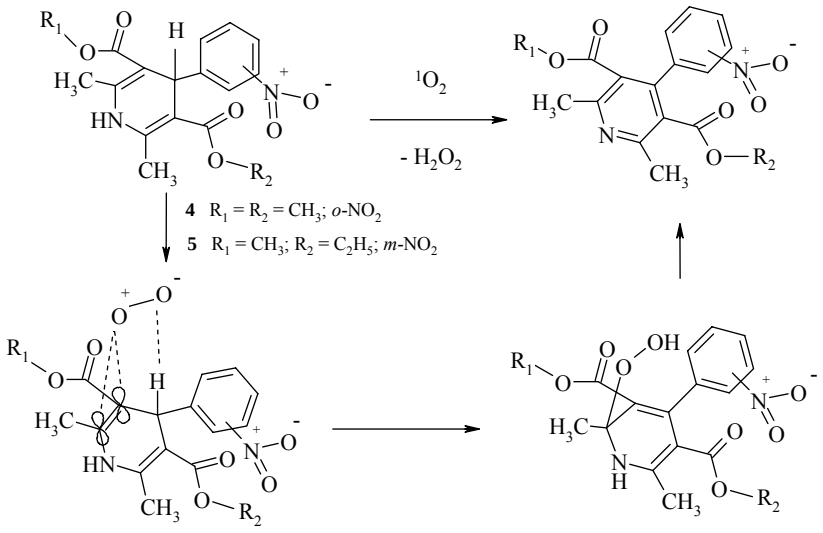
Ab initio calculations favor the biradical mechanism, at least in the gas phase [57], while *semi-empirical* calculations suggest the perepoxide to be a genuine intermediate [58]. Reactions of singlet oxygen are characterized by low activation energies and very fast reaction times. Therefore, a detailed mechanism is in general difficult to establish. Many experimental findings suggest, however, that an interaction with charge-transfer character occurs at the initial steps of the reaction, with the stereochemistry given by the HOMO of the olefin as the electron donor and the π^* LUMO of the oxygen [59].

Recently, the reactivities of two different 1,4-dihydropyridines, namely nifedipine **4** (a symmetrical dihydropyridine diester) and nitrendipine **5** (an unsymmetrical dihydropyridine diester) towards singlet oxygen have been investigated by Pizarro-Urzúa, and Núñez-Vegara [60]. Their proposed mechanism for the oxidation of **4** and **5** by singlet oxygen is given in Scheme 4. As they have shown, the aryl groups are exo-oriented with respect to the molecular plane of DHP ring. According to this mechanism, formation of perepoxide intermediate is involved in the reaction.

Many works have been devoted to the conformational analysis of DHP rings, depending on the steric and electronic factors of the substituents located in 3, 4, and 5 positions. Crystal structure analysis [37,61] and *ab initio* calculations

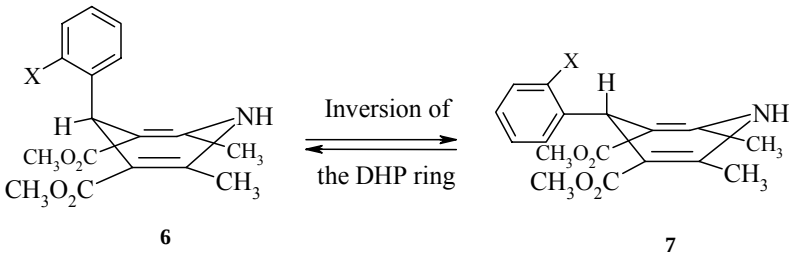


Scheme 3



Scheme 4. Proposed mechanism for the reaction of $O_2(^1\Delta_g)$ with nifedipine **4** and nitrendipine **5** taken from Ref. [60].

[62] of various DHP show the preference of the boat conformation. However, a boat conformation for the DHP ring has considerable consequences with regard to possible conformers. Thus, the aryl substituent may occupy a pseudoaxial position as in **6** or it may be in equatorial position as in **7** (Scheme 5). The *semi-empirical* PM3-calculations of 1,4-dihydropyridines carried out in this study has also confirmed the preference for the conformation with



6 **7**

Scheme 5

Table 3. Deviations of the Distances of 1-N and 4-C from the Molecular Plane, and the Dihedral Angles of the CO-Groups Obtained from *Semi-Empirical* PM3-Calculations

Comp.	R	θ° C_2-C_3-C_7-C_8[a]	θ° C_6-C_5-C_9-C_{10}[a]	d (Å) N-plane	d (Å) 4C-plane
8	H	98.93	-107.61	0.217	0.157
1a	2-$NO_2C_6H_4$	63.79	90.99	0.130	0.060
1b	3-$NO_2C_6H_4$	78.55	-110.32	0.111	0.023
1c	3,4-$(CH_3O)_2C_6H_3$	60.62	-105.47	0.114	0.091
1d	2-Thienyl	65.50	-107.08	0.060	0.097
1e	3-(CH_3O)-4-$(OH)C_6H_3$	-112.50	-106.49	0.114	0.044
1f	C_6H_5	60.37	-105.98	0.136	0.049
1g	4-ClC_6H_4	19.58	-105.78	0.074	0.013
1h	4-$CH_3C_6H_4$	60.41	-105.87	0.118	0.039
1i	3-Pyridyl	59.08	-106.71	0.110	0.043
1j	4-Pyridyl	-106.50	-106.71	0.037	0.043
1k	5-Methyl-2-furyl	59.84	-107.07	0.099	0.111
1l	2-Furyl	63.24	-106.51	0.078	0.149

[a]The (–) sign denote the orientations of the CO groups outside to the boat-conformation.

pseudoaxial occupation of the 4-substituent [63].

Since the 4-H and 1-H (NH) of DHP ring in the preferred conformation are *trans*-orientated to each other, the concerted removal of both hydrogens by $^1O_2$ and oxidation of the ring is not possible. This led us to propose the homolytic and also heterolytic removal of these hydrogens. Heterolytic mechanism should be involved preferentially *via* the paths 5, 7, and 8 by the removal of 1-H attached to the more electronegative nitrogen compared with 4-H and hemolytic mechanism *via* the path 6 by the removal of 4-H attached to the less electronegative carbon atom compared with 1-H. The *semi-empirical* PM3-calculations of the compounds **8** and **1a-1l** show that the extent of deviation of the 4-C and 1-N from the planarity in the boat conformation is dependent on the nature and steric hindrance of 4-substituent as well as on the *cisoid*- and *transoid*- orientation of the CO groups of the acetyl and carboethoxy moiety (Table 3). Therefore, we will propose the exciplex formation of $^1O_2$ from the upper side of the ring (complexation either to the conjugated C=C double bond with $COCH_3$ or to the conjugated C=C double bond with $CO_2C_2H_5$) for the heterolytic removal of 1-H. On the other hand, the exciplex formation of $^1O_2$ from the down side of the ring should be proposed for the homolytic removal of 4-H. By *semi-empirical* PM3- calculations, we can obtain only the

optimized conformation in the gas phase. While the more stable conformation in the solution is dependent on the steric and electronic factors of the substituents, and the type and polarity of the solvent (due to solute-solvent interaction) also play an important role in the involvement of the more stable conformation for the homolytic and heterolytic reactions with $^1O_2$. This leads us to conclude that we should not expect a fast oxidative reaction for any of the compounds considered for this study by using TPP, MB or RB. Therefore, we should compare the average irradiation times for the ability of sensitizers in this reaction.

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