

Photochemical, Solvatochromic, Electrochromic and Kinetic Investigation of New Synthesized Bicyclic Aziridines with Chalcone Moieties

N.O. Mahmoodi* T. Besharati-Seidani, A. Aliakbar and B. Ghalami Choobar

Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box: 41335-1914, Rasht, Iran

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Bicyclic aziridines show exclusive photochromic behavior. Here, we summarize the results of optical and electrochemical properties, such as photochemical, solvatochromic, electrochromic and kinetic behavior of bicyclic aziridines linked to chalcone moieties. The photochromic process for conversion of closed photoisomers to open photoisomers for compounds 1-10 followed zero-order kinetics. For considering the solvatochromic properties of compounds 1, 3, 5, 7 and 9, photochromic properties of these compounds in different solvents were investigated, and the negative solvatochromism were observed. The redox behavior of several derivatives of bicyclic aziridines by cyclic voltammetry was examined for compounds 1, 3, 5 and 6, and irreversible oxidation was observed.

Keywords: Bicyclicaziridine, Chalcone, 1,3-Diazabicyclo[3.1.0]hex-3-enes, Photochromism, Solvatochromism, Cyclic voltammetry

INTRODUCTION

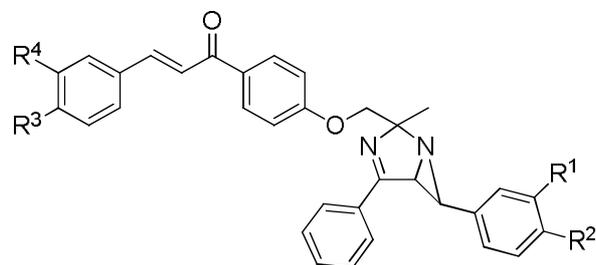
Bicyclic aziridines are a class of photochromic compounds with exclusive reversible photochromic properties both in solution and in solid states [1-2]. Photochromism of bicyclic aziridine can be defined as the photo induced bond cleavage leading to equilibrium between different photoisomers. Such structures commonly named colored open photoisomer form have a distinct absorption spectrum in the visible range and return to the initial colorless closed photoisomer form *via* thermal or photochemical pathways. The coloration-decoloration cycles of these compounds could be repeated several times [3-14].

Solvatochromism can be defined as a color change by a differing in their absorption spectra in the diverse solvents. Two common solvatochromism behaviors based on the polarity of solvent were observed: positive solvatochromism; red-shift in absorption band *via* increase of polarity of solvent and negative solvatochromism; blue-shift in absorption band *via* increase polarity of solvent. With the

rapid growth in the use of optical probes and sensors from 1990s, solvatochromic effect plays an important role. Solvatochromism is used in analysis of liquids, polymer characterization, biological systems such as protein and nucleic acid detection, enzyme-labeled fluorescence, *etc.* [15-16]

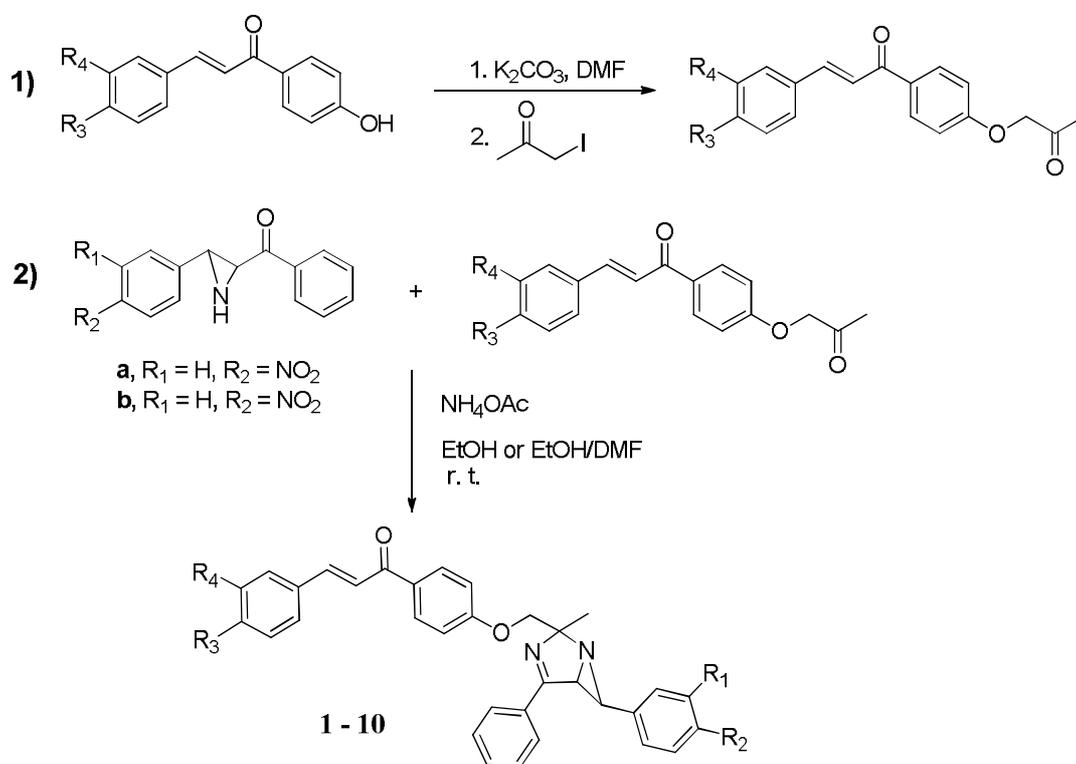
Many organic materials exhibit redox state with distinct electronic (UV-Vis) absorption bands. Electrochromic materials are of interest in commercial applications such as car mirror, windows, display, *etc.* [17]. We synthesized several new bicyclic aziridines with chalcone moiety (Scheme 1) [14]. The general procedure for preparation of photochromic compounds (1,3-diazabicyclo [3,1,0]hex-3-enes) is according to our previous works [3-14]. As shown in Scheme 2, the reaction of hydroxychalcones with freshly prepared iodoacetone in the presence of K_2CO_3 in DMF leads to the formation of alkylated chalcones in 80% yield. One pot reaction of one equivalent of prepared chalcones, one equivalent of premade ketoaziridines, and 5 equivalents of NH_4OAc under anhydrous condition afforded the desired photochromic compounds, 1-10, in good yields (60-80%).

*Corresponding author. E-mail: mahmoodi@guilan.ac.ir



- 1, R¹ = H, R² = NO₂, R³ = H, R⁴ = H
 2, R¹ = NO₂, R² = H, R³ = H, R⁴ = H
 3, R¹ = H, R² = NO₂, R³ = OMe, R⁴ = H
 4, R¹ = NO₂, R² = H, R³ = OMe, R⁴ = H
 5, R¹ = H, R² = NO₂, R³ = Cl, R⁴ = H
 6, R¹ = NO₂, R² = H, R³ = Cl, R⁴ = H
 7, R¹ = H, R² = NO₂, R³ = NO₂, R⁴ = H
 8, R¹ = NO₂, R² = H, R³ = NO₂, R⁴ = H
 9, R¹ = H, R² = NO₂, R³ = H, R⁴ = OH
 10, R¹ = NO₂, R² = H, R³ = H, R⁴ = OH

Scheme 1. Structure of photochromic compounds 1-10



Scheme 2. Concise synthesis route for photochromic compounds 1-10

These compounds have shown unique photochromic properties. Initially, the photochromic behavior of all these compounds was examined in EtOH solution. Kinetic of photo-isomerization of all compounds by UV-Vis spectra was investigated. In other efforts, solvatochromic study of several synthesized bicyclic aziridines was also considered. The electrochemical behavior of several photochromic bicyclic aziridine derivatives in CH₃CN was investigated as well.

EXPERIMENTAL

Photochromic compounds were dissolved in EtOH at 1×10^{-4} M and all of the solutions in UV cuvette were irradiated with 254 nm UV lamp. Absorption spectra were recorded as a function of the irradiation time with a UV-Vis spectrophotometer. All measurements were carried out in air. The solvents used were *n*-hexane, CH₂Cl₂, DMF, CH₃CN and EtOH and were either of analytical grade or bulk solvents and distilled before use. The UV-Vis absorption spectra in the range of 200-800 nm were measured with a Shimadzu UV-2100 spectrophotometer and RayleighUV- 1800 spectrophotometer. Cyclic voltammetry was performed on a voltammetry apparatus model VA Computrace 757. All measurements were carried out with CH₃CN containing 0.1 M *n*-Bu₄NClO₄ as the supporting electrolyte at room

temperature.

RESULTS AND DISCUSSION

Photochromic Properties

Bicyclic aziridines 1-10 exist in two photoisomer forms, closed-ring 1A-10A and open-ring 1B-10B. Ten new bicyclic aziridines with chalcone moieties were synthesized (Scheme 1) [12]. The photochromic properties of compounds 1-10 were investigated by irradiation of EtOH solution of these compounds by exposure to UV light (254 nm) at room temperature (See UV Spectra in Supplementary data). The UV-Vis absorption spectra in the range of 200-800 nm, showed position of λ_{\max} bands for the initial (λ_{\max} A) and photoinduced photoisomers (λ_{\max} B). After irradiation with UV-light, open photoisomer absorbs at longer wavelengths with λ_{\max} red shift compared to the original λ_{\max} . For compounds 1-10, spectral data are reported in Table 1.

The color changes were dependent on the irradiation times. When the irradiation time increased, the absorption peak at UV region gradually decreased and simultaneously a new band grew at the visible region. This allows a reversible switching reaction under UV irradiation between colorless closed photoisomer A into colored open photoisomer B (for example, compound 1A-1B).

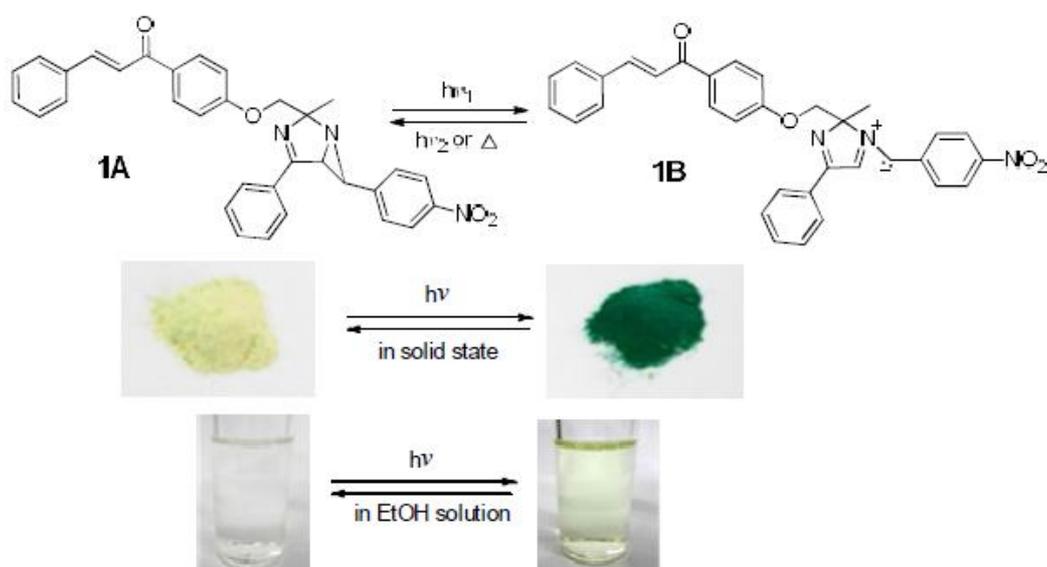


Table 1. Spectral Data for Compounds 1-10 in EtOH Solution by Irradiation with UV Light (254 nm): λ_{\max} A, λ_{\max} B, Irradiation Time

NO	Compound	λ_{\max} A (nm)	ϵ_A ($M^{-1} cm^{-1}$)	λ_{\max} B (nm)	ϵ_B ($M^{-1} cm^{-1}$)	Irradiation time (min)
1	1a	310.0	9022	404.0	2595	0-4
2	2a	320.0	1766	384.0	2441	0-18
3	3a	345.0	1839	432.0	1128	0-6
4	4a	345.5	7444	405.0	377	0-10
5	5a	315.0	2859	420.0	806	0-5
6	6a	324.0	7495	390.0	536	0-14
7	7a	305.0	1258	410.0	274	0-7
8	8a	326.5	3851	383.0	937	0-10
9	9a	308.0	8463	406.0	2400	0-4
10	10a	318.0	9194	385.0	1532	0-10

Table 2. Spectral Data for Compounds 1, 3, 5, 7 and 9 in Different Solvents

	λ_{\max} A (nm) (before irradiation)					λ_{\max} B (nm) (after irradiation)				
	(closed form)					(open form)				
	1	3	5	7	9	1	3	5	7	9
DMF	316	338	318	320	313	-	-	-	-	-
CH ₃ CN	311	336	310	315	309	402	420	420	418	410
EtOH	310	345	315	305	308	404	432	420	410	406
CH ₂ Cl ₂	312	334	315	313	307	426	434	430	430	425
n-hexane	279	279	312	-	-	388, 408, 430	410, 426, 435	-	-	-

The photoisomer B upon heating or remaining in darkness undergoes the back rearrangement to the starting closed photoisomer form A. The isosbestic point indicated the presence of two-component equilibrium systems in the solution. Compound 3 with methoxy group absorbed in

longer wavelength amongst of all 1-10, presumably because the methoxyl groups on the chalcone unit have made a compound with more rigidity. Therefore, compound 3 tended to form the quinoid type of chalcone and had the longer conjugated length.

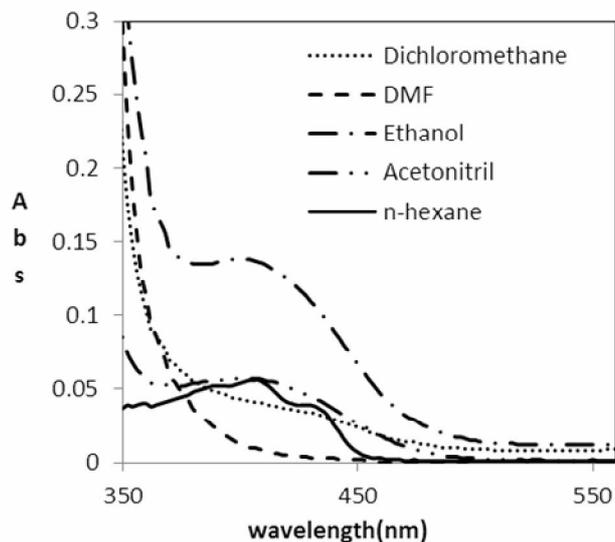


Fig. 1. Solvatochromism of compound 1 in different solvents.

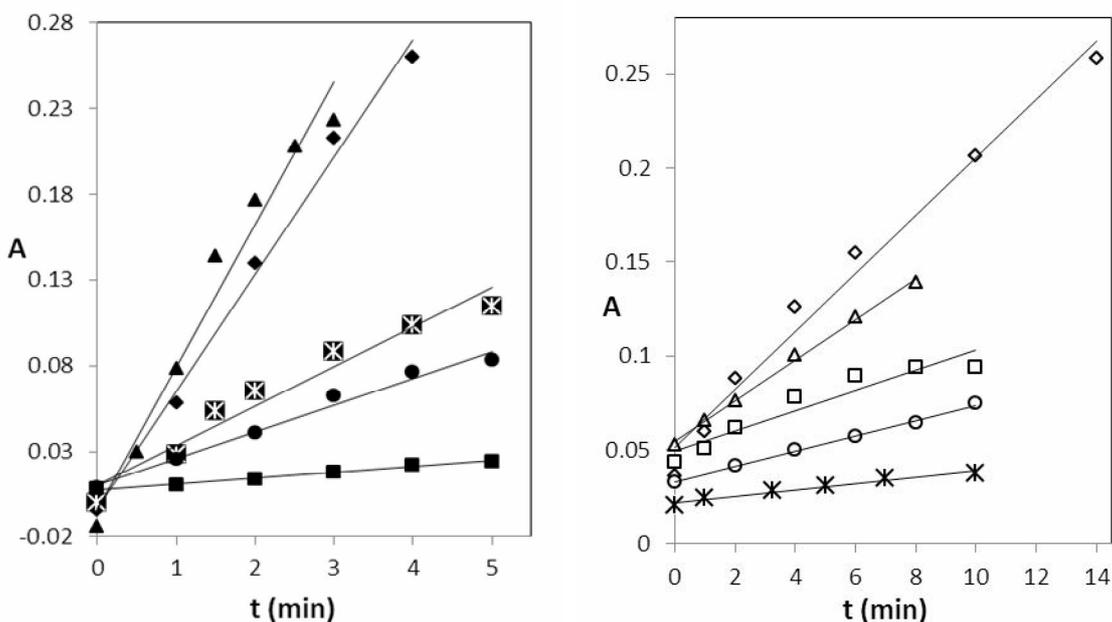


Fig. 2. The plots of A vs. t for compounds 1-10; 1 (\blacklozenge), 2 (\diamond), 3 (\blacksquare), 4 (\otimes), 5 (\bullet), 6 (\circ), 7 (\blacksquare), 8 (\square), 9 (\blacktriangledown) and 10 (∇).

Solvatochromic Study

In solvatochromic investigation, the photoisomerization of compounds 1, 3, 5, 7 and 9 were studied in solvents with different polarities such as CH_3CN , EtOH, DMF, *n*-hexane, CH_2Cl_2 by irradiation at 254 nm. The

UV-Vis spectra for compounds 1, 3, 5, 7 and 9 before and after 8 min were recorded, and results were illustrated in Table 2.

Photo cycloreversion of compound 1 in five different solvents by exposure to UV irradiation were demonstrated in Fig. 1. It displays a negative solvatochromism. This

Table 3. Values of Constant Rate (k) for all Compounds 1-10

Compound	k_{c-o} ($M^{-1} \text{ min}^{-1}$)
1	6.83×10^{-2}
2	1.55×10^{-2}
3	2.31×10^{-2}
4	1.70×10^{-2}
5	1.56×10^{-2}
6	4.10×10^{-3}
7	3.50×10^{-3}
8	5.30×10^{-3}
9	8.32×10^{-2}
10	1.08×10^{-2}

phenomenon is due to the hypsochromic shift for λ_{max} caused by increasing the polarity of solvent. In DMF, upon irradiation with UV light, appreciable color change was not observed. This fact probably is due to the stability of the closed-photoisomer in this solvent. UV spectrum in visible region for open photoisomer of compound 1 in *n*-hexane showed three-shoulder absorption bands. These bands most likely represent different excited states of open photoisomer 1B or perhaps, vibrational bands.

Solvatochromism of other compounds in DMF and *n*-hexane showed the same results. In addition, compounds 3 and 5 also showed negative solvatochromism (see UV spectra of solvatochromic in Supplementary data). Compounds 7 and 9 at visible region in EtOH rather than other solvents indicated a higher blue shift λ_{max} . It is due to the formation of solvent-hydrogen bond that hindered the charge delocalization of chromophore. On the other hand, the λ_{max} for the closed photoisomer forms of 7 and 9 by increasing the polarity of solvent indicated bathochromic shifts (positive solvatochromism). In all used solvents, compound 3 indicated higher red shift λ_{max} rather than other compounds. We attribute this behavior to the electron-donating effect of methoxy groups and its

more-coplanar conformation.

Kinetic Investigation of Photo-isomerization Compounds

The kinetics study for photochromic process of compounds 1-10 was performed to convert the closed photoisomer to open photoisomer. For this aim, the UV spectra of these compounds were recorded in the EtOH solvent with UV-Vis lamp irradiation (254 nm). The concentration of all solutions was 1.0×10^{-4} M. All absorption data were collected at the maximum wavelength of every solution; *i.e.*, at the maximum optical density. The kinetic study of cycloreversion of compounds 1-10 in EtOH shows these processes follow zero-order kinetics as shown in Fig. 2. The relationships between absorbance and exposure time (*A vs. t*) in all solutions upon irradiation with UV light (254 nm) show good linearity (linear correlation factors > 0.99). The slopes of the *A vs. t* lines gave the zero order rate constant, k_{c-o} . To confirm these results, plots of *A vs. t* upon irradiation with UV light indicated the decrease of concentration of closed-form with good linearity (linear correlation factors > 0.99) (See Supplementary data).

The kinetic study of compounds 1-10 indicates the

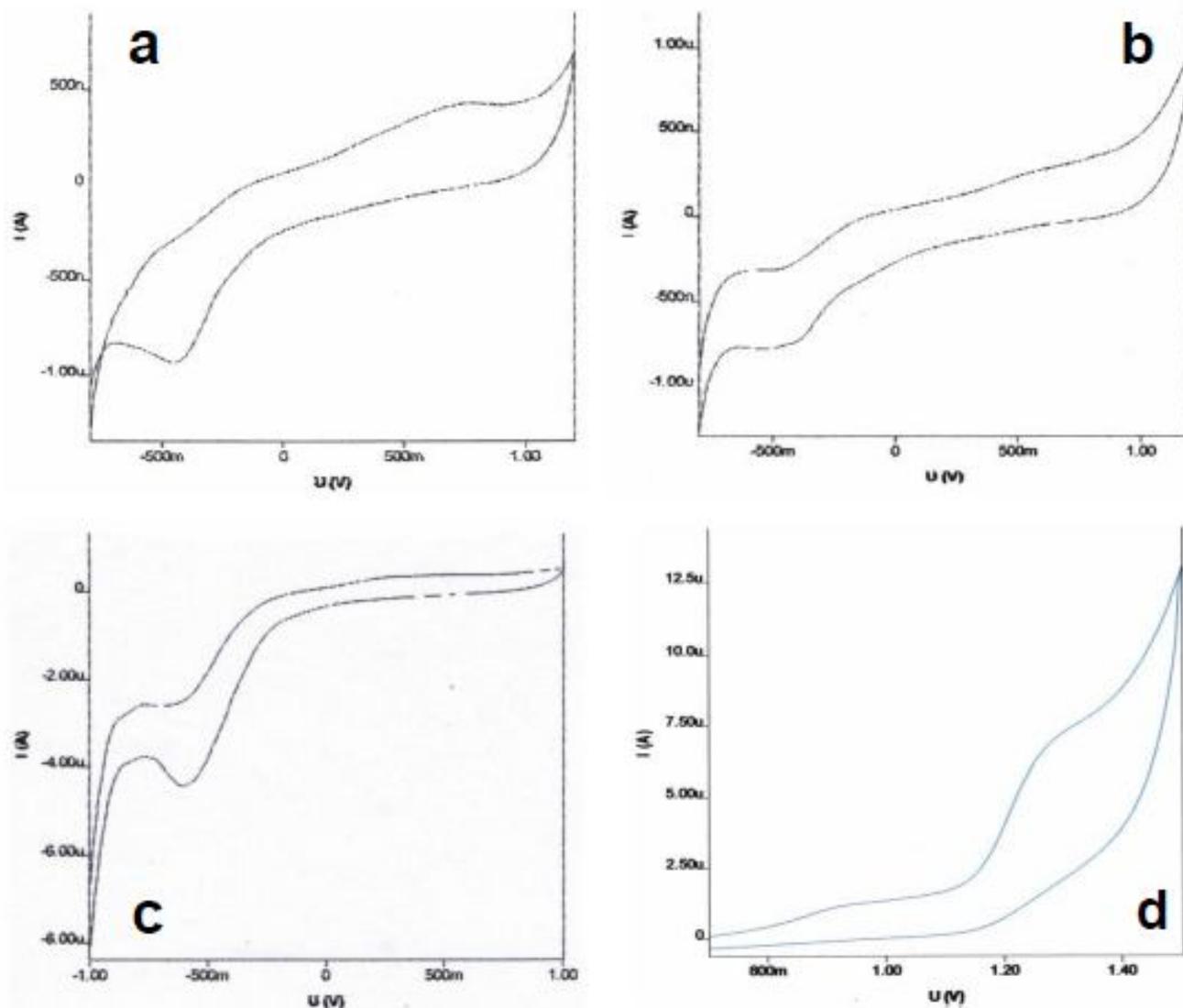
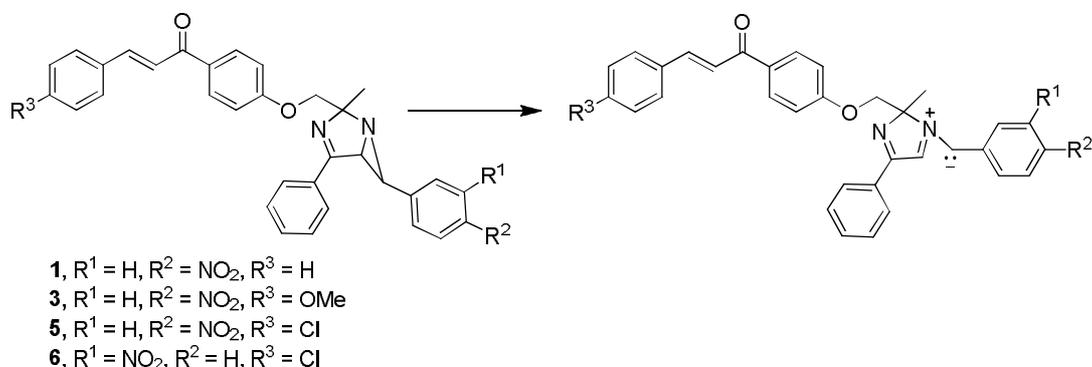


Fig. 3. Cyclic voltammograms of compounds 1, 3, 5 and 6 in CH_3CN : a) 1, b) 3, c) 5 and d) 6.

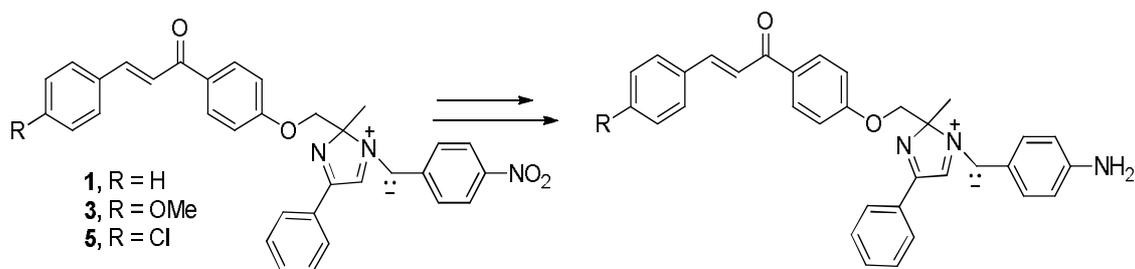
effect of different substituents on the conversion of closed-ring photoisomer. The corresponding values of rate constants are given in Table 3. Among compounds 1-10, compounds with *p*- NO_2 substituent groups in R^2 , compared with *m*- NO_2 groups in R^1 , indicated more rapid cycloreversion. According to Table 3, in compound 9, addition of -OH at the R^4 increases the rate of ring-opening compared to the other compounds. The rate of cycloreversion for compounds 7 and 8 was decreased by replacing H at R^3 with NO_2 .

Electrochemical Study

The investigation of ring opening of bicyclic aziridines was initiated either by UV-light irradiation or by electrochemical oxidation. In this study, the redox potentials of the bicyclic aziridines 1, 3, 5 and 6 are estimated, employing rotating disk electrode (RDE) as a working electrode with saturated calomel electrode (SCE) as reference electrode and Platinum electrode as counter electrode, in CH_3CN . The cyclic voltammograms for



Scheme 3. Oxidation pathway for ring-opening of bicyclic aziridines.



Scheme 4. Electrochemical reduction of bicyclic aziridines

compounds 1, 3, 5 and 6 in CH₃CN are shown in Fig. 3.

Oxidation process attributed to the ring opening of closed-form photoisomer to open-form photoisomer indicated an irreversible oxidation as depicted in Scheme 3. Waves at 0.75, 0.6, 0.29 and 1.27 V are related to the compounds 1, 3, 5 and 6, respectively. They are confirming that the ring conversion processes could be generated by oxidation process too. Oxidation potential for compound 6 as compared to 1, 3 and 5 was higher. This phenomenon indicates that compounds with NO₂ in *para* position in contrast with NO₂ in *meta* position are oxidized more quickly.

Compound 6 shows the irreversible oxidation wave at 1.27 V, while for compounds 1, 3 and 5 on the return cycles a new reduction waves was observed. These new waves are attributed to their corresponding amine groups (Scheme 4). Cyclic voltammograms of isomers of 5 and 6 with *para* and *meta* substituted NO₂ were compared, showing that some peaks have been revealed in region of their irreversible

oxidation at 0.29 and 1.27 V, respectively. The return wave in the voltammogram of 5 appears at -0.44 V owing to the reduction of *p*-nitro group to NH₂. However, similar reduction for *m*-NO₂ of compound 6 was not observed.

CONCLUSIONS

Bicyclic aziridines revealed unique photochromism and solvatochromism behaviors. Kinetic behavior of these compounds with different substitutions on the rate of ring-opening of photoisomers was investigated. Electron donating groups increase the rate of ring-opening of the photoisomer compounds. Electrochromic study of bicyclic aziridines shows an interesting behavior indicating an irreversible oxidation.

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