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Mechanism of hydride abstraction in the electrocyclic phototransformation of heterostilbene

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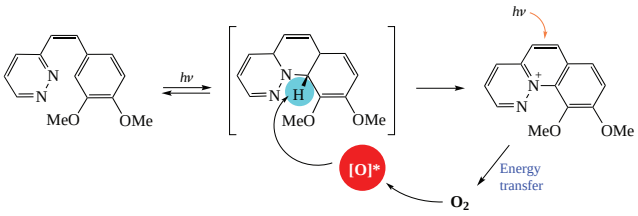
A new mechanism of hydride abstraction in the course of a photochemical electrocyclic reaction of heterostilbene in aqueous solution is reported. The study of electrocyclic transformations of heterostilbenes containing different types of heterocyclic residues revealed that the herein estimated mechanism of hydride abstraction is common for heterostilbene photochemical electrocyclization through the formation of new C–N bond.



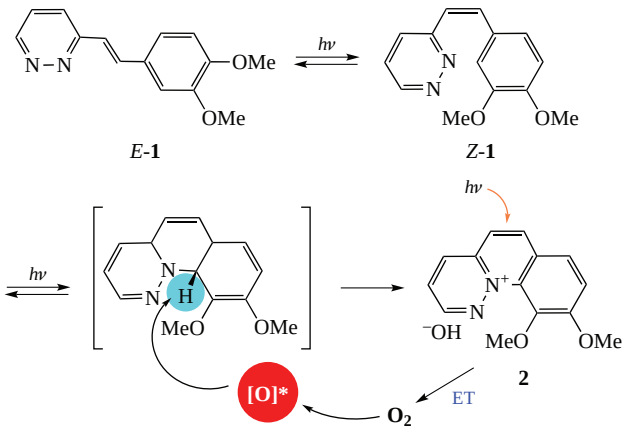
Keywords: heterostilbenes, *E*–*Z*-photoisomerization, electrocyclization, hydride abstraction, regiospecific C–N photocyclization.

Photochemical cyclization of stilbenes and their derivatives is a straightforward strategy for preparing highly diverse phenanthrenes.[1–6] These reactions proceed *via* electrocyclic ring-closure of the *Z*-isomer according to the Woodward–Hoffman rules[7] to form dihydrophenanthrene derivatives, which are highly unstable and either revert back to their *cis*-stilbene form or readily oxidize to the corresponding phenanthrenes. The photocyclizations of stilbenes and related molecules proceed in their lower excited singlet state.[8] The formed unstable product is converted into the phenanthrene derivative in air-saturated solution through the ion-radical reaction involving hydride abstraction by air oxygen. Usually it is advantageous to carry out the photocyclization in the presence of small amounts of iodine additive. The hydride abstraction by iodine is more exothermic than that by oxygen, so the photocyclization in the presence of iodine occurs faster.

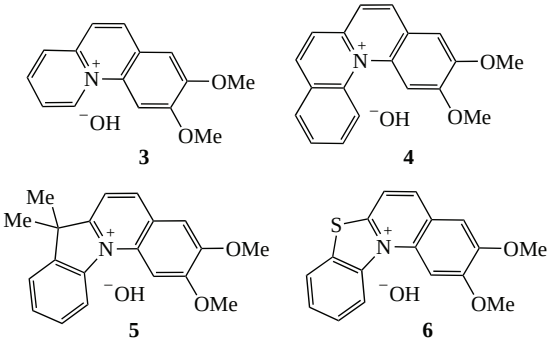
We are developing regiospecific C–N photocyclization of 1-hetaryl-2-phenylethenes resulting in the formation of charged polycyclic heteroaromatics.[9–14] In this reaction, a new C–N bond is formed through the photoinduced electrocyclic ring closure followed by *in situ* oxidation of the resulting hydrobenzo[*c*]-quinolizine intermediate by air oxygen. The process takes place under mild conditions at room temperature, it does not require the use of catalysts and allows one to obtain fused polycyclic cations with good yields. Recently, we have shown that the C–N photocyclization of 2-styrylpyridine[14] and 2-styrylquinolines[9] leads to the efficient and selective formation of benzo[*c*]-quinolizinium derivatives. A lesser known and lesser used variant of this process occurs *via* eliminative mechanism involving the loss of one hydrogen atom from hydrobenzo[*c*]quinolizine derivatives.

In the present work we analyzed the mechanism of hydride abstraction in the photochemical cyclization reaction of heterostilbene derivative *E*-**1** leading to electrocycle **2** (Scheme 1) in aqueous solution (in which the photochemical process is effective). Some results of this study were compared with other reactions giving analogous photochemical products **3**,[14] **4**,[12] **5**[9] and **6**.[10]

Irradiation of compound *E*-**1** in an aqueous solution leads, first of all, to the occurrence of a reversible reaction of *E*–*Z* isomerization (Figure 1). The photoisomerization causes small changes in absorption spectra. More prolong irradiation leads to the remarkable changes in absorption spectra indicating the formation of novel photoproduct **2** (see Figure 1 and Scheme 1).



Scheme 1 *Reagents and conditions*: *E*-**1** ($C = 1 \times 10^{-3}$ M aq.), irradiation, 125 W mercury lamp, 10 min.



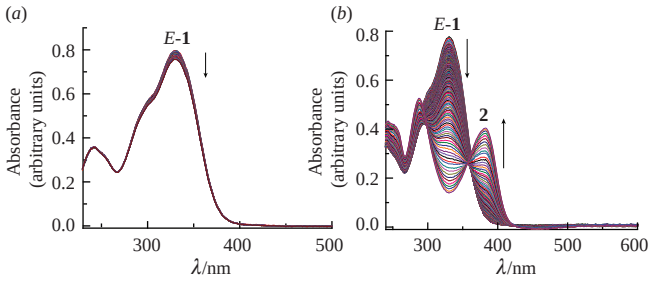


Figure 1 Spectral changes during photolysis of an aqueous solution of *E*-**1** ($C = 3 \times 10^{-5}$ M) after irradiation with a mercury lamp at $\lambda = 365$ nm: (*a*) 0–10 min and (*b*) 0–180 min.

The irradiation of aqueous solutions of compound *E*-**1** with the light of a mercury lamp was carried out under the following conditions: (1) by unfiltered light; (2) by light with $\lambda > 320$ nm and (3) by light with $\lambda = 365$ nm. The monitoring of absorption of reaction mixture was at 380 nm where only electrocyclic product **2** absorbed. It was revealed that the electrocyclization reaction was fully completed in all cases, however the reaction time varied and amounted to 15, 53 and 115 min, respectively (Figure 2). Figure 2 also shows that when irradiation was performed by light with $\lambda > 320$ nm (curves *2* and *3*), the kinetic curve had a section where a gradual accumulation of the product occurred with a further sharp rise and reaching a plateau. This may indicate that the reaction is autocatalytic and the resulting product accelerates its course if it accumulates sufficiently. Based on these results, it would possible to suggest that the electrocyclic product formed in the course of the reaction can be a generator of singlet oxygen, which helps to complete the stage of oxidation of the hydrogenated intermediate. Indeed, the photolysis of compound *E*-**1** in an oxygen-free acetonitrile showed that except *Z*-**1** isomer, no photoproduct was formed.

The generation of singlet oxygen by electrocyclic product **2** was studied by measuring quantum yield according to the reported method.[16] For the measurements a KI trap was used, also we took into account the internal filter from KI_3. The obtained Φ is 5.9% (see Online Supplementary Materials, Figures S1–S5).† The value obtained is not so great that the substance can be used as a photosensitizer, but it is sufficient for it to participate in the generation of singlet oxygen and to act as an autocatalyst for the reaction.

We measured the isomerization and the fluorescence quantum yields of the diazine derivative and its photoproduct (see Online Supplementary Materials, Figures S6–S9 and Table 1).‡ The fluorescence of initial *E*-**1** is insignificant, thus, the photochemical reactions are the main ways of the relaxation of excited state.

Table 1 Optical and photochemical characteristics of compounds *E*-**1** and **2**.

Compound	λ^{abs}_{max}	λ^{fl}_{max} (Φ), $\lambda^{ex} = 390$ nm	$\varphi_{(E-Z)}/\varphi_{(Z-E)}$	φ_{irrev}
1	332	nonfluorescent	0.0054/0.26[a]	0.027[a]
2	383	463 (0.5)	–	–

[a] The quantum yield of the photoreaction was calculated using the program that holds a fourth-order semi-implicit Runge–Kutta numerical integrator. For more details, visit http://pagesperso-orange.fr/cinet.chim/index.html.

Whereas, the fluorescence of compound **2** is high enough, the quantum yield is 50%. The fluorescence proceeds in the lower singlet state and is a concurrent process to the intersystem crossing to triplet state from which the energy transfer (ET) to molecular oxygen occurs. Thus, the high fluorescence of the polynuclear cation **2** is consistent with a low quantum yield of the generation of singlet oxygen. Hence, it can be concluded that irradiating a solution of compound *E*-**1** with the addition of a catalytic amount of product **2** makes it possible to achieve the reaction completion in a shorter period of time. This is useful if the light with $\lambda > 320$ nm is applied to carry out the photochemical transformation. The mild conditions of the photolysis prevent the photodestruction of organic compounds.

Photolysis of an aqueous solution of styryl derivative *E*-**1** with different styryl/photoproduct ratios was carried out by filtered light with $\lambda = 365$ nm (Figure 3, also see Online Supplementary Materials, Figures S10–S15). The best result was achieved at styryl/photoproduct = 31 : 1 ratio, under these conditions the reaction is over up to 65 min *vs.* 115 min when photolysis is carried out without the addition of electrocyclic compound **2**.

We demonstrated that the generation of singlet oxygen or another reactive oxygen species (ROS) is a common characteristic of the electrocyclic products preparing from heterostilbenes containing different heterocyclic part. In Table 2 the measured quantum yields of singlet oxygen generation by compounds **2**–**6** and their yields in the electrocyclic reaction are presented. As one can see from Table 2, the polynuclear products in the electrocyclic reactions are formed with high enough yields which do not depend on ability to singlet oxygen generation. This is because the studied electrocylization is a complicated process ruled by multiple factors.

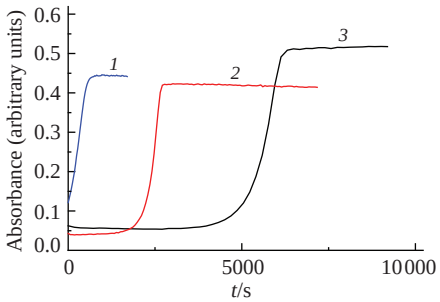


Figure 2 Absorption of photostationary mixture at 380 nm upon irradiation of compound **1** ($C = 3 \times 10^{-5}$ M) with (*1*) full light of a mercury lamp; (*2*) light $\lambda > 320$ nm (filter BS-7) and (*3*) light at 365 nm.

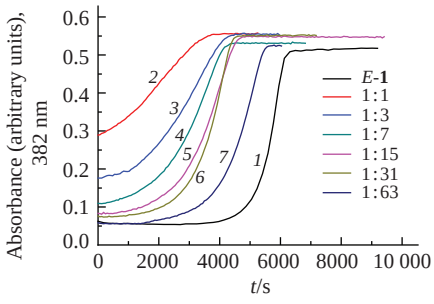


Figure 3 Formation of the photostationary mixture at 382 nm for a styryl/photoproduct mixture (*E*-**1**/**2**) at various ratios. Mercury lamp with filter 365 nm, $C = 3 \times 10^{-5}$ M.

† In the experiments, freshly prepared solutions of standard eosin, compounds **2**–**6** and trap solution KI were used. Irradiation of the solutions was performed on a Fluorolog-3 spectrofluorometer (HORIBA Scientific) with a Xenon lamp 450W as light source. UV spectra were measured using a Cary 300 two-channel spectrophotometer (Varian).

‡ UV-VIS spectra were measured using a Cary 300 two-channel spectrophotometer (Varian). Fluorescence spectra were measured at 20 ± 1 °C on a Cary Eclipse spectrophotometer (Agilent). Coumarin 343 dye in ethanol (quantum yield of fluorescence $\varphi_{fl} = 78.0\%$) was used as a reference for the quantum yield measurements.

Table 2 The chemical yields of polynuclear aromatic products **2**–**6** containing various heterocyclic parts and their efficiency in producing the ROS.

Compound	Φ of singlet oxygen or ROS (%)	Yield of **2**–**6** (%)
2	5.9	60
3	6.7	55
4	2.0	70
5	0.4	88
6	3.5	45

To summarize, the electrocyclic phototransformation of *E*-**1** involves the photoisomerization to *Z*-**1**, cyclization reaction yielding the unstable cyclic product which undergoes hydride abstraction by oxygen to give a polynuclear cationic product **2** (see Scheme 1). As it was mentioned above, the photochemical transformation of stilbenes occurs in their singlet excited state. The triplet excited states of stilbenes exist, but their formation by intersystem crossing is inefficient. The generation of singlet oxygen or ROS should proceed *via* energy transfer (ET) from a higher triplet state of suitable sensitizer molecule. In our case, polynuclear cationic product **2** serves as sensitizer for producing ROS. This mechanism of hydride abstraction in the course of photochemical electrocyclic reaction of heterostilbenes explains the effective occurrence of oxidative cyclization of heterostilbenes under native conditions. The study of electrocylic transformations with participation of heterostilbenes containing different types of heterocyclic residues revealed that the estimated here mechanism of hydride abstraction is common for heterostilbene photochemical electrocyclization through the formation of new C–N bond.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.027.

References

1 J. Grimshaw and A. P. de Silva, *Chem. Soc. Rev.*, 1981, **10**, 181.
2 F. B. Mallory, C. S. Wood and J. T. Gordon, *J. Am. Chem. Soc.*, 1964, **86**, 3094.
3 D. H. Waldeck, *Chem. Rev.*, 1991, **91**, 415.
4 W. H. Laarhoven, *Pure Appl. Chem.*, 1984, **56**, 1225.
5 H. Meier, *Angew. Chem., Int. Ed.*, 1992, **31**, 1399.
6 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
7 R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**, 395.
8 F. B. Mallory and C. W. Mellory, in *Organic Reactions*, Wiley, New York, 1984, vol. 30, ch. 1.
9 O. A. Fedorova, Yu. V. Fedorov, E. N. Andryukhina, S. P. Gromov, M. V. Alfimov and R. Lapouyade, *Org. Lett.*, 2003, **5**, 4533.
10 O. A. Fedorova, E. N. Gulakova, Yu. V. Fedorov, I. E. Lobazova, M. V. Alfimov and G. Jonusauskas, *J. Photochem. Photobiol., A*, 2008, **196**, 239.
11 D. Berdnikova, O. Fedorova, E. Gulakova and H. Ihmels, *Chem. Commun.*, 2012, **48**, 4603.
12 E. N. Gulakova, D. V. Berdnikova, T. M. Aliyeu, Y. V. Fedorov, I. A. Godovikov and O. A. Fedorova, *J. Org. Chem.*, 2014, **79**, 5533.
13 Yu. V. Fedorov, S. V. Tkachenko, E. Yu. Chernikova, I. A. Godovikov, O. A. Fedorova and L. Isaacs, *Chem. Commun.*, 2015, **51**, 1349.
14 D. V. Berdnikova, T. M. Aliyeu, T. Paululat, Yu. V. Fedorov, O. A. Fedorova and H. Ihmels, *Chem. Commun.*, 2015, **51**, 4906.
15 G. M. J. Schmidt, *J. Pure Appl. Chem.*, 1971, **27**, 647.
16 J. Černý, M. Karásková, J. Rakušan and S. Nešpůrek, *J. Photochem. Photobiol., A*, 2010, **210**, 82.

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