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ARTICLE

Photocyclization of diarylethenes: the effect of imidazole on the oxidative photodegradation process

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We have studied the photoreaction of 1,2-diarylethenes under aerobic conditions in the presence of various amines to prevent side processes promoted by singlet oxygen. It has been found that the most amines quite effectively deactivate processes associated with singlet oxygen, but primary and secondary amines unlike tertiary ones, react with substrates resulting in various side products. Among the studied amines, the most effective additive for preventing side processes, including those associated with singlet oxygen is imidazole, which is practically not consumed in photoreaction. It was shown that imidazole can also prevents the photodegradation of organic photochromes in solutions. The results obtained can be used in various branches of science, technology and medicine to improve the photostability of photosensitive organics (dyes).

Introduction

Photochemical transformations are of great interest, both for fundamental research and practical applications.[1,2] They are widely investigated for the development of advanced technologies and materials for various fields of science, technology and medicine.[1,3,4] However, one of the main limiting factors in the widespread practical application of photochemical reactions remains the need to carry out these processes under anaerobic conditions to prevent the formation of singlet oxygen and many side processes associated with it.[5] Aerobic conditions promote the generation of singlet oxygen under UV irradiation in the presence of various sensitizers.[6] In most cases, photosensitive substances involved in photochemical transformations themselves act as photosensitizers to generate singlet oxygen.[7,8] For this reason, the exclusion of the formation of singlet oxygen becomes very complicated. One of the solutions to this issue is the exclusion of singlet oxygen formation in photochemical processes by removing oxygen from the reaction mixture under inert conditions and it, in turn, imposes additional restrictions on the carrying out of photochemical reactions.

Another way to prevent the occurrence of side processes promoted by singlet oxygen is its deactivation (physical quenching or chemical binding) by various substances, including organic compounds (tertiary amines, phenols, sulfides, disulfides, nitrogen heterocycles, etc.).[9]

Our interest in the issue of prevention of side processes associated with singlet oxygen arose in connection with the study of the photorearrangement reaction of 1,2-diarylethenes **I**, leading to the formation of polyaromatic systems and, first of all, naphthalene derivatives **II** (Scheme 1A).[10] We have found that under photoirradiation, the diarylethenes containing a benzene and five-membered heterocyclic residues undergo cyclization with the further sigmatropic rearrangement and opening of the heterocyclic ring.[11,12] However, a more detailed study of this process showed that depending on the reaction conditions, especially in scaling up to the gram level (in preparative reactions), a side reaction may occur. This transformation includes the interaction of the heterocyclic moiety (oxazole ring) with the singlet oxygen resulting to the triacylamines **III** after a number of rearrangements (Scheme 1B).[13]

Scheme 1B shows the mechanism of formation of triacylamine **III** by the reaction of singlet oxygen (formed via photosensitization with diarylethene triplet[7]) with an oxazole residue. In the first, [4+2]-cycloaddition takes place, followed by triacylamine formation after a number of skeletal rearrangements, including a Bayer-Villiger reaction. In this transformation, not only diarylethenes based on oxazole, but also with other heterocyclic residues (imidazole, thiazole, furan, thiophene, etc.) may react.[14] In [4+2]-cycloadditions five-membered heterocycles act as the diene, and the singlet oxygen as the dienophile. Further transformations are dictated by the nature of the heterocyclic residue, in some cases the reaction is accompanied by the opening of the heterocycle, for example azoles,[15] or without opening (furan and thiophene).[16]

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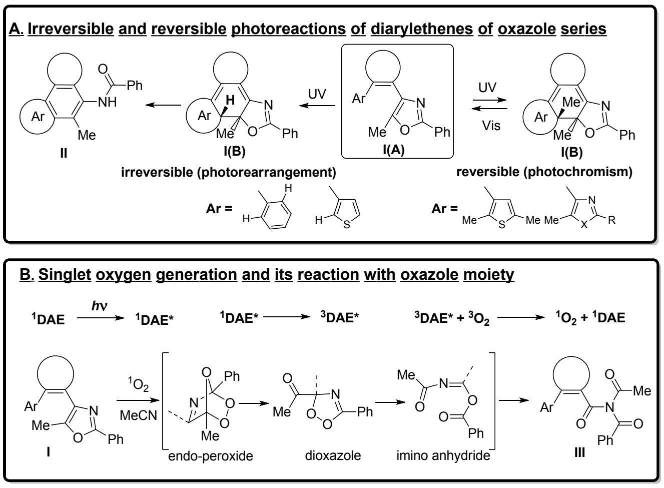

Scheme 1 Photoreactions of diarylethenes of oxazole series.

Another area where it is necessary to take into account the influence of singlet oxygen is the photoswitching of diarylethenes (photochromic properties of diarylethenes).[17] This aspect for diarylethenes, unlike spiropyrans[18] and spirooxazine[19] has been studied poorly and the moreover a systematic study have not performed. Nevertheless several groups have noted that distinct diarylethene derivatives show different types of photochemical side reactions associated with air oxygen. In particular, formation of the DAE oxidative products in the presence of oxygen (in the air) including the oxidation of thiophene ring[20] and the insertion of an oxygen atom between the ethene linker and the aryl residue[21] has been reported. In addition, Hecht and et al. have detected the by-products with a mass $(M+16)^+$ and $(M+32)^+$ upon irradiation DAE solution in the presence of oxygen by UV-light.[22]

Thus, the analysis of the literature has showed that in both reversible and irreversible photochemical reactions of diarylethenes singlet oxygen plays a negative role and favors the formation of undesirable oxidative side products. At the same time, the irreversible photocyclization of diarylethenes is widely used for the synthesis of various polyaromatic compounds including helicenes, graphenes, fluorophores, etc., and photochromic diarylethenes are actively explored to develop new smart materials for optoelectronics and photonics. In this context, it is very important to develop a general concept for the prevention of oxidative side processes promoted by singlet oxygen in the irreversible and photochromic transformations of diarylethenes.

The present work provides important insights on the role of singlet oxygen in the photochemical transformation of diarylethenes and on the protection of organic photochromes from oxidative photodegradation.

Experimental section

General information

Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded in deuterated solvents on a spectrometers working at 300 MHz for ^{1}H, 75 MHz for ^{13}C. Data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; m, multiplet; br, broad), coupling constant in hertz (Hz), integration, and assignment. Mass spectra were obtained on a mass spectrometer (70 eV) with direct sample injection into the ion source. High resolution mass spectra were obtained from a TOF mass spectrometer with an ESI source. All chemicals and solvents were purchased from commercial sources and used without further purification. Silica column chromatography was performed using silica gel 60 (70–230 mesh); TLC analysis was conducted on silica gel 60 F_{254} plates.

Synthesis. Diarylethenes **1a**[11] / **1b**[10] and spiropyranes **7** / **8**[23] were prepared according previously reported methods.

Spectral studies

Absorption spectra and kinetic curves were recorded using an “Agilent 8453” diode array spectrophotometer supplied with a thermostated cell holder. The temperature of solutions was kept at 293 ± 0.2 K. Solutions (2 ml) were stirred in the four-windowed 10×10 cm quartz cell with a magnetic bar driven by a speed controlled motor. Setup consisting of the 200 W Hg Research Arc Source "Newport 66902", liquid IR filter, set of optical bandpass filters and UV-VIS Liquid Light Guide (300-650 nm) from Newport Corp. was used as a light source. The light was brought with Liquid Light Guide to the cell compartment at the right angle to the probe beam of the spectrometer. The monochromatic light intensity at 365 nm was determined to be $7.4\cdot10^{-6}$ $mol\cdot L^{-1}s^{-1}$ using an "Newport Power Meter 2903-C".

Preparative photoreactions

Irradiation of diarylethenes were carried out in 3 ml (d = 5 mm) or 10 ml (d = 10 mm) flat-bottomed vessels from common glass (for analysis of their transparency, see Supporting information in work[11]). The irradiation was carried out by two 8 W UV lamp (365 nm).

Solvent, photosensitizer and amine effect studies

General. Glass vessel (3 ml) was charged by solution of diarylethene **1** (40 mg) in 2 ml of appropriate solvent (if necessary, appropriate photosensitizer or amine were added). The reaction mixture was irradiated by UV (2 lamps, 365 nm, 8 W) without stirring at ambient temperature. Reactions were controlled by TLC, after completion the reaction mixture was poured into water (100 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with water (100 mL), dried with magnesium sulfate, and evaporated in vacuum. The residues were analyzed by ^{1}H NMR spectroscopy in DMSO-d_6 solutions (for copies of these spectra see Sections I, III, IV, V in ESI).

Photosensitizer effect studies

0.1 equivalent of each photosensitizer was added (see Table S1 in Section III of ESI).

Amine effect studies

Diarylethene **1a** was irradiated in the presence of 1 eq. (16 mg) of naphthalene (1 eq.) and 1 eq. of appropriate amine (see Section IV in ESI).

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Synthesis and characterization of new compounds

Synthesis of triacylamines 3

Diarylethene **1a** or **1b** (100 mg, 0.32 mmol) was dissolved in 5 ml of acetone and naphthalene (41 mg, 0.32 mmol) was added. The solution was irradiated until completion of reaction (TLC control). The resulting mixture was purified by column chromatography on silica gel to give target triacylamines **3** as labile amorphous powder.

***N*-Acetyl-*N*-benzoyl-5-oxo-4-phenyl-2,5-dihydrofuran-3-carboxamide (3a).** Yield 11%. Yellow amorphous powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H, CH_3), 5.14 (s, 2H, CH_2), 7.18 (d, J = 7.9 Hz, 2H, H^{arom}), 7.23 (d, J = 7.7 Hz, 2H, H^{arom}), 7.26-7.29 (m, 1H, H^{arom}), 7.39-7.44 (m, 3H, H^{arom}), 7.47-7.53 (m, 2H, H^{arom}). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.35 (s, 3H, CH_3), 5.23 (s, 2H, CH_2), 7.38-7.53 (m, 9H, H^{arom}), 7.62-7.71 (m, 1H, H^{arom}). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 25.7, 70.2, 128.4, 129.0 (2C), 129.3 (2C), 129.6 (2C), 129.8 (2C), 129.9, 130.5, 131.9, 135.3, 151.6, 166.0, 171.2, 172.0, 172.3. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{20}H_{15}NO_5$: 350.1023; Found: 350.1018. MS (EI): m/z (%) = 349 (16) [M]+, 307 (69), 105 (100), 77 (27), 43 (19), 18 (15).

***N*-Acetyl-*N*-(3-oxo-2-phenylcyclopent-1-enecarbonyl)benzamide (3b).** Yield 27%. Yellow amorphous powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H, CH_3), 2.66-2.69 (m, 2H, CH_2), 3.04-3.05 (m, 2H, CH_2), 7.08 (d, J = 7.6 Hz, 2H, H^{arom}), 7.19-7.24 (m, 3H, H^{arom}), 7.35-7.51 (m, 5H, H^{arom}). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.39 (s, 3H, CH_3), 2.60-2.65 (m, 2H, CH_2), 2.87-2.95 (m, 2H, CH_2), 7.18-7.25 (m, 2H, H^{arom}), 7.28-7.46 (m, 7H, H^{arom}), 7.60-7.67 (m, 1H, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.7, 27.9, 34.6, 128.5, 128.7 (4C), 128.8 (2C), 129.2 (2C), 129.8, 131.9, 134.0, 140.4, 161.5, 170.4, 172.0, 172.7, 205.9. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{21}H_{17}NO_4$: 348.1230; Found: 348.1217. MS (EI): m/z (%) = 305 (13) [M-CH_3C(O)+H], 128 (25), 115 (42), 105 (100), 77 (61), 43 (59).

Diarylethenes **4-6** were prepared according to a previously reported method[24] from corresponding hetarylacetic acid and bromoketone.

3-(2,5-Dimethylthiophen-3-yl)-4-(5-methyl-2-phenyloxazol-4-yl)furan-2(5*H*)-one (4). Pale yellow powder, mp = 146-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 5.27 (s, 3H, CH_2), 6.71 (s, 1H, $H^{thiophene}$), 7.43-7.55 (m, 3H, H^{arom}), 7.94-8.10 (m, 2H, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.2, 14.3, 15.2, 71.0, 121.3, 126.2 (2C), 126.6 (2C), 127.1, 128.9 (2C), 129.3, 130.7, 136.7, 136.9, 149.8 (2C), 160.8, 173.4. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{20}H_{17}NO_3S$: 352.1002; Found: 352.0999.

4-(2,4-Dimethyloxazol-5-yl)-3-(2,5-dimethylthiophen-3-yl)furan-2(5*H*)-one (5). Gray powder, mp = 98-100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 5.14 (s, 2H, CH_2), 6.65 (s, 1H, $H^{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.5, 13.9, 14.1, 15.1, 69.1, 119.7, 126.6, 136.4, 137.1, 139.0, 140.6, 143.7, 163.0, 172.6, 174.1. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{15}H_{15}NO_3S$: 290.0845; Found: 290.0838.

4-(2,4-Dimethyloxazol-5-yl)-3-(2,5-dimethylthiophen-3-yl)furan-2(5*H*)-one (6). Pale yellow powder, mp = 189-190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08 (s, 3H, CH_3), 2.40 (s, 6H, CH_3), 5.15 (s, 2H, CH_2), 6.58 (s, 1H, $H^{thiophene}$), 7.35-7.50 (m, 3H, H^{arom}), 7.90-8.01 (m, 2H, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9, 15.1, 16.6, 71.7, 118.0, 120.5, 124.2, 126.4 (2C), 128.0, 128.9 (2C), 130.2, 133.3, 138.4, 139.2, 153.2, 154.8, 168.4, 172.6. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{20}H_{17}NO_2S_2$: 368.0773; Found: 368.0766.

Results and Discussion

Solvent effect

Studies on competition between photorearrangement and interaction with singlet oxygen were carried out on model diarylethenes based on furanone and cyclopentenone derivatives **1a**[11] and **1b**,[10] which were obtained previously in our group (Scheme 2). The choice of these model compounds was dictated by their electron-withdrawing bridges, which accelerate hydrogen migration during photorearrangement.[25] The irradiation of **1** in various solvents by UV light (λ = 365 nm) leads in most cases to the formation of two products: a major product from photoinduced rearrangement **2a,b**[10,11] and a minor product from [4+2]-cycloaddition of an oxazole moiety with singlet oxygen **3a,b** (Scheme 2 and Table 1). The structures of compounds **3a,b** have been proved by ^{1}H, ^{13}C NMR spectroscopy and mass spectrometry, and they are well correlated with literature data.[13] As can be seen from Table 1, in the majority of the solvents studied, the photorearrangement reaction of furanone derivative **1a** proceeds in good yields, while for diarylcyclopentenone **1b**, the yields of triacylamine **3b** are in many cases significantly higher (for copies of NMR spectra see section I in ESI). As noted above, in these reactions diarylethenes act as a photosensitizer, generating singlet oxygen, consequently the formation of triacylamine **3** also depends on the photochemical characteristics of the substrate.

In the case of the cyclopentenone derivative, not only an increase in the formation of triacylamine (ethyl acetate, acetonitrile, toluene, acetone and methylene chloride) is observed, but the prolonged irradiation is required for complete conversion. Especially high yields of **3b** were observed in toluene and acetonitrile, 25 and 31%, respectively.

Scheme 1 Photochemical transformations of diarylethenes bearing benzene and oxazole units.

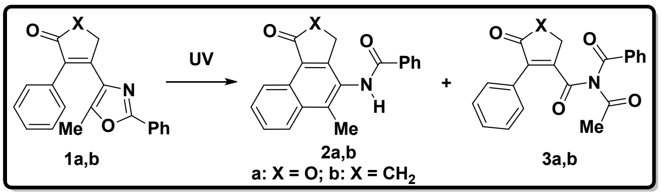

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Table 1 Solvent optimization of the photorearrangement reaction.[a]

	Solvent	Time (h)	Yields[b] for furan-2(5*H*)-ones			Time (h)	Yields[b] for cyclopentenones		
			2a	**3a**	Other by-products		**2b**	**3b**	Other by-products
1	MeCN	10	87	12	<1	17	56	31	13
2	MeCN + imidazole	5	99	0	0	25	99	0	0
3	DMF	3	97	3	0	5	81	19	0
4	NMP	13	99	0	0	5	99	0	0
5	CH_2Cl_2	7	95	5	0	16	80	0	20
6	$CHCl_3$	10	93	7	0	5	76	10	14
7	Acetone	13	86	13	<1	17	72	15	13
8	Acetone + naphthalene	17	70	30	0	13	35	37	28
9	EtOH	9	96	3	<1	17	65	9	26
10	EtOAc	6	88	10	<1	8	34	23	43
11	EtOAc + imidazole	-	-	-	-	25	99	0	0
12	CH_3NO_2	17	80	5	15	17	67	16	17
13	Toluene	26	75	8	17	27	55	25	20

a Typical procedure: solution of **2** (40 mg) in 2 ml of solvent was irradiated by 2 UV lamps (365 nm, 8W) until full conversion of **2**. After common work-up procedure, the residues were analyzed by 1H NMR spectroscopy.

b Yields were determined by 1H NMR spectroscopy.

The best yields of the desired photorearrangement products for both substrates (compounds **2a,b**) have been obtained in *N*-methyl-2-pyrrolidone (entry 4 in Table 1), where the formation of side products, including triacylamine was not observed. The nature of the solvent also affects the photoreaction time. However, the reaction time is not a relevant parameter for this process, since it also depends on many other factors such as concentration, loading, solubility, etc. Nevertheless, we have found that in nonpolar solvents the reaction slows down significantly. In particular, in DMF, the reaction requires 3 hours, whereas in toluene under otherwise identical conditions requires 26 h for competition. In addition, in the case of the cyclopentenone, the formation of other by-products is observed in most solvents. We were unable to establish the structure of these compounds due to the formation of a complex mixture of hard-to-separate substances. In ethyl acetate and ethanol, the yields of unestablished by-products are significantly higher than those of triacylamine **3b**. For this reason, further studies on the prevention of side processes associated with singlet oxygen by amines were carried out only for the furanone derivative **1a**.

Amine effect.

The study to prevent the formation of by-products associated with singlet oxygen was carried out in acetone in the presence of various amines. To more accurately assess the efficiency of amines, the photocyclization of diarylethene **1a** in the presence of an additional sensitizer (naphthalene) has been studied as a model reaction. It is well known that aromatic hydrocarbons (naphthalene, anthracene, phenanthrene, biphenyl, etc.) are good photosensitizers and are capable of generating singlet oxygen upon UV irradiation.[26,27] We have studied the photocyclization of diarylethene **1a** in the presence of various photosensitizers and found that among them, naphthalene more effectively sensitized the generation of singlet oxygen and the yields of triacylamine were 30% (see section III in ESI). In addition, the choice of naphthalene was dictated by another factor. Signals of protons of naphthalene in the ^{1}H NMR spectrum are observed in the form of two multiplets in the range of 7.51 and 7.91 ppm and they are not overlapped by signals of the photoreaction product. It should be noted that, without naphthalene, the yields of triacylamine in acetone did not exceed 13% (Table 1, entry 6).

For the neutralization of singlet oxygen and prevent the formation of a side process - [4+2]-cycloaddition, we have investigated the effect of various commercially available amines on the photorearrangment process (Table 2). In all cases, equimolar amounts of amines were used to prevent the formation of triacylamine. As can be seen from Table 2, practically all amines except pyridine, in equimolar amounts, completely prevent the formation of triacylamine. And only in the reaction with pyridine is the formation of triacylamine (12%), although to a significant degree less, as compared with the reaction without amines in the presence of naphthalene (30%, entry 7 in Table 1).

The use of secondary and primary amines (entries 1-5 in Table 2) leads to the formation of a mixture of hardly separable products, including the desired product (see ^{1}H NMR spectra of the reaction mixtures in ESI). However, the product of the [4+2]-cycloaddition according to ^{1}H NMR was not observed. Along with quenching of singlet oxygen and the photorearrangement reaction, there are probably other chemical transformations involving amines, which result in its consumption.[28,29,30] In the case of DBU the photorearrangement product, as well as triacylamine were not separable and a complex mixture is formed. Perhaps DBU contributes to the formation of other additional side processes. In the case of triethylamine and, along with the target product, the formation of corresponding *N*-oxide is observed[31] (see table S2 in ESI), which, in particular, is indicative of the chemical quenching of singlet oxygen.

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Table 2 The effect of amines on the yields of photoproducts.[a]

	Amines	Yields		
		2a	**3a**	Other by-products
1	*n*-Butylamine	83	0	17
2	Aniline	99[b]	0	0
		94[c]	6	0
3	Morpholine	73	0	27
4	Piperidine	60	0	40
5	TEMP-H	99	0	0
6	DBU	0	0	99
7	Et_3N	99[b]	0	0
		95[c]	5	0
8	DABCO	99[b]	0	0
		99[c]	0	0
9	Pyridine	88	12	0
10	Imidazole	99[b]	0	0
		99[c]	0	0
11	1-Methylimidazole	99[b]	0	0
		89[c]	10	0

[a] Typical procedure: solution of **2** (40 mg), naphthalene (1 eq.) and amine (1 eq.) in 2 ml of acetone was irradiated by 2 UV lamps (365 nm, 8W) until full conversion of **2**. After common work-up procedure, the residues were analyzed by ^1H NMR spectroscopy.

[b] 1 eq. of amine;

[c] 0.1 eq. of amine.

Unfortunately, isolation of the triethylamine *N*-oxide in its pure form failed. However, in the ^1H NMR spectrum, the proton signals are shifted to a weak field, which indicates the formation of the *N*-oxide.[32] A similar pattern is observed for the DABCO. The observed weak-field shift of NMR signals of the hydrogen atoms of DABCO agrees very well with the literature data.[33] And only in the case of imidazole, the use of even catalytic amounts (0.1 equiv) ensures complete deactivation of singlet oxygen. Thus, it has been found that imidazole is an effective additive to prevent by-products associated with singlet oxygen in the diarylethene synthetic photocyclization reactions. Despite the literature data on the oxidative degradation of imidazole and its derivatives by singlet oxygen,[34] we have failed to fix of the imidazole oxidation products, even when scaling the reaction.

It is very interesting to note that the use of *N*-methylimidazole does not have the same effect as in the case of imidazole. A decrease in the amount of *N*-methylimidazole leads to the appearance of triacylamine **3b**. In addition, there is also a shift in the NMR signals of the hydrogen atom of *N*-methylimidazole in a weak field, like triethylamine and DABCO (see Table S2 in ESI).

The effectiveness of imidazole was also demonstrated using photocyclization of diarylethene **1b** in acetonitrile and ethyl acetate solutions. In these solvents without imidazole, the formation of triacylamine **3b** is observed with yields of 31 and 23%, respectively (entries 1 and 10 in Table1) whereas the addition of imidazole leads to the complete disappearance of this product (entries 2 and 11 in Table 1). Moreover, as seen in the Table, imidazole prevents not only the formation of triacylamine **3b**, but also other by-products (entries 2 and 11 in Table 1). Such behavior of imidazole can be explained by the fact that it quenches not only singlet oxygen, but also (or only) triplet (excited) state of diarylethenes. Indirect confirmation of the formation of the triplet state of diarylethenes in this process is the generation of singlet oxygen. In addition, recently, we have demonstrated the formation of triplet state of diarylethenes in photorearrangement reaction.[25] In the future, a more detailed study by flash photolysis of the excited singlet and triplet states of diarylethenes, as well as their transformations without or in the presence of imidazole under aerobic conditions is planned.

Role of imidazole in the photodegradation process of photochromic compounds.

Having in hand the results on the effectiveness of imidazole in preventing oxidative processes in the photocyclization of diarylethenes we have tested it for other processes. It has been studied the photodegradation of photochromic compounds in the presence of imidazole under aerobic conditions (in the presence of air oxygen). Photochromic compounds belong to a relatively small number of families of organic compounds that undergo photoinduced reversible molecular rearrangements between two states characterized by different spectral parameters.[35] These molecules have a few real and many potential applications.[36] One of the main obstacles to the use of photochromic compounds is still the photodegradation.[37]

There are two main photodegradation pathways for the photochromic compounds (Scheme 3). The first of these is related to the structural features of the photochromic molecule, leading to different rearrangements and, as a result, to a decrease in fatigue resistance. For example, photochromic diarylethenes undergo a monomolecular 1,2-dyotropic rearrangement.[22,38] The second channel includes the interaction of the photochromic molecule with singlet oxygen, which also leads to photodegradation.

Scheme 3 Photochromism of model diarylethenes and spiropyrans.

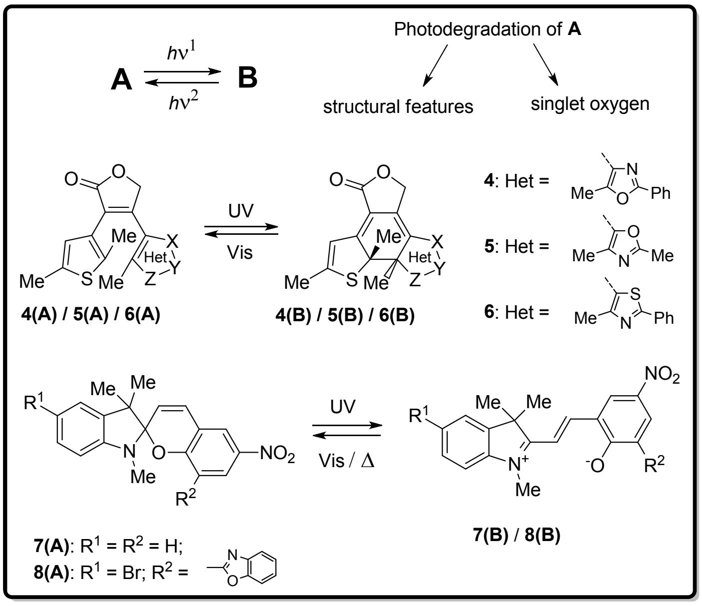

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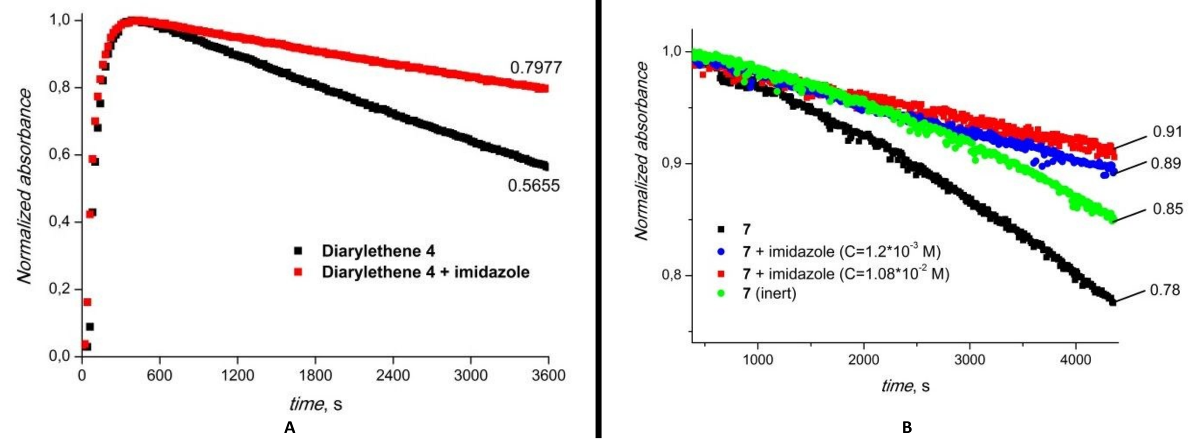
Figure 1.



Dependence of the normalized optical density at the absorption maximum of photoinduced isomer B of DAE 4 on the irradiation time (solvent – CH_3CN, C = 1.4•10^{-5} M, C(imidazole) = 1.03·10^{-3} M, λ^{irr} = 365 nm, T = 293 K).

A

Dependence of the normalized optical density at the absorption maximum 557 nm of merocyanine form B of spiropyran 7 on the irradiation time (solvent – CH_3CN, C = 1.4•10-5 M, λ^{irr} = 365 nm, T = 293 K).

B

To compare the photodegradation of the photochromic compounds in the presence of imidazole, their acetonitrile solutions were investigated under prolonged continuous irradiation similar to the earlier studies.[39] During attainment of the photostationary state of the system its coloration gradually faded and the absorbance at the long wavelength band belonging to the photoinduced isomers decreased. Such spectral behavior is due to irreversible photodestruction of the photochromic system. We have investigated two classes of photochromic compounds: diarylethenes **4 – 6** and spiropyrans **7** and **8** (Scheme 3). The photochromic switching of diarylethenes is based on electrocyclic reaction of a hexatriene system (form **A**) followed by ring-opening of cyclohexadiene system (form **B**).[17a] The photochromism of spiropyrans includes the reversible heterolytic C^{spiro}–O bond cleavage in the cyclic isomer **A** followed by *cis–trans*-isomerization into the metastable merocyanine form **B**.[40]

The photodegradation of photochromic diarylethene **4** (Figure 1A) and spiropyran **7** (Figure 1B) has been studied in solution in the presence of oxygen (in the air) with and without imidazole. For the spiropyran **7** has also been performed additional experiment: the photodegradation has been carried out under inert conditions (argon). The results obtained indicate that imidazole very effectively prevents photodegradation of these photochromic compounds. It was found that the stability of the photochromes depends on the imidazole concentration, the higher it is, the higher the stability. Similar results have been obtained for diarylethenes **5, 6** and spiropyran **8** (see section VII in ESI). The partial photodegradation of these compounds is likely due to the structural features of these photochromic molecules.

Conclusions

Thus, the photocyclization of 1,2-diarylethenes under aerobic conditions in the presence of various amines has been studied to prevent side processes promoted by singlet oxygen. It has been found that most amines effectively quench singlet oxygen, but primary and secondary amines, unlike tertiary ones, react with substrates leading to various by-products. Comprehensive studies have shown that the most effective quencher of singlet oxygen is imidazole, which is practically not consumed in the process of photoreaction. It was shown that imidazole also prevents the photodegradation of photochromic diarylethenes and spiropyrans in solution. An important achievement of this work is the possibility of carrying out photochemical transformations in the presence of oxygen (in the air) without fear of the harmful effect of singlet oxygen.

Conflicts of interest

There are no conflicts to declare.

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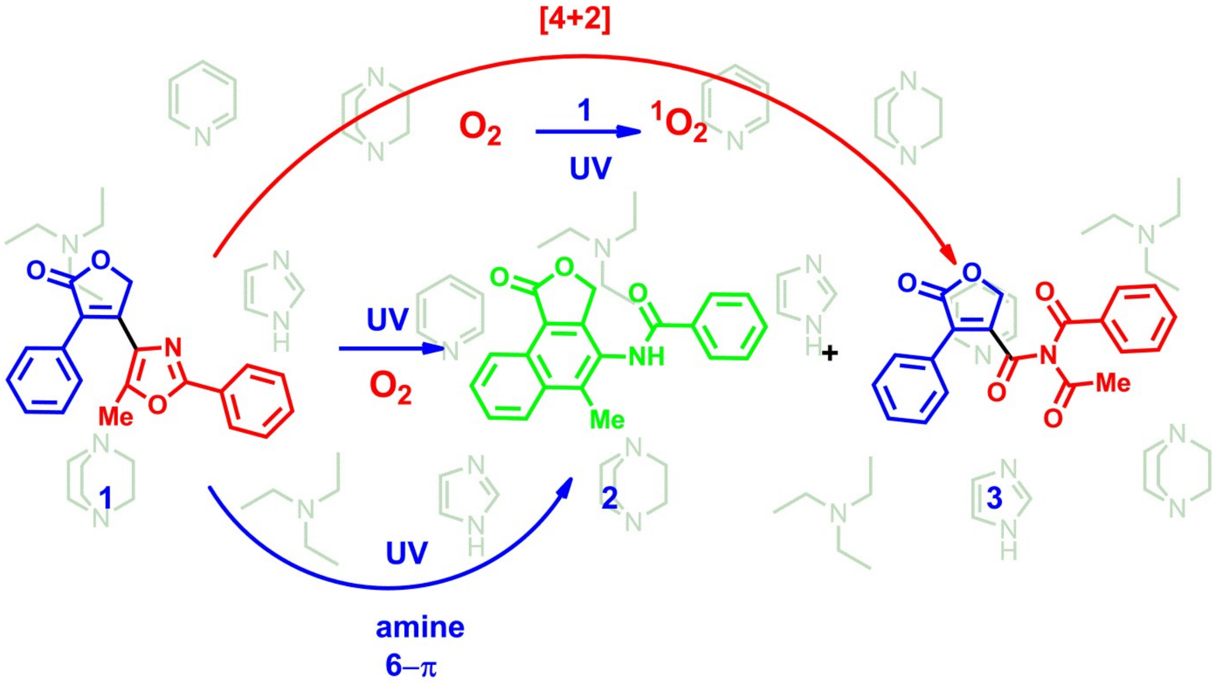

It was found that imidazole prevents the side process of diarylethenes photocyclization and the photodegradation of photochromic compounds.