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General Photoinduced Sequential Electrocyclization/[1,9]-Sigmatropic Rearrangement/Ring-Opening Reaction of Diarylethenes

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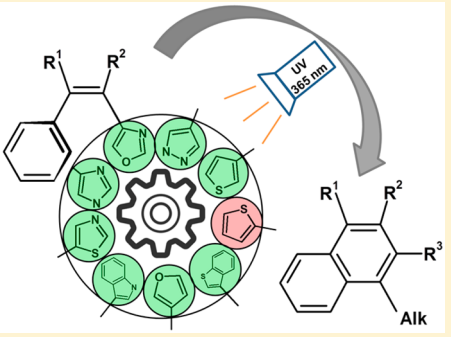
Supporting Information

ABSTRACT: A novel and efficient photochemical transformation of diarylethenes comprising a five-membered heterocyclic ring and phenyl moiety is described. This reaction provides a simple method for the preparation of functionalized naphthalene derivatives via photorearrangement reaction of diarylethenes, and the process is characterized by high efficiency that was determined by NMR monitoring. Some mechanistic aspects of this process have been also explored. It was found that the reaction includes tandem transformation of three basic processes: the photocyclization of the hexatriene system, [1,9]-sigmatropic rearrangement, and heterocyclic ring opening. Diarylethenes with different heterocycle moieties (thiophene, benzo[*b*]thiophene, furan, indole, imidazole, thiazole, oxazole, pyrazole) have been involved into this process, and the target naphthalenes with good yields have been obtained. The opportunity for use in the transformation of diarylethenes with different heterocyclic residues permits synthesis of naphthalenes with desired functional groups. The general character and high efficiency of the reaction promise that the transformation can be an effective synthetic route for the annulation of benzene rings to various aromatic systems, including heterocycles.



INTRODUCTION

Photochemical transformations have long ceased to represent only a fundamental interest and are now actively used for the synthesis of a various classes of organic compounds that are difficult to achieve by conventional chemical methods.[1−3] However, these reactions are underutilized in the development of novel scaffolds for medicines, technology, and material chemistry, although they can provide access to products with rich structural complexity and stereochemical diversity. Among the photochemical reactions, the photocyclization of stilbenes (diarylethenes) is a subject of long-standing interest.[4−6] This reaction has been known for more than 50 years, and different physical and chemical features have been also explored (Scheme 1).[5−7] The photocyclization of stilbenes (diarylethenes) provides convenient access to novel polyaromatic systems, and their heterocyclic derivatives have a significant interest as photochromic compounds, which for the past decades have been widely studied in the development of data storage devices and molecular switches.[8]

The first step of this reaction involves the formation of cyclohexadiene derivatives **II** by a 6π-electrocyclic reaction. The subsequent transformations of the resulting intermediate **II** depend strongly on the nature of substituents R^1 and R^2. When both substituents are alkyl or aryl, such compounds typically exhibit photochromic properties in which the photoinduced form is thermally metastable.[8] Such diarylethenes are chemically inert and do not represent an interest for photochemical organic synthesis. However, the reactivity of compounds **II** varies drastically if at least one of these substituents is hydrogen. Several of their chemical transformations that proceed through an aromatization stage of the cyclohexadiene system of molecule **II** have been described over the past decades. Among them, it should be noted that the oxidation and elimination reactions result in the same products, phenanthrene derivatives or relative polyaromatic systems. In addition, a number of skeletal rearrangement reactions of the molecule **II** have also been reported, leading to polyaromatic systems with different substituents. Thus, the cyclization of stilbenes (diarylethenes) can lead to the formation of the polycyclic systems both with the same number (route 1, Scheme 1) or more than one aromatic ring (route 2), depending on the nature of the substituents (R^1 and R^2) and structure core.

Photocyclization followed by oxidation or elimination has become a respected synthetic protocol for the preparation of phenanthrenes or analogues thereof.[5,6] When the substituents at C^1 and C^2 are hydrogen atoms, the aromatization of intermediate **II** occurs in the presence of oxidants (O_2, I_2). In the event that one of the substituents is a hydrogen atom, or

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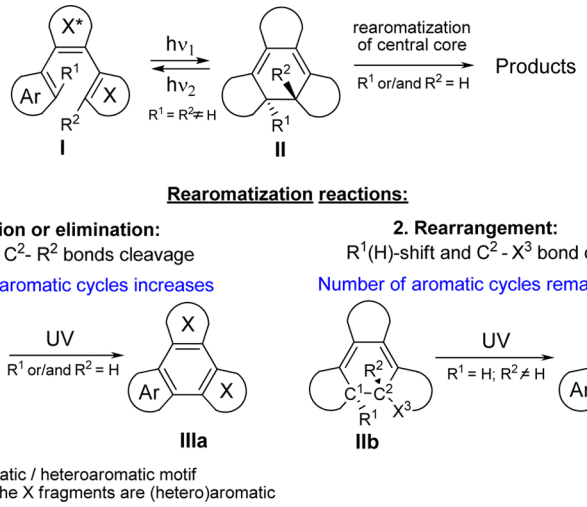
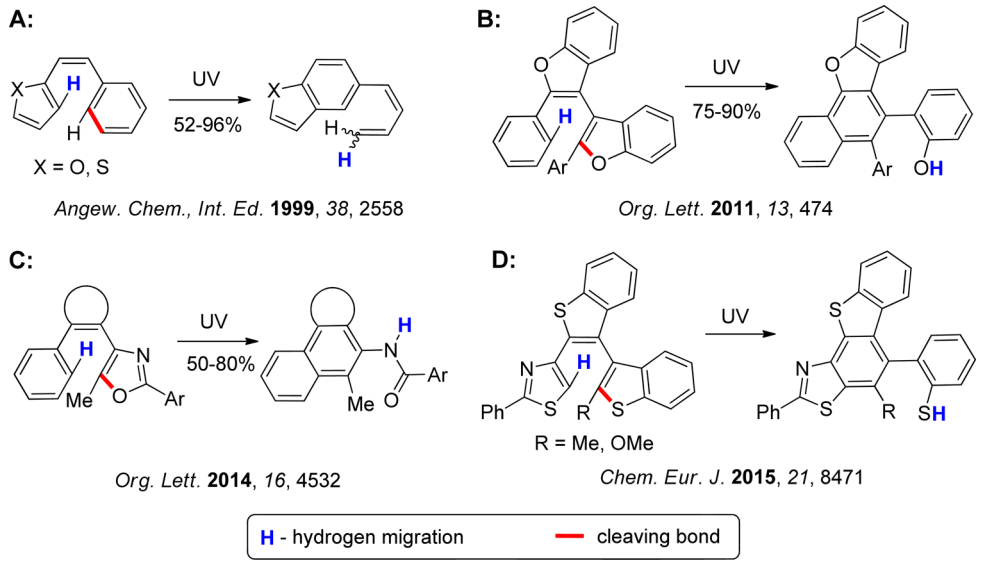
Scheme 1. Photochemical Transformations of Stilbenes/Diarylethenes



Scheme 2. Family of Diarylethene Photorearrangements



the other is halogen or a methoxy group, etc., the aromatization process occurs via the elimination reaction (leaving groups, HHal, MeOH). These methods are widely used in practice for the preparation of polyarenes,[9] including biologically active compounds,[10] organic semiconductors,[11] fluorophores,[12] DNA intercalators,[13] and for the photogeneration of acid agents.[14]

When the above processes are not possible, and one of the substituents is hydrogen, the aromatization of the central core can proceed via sigmatropic rearrangement involving of C^2–X^3 bond cleavage (Scheme 1). This leads to the formation of polyaromatic hydrocarbons through the formal ring opening of one of the aromatic residues, and to date, in contrast to the oxidation or elimination protocol, only a few random examples have been described (Scheme 2). To the best of our knowledge, the first type of this reaction was described for styrylfurans and styrylthiophenes (reaction A, Scheme 2), the photorearrangement of which results in benzofurans and benzothiophenes, respectively.[15] In the continuation of these works, authors have studied the photoreaction of styrylfurans in the presence of acids[16] and bases.[17] Rearrangement of 3,3′-bis(arylbenzofurans) resulting in benzofuran-annulated naphthalenes in high yields has also been reported[18] (reaction B in Scheme 2; synthetic protocols A and B were performed under an inert conditions). Recently, in the course of our studies directed toward the synthesis and the investigation of spectral properties of photochromic diarylethenes,[19] we have found a photoinduced rearrangement of diarylethenes comprising benzene and oxazole derivatives as aryl moieties, the UV irradiation of which results in functionalized naphthalenes with medium to high yields (reaction C in Scheme 2).[20] An important feature of this transformation is its amenability to scale up (scalable process) and enables one to carry out the reaction at the high concentrations and in the presence of oxygen. Finally, more recently, Kawai et al. have published the photorearrangement of diarylethenes, where their tandem photocyclization and thiophene ring-opening processes led to the formation of benzothiazole derivatives (reaction D in Scheme 2).[21] The high yields of the reaction have been demonstrated by ^{1}H NMR monitoring.

The foregoing examples indicate that all of these reactions include tandem photocyclization/sigmatropic rearrangement/ring-opening processes (Scheme 2). The reaction begins by

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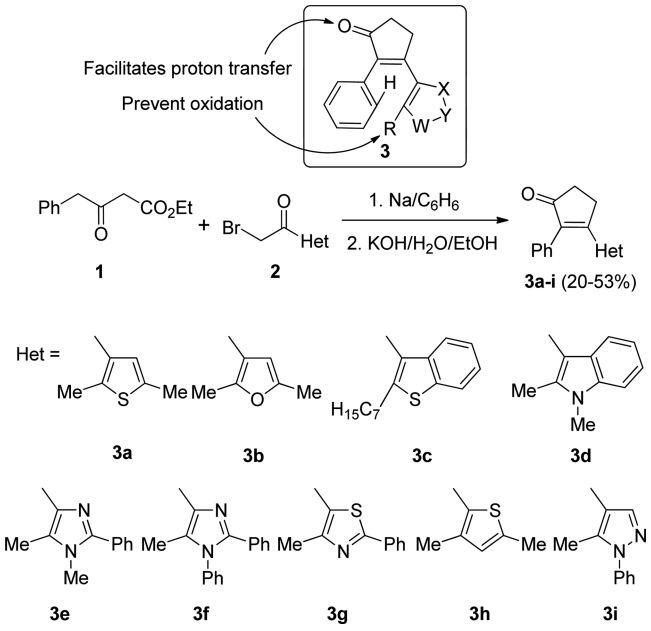
photocyclization of a hexatriene system, followed by H-shift, and the opening of a lateral heterocyclic moiety. The sequence of these processes and their efficiency are highly dependent on some structural features, namely, the lability of the migrating hydrogen atom and the ability to open the aromatic (heteroaromatic) ring. However, the scarcity of available examples does not allow assessing the importance and the potential of this reaction. To elucidate these issues and the opportunity of applications of the reaction in organic synthesis, exploration of the features and scopes of the process is required. The aim of this research is to study the photorearrangement of diarylethenes comprising various heterocyclic moieties along with phenyl residue. The design and elaboration of a new general and effective synthetic process is one of the major challenges in modern organic synthesis, making the development of new technologies, smart materials, and medicines a high priority.[22]

RESULTS AND DISCUSSION

To clarify some features of the phototransformation of diarylethenes, namely, the role and the effect of heterocyclic moieties on the process, a series of diarylethenes that differ only by the heterocyclic residues were explored. The choice of diarylcyclopentenone derivatives as the basic core for the starting diarylethenes (compounds of general formula **3**, Scheme 3) has been caused by some factors. First, recently,

Scheme 3. Synthesis and Structures of Starting Compounds



we have demonstrated that diarylethenes of this type bearing oxazole and phenyl residues readily undergo a photorearrangement reaction.[20] Moreover, it was found that the presence of a carbonyl group in the geminal position with respect to the phenyl fragment promotes the process, leading to an increase in yields of the final products. Another important argument in favor of such structures is their availability by our previously developed synthetic protocol.[19b] To explore the photorearrangement reaction, we have synthesized a series of previously unknown (except **3a**[19b]) 2,3-diarylcyclopent-2-en-1-ones **3**, starting from ethyl 3-oxo-4-phenylbutanoate **1** and 2-bromo-1-hetarylethanones **2** (Scheme 3). It was prepared with the diarylethenes comprising five-membered heterocycles with both one heteroatom (thiophene, furan, benzo[*b*]thiophene, indole) **3a−d,h** and two heteroatoms (imidazole, thiazole, pyrazole) **3e−g,i** with yields ranging from 20 to 53% for two stages.

The photoreaction of diarylethenes has been performed in conventional glass reactors (no need to use only quartz glassware; for details, see in section I in Supporting Information), with stirring in dichloromethane or toluene solutions under irradiation by UV light (λ = 365 nm, $c \approx 6 \times 10^{-2}$ M). In most cases, the irradiation of the diarylethene solution leads to the formation of only 2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one derivatives with good yields (Table 1; for more clarity, the previously published data for oxazole derivative **3j** are also included). The use of various heterocyclic systems has allowed us to synthesize an indanone analogous of naphthalene with various functional substituents. The formal opening of the thiophene or benzothiophene rings (attached to the central double bond of diarylethene by *β*-position) results in the formation of the corresponding thiols **4a,c**; in the first case, the photoreaction product **4a** is a mixture of *E*- and *Z*- isomers. The photoreaction of **3b** leads to naphthalene **4b** with a 2-oxopropyl substituent. Similarly, with a benzothiophene derivative, the photorearrangement of indole diarylethene **3d** results in the formation of corresponding amine **4d**. The phototransformation of azole derivatives with two heteroatoms is similar to the reaction of diarylethenes with one heteroatom and proceeds with cleavage of the carbon−heteroatom bond, giving amidines **4e,f** as imidazole derivatives and thioimide **4g** as thiazole diarylethene.

As mentioned above, the photoreaction products were obtained with sufficiently high yields that were confirmed by ^{1}H NMR monitoring of the reaction process. (^{1}H NMR monitoring of the process was performed for all substrates; see section IV in Supporting Information.) The monitoring of the reaction process for the indole derivative is illustrated in Figure 1. As can be seen from the figure, the photoreaction proceeds with quantitative conversion of the starting compound, leading to a photoproduct, and the formation of any byproducts is not observed. A similar pattern is observed for all other diarylethenes.

Interesting results have been obtained in the irradiation of solutions of diarylethene comprising pyrazole moiety **3i** (Scheme 4). Instead of the expected Schiff base **5**, aldehyde **6** has been isolated, wherein the yields in methylene chloride solution (15%) are significantly lower than that in toluene solution (71%). In methylene chloride solution, along with aldehyde **6**, the formation of numerous side products was also observed. The inconsistent result could be explained by the instability of the photoreaction product **5** in methylene chloride by action of acidic impurities formed by the decomposition of the solvent.

A more complicated pattern was observed in the irradiation of *α*-substituted thiophene derivative **3h** (Scheme 5). ^{1}H NMR monitoring of the photoprocess showed the formation of only two photoproducts: dihydronaphthalene **7** and naphtho[2,1-*b*]thiophene **8** (see section IV in Supporting Information). These compounds were isolated and their structures were proved by different spectral methods including 2D NMR experiments (for complete assignments see the Supporting Information). The mechanism of those products formation is discussed below.

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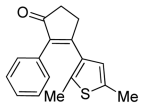
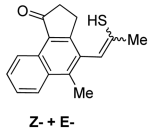
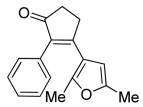
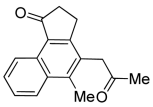
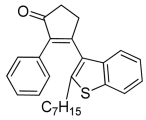
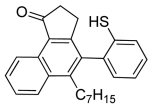
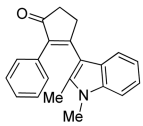
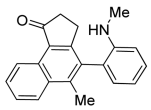
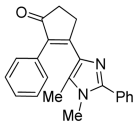
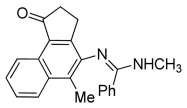
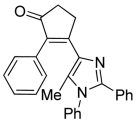
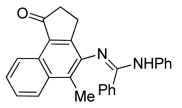
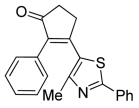
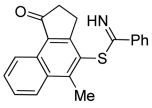
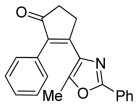
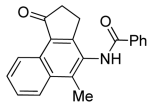
Table 1. Structures of Starting Compounds 3, Photoproducts 4, and Their Isolated Yields[a]

Entry	No	Diarylethene **3**	Photoproduct **4**	Isolated yields
1	**a**		 Z- + E- (1.86 : 1)	70%
2	**b**			69%
3	**c**			55%
4	**d**			77%[b]
5	**e**			75%
6	**f**			61%
7	**g**			79%
8[c]	**j**			80%

[a]Photoreaction was performed in dichloromethane solutions. [b]Photoreaction was performed in toluene solution. [c]Recently published data.[20]

To expand the scope of the reaction and to synthesize other polyaromatic systems, we have performed the photorearrangement of diarylethenes **9** and **10** (Scheme 6). In the first case, instead of the naphthalene system, its isosteric analogue, benzo[*b*]thiophene derivative **11**, has been prepared. The photoreaction of diarylethene **10** leads to the formation of furan-2(*5H*)-one-annulated naphthalene **12**, and the structure of the latter was proven by X-ray analysis (see Figure S4 in the Supporting Information).[23] Both reactions proceed without side processes, and the yields of the final products are rather high. These examples demonstrate the ample opportunities for the rearrangement, including the introduction in the reaction of novel types of diarylethenes, leading to the formation of benzene-annulated heterocycles.

The structures of starting diarylethenes **3**, **9**, and **10** and photoproducts **4**, **6**−**8**, **11**, and **12** have been proved by ^{1}H and ^{13}C NMR and mass spectrometry methods. To prove the structures of some photoproducts, 2D NMR experiments have also been used (compounds **4a** and **4e**; see Supporting Information). Furthermore, the structure of compound **4g** was unambiguously confirmed by X-ray analysis (see Figure S3 in the Supporting Information).[23]

The foregoing results indicate that the photorearrangement of the diarylethenes with different heterocycles has a general nature, and the formation of a polyaromatic system with simultaneous opening of the heterocyclic ring proceeds by the same mechanism. The proposed mechanism of the reaction is shown in Scheme 7.

The first stage of the process is 6π-electron conrotatory photocyclization, leading to the formation of intermediate **13**. This cyclization is a direct reaction of well-known photochromic isomerization, which is typical for diarylethenes.[8] At the next stages, we propose a [1,9]-sigmatropic shift, leading to intermediate **14**, and the spontaneous rearomatization of the latter as a result of migration of a proton and a five-membered heterocycle opening.

This mechanism has been proposed in our previous work.[20] In this study, some evidence was found in favor of the mechanism, namely, regarding the step of sigmatropic rearrangement. It has been shown that this [1,9]-rearrangement proceeds thermally through a suprafacial shift. In addition, the rearrangement product has been isolated and its structure has been proven by NMR and mass spectrometry methods.

To study the rearrangement stage, we have synthesized diarylethene **3k** (Scheme 8), and its photoreaction under similar conditions has been explored. In previous work, it was found that the photorearrangement of diarylethenes bearing a phenyl group at the third position proceeds rather slowly and with relatively low yields compared to structural isomer compounds (2-phenyl-attached diarylethenes).[20]

In structure **15**, the carbonyl group is not conjugated with the cyclohexadiene moiety, which increases the lifetime of this intermediate and allows it to be detected by electron spectroscopy (Figure 2). It was found that the irradiation of the solution of **3k** with UV light (λ = 365 nm) results in the formation of intermediate **15** with an absorption maximum at 525 nm. The kinetic study showed the fast bleaching of the colored intermediate **15** in the absence of irradiation (see Figure 2, inset). This result indicates that the rearrangement proceeds thermally via a suprafacial [1,9]-sigmatropic shift, that is in agreement with the Woodward−Hoffmann rule of conservation of orbital symmetry.[24] According to this rule, the [1,9]-H shift is permitted thermally in the case of a suprafacial shift and photochemically only when there is an antarafacial shift.

The additional confirmation of the proceeding of [1,9]-sigmatropic shift was obtained by the photoreaction of diarylethene **3h**, containing an α-thienyl substituent at the central double bond. As noted above, in the photoreaction of this diarylethene, instead of the expected product **19**, two products were isolated: dihydronaphthalene **7** and naphtho[2,1-*b*]thiophene **8** (Scheme 9).

The first two stages of the diarylethene **3h** photoreaction are also electrocyclization and [1,9]-sigmatropic shift of a hydrogen atom, leading to the intermediate **18** with anticonfiguration of

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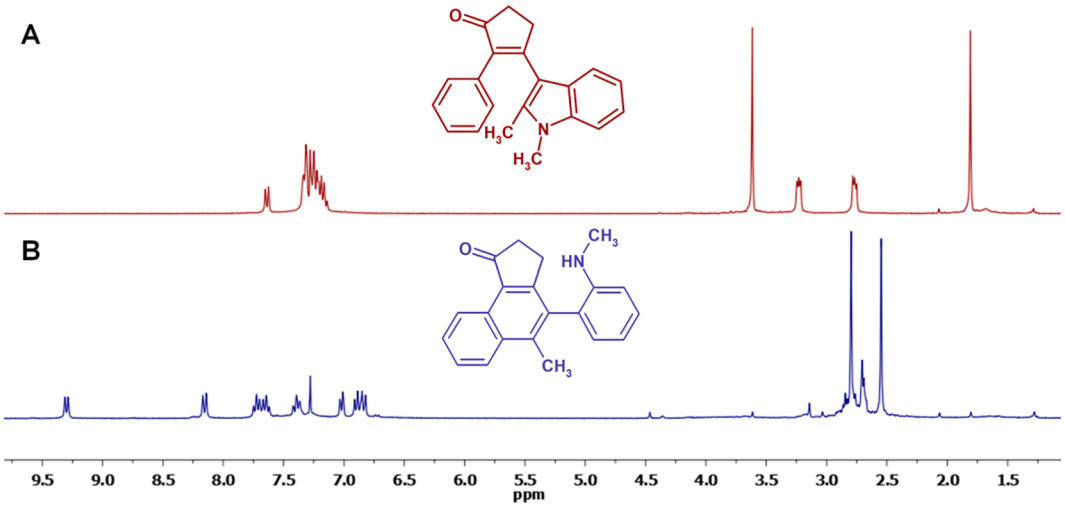
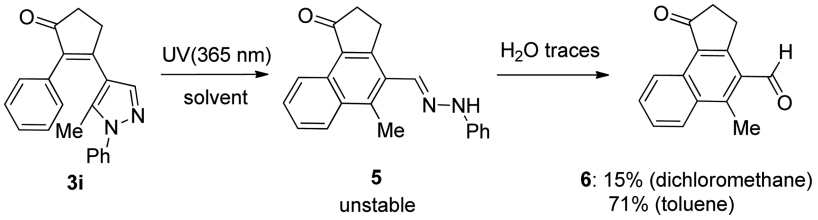
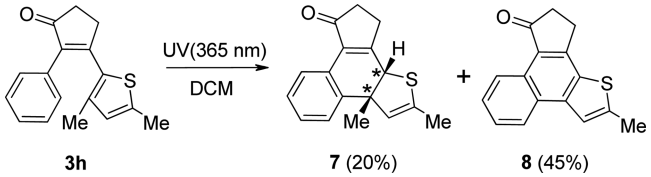


Figure 1. ^{1}H NMR monitoring of diarylethene **3d** photoreaction under UV irradiation (λ = 365 nm) in $CDCl_3$ solution: before irradiation (A) and after 1 h irradiation (B).

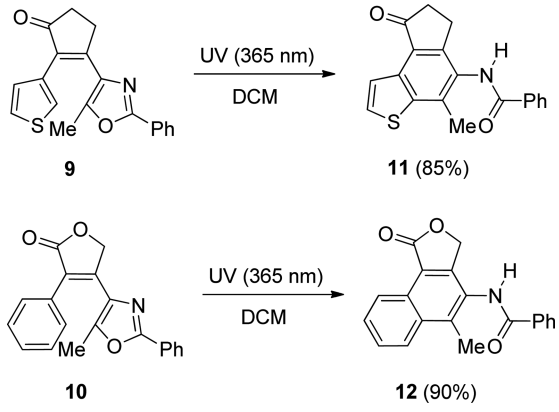
Scheme 4. Photoreaction of Pyrazole Derivative 3i



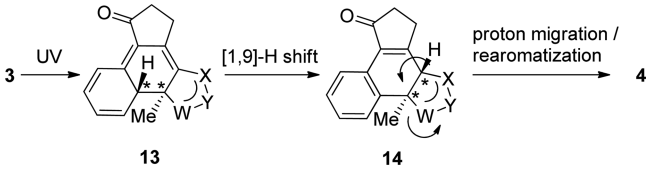
Scheme 5. Photoreaction of Thiophene Derivative 3h



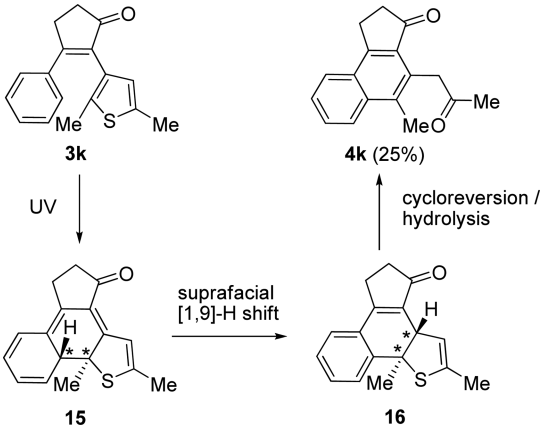
Scheme 6. Photorearrangement of Different Substrates



Scheme 7. Proposed Mechanism of the Photorearrangement



Scheme 8. Photochemical Transformation of Diarylethene 3k



the hydrogen atom and methyl group. Product **7** and intermediate **18** are diastereoisomers, and the conversion of the latter to **7** likely occurs as a result of the keto−enol isomerization, leading to a more stable *syn*-isomer. Similar transformations have been previously described for a number of structurally related compounds.[25,26] The formation of **8** is the result of the elimination of a molecule of methane from compound **17** or **7**. In particular, by a separate experiment, it has been shown that the irradiation of a solution of **7** under similar conditions leads to **8**.

Thus, an expansion of the reaction scope and a more detailed study of separate stages of this transformation allowed us to clarify some aspects of the process. The driving force of this

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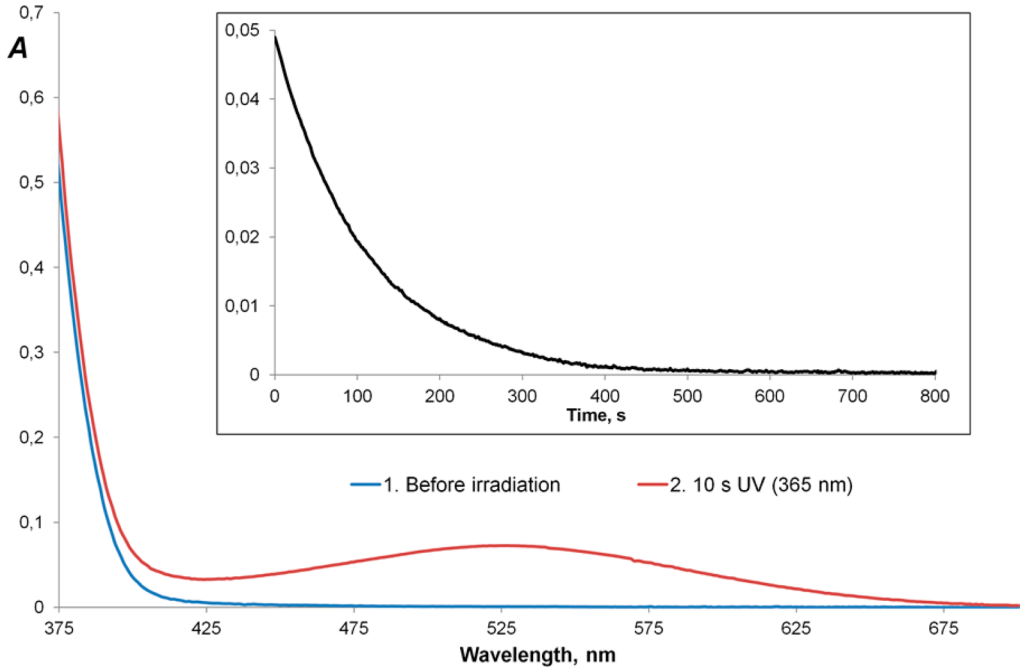
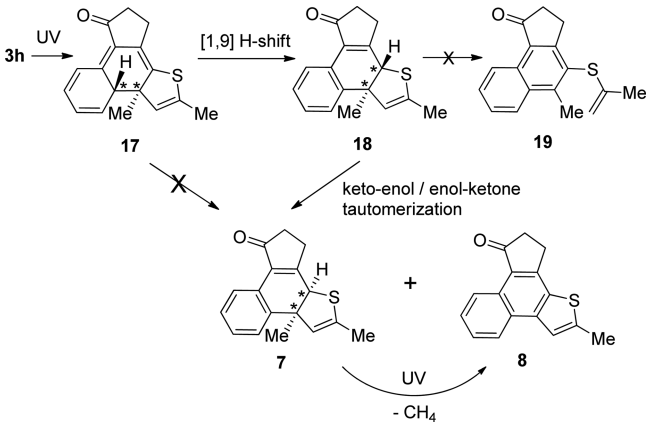


Figure 2. UV−vis spectra of diarylethene **3k** before and after irradiation with UV light (λ = 365 nm) for 10 s in acetonitrile ($c = 1.1 \times 10^{-3}$ M) and thermal decomposition of colored intermediate **15** observed at 525 nm (inset).

Scheme 9. Photoreaction of the Inverse Thiophene Derivative



rearrangement is the restoration initially of aromaticity of the benzene ring and then of the naphthalene system, leading to a thermodynamically more stable structure. Another important condition for this reaction to proceed is the opening of a heterocyclic ring with the cleavage of the carbon−heteroatom bond. It should be noted that the presence of a carbon−carbon bond instead of carbon−heteroatom (diarylethene **3h**) prevents the ring-opening process and leads to restoration of aromaticity by elimination of the methane molecule, although in the scientific literature, a close example of carbon−carbon bond cleavage reaction leading to ring opening is described.[27]

CONCLUSIONS

In summary, we have studied a novel photochemical transformation of diarylethenes comprising a five-membered heterocyclic ring (thiophene, benzo[*b*]thiophene, furan, indole, imidazole, pyrazole, thiazole, pyrazole, and oxazole) and benzene derivatives. It was found that the reaction includes tandem photocyclization/sigmatropic rearrangement/ring-opening processes. Based on this transformation, a general and efficient method for the preparation of functionalized naphthalene derivatives has been proposed. NMR monitoring has indicated that the process proceeds without side products and with good yields of final products. High efficiency of the reaction and the opportunity to carry out the process under mild conditions promises that the transformation can be an effective practical synthetic protocol for the annulation of the benzene ring to various aromatic systems, including heterocycles.

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 spectrometers working at 200 or 300 MHz or 400 or 600 MHz for ^{1}H and 75, 101, or 151 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. Melting points (mp) were recorded using an apparatus and not corrected. 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 F254 plates.

Photochemical Studies. UV−vis spectra were recorded in 1.0 cm quartz cuvettes. The experimental measurements were performed at 293 K in the presence of air in solutions of acetonitrile.

Photochemical Synthesis. Photochemical reactions were performed in commercial 10 mL flat-bottomed glass vessels (for details, see section I in Supporting Information). The irradiation was carried out by 6 W UV lamp (365 nm light).

Synthesis and Characterization of Starting Diarylethenes. Diarylethenes **3a** and **3k** were prepared according to literature procedures.[19b] Diarylethenes **3b−i** and **9** were prepared according previously reported method[19b] from corresponding ethyl 3-oxo-4-

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arylbutanoates[28] and corresponding 2-bromo-1-arylethanones. 2-Bromo-1-arylethanones were prepared from corresponding ketones by bromination with Br_2 in $CHCl_3$. Diarylethene **10** was synthesized from phenylacetic acid and 2-bromo-1-(5-methyl-2-phenyl-1,3-oxazol-4-yl)ethanone according to a previously reported method.[29]

2,3-Diarylcyclopent-2-en-1-ones (General Procedure). To a solution of ketoester **1** (10 mmol) in absolute benzene (30 mL) was added sodium (0.23 g, 10 mmol). The reaction mixture was stirred for 2 h, and bromoketone **2** or **23** (10 mmol) was added portionwise. The mixture was kept overnight and then poured into water (150 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL) and evaporated in vacuum. The residue was dissolved in ethanol (37 mL), and a solution of KOH (2.80 g, 50 mmol) in water (37 mL) was added. The reaction mixture was refluxed until completion of the reaction (monitored by TLC), then cooled, poured into water (100 mL), and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography by petroleum ether/ethyl acetate (2:1 or 3:1 or 4:1).

*3-(2,5-Dimethylfuran-3-yl)-2-phenylcyclopent-2-en-1-one (**3b**):* Yellow amorphous powder, 20% yield (504 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.04 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.61−2.70 (m, 2H, CH_2), 2.90−3.00 (m, 2H, CH_2), 5.69 (s, 1H, H^{furan}), 7.22−7.45 (m, 5H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.2, 14.2, 30.0, 34.7, 106.3, 117.8, 127.5, 128.3, 129.3, 133.0, 138.2, 150.4, 150.5, 162.5, 207.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{17}O_2$ 253.1223, found 253.1220; MS (EI) m/z (%) = 252 (15) $[M]^+$, 237 (10) $[M - CH_3]^+$, 43 (100).

*3-(2-Heptyl-1-benzothiophen-3-yl)-2-phenylcyclopent-2-en-1-one (**3c**):* White powder, 26% yield (1.01 g); mp 95−98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.89 (t, J = 6.9 Hz, 3H, CH_3), 1.03−1.51 (m, 10H, $(CH_2)_5$), 2.31−2.65 (m, 2H, CH_2), 2.73−2.91 (m, 3H, 1/2 CH_2+CH_2), 3.16−3.33 (m, 1H, 1/2 CH_2), 7.13−7.40 (m, 7H, H^{arom}), 7.50−7.59 (m, 1H, H^{arom}), 7.76−7.87 (m, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.1, 22.6, 29.0, 29.3, 29.4, 31.3, 31.7, 35.4, 51.0, 121.8, 122.4, 124.0, 124.5, 127.1, 127.9, 128.1, 128.5, 128.8, 129.4, 131.4, 134.3, 138.5, 138.9, 142.6, 143.0, 166.3, 207.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{29}OS$ 389.1934, found 389.1928; MS (EI) m/z (%) = 388 (95) $[M]^+$, 289 (100) $[M - C_7H_{15}]^+$.

*3-(1,2-Dimethyl-1H-indol-3-yl)-2-phenylcyclopent-2-en-1-one (**3d**):* Yellow powder, 29% yield (873 mg); mp 196−198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.81 (s, 3H, CH_3), 2.71−2.83 (m, 2H, CH_2), 3.18−3.28 (m, 2H, CH_2), 3.62 (s, 3H, CH_3), 7.13−7.37 (m, 8H, H^{arom}), 7.61 (d, J = 7.8 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.9, 29.8, 31.3, 35.5, 109.2, 109.7, 119.7, 120.3, 121.5, 126.3, 127.0, 128.2, 129.1, 133.5, 135.8, 137.5, 137.8, 167.0, 207.5; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{21}H_{20}NO$ 302.1539, found 302.1543; MS (EI) m/z (%) = 301 (50) $[M]^+$, 45 (100).

*3-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-2-phenylcyclopent-2-en-1-one (**3e**):* Yellow powder, 53% yield (1.74 g); mp 148−150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.50 (s, 3H, CH_3), 2.61−2.71 (m, 2H, CH_2), 3.12−3.22 (m, 2H, CH_2), 3.48 (s, 3H, CH_3), 7.24−7.38 (m, 5H, H^{arom}), 7.41−7.52 (m, 3H, H^{arom}), 7.62 (d, J = 6.7 Hz, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.4, 29.9, 31.9, 34.9, 127.2, 128.3, 128.6, 128.7, 128.9 (2C), 129.2, 130.5, 133.6, 133.9, 137.0, 148.4, 165.1, 207.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{22}H_{21}N_2O$ 329.1648, found 329.1643; MS (EI) m/z (%) = 328 (100) $[M]^+$, 313 (40) $[M - CH_3]^+$.

*3-(1,2-Diphenyl-5-methyl-1H-imidazol-4-yl)-2-phenylcyclopent-2-en-1-one (**3f**):* White powder, 49% yield (1.91 g); mp 155−157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.32 (s, 3H, CH_3), 2.69−2.80 (m, 2H, CH_2), 3.30−3.43 (m, 2H, CH_2), 7.06−7.58 (m, 15H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.9, 29.8, 35.0, 127.3, 127.8, 128.2 (2C), 128.3, 128.4, 129.0, 129.3, 129.7, 130.1, 130.4, 133.5, 134.4, 136.8, 137.6, 147.5, 164.9, 207.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{27}H_{23}N_2O$ 391.1805, found 391.1804; MS (EI) m/z (%) = 390 (30) $[M]^+$, 180 (95), 77 (100) $[C_6H_5]^+$.

*3-(4-Methyl-2-phenyl-1,3-thiazol-5-yl)-2-phenylcyclopent-2-en-1-one (**3g**):* Yellow crystals, 39% yield (1.29 g); mp 92−94 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.04 (s, 3H, CH_3), 2.68−2.81 (m, 2H, CH_2), 2.99−3.14 (m, 2H, CH_2), 7.23−7.54 (m, 8H, H^{arom}), 7.82−7.97 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 17.6, 32.1, 35.0, 126.5, 127.8, 128.3, 128.7, 129.0, 129.2, 130.5, 131.9, 133.0, 140.8, 152.9, 159.5, 168.2, 206.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{21}H_{18}NOS$ 332.1104, found 332.1098; MS (EI) m/z (%) = 331 (85) $[M]^+$, 316 (50) $[M - CH_3]^+$, 77 (100) $[C_6H_5]^+$.

*3-(3,5-Dimethylthiophen-2-yl)-2-phenylcyclopent-2-en-1-one (**3h**):* Yellow powder, 37% yield (992 mg); mp 114−117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.67 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.64−2.77 (m, 2H, CH_2), 2.95−3.08 (m, 2H, CH_2), 6.48 (s, 1H, $H^{thiophene}$), 7.23−7.41 (m, 5H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 15.4, 16.0, 32.0, 35.0, 127.7, 128.4, 129.3, 130.2, 131.1, 132.8, 138.1, 138.6, 142.3, 162.8, 206.8; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{17}OS$ 269.0995, found 269.0995; MS (EI) m/z (%) = 268 (90) $[M]^+$, 253 (30) $[M - CH_3]^+$, 211 (100).

*3-(5-Methyl-1-phenyl-1H-pyrazol-4-yl)-2-phenylcyclopent-2-en-1-one (**3i**):* White crystals, 44% yield (1.38 g); mp 138−141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.82 (s, 3H, CH_3), 2.67−2.78 (m, 2H, CH_2), 3.01−3.13 (m, 2H, CH_2), 7.24−7.50 (m, 10H, H^{arom}), 7.64 (s, 1H, $H^{pyrazole}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 12.6, 30.3, 34.7, 117.5, 125.2, 127.7, 128.3, 128.6, 129.2 (2C), 133.1, 137.7, 138.1, 139.0, 139.8, 161.9, 206.8; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{21}H_{19}N_2O$ 315.1492, found 315.1486; MS (EI) m/z (%) = 314 (35) $[M]^+$, 299 (10) $[M - CH_3]^+$, 77 (100) $[C_6H_5]^+$.

*3-(5-Methyl-2-phenyl-1,3-oxazol-4-yl)-2-thiophen-3-ylcyclopent-2-en-1-one (**9**):* Yellow powder, 25% yield (803 mg); mp 155−157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.91 (s, 3H, CH_3), 2.65−2.72 (m, 2H, CH_2), 3.05−3.12 (m, 2H, CH_2), 7.13 (d, J = 5.0 Hz, 1H, $H^{thiophene}$), 7.26−7.33 (m, 1H, $H^{thiophene}$), 7.43−7.52 (m, 3H, H^{arom}), 7.62−7.68 (m, 1H, $H^{thiophene}$), 8.00−8.10 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.7, 29.3, 34.6, 125.0, 125.2, 126.2, 127.0, 127.7, 128.8, 130.5, 131.9, 133.2, 134.6, 148.0, 159.6, 160.7, 207.2; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{19}H_{15}NO_2SNa$ 344.0716, found 344.0705; MS (EI) m/z (%) = 321 (20) $[M]^+$, 43 (100).

*4-(5-Methyl-2-phenyl-1,3-oxazol-4-yl)-3-phenylfuran-2(5H)-one (**10**):* Yellow crystals, 56% yield (890 mg) obtained from 5 mmol of initial phenylacetic acid; mp 197−200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.79 (s, 3H, CH_3), 5.24 (s, 2H, CH_2), 7.33−7.67 (m, 8H, H^{arom}), 7.91−8.11 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 12.0, 70.8, 125.3, 126.2, 126.4, 126.7, 128.6, 128.8, 128.9, 129.1, 129.3, 130.7, 148.9, 149.3, 160.9, 173.3; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{16}NO_3$ 318.1125, found 318.1121; MS (EI) m/z (%) = 317 (100) $[M]^+$.

Photochemical Rearrangement of Diarylethenes (General Procedure). Diarylethene (0.5 mmol) was dissolved in 8 mL of appropriate solvent (dichloromethane or toluene), and the reaction mixture was irradiated (UV, λ = 365 nm, 6W) with stirring in a 10 mL flat-bottomed glass vessel. After completion of the reaction (TLC control), the solution was evaporated under vacuum, and the residue was purified by column chromatography eluting by light petroleum/ethyl acetate (compounds **4a−d**, **6−8**, and **19**) or by recrystallization from small amount of CH_2Cl_2 (compounds **4e−g**, **11**, and **12**).

*5-Methyl-4-(2-sulfanylprop-1-en-1-yl)-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (**4a**):* Diarylethene **3a**, solvent = dichloromethane, irradiation time = 6 h; isolated mixture of *E*- and *Z*-isomers (for more details, see section II.4 in Supporting Information); light yellow powder (93 mg, 70%); mp 97−100 °C. *Z*-isomer (65%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.31 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 2.72−2.80 (m, 2H, CH_2), 2.76 (s, 1H, SH), 3.02−3.10 (m, 2H, CH_2), 6.43 (s, 1H, CH), 7.55−7.71 (m, 2H, H^{arom}), 8.11 (d, J = 7.9 Hz, 1H, H^{arom}), 9.24 (d, J = 8.1 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 16.6, 25.5, 26.4, 36.7, 120.2, 124.3, 124.7, 126.5, 128.2, 128.8, 129.4, 132.2, 132.4, 133.3, 141.1, 158.4, 207.5. *E*-isomer (35%): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.83 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 2.72−2.80 (m, 2H, CH_2), 2.95−3.02 (m, 2H, CH_2), 3.10 (s, 1H, SH), 6.58 (s, 1H, CH), 7.55−7.71 (m, 2H, H^{arom}), 8.09 (d, J = 7.3 Hz, 1H, H^{arom}), 9.24 (d, J = 8.1 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 16.9, 22.5, 25.8, 36.7, 122.8, 124.2, 124.6, 126.6, 128.2,

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128.6, 128.8, 132.1, 132.3, 133.3, 140.5, 158.3, 207.4; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{17}OS$ 269.0995, found 269.0997; MS (EI) m/z (%) = 268 (100) $[M]^+$, 253 (10) $[M - CH_3]^+$.

*5-Methyl-4-(2-oxopropyl)-2,3-dihydro-1H-cyclopenta[a]-naphthalen-1-one (**4b**):* Diarylethene **3b**, solvent = dichloromethane, irradiation time = 8 h; white powder (87 mg, 69%); mp 155−157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.29 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 2.71−2.85 (m, 2H, CH_2), 2.96−3.11 (m, 2H, CH_2), 4.02 (s, 2H, CH_2), 7.55−7.73 (m, 2H, H^{arom}), 8.10 (d, J = 8.2 Hz, 1H, H^{arom}), 9.25 (d, J = 8.0 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 16.1, 25.5, 29.8, 36.6, 44.8, 124.3 (2C), 126.7, 128.1, 128.2, 128.8, 129.5, 132.2, 141.3, 157.9, 204.9, 207.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{17}O_2$ 253.1223, found 253.1225; MS (EI) m/z (%) = 252 (45) $[M]^+$, 209 (100).

*5-Heptyl-4-(2-sulfanylphenyl)-2,3-dihydro-1H-cyclopenta[a]-naphthalen-1-one (**4c**):*[30] Diarylethene **3c**, solvent = dichloromethane, irradiation time = 7 h; yellow amorphous powder (107 mg, 55%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.13−1.40 (m, 8H, $(CH_2)_4$), 1.51−1.78 (m, 2H, CH_2), 2.68−3.11 (m, 6H, CH_2), 3.17 (s, 1H, SH), 7.18−7.37 (m, 3H, H^{arom}), 7.46−7.49 (m, 1H, H^{arom}), 7.62−7.75 (m, 2H, H^{arom}), 8.17 (d, J = 8.3 Hz, 1H, H^{arom}), 9.35 (d, J = 7.8 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.1, 22.6, 25.6, 28.7, 30.1, 30.5, 30.8, 31.6, 36.8, 124.6, 124.9, 125.7, 126.7, 128.5, 128.6, 128.8, 129.1, 129.8, 130.2, 131.6, 131.9, 135.1, 136.5, 146.0, 157.9, 207.4; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{29}OS$ 389.1934, found 389.1935; m/z $[M + H_2O + H]^+$ calcd for $C_{26}H_{31}O_2S$ 407.2039, found 407.2033; MS (EI) m/z (%) = 388 (65) $[M]^+$, 247 (100).

*5-Methyl-4-[2-(methylamino)phenyl]-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (**4d**):* Diarylethene **3d**, solvent = toluene, irradiation time = 5 h; white powder (116 mg, 77%); mp 180−183 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.55 (s, 3H, CH_3), 2.66−2.85 (m, 4H, CH_2), 2.80 (s, 3H, CH_3), 6.81−6.94 (m, 2H, H^{arom}), 7.02 (d, J = 7.3 Hz, 1H, H^{arom}), 7.35−7.44 (m, 1H, H^{arom}), 7.60−7.76 (m, 2H, H^{arom}), 8.15 (d, J = 8.4 Hz, 1H, H^{arom}), 9.30 (d, J = 8.2 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 16.7, 25.7, 30.8, 36.7, 110.3, 117.4, 123.7, 124.4, 124.7, 126.6, 128.5, 129.1, 129.2, 129.6, 129.8, 132.3, 133.7, 142.0, 145.9, 159.1, 207.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{21}H_{20}NO$ 302.1539, found 302.1537; MS (EI) m/z (%) = 301 (100) $[M]^+$, 286 (20) $[M - CH_3]^+$.

*N-Methyl-N′-(5-methyl-1-oxo-2,3-dihydro-1H-cyclopenta[a]-naphthalen-4-yl)benzenecarboximidamide (**4e**):* Diarylethene **3e**, solvent = dichloromethane, irradiation time = 5 h; white crystals (123 mg, 75%); mp 165−167 °C (for 2D NMR HSQC and NOESY data, see section II.5 in Supporting Information); ^{1}H NMR (600 MHz, DMSO-d_6) δ = 2.39 (s, 3H, CH_3), 2.57−2.66 (m, 2H, CH_2), 2.69−2.83 (m, 1H, 1/2 CH_2), 2.96 (br s, 3H, CH_3), 2.90−3.02 (m, 1H, 1/2 CH_2), 7.14−7.35 (m, 6H, NH+H^{arom}), 7.40−7.54 (m, 2H, H^{arom}), 7.84−7.95 (m, 1H, H^{arom}), 8.90−9.01 (m, 1H, H^{arom}); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 14.5, 25.0, 29.2, 36.9, 123.4, 124.2, 125.5, 125.7, 126.5, 127.8, 128.6, 128.7, 128.9, 129.8, 133.1, 136.0, 146.0, 154.9, 158.2, 207.5; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{22}H_{21}N_2O$ 329.1648, found 329.1651; MS (EI) m/z (%) = 328 (10) $[M]^+$, 313 (10) $[M - CH_3]^+$, 119 (100).

*N-Phenyl-N′-(5-methyl-1-oxo-2,3-dihydro-1H-cyclopenta[a]-naphthalen-4-yl)benzenecarboximidamide (**4f**):* Diarylethene **3f**, solvent = dichloromethane, irradiation time = 5 h; white crystals (119 mg, 61%); mp 217−220 °C (for the temperature dependence of the ^{1}H NMR spectrum of **4f**, see section V in Supporting Information); ^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ = 2.62 (s, 3H, CH_3), 2.63−2.70 (m, 2H, CH_2), 2.93−3.15 (m, 2H, CH_2), 6.99−7.10 (m, 1H, H^{arom}), 7.16−7.59 (m, 11H, H^{arom}), 7.93−8.03 (m, 1H, H^{arom}), 9.10−9.19 (m, 1H, H^{arom}); ^{13}C NMR (100 MHz, $CDCl_3$, 333 K) δ = 14.2, 24.6, 36.7, 123.6, 123.7, 124.2, 126.3, 126.7, 128.5, 128.9, 129.2, 129.6, 129.7, 130.0, 130.1, 133.1, 134.9, 153.0, 154.9, 206.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{27}H_{23}N_2O$ 391.1805, found 391.1799; MS (EI) m/z (%) = 390 (20) $[M]^+$, 298 (75) $[M - CH_3 - C_6H_5]^+$, 77 (100) $[C_6H_5]^+$.

*5-Methyl-1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalen-4-yl Benzenecarbimidothioate (**4g**):* Diarylethene **3g**, solvent = dichloromethane, irradiation time = 5 h; light yellow powder (130 mg, 79%); mp 136−138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.75−2.88 (m, 2H, CH_2), 2.99 (s, 3H, CH_3), 3.14−3.26 (m, 2H, CH_2), 7.50−7.89 (m, 5H, H^{arom}), 8.15−8.30 (m, 3H, H^{arom}), 9.33 (d, J = 8.4 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 18.0, 26.5, 36.6, 121.9, 124.7, 125.5, 127.5, 128.8, 130.3, 130.4, 131.4, 131.9, 132.4, 132.7, 135.8, 137.2, 151.5, 161.1, 206.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{21}H_{18}NOS$ 332.1104, found 332.1107; MS (EI) m/z (%) = 331 (5) $[M]^+$, 316 (10) $[M - CH_3]^+$, 228 (90) $[M - PhCN]^+$, 103 (100) $[PhCN]^+$.

*5-Methyl-4-(2-oxopropyl)-1,2-dihydro-3H-cyclopenta[a]-naphthalen-3-one (**4k**):* Diarylethene **3k**, solvent = dichloromethane, irradiation time = 20 h; yellow powder (31 mg, 25%); mp 150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.35 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 2.75−2.86 (m, 2H, CH_2), 3.34−3.44 (m, 2H, CH_2), 4.55 (s, 2H, CH_2), 7.58−7.75 (m, 2H, H^{arom}), 8.07 (d, J = 8.0 Hz, 1H, H^{arom}), 8.14 (d, J = 8.5 Hz, 1H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.2, 23.4, 29.8, 36.6, 42.9, 124.7, 125.3, 126.3, 127.4, 129.4, 129.8, 132.0, 133.4, 135.7, 155.8, 206.1, 207.9; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{17}O_2$ 253.1223, found 253.1239; MS (EI) m/z (%) = 252 (25) $[M]^+$, 210 (100).

*5-Methyl-1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalene-4-carbaldehyde (**6**):* Diarylethene **3i**, solvent = dichloromethane, irradiation time = 15 h (17 mg, 15%); solvent = toluene, irradiation time = 10 h (80 mg, 71%); white powder; mp 172−175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.71−2.87 (m, 2H, CH_2), 3.10 (s, 3H, CH_3), 3.44−3.57 (m, 2H, CH_2), 7.60−7.87 (m, 2H, H^{arom}), 8.27 (d, J = 8.2 Hz, 1H, H^{arom}), 9.32 (d, J = 8.4 Hz, 1H, H^{arom}), 10.85 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.6, 26.4, 36.7, 124.5, 125.2, 127.4, 128.7, 129.7, 130.2, 131.2, 132.0, 148.2, 157.5, 191.8, 207.1; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{13}O_2$ 225.0910, found 225.0919; MS (EI) m/z (%) = 224 (100) $[M]^+$.

*2,10b-Dimethyl-3a,9,10,10b-tetrahydro-8H-cyclopenta[3,4]-naphtho[2,1-b]thiophene-8-one (**7**):* Racemic mixture of (*R*,*S*) and (*S*,*R*) isomers; diarylethene **3h**, solvent = dichloromethane, irradiation time = 10 h; yellow powder (26 mg, 20%); mp 185−7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.46 (s, 3H, CH_3), 1.96−1.98 (m, 3H, CH_3), 2.59−2.67 (m, 3H, CH_2 + 1/2CH_2), 2.75−2.83 (m, 1H, 1/2CH_2), 4.63 (s, 1H, CH), 5.60−5.62 (m, 1H, CH), 7.25−7.34 (m, 3H, H^{arom}), 8.48 (d, J = 7.5 Hz, 1H, H^{arom}); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 16.7, 28.6, 29.1, 35.8, 54.1, 58.1, 124.2, 125.8, 126.2, 126.7, 127.6, 129.0, 133.0, 136.5, 140.0, 167.3, 206.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{17}H_{17}OS$ 269.0995, found 269.0990; MS (EI) m/z (%) = 268 (85) $[M]^+$, 253 (70) $[M - CH_3]^+$, 211 (100).

*2-Methyl-9,10-dihydro-8H-cyclopenta[3,4]naphtho[2,1-b]-thiophene-8-one (**8**):* Diarylethene **3h**, solvent = dichloromethane, irradiation time = 10 h; yellow crystals (57 mg, 45%); mp 179−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.78 (s, 3H, CH_3), 2.85−2.91 (m, 2H, CH_2), 3.21−3.27 (m, 2H, CH_2), 7.60−7.67 (m, 2H, H^{arom}), 7.71 (s, 1H, H^{arom}), 8.25 (d, J = 8.3 Hz, 1H, H^{arom}), 9.29 (d, J = 7.4 Hz, 1H, H^{arom}); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 16.7, 24.9, 36.5, 121.5, 123.6, 124.7, 126.6, 127.2, 127.3, 127.4, 128.3, 133.2, 141.9, 146.0, 153.5, 206.2; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{13}OS$ 253.0682, found 253.0683; MS (EI) m/z (%) = 252 (100) $[M]^+$.

*N-(4-Methyl-8-oxo-7,8-dihydro-6H-indeno[5,4-b]thiophen-5-yl)-benzamide (**11**):* Diarylethene **9**, solvent = dichloromethane, irradiation time = 5 h; yellow crystals (136 mg, 85%); mp 264−266 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 2.55 (s, 3H, CH_3), 2.66−2.82 (m, 2H, CH_2), 3.00−3.20 (m, 2H, CH_2), 7.50−7.71 (m, 3H, H^{arom}), 7.96−8.19 (m, 4H, H^{arom}), 10.25 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 17.4, 24.6, 36.5, 122.0, 128.1, 128.2, 129.0, 129.4, 130.7, 132.3, 133.3, 134.5, 136.7, 141.2, 153.7, 166.2, 205.6; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{15}NO_2SNa$ 344.0716, found 344.0708; MS (EI) m/z (%) = 321 (50) $[M]^+$, 105 (100) $[C_6H_5CO]^+$.

*N-(5-Methyl-1-oxo-1,3-dihydronaphtho[1,2-c]furan-4-yl)-benzamide (**12**):* Diarylethene **10**, solvent = dichloromethane, irradiation time = 5 h; white crystals (142 mg, 90%); mp 242−244 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 2.70 (s, 3H, CH_3), 5.43 (s, 2H, CH_2), 7.50−7.90 (m, 5H, H^{arom}), 7.99−8.19 (m, 2H, H^{arom}),

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8.22−8.38 (m, 1H, H^{arom}), 8.81−9.00 (m, 1H, H^{arom}), 10.47 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 14.9, 69.0, 118.0, 123.0, 126.1, 127.7, 127.8, 128.3, 128.4, 128.8, 129.0, 132.4, 133.3, 134.1, 139.2, 148.3, 166.2, 171.3; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{16}NO_3$ 318.1125, found 318.1125; MS (EI) m/z (%) = 317 (100) $[M]^+$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02237.

^1H and ^{13}C NMR and HRMS spectra for new compounds; 2D NMR characterization of photoproducts **4a**, **4e**, **7**, and **8**; ^1H NMR monitoring of photoreaction for diarylethenes **3** (PDF)

Crystallographic file for compound **12** (CIF)

Crystallographic file for compound **4g** (CIF)

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Notes

The authors declare no competing financial interest.

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(30) Photoproduct **4c** is unstable in the air due to oxidation and formation of appropriate disulfide. This was proven by MS characterization of the decomposition product: HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{52}H_{55}O_2S_2$ 775.3638, found 775.3612. For the spectrum, see section VIII in Supporting Information.

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