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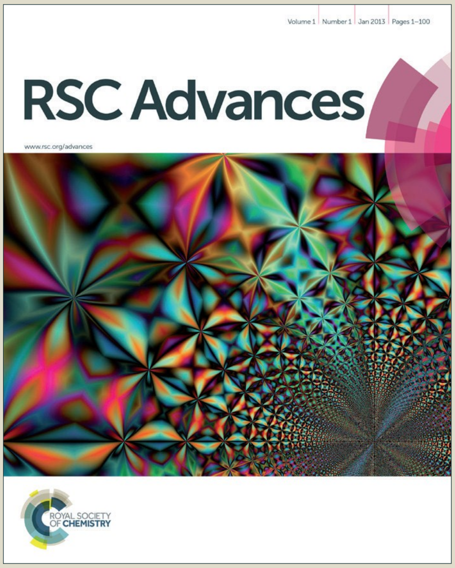

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COMMUNICATION

Facile synthesis of photoactive diaryl(hetaryl)cyclopentenes by ionic hydrogenation

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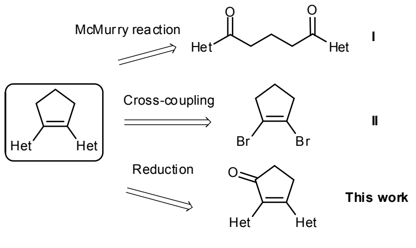
A facile synthetic approach to photoactive diarylethenes comprising a cyclopentene ring as an ethene bridge was developed based on reduction of 2,3-diaryl(hetaryl)cyclopent-2-en-1-ones through ionic hydrogenation reaction. The method provides an access to unsymmetrical photoswitchable diarylethenes containing benzene, thiophene, or azoles (thiazole, oxazole, imidazole) as aromatic moieties in 40-71% yields. Diarylethenes comprising two heterocyclic moieties show typical photochromic properties, with absorption maxima of the photoinduced form in the blue region (yellow photochromes).

Photochromic diarylethenes are promising candidates for the development of photoswitchable materials and devices.[1] Nowadays, synthetic organic chemistry gives access to a great variety of diarylethenes, which in turn allows the investigation of relationships between the structure of diarylethene molecules and their photochromic properties. The electronic and steric effects of the so-called ethene bridge, the fragment with a central double bond, greatly influence the photochromic properties, including on the absorption maxima and quantum yields. Strong electron-withdrawing moieties (perfluorocyclopentene, maleic anhydride, maleimide, cyclopentenone, etc.) are commonly used as ethene bridges in photochromic diarylethenes, while there is only one truly electron-neutral core, cycloalkene (mainly cyclopentene).[2-4] Photochromic diarylethenes of the cyclopentene series have several advantages. First, the cyclopentene ethene bridge provides a shift of the absorption maxima of the photoinduced form to the blue region giving rise to yellow developing photochromic compounds. It is indispensable to prepare red and yellow developing diarylethene derivatives for their application as full-color display and in many other fields.[5-10] Most of diarylethenes based on perfluourocyclopentenes, maleic anhydride, maleimides, cyclopentenone and other carbo- and heterocyclic derivatives belong to red photochromes. Yellow developing photochromes are practically very few and they basically belong to either inverse diarylethenes or cyclopentene derivatives. Second, in the case of photochromes of the cyclopentene series the spectral and kinetic properties depend only on the nature and substituents of aryl moieties, which greatly simplifies the management of these characteristics. Besides, it is of interest to study this family of diarylethenes in order to develop different types of light-controlling materials and devices.[11-17] In addition, the elaboration of an alternative and effective synthetic protocol is one of the major challenges in modern organic synthesis having a high priority in the development of new technologies and smart materials.[18-20] However, the synthesis of these compounds remains a difficult task and has a lot of limitations.

There are two synthetic protocols for the preparation of diarylcyclopentenes (Scheme 1). One method is based on the intramolecular McMurry cyclization of 1,5-diarylpentane-1,5-diones (pathway **I** in Scheme 1).[2,21-24] Another approach involves the Pd-catalyzed cross-coupling of 1,2-dibromocyclopentene (pathway **II** in Scheme 1).[4,11,12,25,26] These methods are quite suitable for thiophene and benzothiophene derivatives, including unsymmetric,[23] but they are generally limited to azole compounds (oxazole, imidazole, thiazole) because the starting compounds are difficult to access and the reaction requires harsh conditions. In addition, an alternative synthesis was used for the preparation of diarylcyclopentene derivatives by the reduction of the carbonyl group in diarylcyclopentenones.[27] The method includes the following three steps: the reduction of diarylcyclopentenones with sodium borohydride to hydroxy derivatives followed by tosylation and reduction with sodium hydride in the last steps, however it is difficult to evaluate the experimental opportunities of the method as the synthesis was carried out only for a single substrate.



Scheme 1 Recent approaches to the synthesis of photochromic diarylcyclopentenes

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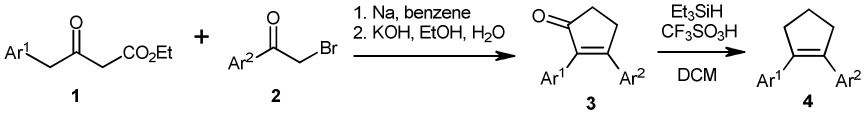
In the last decades photochromic diarylethenes bearing azole units[28-32] have attracted much attention because of their potential ability to form hydrogen bond and the possibility of its application as an effective tool for the spatiotemporal control of switchable biological systems.[33]

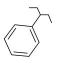
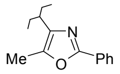
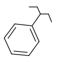
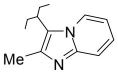
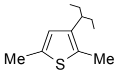
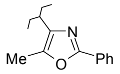
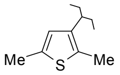
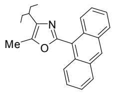
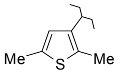
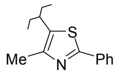
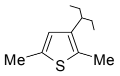
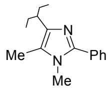
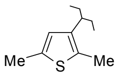
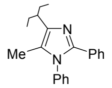
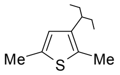
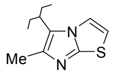
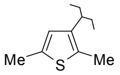
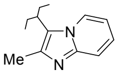
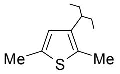
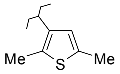
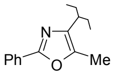
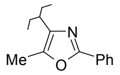
Therefore, the development of an alternative method for the preparation of diary(hetaryl)lcyclopentenes based on azoles, primarily unsymmetrical, is of most importance for the design of new smart materials for various fields of science, medicine and technology. In this study, we present a novel method for the synthesis of diaryl(hetaryl)cyclopentenes by ionic hydrogenation of appropriate cyclopentenone derivatives.

Earlier, we have proposed a new type of photochromic diarylethenes **3** based on the cyclopentenone core as an ethene bridge (Scheme 2).[34] These compounds can be synthesized from readily available ketoesters **1** and bromoketones **2** based on thiophene, benzothiophene, benzene,[34,35] oxazole,[36,37] imidazole[38] derivatives, as well as some other heterocyclic compounds.[39] Due to the possibility of varying the heterocyclic moieties, 2,3-diaryl(hetaryl)cyclopent-2-en-1-ones can be considered as suitable synthons for the synthesis of diarylcyclopentene derivatives. We have found that the ionic hydrogenation (Kursanov reaction)[40] in Olah's modification[41] is a convenient method for carbonyl reduction. In this reaction triethylsilane serves as a reducing agent in the presence of trifluoromethanesulfonic acid. A wide range of 2,3-di(het)arylcyclopent-2-en-1-ones **3** were tested in the ionic hydrogenation reaction (Scheme 2, Table 1).



Scheme 2 Synthetic protocol for the preparation of diarylcyclopentenes **4**

Table 1 Structures and spectral properties of diarylethenes **3** and **4**

№	Ar^1	Ar^2	Yield of **3**[a]	Yield of **4**	Diarylethene **3**		Diarylethene **4**	
					λ_{max}(A)[b]	λ_{max}(B)[c]	λ_{max}(A)[b]	λ_{max}(B)[c]
3a/4a			35%	71%	300	-[d]	294	-[d]
3b/4b			52%	64%	362	-[e]	319	-[e]
3c/4c			40%	65%	298	523	290	452
3d/4d			15%	61%	251, 385	-[f]	250, 385	-[f]
3e/4e			32%	60%	343	501	325	420
3f/4f			21%	50%	329	555	293	460
3g/4g			35%	40%	327	558	296	481
3h/4h			20%	57%	346	540	284	424
3i/4i			34%	48%	359	565	304	500
3j/4j			60%	0%				
3k/4k			33%	0%				

[a]The yields of **3** are given for two steps; [b]The absorption maxima of the open-ring isomer, nm; [c]The absorption maxima of the closed-ring isomer, nm; [d]The irreversible photorearrangement affords a naphthalene derivative [ref 42]; [e]Stable under irradiation; [f]Photochromic properties are poorly manifested.

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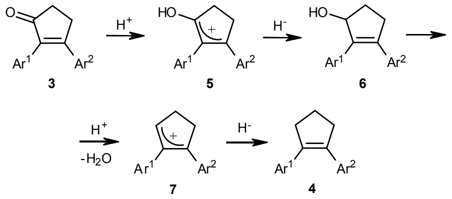
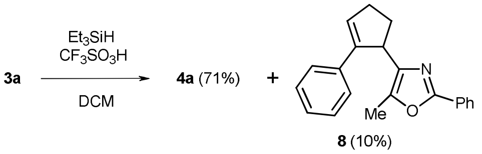
The nature of the heterocycle attached to the central double bond strongly affects the ionic hydrogenation process. The reduction of ketones, including benzene or 2,5-dimethylthiophene at position 2 of the cyclopentenone and azoles at position 3 (compounds **3a-i**), proceeded smoothly in 40-71% yields. The ionic hydrogenation of diarylethenes bearing oxazolyl and thiazolyl moieties (compounds **3a-e**) was accomplished at room temperature, whereas the reduction of imidazole (**3f,g**), imidazo[2,1-*b*]thiazole (**3h**) and imidazo[1,2-*a*]pyridine (**3i**) derivatives requires prolonged heating under reflux. This can be explained by strong basicity of the imidazole rings, resulting in the protonation of the starting diarylethenes, thus decelerating the ionic hydrogenation process. Meanwhile, we failed to reduce bis-(2,5-dimethylthien-3-yl)cyclopentenone **3j**. Even after prolonged heating under reflux (for more 12 hrs), no conversion was observed and the starting compound was completely returned (for details see Supplementary data). The increase of the reaction temperature (refluxing in dichloroethane) also does not lead to the desired results, there is observed only a gradual degradation of the starting cyclopentenone. The proposed mechanism of this transformation involves two-fold stepwise protonation-hydride transfer reaction (Scheme 3). Apparently, the protonation of **3j** produces the more stabilized carbocation intermediate **5**, which completely inhibits the hydride transfer and the further reduction of carbonyl groups.[41] Another limitation of this reaction is that it is difficult to reduce bis-oxazolyl derivative **3k**. In this case, the reaction was accompanied by a number of side processes and the target product was not isolated.



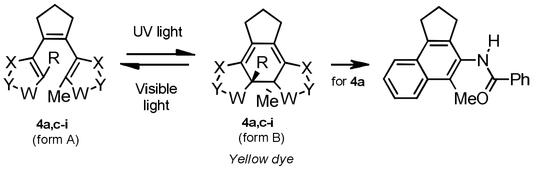
Scheme 3 Proposed mechanistic pathway of the ionic hydrogenation of the diarylcyclopentenones

As can be seen in Table 1, the reduction of diarylcyclopentenones **3a-i** proceeds in moderate yields (48-71%). It should be noted that in all the cases except diarylethene **3a**, the reaction gives no by-products and only a slight resinification is observed. An interesting result was obtained in the reduction of **3a**. Thus, the reaction affords by-product **8** in 10% yields along with the target diarylcyclopentene **4a** in 71% yield (Scheme 4). The formation of this isomer could be explained by [1,3]-H shift of diarylethene **4a**.



Scheme 4 The ionic hydrogenation of the cyclopentenone **3a**.

Depending on the nature of aryl moieties, diarylethenes **4** showed different behavior under UV irradiation. Diarylethene **4a** based on oxazole and benzene rings underwent a photorearrangement to a naphthalene derivative.[42] Compound **4b** (bearing benzene and imidazo[1,2-*b*]pyridine as the substituents), as well as parent ketone **3b**, showed unexpected stability under the action of light. On the contrary, compounds **4c,e-i** comprising two heterocycles as aryl moieties (excluding anthracene derivative **4d**, which has no photochromic properties because of strong fluorescence) exhibited typical photochromic properties (Scheme 5).



Scheme 5 Photocyclization of diarylcyclopentenes

Figure 1 presents the absorption spectra of a solution of **4f** before and after UV irradiation. Initial isomer **A** has a maximum at 293 nm; photoisomer **B**, at 460 nm. A reverse photoreaction occurs under the action of visible light. As can be seen in Table 1, the reduction of the carbonyl group in diarylethenes **3** resulted in a hypsochromic shift of the maxima of both the initial and photoinduced forms. It should be noted that photochromic diarylethenes **3c,e-i** characterized by absorption maxima in the blue region of the visible spectrum, in other words, they are yellow photochromes. Earlier, the lack of examples of such photochromes has been noted,[5,6] and solutions to this issue have been proposed in a number of studies.[7-10] As can be seen in Table 1, the introduction of various azole groups into cyclopentene-based diarylethenes gives rise to photochromes with absorption maxima of form **B** in the range from 420 to 500 nm. We supposed that a new synthetic strategy for the preparation of azole-containing diaryl(hetaryl)cyclopentenes opens up new opportunities to access the photochromic compounds with specified spectral properties including absorption maxima.

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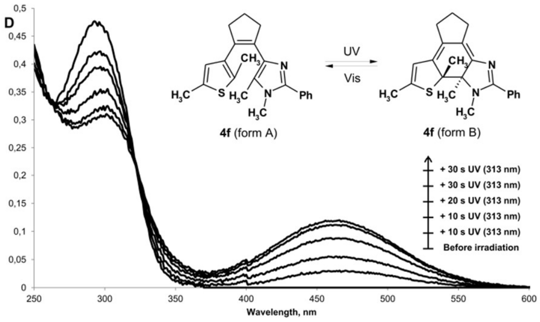

Figure 1. Changes of an absorption spectrum of compound **4f** under irradiation with UV light (313 nm, 6W lamp) in acetonitrile ($c \approx 10^{-5}$ M).

Conclusions

In summary, we have proposed a new synthetic approach for the preparation of photoactive diaryl(hetaryl)cyclopentenes. The method allows the synthesis of unsymmetrical products bearing thiophene, benzene or various azoles as aryl moieties starting from appropriate available ketones in 40-71% yields.

Acknowledgements

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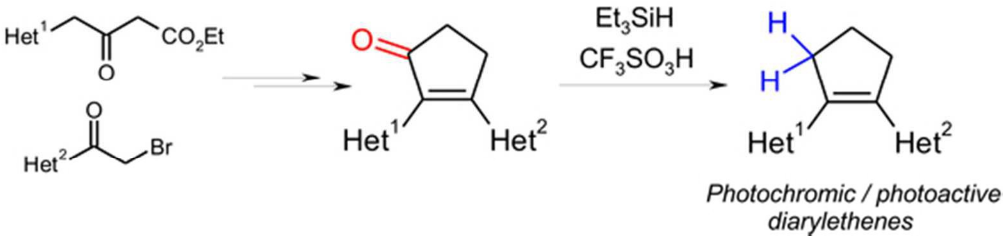

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