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Regiodivergent Synthesis of Bis(4-oxycoumarin)-based Dioxabicycles: Exploration of [4 + 4] (Heterocyclo)reversion/addition and 1,5-Hydrogen Shift Photochromism

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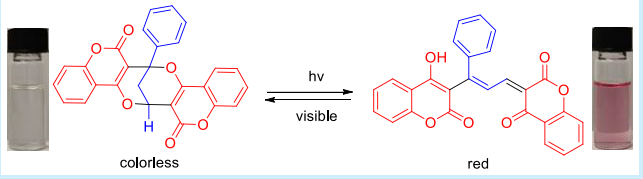
ABSTRACT: Two isomeric dioxabicyclic molecular skeletons were constructed by employing the concepts of divergent synthesis. A base-mediated and an acid-catalyzed pseudo-three-component reaction of two equivalents of 4-hydroxycoumarin and (*Z*)-3-chloro-3-phenylacrylaldehyde yielded the corresponding bis(4-oxycoumarin)-based 2,6- and 2,8-dioxabicycles, respectively. The prepared colorless 2,6-dioxabicycles turned red upon UV irradiation and underwent the reverse reaction when exposed to visible light. The photochromism was proposed to proceed via a sequential [4 + 4] (heterocyclo)addition/reversion and 1,5-hydrogen shift on the basis of photogenerated product-trapping experiments.

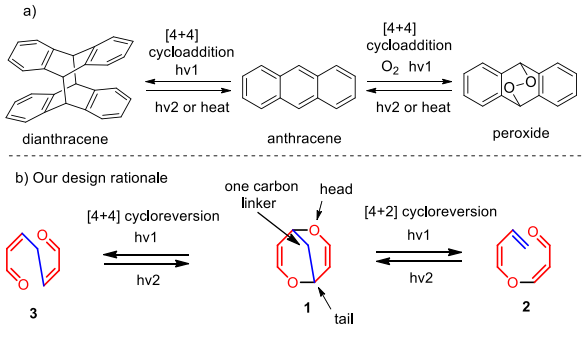


Photochromism is defined as the reversible transformation of a chemical species between two forms by the absorption of electromagnetic radiation, in which the two forms have different absorption spectra. Compounds with photochromic properties may have wide applications in the areas of electronic display,[1] information storage,[2] and so on.[3] Various organic compounds exhibiting photochromism and their unique properties have been reported in the literature,[4] to name a few, the trans/cis isomerization of azobenzene,[5] the electrocyclic ring-opening/closing reaction of diarylethenes,[6] napthopyranes,[7] and the dimerization photoreaction of anthracene[8] (Scheme 1a).

The photochromic property of anthracene not only results in a change of absorption but also leads to a large change in the dipole between two states, which can be used for many different applications, including smart materials,[9] photoactive receptors,[10] and the modulation of magnetic properties.[11] Nevertheless, because of its low conversion efficiencies and its tendency to undergo side reactions with oxygen,[12] anthracene photochromism is not as widely used as the unimolecular photoreactions of azobenzenes or diarylethenes. Whereas the efficiency of anthracene dimerization may be substantially enhanced by connecting two anthracenes together via a linker,[8e] the resulting bisanthracene still suffers from the undesired competition of unsymmetrical dimerization as well as other side reactions such as [4 + 2], [2 + 2], or [6 + 6] cycloadditions. Therefore, the development of an oxygen-insensitive, regiospecific [4 + 4] cycloaddition-based photochromic dye with sharp color variation as an output property remains to be a challenging task for organic chemists. In our continuing efforts to explore photochromic colorants with novel molecular scaffolds as well as new photochromic mechanisms, we proposed to design 2,6-dioxabicycle-based photochromic dye **1** in which two oxygen atoms were introduced onto the molecule, aiming to eliminate the possible oxygenation reaction and other undesired cycloadditions (Scheme 1b).

To enhance the ring-opening/closing efficiency upon irradiation, the proposed bicycle **1** was assembled by connecting two molecules of diene from head to tail (i.e., oxygen to carbon), followed by bridging via a one-carbon

Scheme 1. (a) Photodimerization and Oxidation of Anthracene and (b) Design Rationale for the Potential 2,6-Dioxabicycle-based Photochromic Dye 1



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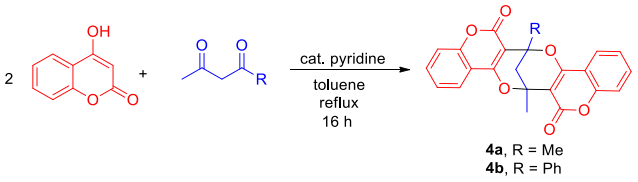
linker between the two tail carbons. We hypothesized that when compound **1** is irradiated, compound **2** will be generated if the reaction proceeds with a [4 + 2] cycloreversion mechanism, whereas compound **3** will be formed if the reaction proceeds with a [4 + 4] cycloreversion mechanism. Here we report the efficient synthesis of bis(4-oxycoumarin)-based dioxabicycles via a multicomponent reaction. The photochromic properties and the plausible mechanism of the prepared compounds were investigated by the trapping and subsequent characterization of the photogenerated product.

In contrast with anthracene, in which benzene is used to stabilize the cyclic adduct (dianthracene), we intended to employ a coumarin moiety to serve this purpose. After a literature search, we realized that the coumarin-based 2,6-dioxabicycle **4a** has been previously prepared[13] by the pseudo-three-component reaction of 2 equiv of 4-hydroxycoumarin with pentane-2,4-dione, as shown in Scheme 2. To investigate

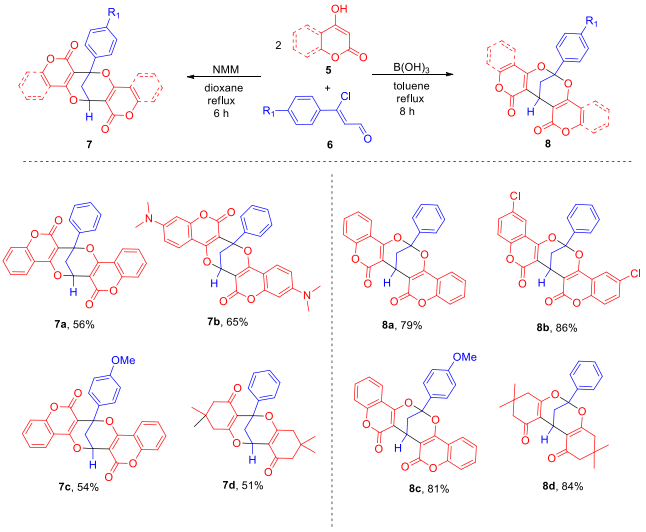
Scheme 2. Pseudo-Three-Component Synthesis of 2,6-Dioxabicycles 4a and 4b



their potential photochemical properties, we synthesized the 2,6-dioxabicycles **4a** and **4b** accordingly, but they were found be light-insensitive. This crucial information prompted us to relook into our proposed design strategy, and we speculated that the replacement of the bridgehead methyl group of **4b** with a hydrogen atom might lead to a light-sensitive dioxabicycle.

Our previous efforts on the photochromism of oxazabicycles[14] and divergent synthesis of lamellarins and their derivatives[15] propelled us to judiciously choose 4-hydroxycoumarin and (*Z*)-3-chloro-3-phenylacrylaldehyde to construct the designed dioxabicyclic core. To begin with, the reaction of 4-hydroxycoumarin (**5**) with (*Z*)-3-chloro-3-phenylacrylaldehyde (**6**, R_1 = H) in the presence of triethylamine (1 equiv) as a base in toluene under refluxed conditions for 4 h furnished the 2,6-dioxabicycle **7a** in 32% yield. Interestingly, a minor product (<5%) of 2,8-dioxabicyclic isomer **8a** was also detected. This observation led us to further explore the possible divergent synthesis of **7a** and **8a** by screening of reaction conditions with different acids and bases. As a result, we found that when 4-hydroxycoumarin (**5**) was reacted with **6** (R_1 = H) using *N*-methylmorpholine (NMM, 1.5 equiv) as a base in dioxane at 90 °C for 6 h, the 2,6-dioxabicycles **7a−d** were obtained as the exclusive products (Scheme 3). In contrast, when the reaction was carried out in the presence of a catalytic amount of $B(OH)_3$ in toluene at 120 °C for 8 h, the 2,8-dioxabicycles **8a−d** were generated in good yield, exclusively. The structures of dioxabicyclic isomers **7a−d** and **8a−d** can be easily differentiated by their proton NMR spectra. The characteristic triplet absorption peaks that appeared at a chemical shift of 5.50 to 6.05 ppm were assigned to the bridgehead hydrogen for 2,6-dioxabicycles **7a−d**, whereas those at 4.40 to 4.82 ppm were assigned to 2,8-dioxabicycles **8a−d**. The molecular structures of dioxabicycles **7a** and **8a** were further verified by the X-ray crystallography. (See the SI.)

Scheme 3. Pseudo-Three-Component Synthesis of Dioxabicycles 7a−d and 8a−d



The mechanism for the formation of dioxabicycle **7a** under basic conditions via this pseudo-three-component reaction is proposed to proceed with a sequence of 1,4-addition, cyclization, 1,2-addition, and a cyclization process. Intriguingly, the proposed sequence of 1,4- and 1,2-additions is reversed when the reaction is performed under acidic conditions, generating dioxabicycle **8a** as the major product. (See the SI for details.)

With dioxabicycles **7a−d** and **8a−d** in hand, we then evaluated their photochromic properties. Upon ultraviolet irradiation (352 nm) in acetonitrile, the 2,8-dioxabicycles **8a−d** were found to be light-insensitive and remain intact even under prolonged irradiation. Conversely, the 2,6-dioxabicycles **7a−c** turned from colorless to red soon after irradiation (except for **7d**, in which the color variation was not so obvious). For instance, with the increase in the exposure time of **7a** to UV light, a new absorption band with a peak wavelength around 554 nm gradually increased on the UV−vis spectra, as shown in Figure 1. When irradiated with visible light (580 nm), the photogenerated product in acetonitrile decayed away with the disappearance (i.e., turning colorless) of the 554 nm band (Figure 1, inset). The photochromic process was reversible and could be repeated 10 times without a significant loss of absorption at the 554 nm band. Furthermore, the photogenerated product of **7a** was found to be stable in the dark at room temperature for at least 72 h and at 80 °C for 10 h. These observations suggest that the conversion between **7a** and its photogenerated product can be categorized as a P-type photochromism. It should be noted that whereas the coumarin moiety was employed to harness the fluorescence emission as a potential output property in our original design, unfortunately, in the current system, we did not observe the fluorescence emission for either **7a** or its photogenerated product.

Although the photogenerated product of **7a** was thermally stable, all attempts to isolate it failed, mainly due to the low photoconversion yield. Moreover, some photogenerated product reverted back to the original form in daylight during the purification process. To gain insights into the structure of the photogenerated product, the compounds generated by the irradiation of **7b** and **7c** were trapped *in situ* by an excess of diazomethane in acetonitrile and hydrogen gas in the presence

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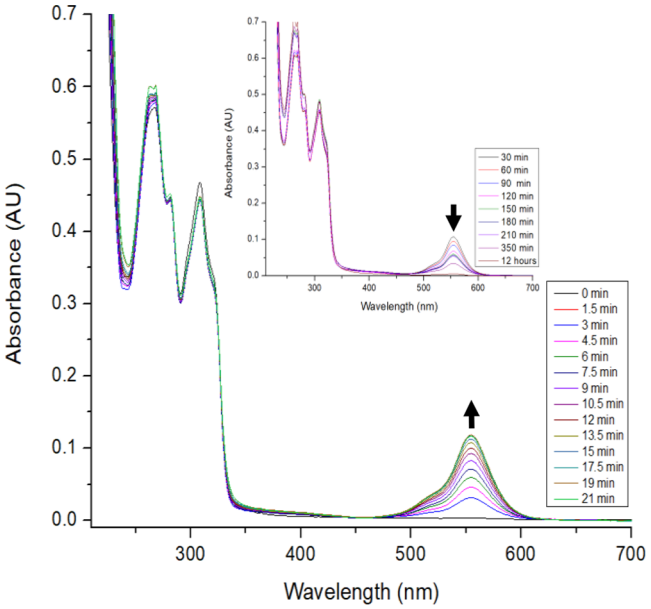
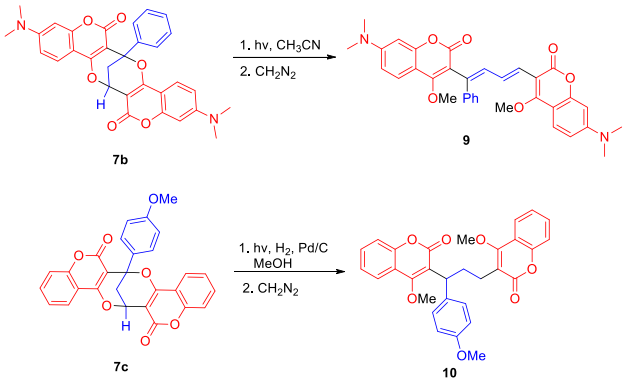


Figure 1. Absorption spectra of **7a** (3.5×10^{-5} M in CH_3CN) obtained with different exposure times (352 nm), 0−21 min, in increments of 1.5 to 2 min. (inset) Absorption spectra of the photogenerated product (3.5×10^{-5} M in CH_3CN) obtained with different exposure times (580 nm), 0−12 h, in increments of 0.5 to 6 h.

of palladium on carbon in methanol followed by diazomethane to afford compounds **9** and **10**, respectively, as shown in Scheme 4. The molecular structures of both **9** and **10** were

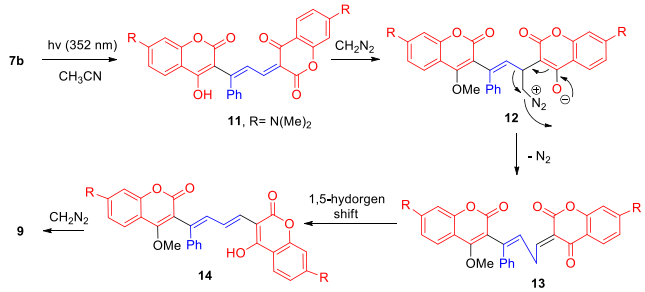
Scheme 4. Trapping of the Photogenerated Product



fully characterized by spectroscopic analysis. (See the SI for details.) The isolation of **9** and **10** indicates that the photogenerated product of **7b** reacted with 3 equiv of diazomethane, and the photogenerated product of **7c** reacted with 2 equiv of hydrogen and diazomethane gases each during the trapping process. On the basis of the *in situ* diazomethane and hydrogen trapping results depicted in Scheme 4, the structures of the photogenerated products of **7b** and **7c** were then elucidated.

Scheme 5 outlines the proposed mechanism for trapping of the photogenerated product **11**. Upon irradiation, the dioxabicycle **7b** is converted to the ring-opened product **11**. In the presence of an excess of diazomethane, the photogenerated product **11** is then swiftly methylated, followed by the 1,4-addition of the second equivalent of diazomethane to

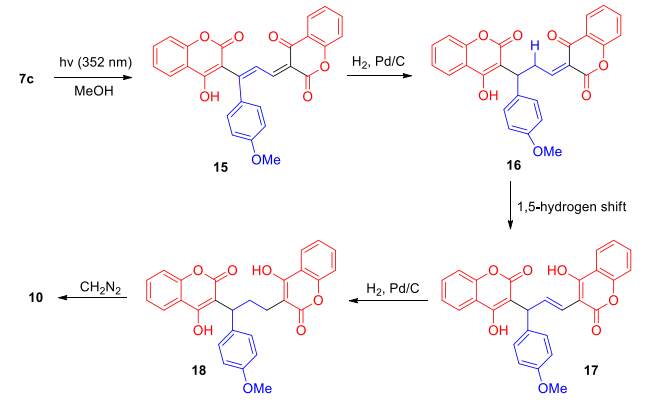
Scheme 5. Proposed Mechanism for Trapping of the Photogenerated Product 11



give the zwitterion **12**. The subsequent 1,2-vinyl migration of **12** to insert the methylene group into the molecular backbone along with expelling of nitrogen gas affords the compound **13**. The facile 1,5-hydrogen shift of **13** from the central methylene hydrogen to the coumarin carbonyl oxygen atom yields the 4-hydroxycoumarin **14**. The final methylation of **14** with the third equivalent of diazomethane affords the isolated compound **9**.

Similar to that of **11**, we speculate that the photogenerated product **15** is formed upon the exposure of **7c** to UV irradiation, as outlined in Scheme 6. The central double bond

Scheme 6. Proposed Mechanism for Trapping of the Photogenerated Product 15



of **15** is then hydrogenated by the exposure to the first equivalent of hydrogen gas to give the compound **16**. The subsequent 1,5-hydrogen shift of the methylene hydrogen to the coumarin carbonyl oxygen atom of **16** yields the olefin **17**. Further hydrogenation of the central double bond of **17** with the second equivalent of hydrogen gas affords **18**, which is unstable and hence is methylated with 2 equiv of diazomethane to receive the isolated product **10**.

Scheme 7 depicts the plausible mechanism for the photochromic switch between **7a** and the photogenerated **20** on the basis of the aforementioned two trapping experiments. Upon irradiation, the 2,6-dioxabicycle **7a** presumably proceeds with [4 + 4] heterocycloreversion to give the bis(chromane-2,4-dione) **19**, which can easily undergo a 1,5-hydrogen shift from the central methylene hydrogen to the carbonyl oxygen atom to yield the red photogenerated product **20**. The color of **20** can presumably be attributed to the intramolecular charge transfer between the electron-rich 4-hydroxycoumarin moiety and the electron-poor 3-methylenechromane-2,4-dione moiety.[16] This hypothesis is partially supported by the UV−vis

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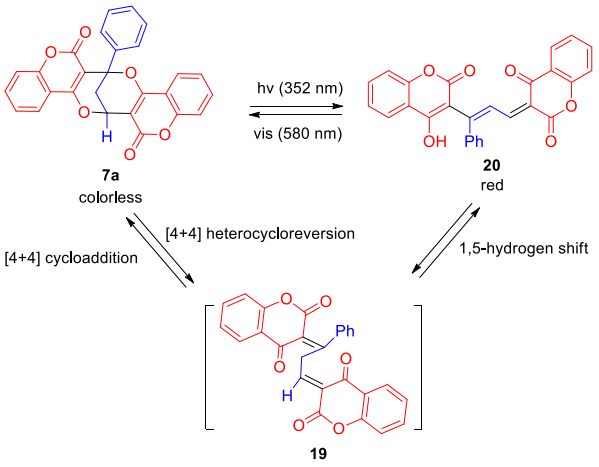
Scheme 7. Proposed Photochromic Mechanism between 7a and 20



absorption spectra of the photogenerated compound in solvents with different polarities. (See the SI.) When exposed to visible light, the colored **20** can be reverted back to the colorless 2,6-dioxabicycle **7a** via the reverse process, that is, a 1,5-hydrogen shift and a [4 + 4] heterocycloaddition. To the best of our knowledge, the interconversion between ring-closed **7a** and ring-opened **20** represents the first photochromic system that involves the combination of a [4 + 4] heterocycloreversion/heterocycloaddition with a 1,5-hydrogen shift as the switching mechanism.

Although, unlike their isomeric 2,6-dioxabicycles **7a–d**, the 2,8-dioxabicycles **8a–d** were found to be photochemically inactive, the structural resemblance of the 2,8-dioxabicyclic core to the bridged [3.3.1]dioxabicyclic natural products such as dracoflavans,[17] sanctis A–C,[18] diinsinin,[19] and procyanidin A1 and A2[20] makes them potential candidates for the future evaluation of their biological activities.

In summary, an efficient one-pot, divergent synthesis of the 2,6-dioxabicycles **7a–d** and 2,8-dioxabicycles **8a–d** by base-mediated and acid-catalyzed pseudo-three-component reactions of (*Z*)-3-chloro-3-phenylacrylaldehyde and 4-hydroxycoumarin is presented. The prepared colorless 2,6-dioxabicycles **7a–d** were found to be photochromic. They turned red upon UV irradiation and underwent the reverse reaction when exposed to visible light. The *in situ* trapping of the photogenerated products of **7b** and **7c** by diazomethane and hydrogen gases confirms the formation of the colored species **11** and **15**, respectively. Our studies suggest that the photochromism of 2,6-dioxabicycles involves the [4 + 4] heterocycloreversion of the dioxabicyclic skeleton followed by the 1,5-hydrogen shift of the methylene hydrogen to the adjacent carbonyl oxygen atom. The colored photogenerated product can be reverted back to the starting material via the reverse process, that is, a 1,5-hydrogen shift and a [4 + 4] heterocycloaddition. The further exploration of the possibility of an extension of this photochromic dioxabicyclic molecular scaffold to the trioxabicyclic scaffold is currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00904.

Experimental details and spectral data of **4a,b**, **7a–d**, **8a–d**, **9**, and **10** (PDF)

Accession Codes

CCDC 1952779–1952780 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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