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Radical Cation Diels−Alder Reactions by TiO_2 Photocatalysis

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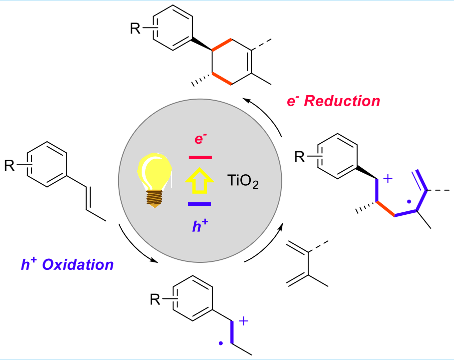
Supporting Information

ABSTRACT: Radical cation Diels−Alder reactions by titanium dioxide (TiO_2) photocatalysis in lithium perchlorate/nitromethane solution are described. TiO_2 photocatalysis promotes reactions between electron-rich dienes and dienophiles, which would otherwise be difficult to accomplish due to electronic mismatching. The reactions are triggered by hole oxidation of the dienophile and are completed by the excited electron reduction of the radical cation intermediate at the dispersed surface in the absence of any sacrificial substrate.



Light has long been recognized for its potential to catalyze chemical reactions, which is widely referred to as photocatalysis. Photoexcited catalysts generate radical ion species from neutral starting materials via oxidative and/or reductive single electron transfer (SET). These species can act as reactive intermediates in further transformations. A wide variety of organic chromophores have been devised and used as photocatalysts to trigger chemical reactions through SET, a process which is more commonly called photoinduced electron transfer.[1] Furthermore, since the early works by MacMillan,[2] Yoon,[3] and Stephenson,[4] the use of transition metal complexes as photocatalysts has occupied a central place in new reaction development in the field of synthetic organic chemistry.[5] The chromophores and complexes are soluble small molecules, and therefore, they can both undergo homogeneous SET.

Since the pioneering work by Fujishima and Honda,[6] heterogeneously dispersed semiconductors have also been studied as photocatalysts to induce oxidative and/or reductive SET at the surfaces. The hole/excited electron pair generated upon irradiation can act as an oxidant and reductant, even in the absence of sacrificial substrates that are generally needed for homogeneous photocatalysts. Although semiconductor photocatalysis can achieve various useful redox transformations,[7] its application in the field of synthetic organic chemistry is somewhat less widespread. This is probably due to reactive oxygen species (ROS) produced at the surfaces in aqueous aerobic conditions that cause the decomposition of organic compounds via carbon−carbon bond cleavage.[8] Nevertheless, challenging carbon−carbon bond formation has been accomplished, mainly by using titanium dioxide (TiO_2) as a typical semiconductor photocatalyst.[9] Generally, the reactions must be carried out under dry anaerobic conditions to prevent the production of ROS. However, Wang demonstrated that these conditions would not be required if the reaction of the carbon-centered radical cation with a carbon nucleophile was sufficiently more favorable than the undesired oxygenation by ROS.[10]

We have been developing novel cycloadditions involving carbon−carbon bond formation by electrocatalysis in lithium perchlorate/nitromethane ($LiClO_4/CH_3NO_2$) solution,[11] which has proven to be beneficial in reactions between carbon-centered radical cations and carbon nucleophiles.[12] Recently, we demonstrated that TiO_2 photocatalysis in combination with a $LiClO_4/CH_3NO_2$ solution was a powerful redox option to catalyze [2 + 2] cycloadditions (Scheme 1a).[13] It is believed that the reactions are triggered by hole oxidation of electron-rich alkenes, generating highly reactive radical cation species, which are then trapped by unactivated alkene nucleophiles. The resulting radical cation intermediates were reduced by excited electrons to complete the net redox-neutral reactions, affording [2 + 2] cycloadducts. We envisioned that such SET-catalyzed cycloadditions by TiO_2 photocatalysis should find further applications in synthetic organic chemistry. Described herein are radical cation Diels−Alder reactions by TiO_2 photocatalysis (Scheme 1b).

The present work began with the reaction between *trans*-anethole (**1**) and 2,3-dimethyl-1,3-butadiene (**2**) as a model using Aeroxide P25 (Table 1).[14] Such electronically mismatched Diels−Alder reactions have been made possible by the use of Ru complexes as photocatalysts.[15] Extensive efforts to explore earth-abundant materials as alternatives have added Cr[16] and Fe[17] complexes and graphitic carbon nitride[18] to the growing toolbox of photocatalysts that enable the reaction. TiO_2 was also found to catalyze the reaction, affording cycloadduct **3** in excellent yield (entry 1). When the reaction was carried out in the absence

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Scheme 1. Cycloadditions by TiO_2 Photocatalysis

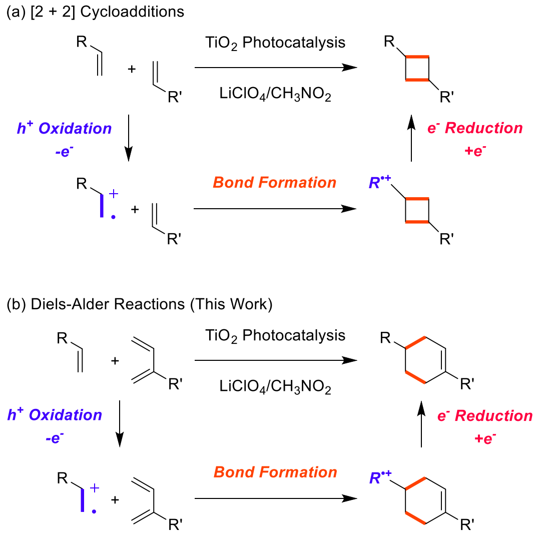
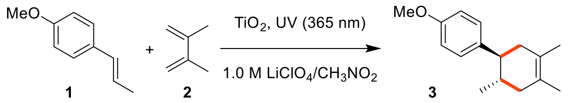


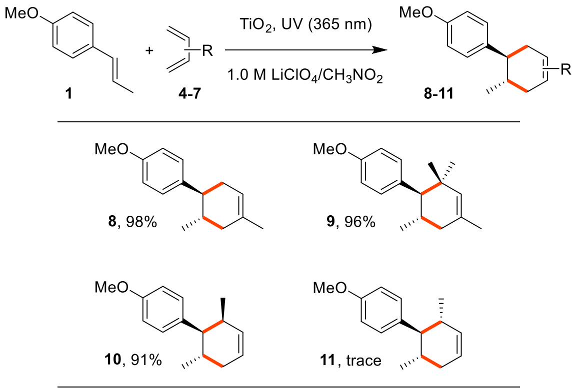
Table 1. Optimization of the Conditions for the Diels–Alder Reaction



entry	conditions[a]	yield (%)[b]
1		97 (0)
2	no TiO_2	71 (0)
3	no light	6 (78)
4	no TiO_2, no light	trace (79)
5	no $LiClO_4$	trace (61)

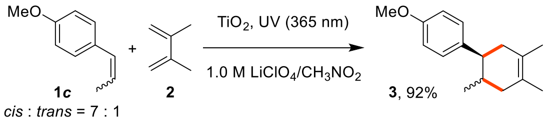
[a] Unless otherwise stated, reactions were carried out on a 0.20 mmol scale of *trans*-anethole (**1**) with 2 equiv of 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h. [b] Determined by ^{1}H NMR analysis using benzaldehyde as an internal standard. Recovered starting material is reported in parentheses.

Scheme 2. Scope of Dienes for the Diels–Alder Reaction[a]



[a] Reactions were carried out on a 0.20 mmol scale of *trans*-anethole (**1**) with 2 equiv of the dienes **4**–**7** and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h. Yields were determined by ^{1}H NMR analysis using benzaldehyde as an internal standard.

Table 2. Diels–Alder Reaction of *cis*-Anethole (**1*c***) and 2,3-Dimethyl-1,3-butadiene (**2**)



entry[a]	concentration of **2**	*cis*/*trans*[b]
1	10 mM (0.20 equiv)	1:11
2	100 mM (2 equiv)	1:6
3	1000 mM (20 equiv)	1:7

[a] Reactions were carried out on a 0.20 mmol scale of *cis*-anethole (**1*c***) with 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h. [b] Determined by ^{1}H NMR analysis.

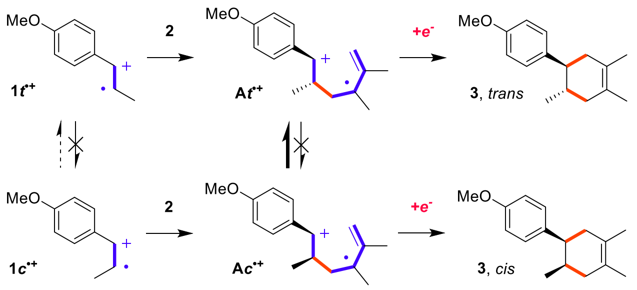
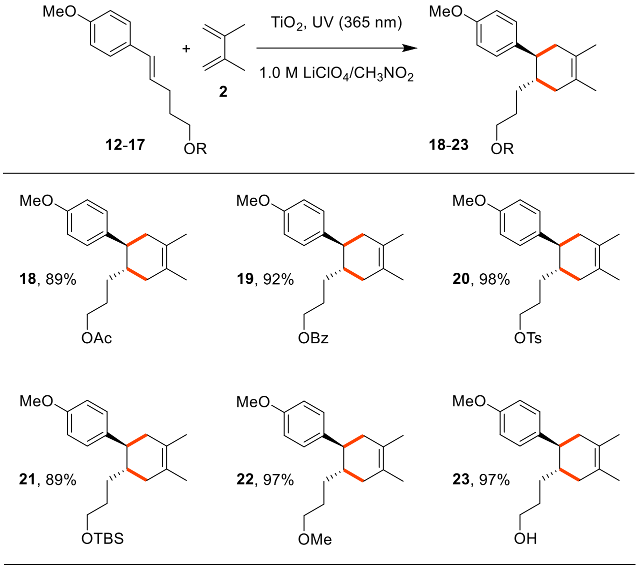


Figure 1. Plausible reaction mechanism for the isomerization.

Scheme 3. Scope of *trans*-Anetholes for the Diels–Alder Reaction[a]



[a] Reactions were carried out on a 0.20 mmol scale of *trans*-anethole derivatives (**12**–**17**) with 2 equiv of 2,3-dimethyl-1,3-butadiene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h. Yields were determined by ^{1}H NMR analysis using benzaldehyde as in internal standard.

of TiO_2, the yield decreased somewhat (entry 2).[19] This difference is significant as no starting material was recovered. Although the mechanisms are still unclear, the decrease was mainly a result of the dimerization of **1**. The reaction was slightly catalyzed by TiO_2 even under dark conditions, which might be due to acid/base sites on the surface (entry 3). In the absence of TiO_2 under dark conditions, only a trace amount of **3** was obtained (entry 4). It was also confirmed that $LiClO_4$ was essential for the reaction (entry 5).

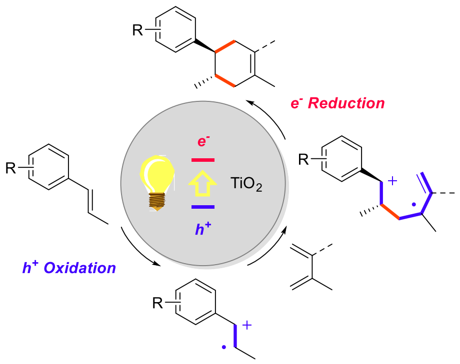


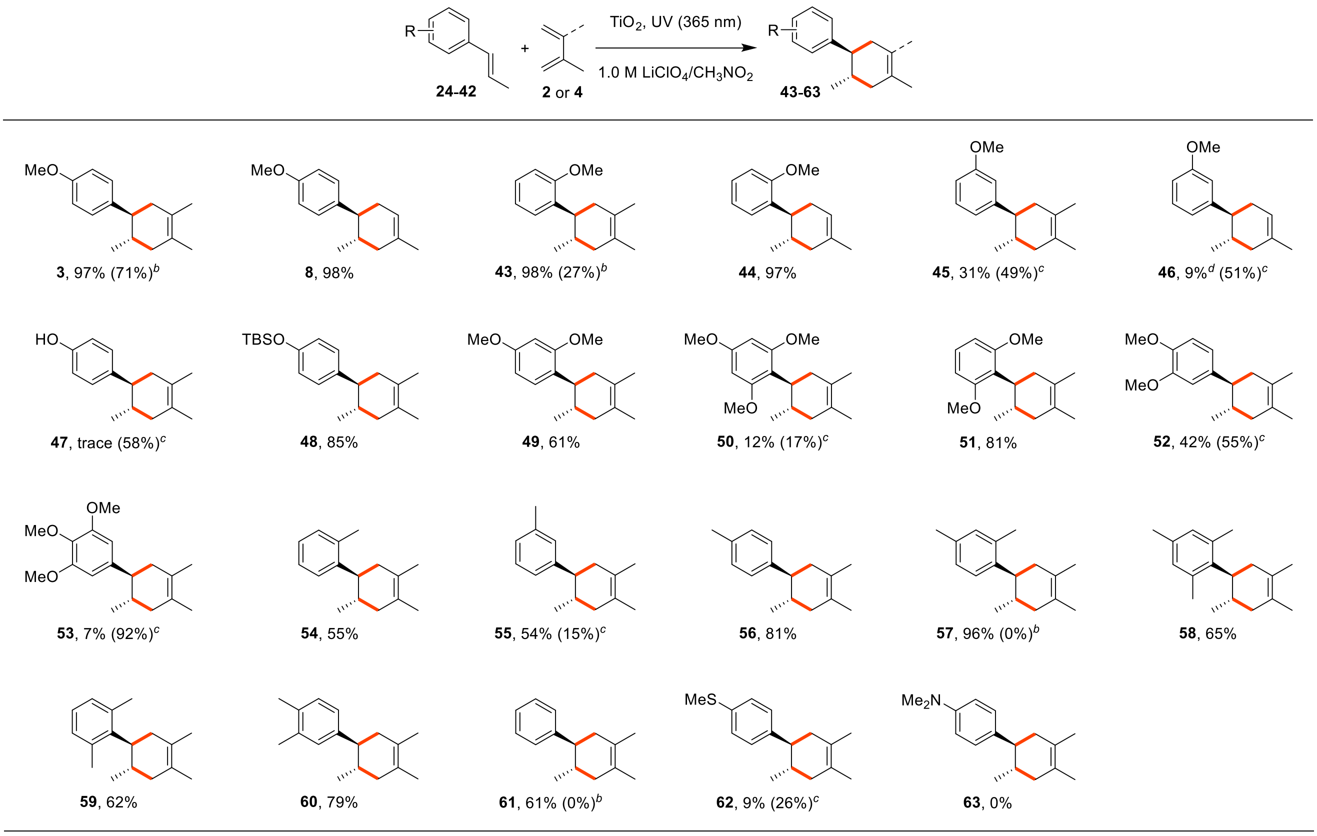
Figure 2. Plausible reaction mechanism for the Diels−Alder reaction.

With the optimized conditions in hand, the reactions of **1** with several dienes **4**−**7** were conducted (Scheme 2). Isoprene **4** gave the cycloadduct **8** in excellent yield without any difficulty, and the sterically bulky diene **5** was also found to be a successful substrate. As expected, cycloadduct **10** was obtained in good yield from (*E*)-1,3-pentadiene (**6**), whereas the use of (*Z*)-1,3-pentadiene (**7**) was unsuccessful. Whereas *trans*-cycloadducts were selectively formed from *trans*-anethole (**1***t*), *cis*-anethole (**1***c*) was found to give a mixture of *cis*- and *trans*-cycloadducts (**3**) with **2** (Table 2). This observation is consistent with previous reports,[20] suggesting that the reaction proceeds via a stepwise pathway, and a loss of stereochemistry can potentially happen by bond rotation of the anethole radical cation ($\mathbf{1}^{\bullet+}$) and/or that of the radical cation intermediate ($\mathbf{A}^{\bullet+}$) (Figure 1). Bond rotation of $\mathbf{1}^{\bullet+}$ would be suppressed in the presence of a large excess of the diene **2**; however, the *cis*/*trans* ratio for cycloadduct **3** was not significantly affected by the concentration of diene **2**. This indicated that loss of stereochemistry was likely to occur by bond rotation of the radical cation intermediate $\mathbf{A}^{\bullet+}$. However, the possibility that bond rotation of $\mathbf{1}^{\bullet+}$ was much faster than trapping by diene **2** cannot entirely be ruled out.

To test the functional group tolerance, several *trans*-anethole derivatives (**12**−**17**) equipped with oxygen functionalities were prepared and used for the reaction with **2** (Scheme 3). As the oxygen electron(s) can potentially trap the radical cation,[21] an electron-withdrawing protective group is generally required. However, in addition to the substrates with an electron-withdrawing protective group (**18**−**20**), (silyl)ethers (**21**, **22**) and even a free alcohol (**23**) were found to be compatible with the reaction. This is probably attributed to the use of the $LiClO_4/CH_3NO_2$ solution, which facilitates reactions between carbon-centered radical cations and carbon nucleophiles.

The scope of the aromatic ring in the Diels−Alder reaction was investigated using variously substituted *β*-methylstyrenes (**24**−**42**) in combination with **2** or isoprene (**4**) (Figure 2 and Scheme 4). In addition to *para*-methoxy substitution (**3**, **11**), *ortho*-variants (**43**, **44**) were comparably effective for the reaction. On the other hand, *meta*-substitution (**45**, **46**) was significantly less effective, which was in good accordance with our previous observations. Although free phenol **47** was incompatible for the reaction, a silyl protective group (**48**)

Scheme 4. Scope of *β*-Methyl Styrene Derivatives for the Diels−Alder Reaction[a]



[a] Reactions were carried out on a 0.20 mmol scale of substituted *β*-methylstyrenes (**24**−**42**) with 2 equiv of 2,3-dimethyl-1,3-butadiene (**2**) or isoprene (**4**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 2 h. Yields were determined by ^1H NMR analysis using benzaldehyde as an internal standard. [b] Yields in the absence of TiO_2. [c] Recovered starting material. [d] Inseparable mixture.

was found to mask this functionality. Installation of additional methoxy group(s) generally had a negative impact over the reaction (**49−53**), especially for *meta*-substitution (**52**, **53**). In the case of 2,4,6-trimethoxy substitution (**50**), the radical cation is potentially stabilized on the aromatic ring, rendering the styrene double bond less reactive. In the previous reports, the aromatic ring of the *β*-methylstyrenes was electron-rich, e.g., substituted with alkoxy group(s), and most examples of this class were demonstrated by using **1**. However, *β*-methylstyrenes with weakly electron-donating methyl group(s) (**54−60**) were found to be productive under TiO_2 photocatalysis. Compared with the positional effect of the methoxy group(s), that of methyl group(s) seemed to have less impact, possibly because the electron density in the aromatic ring and steric hindrance around the styrene double bond should be balanced. Furthermore, a nonsubstituted *β*-methylstyrene that was previously reported to be an unsuccessful substrate under Ru complex photocatalysis and electrocatalysis gave the cycloadduct **61** in acceptable yield.

In conclusion, we have demonstrated that TiO_2 photocatalysis in combination with the use of a $LiClO_4/CH_3NO_2$ solution is a powerful redox option to catalyze radical cation Diels−Alder reactions. The $LiClO_4/CH_3NO_2$ solution facilitates reactions between carbon-centered radical cations and carbon nucleophiles, even in the presence of a nucleophilic oxygen functionality. We believe that TiO_2 photocatalysis should find complementary applications in synthetic organic chemistry that would be difficult to accomplish by molecular photocatalysis or electrocatalysis. Further design and development of reactions by TiO_2 photocatalysis are under investigation in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00526.

> Additional figures, general remarks, synthesis and characterization data, including copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(19) This is an exceptional example, and TiO_2 is crucial for most other cases.

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