


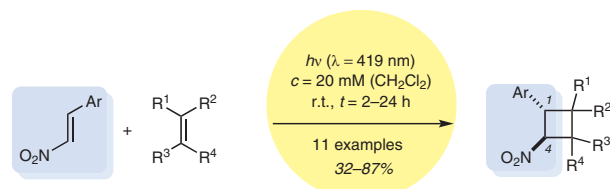
# Intermolecular [2+2] Photocycloaddition of $\beta$ -Nitrostyrenes to Olefins upon Irradiation with Visible Light

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Dedicated to Victor Snieckus, a dear colleague and friend, on  
the occasion of his 80<sup>th</sup> birthday



Received: 19.06.2017

Accepted after revision: 30.06.2017

Published online: 31.08.2017

DOI: 10.1055/s-0036-1588524; Art ID: st-2017-r0492-l

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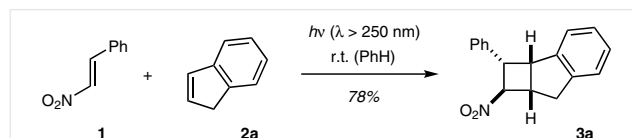
**Abstract** The title compounds were found to undergo a [2+2] photocycloaddition with olefins at  $\lambda = 419$  nm in  $\text{CH}_2\text{Cl}_2$  as the solvent. The resulting cyclobutanes were isolated in yields of 32–87% (11 examples) and showed a defined relative configuration at C1/C4 in the major diastereoisomer (nitro and aryl *trans*). The analysis of side products and triplet sensitization experiments support a mechanistic scenario in which a 1,4-diradical is formed as a key intermediate.

**Key words** cycloaddition, cyclobutanes, diastereoselectivity, nitro compounds, photochemistry, stereoselective synthesis, umpolung, visible light

Although [2+2] photocycloaddition chemistry<sup>1</sup> originates historically<sup>2</sup> from experiments performed with visible light, the advent of artificial UV light sources led – starting in the middle of the 20<sup>th</sup> century – to the almost exclusive use of short-wavelength ( $\lambda = 250$ –380 nm) irradiation in all areas of photochemistry. Interest in reactions that were promoted by long-wavelength ( $\lambda > 380$  nm) irradiation was spurred in the 1970s and in the 1980s by the desire to find suitable energy storage systems mainly based on the [2+2] photocycloaddition of norbornadienes to quadricyclenes.<sup>3</sup> Aromatic carbonyl compounds<sup>4</sup> and transition-metal salts<sup>5</sup> were found to act as triplet sensitizers in this transformation allowing the reaction to occur with visible light. More recently, triplet energy sensitization has been employed for enantioselective [2+2] photocycloaddition reactions that are promoted by visible light<sup>7</sup> in the presence of an appropriate sensitizer.<sup>8</sup> In the context of our work on the activation of chromophors by Lewis or Brønsted acids,<sup>9</sup> we became interested in the photochemistry of nitrostyrenes.<sup>10</sup> The compound class seemed amenable to un-

dergo direct intermolecular [2+2] photocycloaddition reaction upon excitation with visible light and we report in this communication on our preliminary results on this topic.

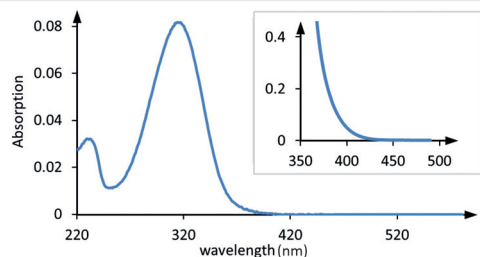
Already in the 19<sup>th</sup> century, the [2+2] photodimerization of *trans*- $\beta$ -nitrostyrene was observed to occur upon exposure to sunlight.<sup>11</sup> However, reactions with olefins in the spirit of an intermolecular [2+2] photocycloaddition have remained rare and were performed exclusively with short-wavelength light. Chapman et al. mentioned in a review on the photochemistry of unsaturated nitro compounds the reaction with olefins but did not provide any experimental details.<sup>12,13</sup>



**Scheme 1** [2+2] Photocycloaddition of *trans*- $\beta$ -nitrostyrene (**1**) and indene (**2a**) as reported by Majima et al.<sup>14</sup>

Later, Majima et al. employed the reaction of *trans*- $\beta$ -nitrostyrene (**1**) and indene (**2a**) to form cyclobutane **3a** (Scheme 1).<sup>14</sup> A high-pressure mercury lamp was employed as the light source in this transformation. In more recent work, pyrex-filtered irradiation was used to study the reaction of nitrostyrenes with silyl enol ethers.<sup>15,16</sup>

Inspection of the UV-Vis spectrum<sup>17</sup> of *trans*- $\beta$ -nitrostyrene in  $\text{CH}_2\text{Cl}_2$  (Figure 1) reveals a strong absorption centered at  $\lambda = 312$  nm ( $\epsilon = 16500$   $\text{M}^{-1}$   $\text{cm}^{-1}$ ). This band has been previously assigned to an allowed  $\pi\pi^*$ -transition with significant charge-transfer character.<sup>18,19</sup> At high concentration it is evident that the absorption continues into the visible region of the electromagnetic spectrum in line with the fact that *trans*- $\beta$ -nitrostyrene (**1**) is a yellow-colored solid.



**Figure 1** UV-Vis spectrum of *trans*- $\beta$ -nitrostyrene in  $\text{CH}_2\text{Cl}_2$  solution ( $c = 0.05 \text{ mM}$ ), the inset shows the long-wavelength absorption measured at  $c = 5 \text{ mM}$

In view of the apparent long-wavelength absorption of *trans*- $\beta$ -nitrostyrene (**1**), its reaction with indene was revisited. The concentration, the solvent, and the stoichiometry (3.1 equiv indene) were taken from previous work,<sup>14</sup> and the reaction was run for 23 hours (Table 1). We were pleased to find that conversion was not only complete when the mixture was irradiated with fluorescent lamps<sup>20</sup> at  $\lambda = 300, 350,$  and  $366 \text{ nm}$ , but also at  $\lambda = 419 \text{ nm}$  (Table 1, entries 1–4). In all cases, it was observed that major diastereoisomer **3a** was accompanied by a minor diastereoisomer to which structure **3a'** was assigned based on NOESY experiments. The diastereomeric ratio (d.r.) varied at around 3:1. Best yields were recorded at  $\lambda = 350 \text{ nm}$  (Table 1, entry 2) and  $\lambda = 419 \text{ nm}$  (Table 1, entry 4). Clearly, the [2+2] photocycloaddition was promoted by visible light as even long-wavelength light-emitting diodes (LEDs) led to a significant conversion at  $\lambda = 457 \text{ nm}$  and at  $\lambda = 470 \text{ nm}$  (Table 1, entries 5, 6). At  $\lambda = 517 \text{ nm}$ , there was essentially no conversion after 23 hours (Table 1, entry 7).

**Table 1** Conversion, Yield, and Diastereomeric Ratio in the Intermolecular [2+2] Photocycloaddition Reaction to Products **3a/3a'** in Correlation to the Irradiation Wavelength

Entry	$\lambda \text{ (nm)}^a$	Conv. (%)	Yield (%) <sup>b</sup>	d.r. ( <b>3a/3a'</b> ) <sup>c</sup>
1	300	100	49	77:23
2	350	100	83	80:20
3	366	100	64	77:23
4	419	100	75	75:25
5	457	71	50	75:25
6	470	42	18	73:27
7	517	<5	– <sup>d</sup>	–

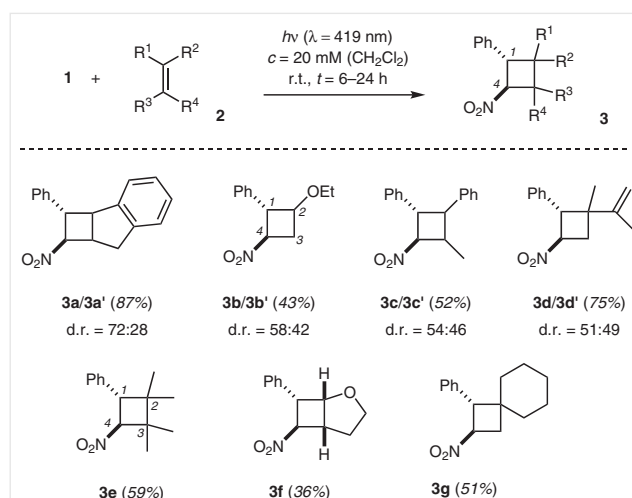
<sup>a</sup> For the emission spectra of the light sources, see ref.<sup>20</sup>

<sup>b</sup> Yield of isolated products **3a** and **3a'** as a mixture of diastereoisomers.

<sup>c</sup> The diastereomeric ratio (d.r.) was determined by integration of appropriate <sup>1</sup>H NMR signals.

<sup>d</sup> No significant amounts of the respective products were isolated.

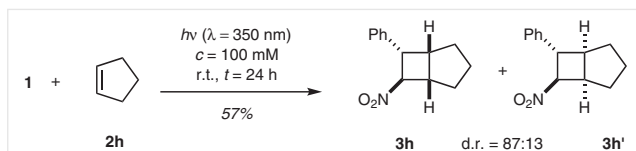
Further experiments were undertaken to identify a less problematic solvent but benzene and to optimize the reaction conditions at  $\lambda = 419 \text{ nm}$ . While toluene was found less suited to substitute benzene, dichloromethane turned out to be an excellent solvent. A larger excess of the olefin led to higher product yields and the concentration was lowered to  $20 \text{ mM}$  in order to allow for small-scale reactions with more precious, not commercially available nitrostyrenes (vide infra). At optimized conditions<sup>21</sup> the [2+2] photocycloaddition products **3a/3a'** were obtained in a yield of 87% after 24 hours of irradiation at  $\lambda = 419 \text{ nm}$ . A variety of other olefins was employed in the reaction, and the results are summarized in Scheme 2.



**Scheme 2** Visible-light-induced [2+2] photocycloaddition of various olefins **2** to *trans*- $\beta$ -nitrostyrene (**1**)

It should be noted that the reactions were not always complete and that in some cases substantial amounts (up to 22%) of starting material were recovered, mostly as *cis*- $\beta$ -nitrostyrene. Yields refer to isolated products, however, and are not corrected for conversion. With olefins **2b,d,f,g**, the fact that the polarity of the excited state is opposite to the ground state polarity (photochemical *umpolung*) becomes particularly apparent. C–C bond formation occurs formally between two – in the ground state – electrophilic centers (C1–C2) and between two nucleophilic centers (C3–C4). The reactions with olefins **2b–d** led to a mixture of diastereoisomers the relative configuration of which could be in most cases elucidated by NOESY experiments (see Supporting Information for further details). Cyclobutanes **3e–g** were obtained as single products. For the reaction of the electron rich olefin **2b**, it was checked that there was no reaction in the absence of irradiation.<sup>22</sup>

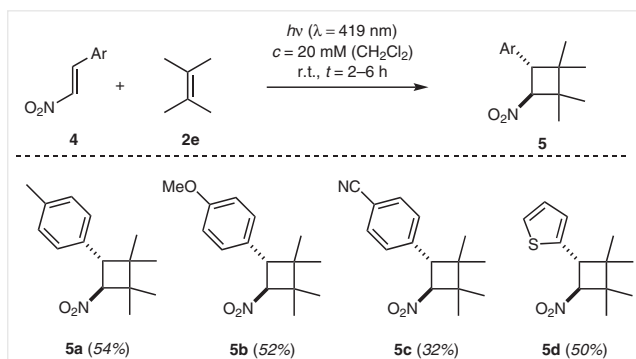
Contrary to unsaturated hydrocarbons **2e** and **2g**, cyclopentene **2h** did not react with a sufficient rate at  $\lambda = 419 \text{ nm}$ . The [2+2] photocycloaddition could, however, be successively conducted if nitrostyrene **1** was irradiated in a



**Scheme 3** Intermolecular [2+2] photocycloaddition of cyclopentene (**2h**) to *trans*- $\beta$ -nitrostyrene (**1**)

solution of cyclopentene at  $\lambda = 350$  nm (Scheme 3). The products were found to be a mixture of diastereoisomers in which product **3h** with the nitro group in *exo* position to the cyclopentyl ring prevailed (d.r. = 87:13).

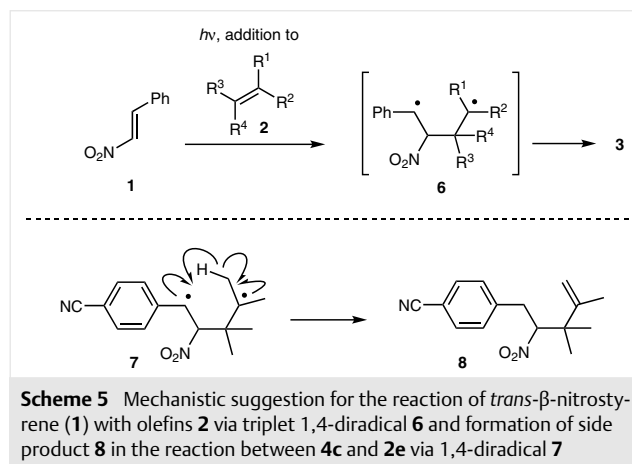
Some preliminary experiments were conducted with other aromatic nitroolefins **4** (Scheme 4). 2,3-Dimethyl-2-butene (**2e**) was employed as the reaction partner since its use avoids the formation of regio- or diastereomeric cyclobutane products. It was found that electron-rich aryl groups (*para*-tolyl, *para*-anisyl, 2-thiophenyl) in 2-position of the respective nitroethenes (**4a**,<sup>23</sup> **4b**,<sup>23</sup> **4d**<sup>24</sup>) led in their [2+2] photocycloaddition to results similar to those of *trans*- $\beta$ -nitrostyrene. Reaction times were short (2–4 h) and cyclobutanes **5a**, **5b**, and **5d** were obtained in yields of 50–54%. The reaction with the *para*-cyano-substituted nitrostyrene **4c**<sup>25</sup> was less chemoselective and gave product **5c** in a yield of only 32% after a longer reaction time (6 h). A side product could be isolated (vide infra).



**Scheme 4** Visible-light-induced [2+2] photocycloaddition of some 2-aryl-substituted nitroethenes **4** and 2,3-dimethyl-2-butene (**2e**)

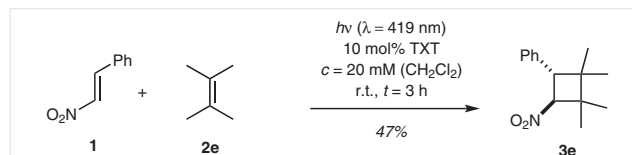
If 2,3-dimethyl-2-butene was subjected to [2+2] photocycloaddition with *cis*- $\beta$ -nitrostyrene instead of *trans*- $\beta$ -nitrostyrene the reaction was slower. The reaction product was exclusively the *trans*-substituted cyclobutane **3e** that was isolated in 43% yield. Irradiation of *trans*- $\beta$ -nitrostyrene at  $\lambda = 419$  nm in the absence of an olefin established an equilibrium<sup>26</sup> between the *cis* and the *trans* diastereoisomer in a ratio of 86:14.<sup>27</sup> This finding is in accord with the higher extinction coefficient of the *trans* diastereoisomer within the wavelength range of the light source.<sup>20c</sup> The absorption maximum of *cis*- $\beta$ -nitrostyrene is centered at  $\lambda = 309$  nm ( $\epsilon = 5200$  M<sup>-1</sup> cm<sup>-1</sup>) in CH<sub>2</sub>Cl<sub>2</sub> solution.<sup>26b</sup>

Mechanistically, there is no indication for a reaction course which would deviate from the pathway of typical [2+2] photocycloaddition reactions.<sup>1</sup> In this regard, it seems likely that olefin **2** adds to the excited substrate, for example, *trans*- $\beta$ -nitrostyrene (**1**), most likely on the triplet hypersurface (Scheme 5). A 1,4-diradical **6** is formed as intermediate which collapses after intersystem crossing to product **3**. Evidence for the postulated structure of diradical **6** is based on the constitution of the products and side products. Indeed, olefins such as **8** were isolated in a few instances and their formation is readily explained by a hydrogen abstraction in the intermediate 1,4-diradical. In the reaction of olefin **2e** with styrene **4c**, byproduct **8** was obtained in 5% yield and is putatively formed via intermediate **7**.



**Scheme 5** Mechanistic suggestion for the reaction of *trans*- $\beta$ -nitrostyrene (**1**) with olefins **2** via triplet 1,4-diradical **6** and formation of side product **8** in the reaction between **4c** and **2e** via 1,4-diradical **7**

Further support for the hypothesis that the reaction proceeds via a triplet intermediate was obtained from the reaction of styrene **1** and olefin **2e**. In the absence of an additive the reaction was complete after 12 hours (Scheme 2), while a significant rate increase was noted upon addition of the triplet sensitizer 9*H*-thioxanthen-9-one (thioxanthone).<sup>28</sup> No  $\beta$ -nitrostyrene was detected after three hours and product **3e** was obtained in 47% yield (Scheme 6).



**Scheme 6** Rate increase of the reaction between *trans*- $\beta$ -nitrostyrene (**1**) and **2e** in the presence of a triplet sensitizer (TXT = thioxanthone)

In summary, we have shown that nitro-substituted cyclobutanes can be accessed by a visible-light-induced [2+2] photocycloaddition of various 2-arylnitroethenes and olefins. The yields are moderate to good (32–87%) and can possibly be further improved by adjusting the wavelength and the reaction temperature. Given the straightforward reduc-

tion of nitro compounds to amines,<sup>11c,14,29</sup> the method offers also access to various aminocyclobutanes. Mechanistically, it remains open to what degree a charge transfer<sup>30</sup> occurs upon encounter of the photoexcited nitro compound and the olefin. In addition, it might be worth to study whether other nitroethenes but nitrostyrenes are equally suited for [2+2] photocycloaddition reactions. Work along these lines is in progress in our laboratories and will be reported in due course.

## Funding Information

Financial support by the European Research Council under the European Union's Horizon 2020 research and innovation programme (grant agreement No 665951 – ELICOS) is gratefully acknowledged.

## Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0036-1588524>.

## Primary Data

Primary data for this article are available online at <https://zenodo.org/record/4610511> and can be cited using the following DOI: 10.5281/zenodo.4610511. Please note that the DOI for the Primary Data associated with this article was updated on April 20, 2021.

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- (21) **Representative Procedure**  
29.8 mg of nitrostyrene **1** (199  $\mu$ mol, 1.00 equiv) and 10.0 equiv of olefin **2e** (168 mg, 2.00 mmol) were dissolved in degassed, dry  $\text{CH}_2\text{Cl}_2$  ( $c = 20$  mM). The reaction solution was irradiated at

$\lambda = 419$  nm in a Duran tube at r.t., and the reaction progress was monitored by TLC. When no further conversion was observed by TLC ( $t = 12$  h), the reaction was stopped and all volatiles were removed. Purification by column chromatography (pentane/Et<sub>2</sub>O = 20:1) gave product **3e** as a yellow oil (27.5 mg, 118  $\mu$ mol, 59%). When performed on a mmol scale (150 mg **1**), product **3e** was obtained in 56% yield (132 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 0.71$  (s, 3 H, CH<sub>3</sub>-2), 1.15 (s, 3 H, CH<sub>3</sub>-3), 1.19 (s, 3 H, CH<sub>3</sub>-2), 1.24 (s, 3 H, CH<sub>3</sub>-3), 3.97 (d, <sup>3</sup>J = 10.1 Hz, 1 H, H-1), 4.91 (d, <sup>3</sup>J = 10.1 Hz, 1 H, H-4), 7.08–7.13 (m, 2 H, *ortho*-H<sub>Ar</sub>), 7.23–7.28 (m, 1 H, *para*-H<sub>Ar</sub>), 7.30–7.37 (m, 2 H, *meta*-H<sub>Ar</sub>) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 300 K):  $\delta = 19.5$  (q, CH<sub>3</sub>-3), 21.5 (q, CH<sub>3</sub>-2), 22.8 (q, CH<sub>3</sub>-3), 24.3 (q, CH<sub>3</sub>-2), 39.3 (s, C-2), 44.9 (s, C-3), 49.4 (d, C-1), 84.9 (d, C-4), 127.0 (*ortho*-C<sub>Ar</sub>H), 127.1 (d, *para*-C<sub>Ar</sub>H), 128.6 (d, *meta*-C<sub>Ar</sub>H), 136.4 (s, C<sub>Ar</sub>) ppm.

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