

# Photocatalyzed Amidoarylation of 1,3-Butadiene

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.201#####>. ((Please delete if not appropriate))

**Abstract.** 1,3-Butadiene is involved in a photocatalyzed amidoarylation reaction that allows the synthesis of *N*-allyl amides. The reaction was evaluated on a wide range of aryl diazonium salts and nitriles as co-reactants. Selectivity issues were studied from the help of a computational approach.

**Keywords:** Visible-light-promoted photocatalysis; 1,3-butadiene; Diazonium salts;

Catalytic functionalization of 1,3-dienes has provided a wide range of chemical building blocks of great importance in organic chemistry. 1,3-Butadiene is the simplest member of the series of conjugated dienes. Its annual production of over 12Mt is essentially dedicated to the production of synthetic rubbers and high-added value fine chemicals. This diene is currently obtained as a side product of ethylene production by oil cracking. Alternatively, in a global context oriented towards the valorization of bio-based chemicals, it has long been established that 1,3-butadiene could be formed by biomass conversion. In particular, the two main industrially proven technology known as Lebedev and Ostromislensky processes are based on the conversion of ethanol.

1,3-Butadiene is a versatile and remarkable C4 platform molecule for a large number of catalytic transformations.<sup>1-21</sup> Among those, metal-catalyzed multicomponent reactions are useful and straightforward synthetic approaches to provide difunctionalized diene derivatives, in particular for arylative transformations.<sup>22-28</sup> Besides, over the past decade, visible light photoredox catalysis has continued to generate an impressive interest. The use of visible light to promote reactions represents a very promising alternative. Since the revival of this field in 2008, various photoredox organic transformations have been highlighted. Surprisingly, only two articles have scarcely described the use of 1,3-butadiene under photocatalytic initiation.

**Table 1.** Optimization of the Reaction Conditions



| Entry          | Variation from the standard conditions  | Yield (%) <sup>a</sup><br>(1:b ratio) |
|----------------|---|---------------------------------------|
| 1 <sup>b</sup> | None  | 75 (1:2.8)                            |
| 2              | [Ir(dtbbpy)(ppy) <sub>2</sub> ] <sub>2</sub> PF <sub>6</sub> as photocatalyst | 51 (1:3.5)                            |
| 3 <sup>c</sup> | Eosin Y as photocatalyst  | traces                                |
| 4 <sup>c</sup> | Fluorescein as photocatalyst  | traces                                |
| 5 <sup>c</sup> | Rhodamine B as photocatalyst  | traces                                |
| 6 <sup>c</sup> | Rhodamine 6G as photocatalyst   | traces                                |
| 7              | 0.5 mol % Ru(bpy) <sub>3</sub> Cl <sub>2</sub>                                | 73 (1:2.8)                            |
| 8              | 0.2 mol % Ru(bpy) <sub>3</sub> Cl <sub>2</sub>                                | 57 (1:2.2)                            |
| 9              | 0.1 mol % Ru(bpy) <sub>3</sub> Cl <sub>2</sub>                                | 50 (1:2.7)                            |
| 10             | 2 equiv. of H <sub>2</sub> O  | 64 (1:3.5)                            |
| 11             | 5 equiv. of H <sub>2</sub> O  | 46 (1:4.6)                            |
| 12             | 25.4 equiv of 1,3-butadiene   | 51 (1:3.2)                            |
| 13             | 6.4 equiv of 1,3-butadiene  | 66 (1:2.4)                            |
| 14             | 3.8 equiv of 1,3-butadiene  | 59 (1:2.8)                            |
| 15             | 5 h reaction time   | 60 (1:3.5)                            |
| 16             | 40 h reaction time  | 46 (1:4.3)                            |
| 17             | In absence of catalyst  | 0                                     |
| 18             | In absence of catalyst  | 0                                     |

<sup>a</sup>Isolated yields. <sup>b</sup>Reaction conditions: **1a** (0.45 mmol), 1,3-butadiene (5.7 mmol), H<sub>2</sub>O (0.45 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (1 mol %) in acetonitrile (2 mL) were irradiated using a 11 W LED ( $\lambda_{\max}$  = 447 nm). <sup>c</sup>Irradiation (LED  $\lambda_{\max}$  = 530 nm).

In 2017, T. Rovis has thus reported the hydroaminoalkylation of conjugated dienes using a unified cobalt and photoredox catalytic system.<sup>29</sup> In 2018, T. Yoon has performed [3+2] cycloaddition with various alkenes including 1,3-butadiene by a tandem

Lewis acid / photoredox catalysis.<sup>30</sup> As such, the transformation of 1,3-butadiene in a context of photocatalysis is, to date, limited to scope studies in organic chemistry. Photocatalytic transformations of 1,3-butadiene would open new valorization pathways for this industrially relevant molecule.

In this context and inspired by a tandem photoredox Meerwein-Ritter reaction described by B. König on styrene derivatives,<sup>31</sup> we now describe herein a photocatalyzed amidoarylation of 1,3-butadiene.

The 4-methoxybenzenediazonium tetrafluoroborate **1a** was chosen as model substrate to explore the feasibility of the reaction in the presence of 1,3-butadiene and water in acetonitrile as solvent (Table 1). Satisfyingly, in the presence of 1 mol % of Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, the reaction led to the linear/branched-adducts **1-2a/b-2a** with 75 % yield and a 1:2.8 ratio (entry 1). The yield in **2a** decreased to 51% when the reaction was catalyzed with [Ir(dtbbpy)(ppy)<sub>2</sub>][PF<sub>6</sub>] (entry 2). Only traces of product were observed when the transformation was initiated with various xanthenes dyes as organophotocatalysts (entries 3-6). Although the yield remained stable in the presence of 0.5 mol % of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (entry 7), lower catalyst loadings led to a significantly reduced efficiency of the transformation (entries 8, 9). In addition, the yield was affected when the amount of water was increased (entries 10, 11). To conclude this optimization set of experiments, it was found that 12.7 equivalents of 1,3-butadiene was optimal for the transformation (entry 1 vs entries 12-14) and the reaction has to run for 16 h (entry 1 vs entries 15, 16). It is worth noticing that no *Z*-isomer was observed on the linear product linear-**2a**. Last but not least, control experiments demonstrated the strict requirement of both catalyst and light for the reaction to occur (entries 17-18).

Following this preliminary study, the optimized conditions for the photocatalyzed amidoarylation were 1 mol % of Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 12.7 equivalent of 1,3-butadiene, 1 equivalent of water, a 0.23 M concentration of aryldiazonium salt and irradiation during 16 h with a blue LED ( $\lambda_{\text{max}} = 447$  nm, 11W).

The scope of the reaction was then extended and evaluated on diversely substituted aryl diazonium tetrafluoroborate salts (Table 2). From this study, it was observed that electron withdrawing as well as donating groups are tolerated in this photoredox process and variously meta- or para-substituted phenyl diazonium salts allowed the synthesis of allylic *N*-allylamides with 57-77% yields.

Furthermore, starting from diazonium **1a**, various nitriles were evaluated in the reaction (Table 3). Propionitrile and **benzonitrile** were respectively converted in **2ab** and **2ac** with 57% and 46% yield. Despite of the steric hindrance, *i*PrCN and *t*BuCN were also efficiently reacted thus affording **2ad** and **2ae** with respectively 55% and 33% yield. Finally, whereas monochloroacetonitrile was converted in **2af** with 60% yield, the trichlorinated derivative proved to be inert.

**Table 2.** Scope of the Amidoarylation Reaction<sup>a</sup>



| Entry | Reagent   | R                      | Product   | Yield (%)<br>(l:b-ratio) |
|-------|-----------|------------------------|-----------|--------------------------|
| 1     | <b>1a</b> | 4-OMe                  | <b>2a</b> | 75 (1:2.8)               |
| 2     | <b>1b</b> | 4-OPh                  | <b>2b</b> | 77 (1:2.4)               |
| 3     | <b>1c</b> | 3,4-OCH <sub>2</sub> O | <b>2c</b> | 57 (1:1.6)               |
| 4     | <b>1d</b> | 4-Ph                   | <b>2d</b> | 70 (1:1.9)               |
| 4     | <b>1e</b> | 4-Me                   | <b>2e</b> | 72 (1:2.4)               |
| 5     | <b>1f</b> | 3,4-Me                 | <b>2f</b> | 60 (1:2.4)               |
| 6     | <b>1g</b> | 4- <i>i</i> Pr         | <b>2g</b> | 61 (1:1.9)               |
| 7     | <b>1h</b> | H                      | <b>2h</b> | 61 (1:1.8)               |
| 8     | <b>1i</b> | 4-F                    | <b>2i</b> | 70 (1:1.9)               |
| 9     | <b>1j</b> | 4-Br                   | <b>2j</b> | 70 (1:1.3)               |
| 10    | <b>1k</b> | 4-NO <sub>2</sub>      | <b>2k</b> | 61 (1:1.7)               |
| 11    | <b>1l</b> | 4-CO <sub>2</sub> Me   | <b>2l</b> | 60 (1:1.2)               |
| 12    | <b>1m</b> | 3-NO <sub>2</sub>      | <b>2m</b> | 31 (1:1.9)               |
| 13    | <b>1n</b> | 3-OMe                  | <b>2n</b> | 37 (1:1.1)               |

<sup>a</sup>Reaction conditions: **1** (0.45 mmol), 1,3-butadiene (5.7 mmol), H<sub>2</sub>O (0.45 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (1 mol %) in acetonitrile (2 mL) were irradiated using a blue 11 W LED ( $\lambda_{\text{max}} = 447$  nm).

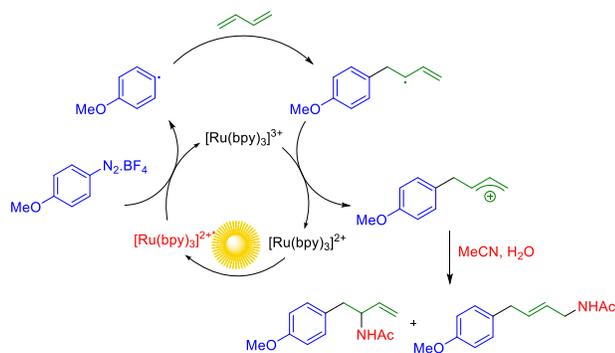
**Table 3.** Screening of Nitriles<sup>a</sup>

| Entry | Nitrile              | Product    | Yield (%) <sup>b</sup><br>(l:b-ratio) |
|-------|----------------------|------------|---------------------------------------|
| 1     | MeCN                 | <b>2a</b>  | 75 (1:2.8)                            |
| 2     | EtCN                 | <b>2ab</b> | 57 (1:4.5)                            |
| 3     | <i>i</i> PrCN        | <b>2ac</b> | 55 (1:4)                              |
| 4     | <i>t</i> BuCN        | <b>2ad</b> | 33 (1:3.8)                            |
| 5     | CCl <sub>3</sub> CN  | <b>2ae</b> | 0 (-)                                 |
| 6     | CH <sub>2</sub> ClCN | <b>2af</b> | 60 (1:3.8)                            |
| 7     | <b>PhCN</b>          | <b>2ag</b> | 46 (1:4.3)                            |

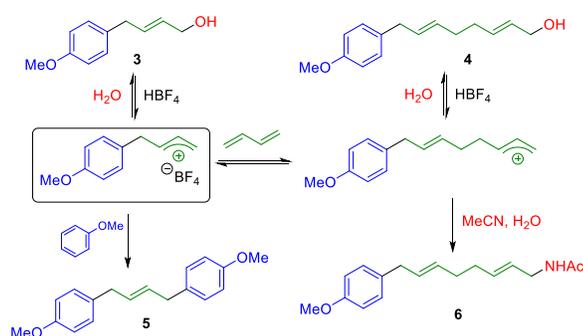
<sup>a</sup>Reaction conditions: **1a** (0.45 mmol), 1,3-butadiene (5.7 mmol), H<sub>2</sub>O (0.45 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (1 mol %) in nitrile (2 mL) were irradiated using a blue 11 W LED ( $\lambda_{\text{max}} = 447$  nm). <sup>b</sup>Isolated yields.

The mechanism proposed for this reaction is described in the scheme 1 with the aryl diazonium salt **1a**. The absorption of a photon promotes the photocatalyst Ru(bpy)<sub>3</sub><sup>2+</sup> into an excited state Ru(bpy)<sub>3</sub><sup>2+\*</sup> able to reduce the aryl diazonium into the corresponding aryl radical. Addition of the latter onto 1,3-butadiene leads to the allylic radical which upon oxidation with Ru(bpy)<sub>3</sub><sup>3+</sup> provides the allylic carbocation. Addition of the acetonitrile onto the primary or secondary carbocation followed by a Ritter reaction in presence of water furnished the linear or branched acetamides. Mechanistically, it is of interest to note that aside from the expected product, in some cases, trace amounts of side products were identified

by mass spectroscopy (scheme 2).<sup>32</sup> As such, the allylic



**Scheme 1.** Proposed Mechanism



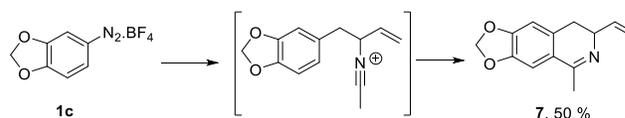
**Scheme 2.** Side products formation

alcohol derivative **3** and diaryl adduct **5** would result from the addition of a molecule of water or anisole<sup>33</sup> respectively onto the allylic carbocation. Furthermore, trace amounts of C-8 products **4** and **6** resulting from the addition of one molecule of butadiene to the allylic carbocation were observed. It is worth noticing that neither polybutadienes nor higher oligomers were obtained during this process. This is consistent with a fast reaction of the cation with the nitrile.

Interestingly, when the reaction was performed with the methylenedioxy-containing adduct **1c**, besides the formation of **2c** (Table 2, entry 3), 25 % of 3,4-dihydroisoquinoline **7** was isolated as well. Conducting the reaction in absence of water led to increase the yield of **7** to 50 % (Scheme 3). This product results from the Friedel-Crafts addition of the electron rich aromatic ring to the nitrilium intermediate. Further experiments are ongoing to improve the yield of this relevant reaction.

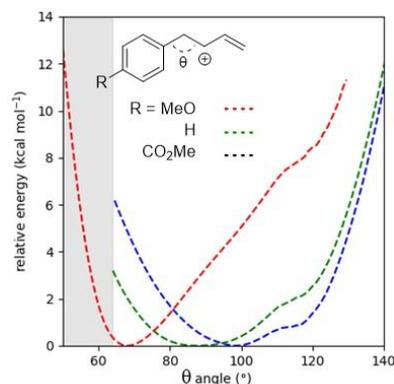
From the amidoarylation process, it was observed that the branched isomer was always favored over the linear one. To rationalize this selectivity issue, a computational study was undertaken on the formation of **2a**, **2h** and **2l**. These products formation were selected to cover the whole electronic span from electron-donating to electron-withdrawing groups. As a first postulate, we assumed that the reactivity of the

allylic cationic intermediate toward a nucleophile such

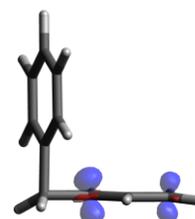


<sup>a</sup>Reaction conditions: **1c** (0.45 mmol), 1,3-butadiene (5.7 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (1 mol %) in acetonitrile (2 mL) were irradiated using a blue 11 W LED ( $\lambda_{\text{max}} = 447 \text{ nm}$ ).

**Scheme 3.** Dihydroisoquinoline formation<sup>a</sup>



**Figure 1.** Relative energy calculated against the value of the bond angle Ar-C-C<sup>+</sup>



**Figure 2:** Fukui function (isovalue = 0.0015 au) for the intermediate originating from **1c**

as acetonitrile can be a clue of the regioselectivity. However, during the geometry optimization of these three structures, an interesting issue was encountered as several computations led to the formation of a bridge arylum intermediate. This surprising result was not confirmed by experimental results.<sup>34</sup> Therefore, a more careful examination of the geometries was processed and the energy of the intermediate molecule was computed against the value of the bond angle Ar-C-C<sup>+</sup>. The obtained curves are depicted in Figure 1.

An interesting trend is observed where the optimal angle decreases with the increase of the electron-donating nature of the aryl substituent. This observation is consistent as the electron donating character increases the electron density on the ipso

carbon (C<sub>ipso</sub>) of the benzene ring. Thus, the Coulomb interaction between this latter and allylic carbocation (C<sup>+</sup>) drives the value of the angle. This interaction could be a first explanation to the aforementioned regioselectivity of the reaction. Indeed, to enhance the C<sub>ipso</sub>-C<sup>+</sup> interaction, the cationic character of C<sup>+</sup> should be enforced, leading to an increased significance of the related mesomer form.

With the aim to confirm this assumption, the electrophilic Fukui function  $f^+(\mathbf{r})$  for the cationic intermediates was calculated.<sup>35</sup> It has been computed using a finite difference method, and the result of this computational analysis in the case of the intermediate originating from **1h** is depicted in Figure 2.<sup>36</sup>

As result of this computation study, the Fukui function is in line with the stabilizing Coulomb interaction formulated above. Indeed, the lobe of non-terminal allylic carbocation is oriented towards the ipso carbon of the benzene moiety. Consequently, the volume of the lobe and thus the cationic character of this carbocation is confirmed to be higher than the terminal allylic carbocation.

In conclusion, we have developed a straightforward visible light photoinduced amidoarylation reaction of 1,3-butadiene. This multicomponent reaction yields  $\alpha$ -allylamides from a good range of aryl diazonium salts and nitriles. We believe that this process represents an opening wedge in the valorization of 1,3-butadiene through photocatalyzed transformation. Interestingly, it was found that 3,4-dihydroisoquinoline can be formed from sufficiently electron rich aromatic diazonium salts. Additionally, the favorable formation of the 1,2-isomer over the 1,4-isomer was rationalized by computational studies.

## Experimental Section

### Typical procedure for the synthesis of acetamide derivatives.

Buta-1,3-diene was condensed at -20 °C in a graduate tube and the appropriate amount (0.5 mL, 12.7 eq, 5.73 mmol) was cannulated into a pre-cooled (at -20 °C) Schlenk flask containing the diazonium salt (1 eq, 0.45 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (3.3 mg, 1 mol%, 0.005 mmol), acetonitrile (2 mL) and water (8.5  $\mu$ L, 1 eq, 0.45 mmol). After 16h under 11 W blue light irradiation, the crude product was transferred into a round-bottom flask and concentrated by evaporation. Both linear and branched product were isolated by column chromatography on silica gel (from DCM to DCM/AcOEt 80/20).

## Acknowledgements

Chevreur institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche, Région Nord – Pas de Calais and FEDER are acknowledged for supporting and funding this work. This work was granted access to the HPC resources of CINES (Centre Informatique National de l'Enseignement Supérieur) and

IDRIS (Institut du Développement et des Ressources en Informatique Scientifique) under the allocations A0050806933 made by GENCI (Grand Équipement National de Calcul Intensif). We also would like to thank Romain Jooris and Céline Delabre for their technical support.

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- [32] For clarity, only the linear products were represented.
- [33] Anisole was supposedly formed from the hydrogen atom transfer reaction between the solvent and the aryl radical.
- [34] No product resulted from this intermediate was observed.
- [35] *This function* localizes the electrophilic part of the molecules (e.g. those that bear the most important part of the increase of the electron density if the number of electron increases). For this purpose, *this function is defined for each point of the space from the electron density  $\rho(r)$  and from the number of electrons  $N$  according to the equation:  $f^+(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v, N > N_0}$*
- [36] A similar representation was obtained for the intermediate originating from **1d** (see supporting information).

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