

More Chips to Nitroolefins: Decatungstate Photocatalysed Hydroalkylation Under Batch and Flow Conditions

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Abstract: The hydroalkylation of nitroalkenes and β -nitroacrylates via a photocatalytic strategy has been optimised under both batch and continuous flow conditions. This target has been achieved by exploiting the potentialities of the decatungstate anion as a versatile hydrogen atom transfer (HAT) photocatalyst for the generation of alkyl radicals from aliphatic heterocycles, amides and cycloalkanes.

Keywords: Hydrogen Atom Transfer (HAT); Photocatalysis; Flow Chemistry; Nitroalkenes; Hydroalkylation, tetrabutylammonium decatungstate (TBADT)

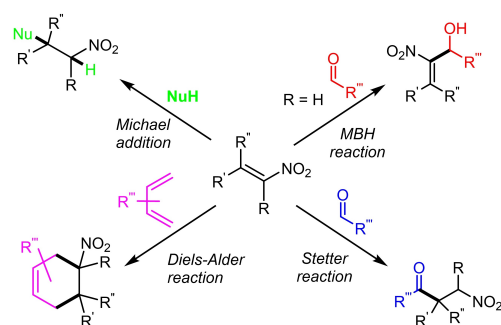
Introduction

Among the different classes of electron-poor olefins, the popularity of nitroalkenes as key intermediates on the route to highly functionalized molecules and biologically active targets^[1] is related to their peculiar dual reactivity. The high electron-withdrawing character of the nitro group makes these compounds extremely reactive species in pivotal synthetic processes, including Michael addition,^[2] Diels-Alder cycloaddition,^[3] Morita-Baylis-Hillman (MBH)^[4] and Stetter reactions (Scheme 1a).^[5] Moreover, the nitro group can be smoothly converted under mild conditions into a plethora of different functional groups, including amines, oximes, aldehydes, ketones and carboxylic acids,^[6] or even removed via a denitration reaction.^[7] More recently, the behaviour of nitroalkenes under irradiation conditions has been also investigated, and their reactivity applied to [2 + 2] cycloadditions,^[8]

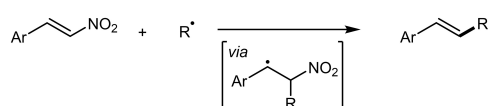
as well as a tool to perform both stereo-^[9] and regioisomerizations.^[10]

On the other hand, the reactivity of nitro compounds under conditions involving open-shell species, has been explored only to a limited extent. As for nitroalkenes, the attention has been mainly focused on their role as traps for both thermally and photochemically generated radical intermediates.^[11] In particular, photocatalytic strategies have been recently under the spotlight as a tool for the smooth generation of valuable organoradical intermediates,^[12] due to the mildness of the involved conditions. However, in these processes the use of nitroalkenes as radical acceptors is mainly limited to β -nitrostyrene derivatives, wherein quantitative -NO₂ loss results in a formal *ipso*-substitution process (Scheme 1b).^[11] Such strategy has been successfully applied to the preparation of a variety of synthetic targets including stilbenes,^[13] chalcones,^[14] vinyl thiocyanates^[15] and trifluoromethyl

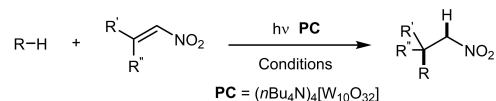
a) Typical reactivity of nitroalkenes



b) Radical mediated ipso substitution reaction on nitroalkenes



c) This work: Hydroalkylation of nitroalkenes via photocatalyzed HAT



Scheme 1. a) Common reactivity of nitroalkenes; b) radical denitrative reactivity of β -nitrostyrenes (usual reactivity) and c) photocatalyzed hydroalkylation of nitroalkenes (this work).

alkenes,^[16] as well as to the alkenylation of cyclic ethers^[17] and unactivated alkenes^[18] (Scheme 1b). To the best of our knowledge, the nitro group was retained in the final product only in a couple of instances, namely in the preparation of Diels-Alder adducts (only one example reported)^[19] and in the alkylation of indoles^[20] photocatalyzed by chromium-complexes and rose Bengal, respectively.

Following our interest in the application of tetrabutylammonium decatungstate (TBADT, $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$)^[21] as the photocatalyst for the generation of carbon-centered radicals through a hydrogen atom transfer (HAT) step,^[22] we report herein our efforts in the hydroalkylation of nitroalkenes and β -nitroacrylates with a range of hydrogen donors (R-H, see Chart S1 for further details) for the preparation of functionalized nitroalkane products (Scheme 1c).

Results and Discussion

At the outset of our investigation, we focused the attention on the hydroalkylation of (*E*)-1-nitrooct-1-ene **1a** with 2,2-dimethyl-1,3-dioxolane **2a** in the role of H-donor to afford adduct **3** (see Table 1 and the Supporting Information for further details), adapting conditions previously adopted for the C-H bond functionalization of oxygenated heterocycles.^[23] When a MeCN solution (5 mL contained in a Pyrex vessel)

Table 1. Optimization of β -nitroalkenes hydroalkylation.^[a]

Entry	Variation from standard conditions	3 , GC Yield ^{b)}
1	none	83%
2	room temperature (rt)	39%
3	$\lambda = 390 \text{ nm}$ (50% power)	41% ^{c)}
4	$\lambda = 427 \text{ nm}$	37%
5	$\lambda = 456 \text{ nm}$	n.d.
6	TBADT omitted	n.d.
7	in the dark	n.d.
8	TEMPO (1 equiv.) as an additive	traces
9	flow conditions, rt	90%
10	flow conditions, 0 °C	89%

^[a] Reaction conditions: an Ar-bubbled MeCN solution (5 mL) containing **1a** (0.5 mmol, 0.1 M), **2a** (5 equiv.), and TBADT (2 mol%) was irradiated with a LED lamp (40 W, $\lambda = 390 \text{ nm}$) under either batch (grey background) or flow conditions (blue background). V_R : reactor volume; n.d.: not detected.

^[b] Gas chromatography (GC) yields are based on the amount of **3** vs *n*-dodecane ($1 \mu\text{L} \cdot \text{mL}^{-1}$) used as internal standard.

^[c] 50% of unreacted **1a** has been detected via GC analysis.

of **1a** (0.1 M) and **2a** (5 equiv.) was irradiated with a 390 nm LED lamp (40 W power) for 6 h at 0 °C (ice bath) in the presence of TBADT (2 mol%) under Ar atmosphere, product **3** was obtained in 83% yield according to GC analysis (entry 1). By performing the reaction at room temperature (25 °C; entry 2), product **3** was again formed, although in a significantly diminished yield (39% by GC analysis). Reducing the power (the switch has been set at 50% level) of the 390 nm LED lamp employed or moving to a less energetic wavelength (427 and 456 nm lamps were used; 40 W power) proved to be detrimental for the reaction outcome (entries 3–5). Finally, control experiments demonstrated that both light and TBADT are mandatory for the formation of **3** (entries 6, 7). At the same time, only trace amounts of **3** were formed when 2,2,6,6-tetramethylpyrrolidine-*N*-oxyl (TEMPO, 1 equiv.) was added to the reaction mixture (entry 8; see SI for GC-MS analysis and further details).

Then, we moved to flow conditions^[12d] by exploiting a 3D-printed reactor made of polypropylene recently described by some of us and used for the hydrofunctionalization of alkenoic acids under TBADT-photocatalyzed conditions (channels diameter:

1 mm; reactor volume (V_R): 4.1 mL; see SI for further details).^[24] Gratifyingly, upon adopting the same reaction parameters as those previously reported, namely by circulating the mixture by means of a syringe pump with a $2 \text{ mL} \cdot \text{h}^{-1}$ flow rate (residence time: 2 h 3'),^[24] the desired product **3** was obtained in excellent GC yield (*ca.* 90%), independently from the temperature (entries 9, 10).

Having established the optimal reaction conditions, we isolated the nitroalkane products on 0.5 mmol scale and evaluated the reaction scope (Table 2; see also Chart S1 for the complete substrates list). Thus, product **3** was obtained in 81% and 89% isolated yield by adopting the conditions gathered in Table 1, entries 1 and 9, respectively. Flow conditions were also

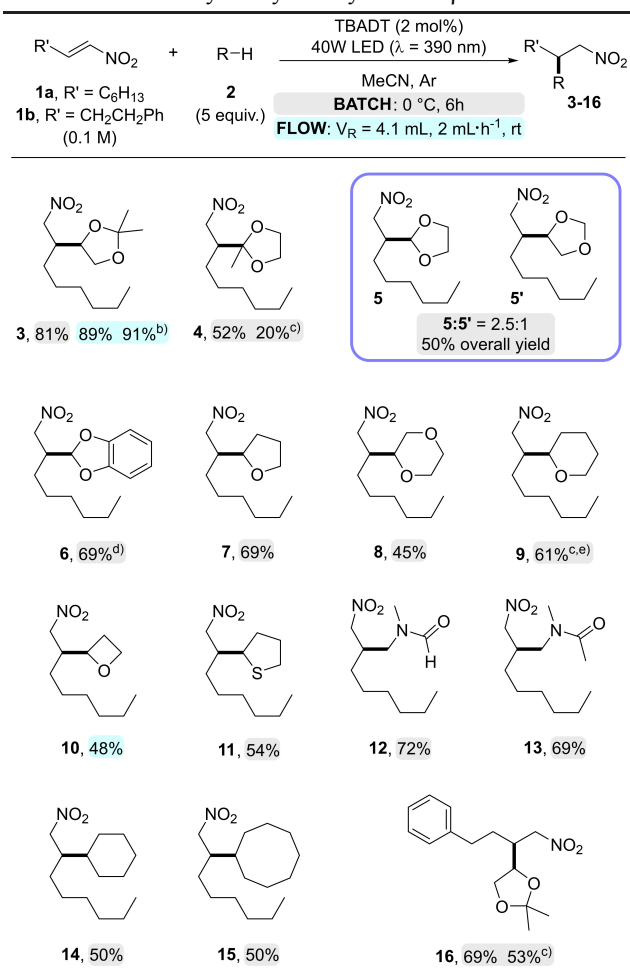
exploited to perform the model reaction between **1a** and **2a** on a larger scale (2 mmol). For practical reasons, the reaction was carried out at room temperature (compare entries 9 and 10, Table 1), which allowed to isolate the desired product **3** in 91% yield (471 mg).

A change in the substitution pattern onto the 1,3-dioxolane ring led to a different outcome in terms of regioselectivity. Thus, while the functionalization of 2-methyl-1,3-dioxolane **2b** cleanly led to product **4** in 52% yield under batch conditions (20% at room temperature) via the exclusive functionalization of the acetal position, a mixture of regioisomers **5** and **5'** (2.5:1 ratio) was obtained when subjecting 1,3-dioxolane **2c** to optimized conditions. We further explored the reactivity of oxygenated 5-membered rings, as exemplified by the adoption of 1,3-benzodioxole **2d** (1.5 equiv. only used) and tetrahydrofuran **2e** as the H-donors, which allowed to isolate adducts **6** and **7** in 69% yield. Products **8** and **9** were formed in 45% and 61% yield, respectively, upon functionalization of the 6-membered oxygenated ring of 1,4-dioxane **2f** and tetrahydropyran **2g**. In the latter case, the reaction took place at room temperature upon irradiation for 1 h only. On the other hand, the elaboration of the 4-membered ring in oxetane **2h** proved more challenging and the corresponding adduct **10** could be isolated in 48% yield, only upon adoption of flow conditions.

We next considered the opportunity to adopt substrates decorated with different heteroatoms. Thus, tetrahydrothiophene **2i** smoothly reacted with **1a** to afford product **11** in 54% isolated yield, while both *N,N*-dimethyl formamide **2j** and *N,N*-dimethyl acetamide **2k** delivered adducts **12** and **13**, resulting from the selective functionalization at the α -to-*N* methyl group in 72% and 69% yields.^[25] On the other hand, a sluggish reaction was observed when adopting *N*-Boc pyrrolidine as substrate (data not reported).^[25a] Cycloalkanes also worked as competent substrates, as showcased by the functionalization of cyclohexane **2l** and cyclooctane **2m** to afford products **14** and **15**, both in 50% isolated yield. Finally, we modified the structure of the nitroalkene reaction partner by introducing an aromatic substituent. Thus, the reactivity of (*E*)-(4-nitrobut-3-en-1-yl)benzene **1b** was preserved, delivering **16** in good yield via hydroalkylation with the model H-donor **2a**. On the other hand, β -nitrostyrene **1c** led to the formation of a complex mixture when reacted with **2a** (data not reported).

In order to demonstrate the versatility of this approach under continuous flow conditions^[12d] and its usefulness towards the synthesis of highly functionalized materials, we extended the photoalkylation studies to (*E*)- β -nitroacrylates **1d-i** (see Chart S1), which recently demonstrated a high reactivity upon direct

Table 2. Photocatalyzed hydroalkylation of β -nitroalkenes.^[a]



^[a] Isolated yields for reactions performed under batch (grey background; see entry 1 in Table 1) or flow conditions (blue background; see entry 9 in Table 1) on a 0.5 mmol scale.

^[b] Reaction performed on a 2 mmol scale.

^[c] Reaction performed at room temperature.

^[d] 1.5 equiv. of 1,3-benzodioxole **2d** were used.

^[e] Reaction mixture irradiated for 1 h.

photoirradiation, smoothly leading to the corresponding (*Z*)-stereoisomers.^[9] Nevertheless, we surmised model β -nitroacrylate **1d** to photocatalytic conditions in the presence of hydrogen-donor 1,3-benzodioxole **2d** (only 1.3 equiv. were sufficient in this case) for the preparation of hydroalkylated product **17** (Table 3).

As demonstrated above, temperature may play a key-role for achieving a good reactivity profile, therefore we moved from the 3D-printed reactor^[24] to a Syrris Asia flow apparatus, which offers the possibility to modify the temperature over a wide range (−40 to +80 °C). This reaction setup is equipped with a 54 W LED irradiation system (4 LED modules; $\lambda = 385$ nm) and light can be set at different intensity levels. When the reaction was carried out at +20 °C while maintaining a 2 mL·h^{−1} flow rate, alkylated product **17** was prepared in 48% yield (entry 1), while decreasing the temperature to +5 °C resulted in a slight improvement of the alkylation yield (50% yield, entry 2). On the other hand, the adoption of stop-flow conditions led to an unsatisfactory yield of **17** (entry 3). Better results have been obtained when setting the temperature to −10 °C (53% yield, entry 4). Next, we evaluated the impact of lamp power on the reaction outcome (compare entries 4–7). Thus, the best performance was found when setting the light intensity at 25% (61% yield, entry 6). On the other hand, a further decrease of

the temperature was found detrimental to the process efficiency (entry 8).

The optimized protocol was next applied to the synthesis of α -(1,3-benzodioxolan-2-yl) β -nitro esters **17–23** (0.5 mmol scale), that have been isolated in good amounts, independently from the nature of the substituents on β -nitroacrylates **1d–i** (see Table 4). Also in this case, we performed our model reaction on a 2 mmol scale, obtaining a yield of product **17** (62%, 366 mg) comparable to that obtained on a 0.5 mmol one. Notably, even the presence of a 1,3-dioxolane ring on olefin **1h** did not alter reactivity, allowing to prepare compound **21** in a good yield. Similar results have been obtained when using 5-methyl-1,3-benzodioxole **2n** as H-donor, with the desired products **22** and **23** isolated in 50 and 47% yield, respectively.

The successful realization of the reported strategy demonstrates the unique properties of the TBADT photocatalyst, that preserves the nitro group upon irradiation, in contrast to previous examples wherein the NO₂-moiety was lost at the end of the process (see Scheme 1b); similarly, the photocatalyzed reduction of nitroalkenes to oximes has been reported.^[26]

The excitation of the decatungstate anion calls for the use of a light source emitting at *ca.* 390 nm, wherein the employed nitroolefins may absorb as well. Figure S1 gathers the UV-Vis spectra of model compounds **1a,c,d**, along with that of the employed photocatalyst. As apparent, compounds **1a,d** exhibit only a modest absorption at wavelengths > 300 nm, which does not hamper photocatalyst excitation and

Table 3. Optimization of β -nitroacrylates hydroalkylation.^[a]

Entry	Temperature (°C)	Light intensity (% power)	17 , GC Yield ^{b)}
1	20	50	48%
2	5	50	50%
3 ^{c)}	5	50	40%
4	−10	50	53%
5	−10	100	49%
6	−10	25	61%
7	−10	15	35%
8	−20	25	43%

^[a] Reaction conditions: an Ar-bubbled MeCN solution (5 mL) containing **1d** (0.5 mmol, 0.1 M), **2d** (1.3 equiv.), and TBADT (2 mol%) was irradiated with a LED lamp (54 W, $\lambda = 385$ nm; light intensity has been set at different levels) in a Syrris Asia photoreactor. V_R : reactor volume.

^[b] Gas chromatography (GC) yields are based on the amount of **17** vs *n*-dodecane (1 μ L·mL^{−1}) used as internal standard.

^[c] Reaction carried out under stop-flow conditions.

Table 4. Photocatalyzed hydroalkylation of (*E*)- β -nitroacrylate-**S**.^[a]

17 , 61% 62% ^{b)}	18 , 53%	19 , 54%	20 , 56%
21 , 49%	22 , 50%	23 , 47%	

^[a] Isolated yields for reactions performed with the Syrris Asia photoreactor on a 0.5 mmol scale (see entry 6 in Table 3).

^[b] Reaction performed on a 2 mmol scale.

allows to observe the desired hydroalkylation reactivity. On the other hand, the UV-Vis spectrum of β -nitrostyrene **1c** features an intense absorption in the near UV range tailing at wavelengths > 380 nm, thus preventing photocatalyst excitation. At this stage, we cannot exclude that the recently reported *E/Z*-isomerization of β -nitroacrylates^[9] may take place under our conditions as well. However, the photocatalyzed hydroalkylation reaction would consistently lead to the formation of the desired product independently from the stereochemistry of the starting β -nitroacrylate.

The impact of the temperature on the process efficiency likewise deserves some comments. As for the hydroalkylation of simple nitroolefins, working at low temperature (0°C) under batch conditions is required to obtain a good yield of product, while this parameter has a limited effect on the reaction outcome under flow conditions. Our hypothesis is that the shorter reaction times needed under flow *vs* batch conditions (*ca.* 2 *vs* 6 hours, respectively) limit the possibility for the product to undergo undesired decomposition pathways. An analogous reasoning can be applied to the hydroalkylation of β -nitroacrylates, which calls for the adoption of even lower temperatures (-10°C), also under flow conditions.

Mechanism-wise (see Scheme 2), this process capitalizes on the capability of excited TBADT to cleave aliphatic C–H bonds in hydrogen donors **2**, encompassing aliphatic heterocycles, amides and even cycloalkanes. Thus, the radical nature of the process has been confirmed by the experiment run in the presence of the TEMPO additive (see Table 1), which shut down the formation of the desired nitroalkane product and led to the formation of an adduct between TEMPO and the adopted H-donor. In the proposed mechanistic scenario, the photogenerated alkyl radical intermediates **I** \cdot were then intercepted by nitroolefins **1** through a conjugate addition, leading to radical adducts **II** \cdot . An interesting point is the regioselectivity of the radical addition step, which consistently took place at the β -position with respect to the nitro group. While this was expected in the case of simple β -nitroalkenes, a

mixture could have been obtained with β -nitroacrylates. However, this was not the case and all the reported examples cleanly led to the same reactivity pattern, thus avoiding any further denitrative process (see Scheme 1b). In the final step, the recovery of the photocatalyst is coupled with the formation of the final hydroalkylated products **III** through a back-HAT step.

Conclusions

The present work enables the hydroalkylation of a diverse set of nitroolefins under photocatalyzed conditions, representing one of the few examples allowing to maintain the multi-potent nitro functionality in the final product. The success of this 100% atom-economic transformation is entrusted to the unique properties of the decatungstate anion, which can cleave (strong) C–H bonds upon irradiation, smoothly delivering the corresponding alkyl radicals.

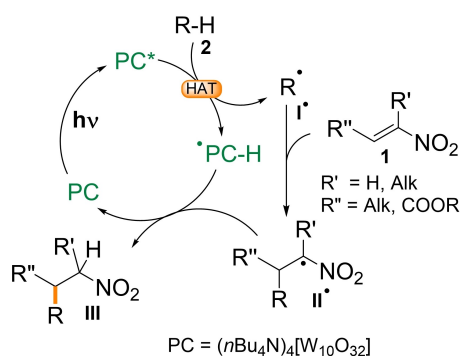
The optimized protocol can be run indifferently under either batch or flow conditions, and the control of both reaction temperature and light intensity has been observed to impact significantly over the performance of the transformation.

Experimental Section

Typical procedure for nitroolefins hydroalkylation A solution of nitroalkene **1** (0.5 mmol, 0.1 M), hydrogen donor **2** (0.65–2.5 mmol, 0.13–0.5 M; 1.3–5 equiv.) and TBADT (2 mol%, 2 mM) in 5 mL of MeCN was deaerated (by argon bubbling for 10 minutes) and irradiated under either batch (General Procedure A) or flow (General Procedures B or C) conditions (see Supporting Information for further details). The progress of the reaction was monitored by GC-FID and, upon completion, the crude mixture was poured into a round-bottom flask and the solvent removed via rotary evaporation. Then, the reaction product was isolated by column chromatography using SiO_2 as stationary phase and mixtures of cyclohexane/ethyl acetate as eluants.

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Scheme 2. Proposed reaction mechanism.

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