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To be cited as: *ChemSusChem* 10.1002/cssc.201901725

Link to VoR: http://dx.doi.org/10.1002/cssc.201901725

A Journal of
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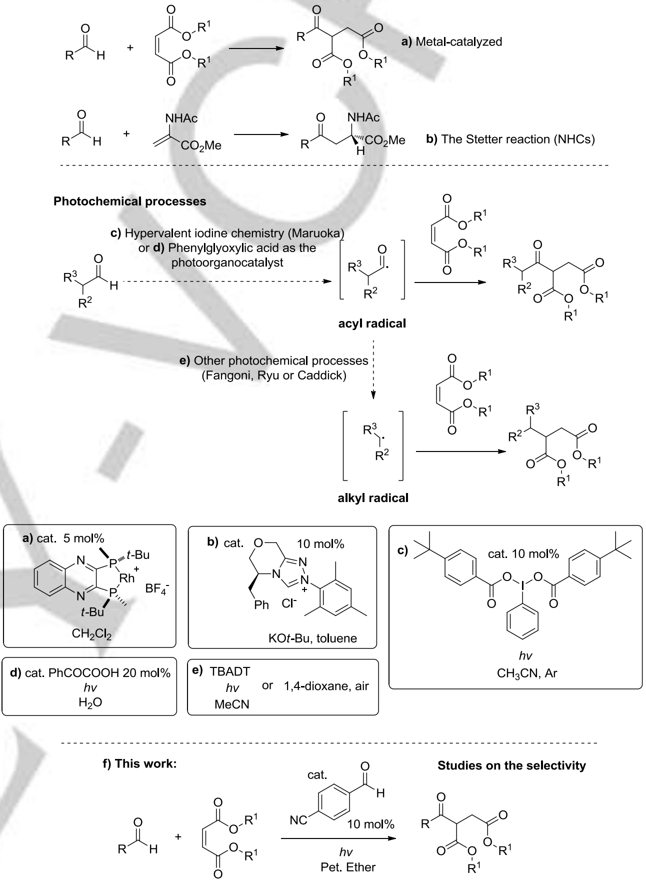
Photochemical Hydroacylation of Michael Acceptors Utilizing an Aldehyde as the Photoinitiator

Ioanna K. Sideri,[a] Errika Voutyritsa[a] and Christoforos G. Kokotos*[a]

Abstract: The hydroacylation of Michael acceptors constitutes a useful tool for the formation of new C-C bonds. In this work, an environmentally friendly procedure was developed, utilizing 4-cyanobenzaldehyde as the photoinitiator and household bulbs as the irradiation source. A great variety of substrates was well-tolerated leading to good yields, while mechanistic experiments were performed for the catalyst's possible mechanistic pathway. Also, the inherent selectivity problem regarding *α,α*-disubstituted aldehydes (decarbonylation problem) was studied and addressed.

Introduction

Photoredox catalysis is an increasingly important tool in Organic Synthesis, having multiple applications in novel and/ or already-existing organic transformations.[1] In the majority of these cases, metal-based catalysts (mainly based on ruthenium or iridium) are used to promote these transformations. These complexes have the ability to present different electronic properties, depending on the ligand that are coordinated with. Nevertheless, they can be highly toxic, difficult to be removed from the final product and also in most cases are expensive. To solve these problems, Photoorganocatalysis came into the scene, which is more sustainable, eco-friendly and gradually becomes equally effective, as entirely organic catalysts are utilized upon the same transformations.[2] The last few years, we have initiated a program with the aim being to contribute to this domain by developing a phootorganocatalytic protocol, utilizing common household lamps and a commercially available small organic molecule as the photocatalyst.[3] One of these applications was the green photochemical C-H activation of aldehydes, leading to the hydroacylation of electron-deficient olefins (Scheme 1**d**).[4] There are quite a few examples dealing with the C-C bond activation for this hydroacylation, such as via metal catalysis (Scheme 1**a**),[5] the Stetter reaction (*N*-heterocyclic carbenes) (Scheme 1**b**),[6] or via photochemical processes (Scheme 1**e**).[7-9] In our previous work,[4] we were able to overcome existing problems in literature, regarding this transformation: wider substrate scope, including aromatic aldehydes and the most important problem of the poor selectivity of α,α-disubstituted aldehydes. When branched aldehydes are used, the acyl radical would often decarbonylate, due to the increased stability of the secondary alkyl radical formed, leading to undesired products (Scheme 1, middle). In our case, phenylglyoxylic acid was used as the photocatalyst and it performed remarkably well, affording high selectivity.[4] Maruoka also provided a solution to this matter by employing a hypervalent iodine photoinduced protocol, yet using a non-commercial catalyst (Scheme 1**c**).[10] During our studies, upon the mechanistic aspect of the reaction and the selectivity as well, the good performance exhibited by benzaldehyde triggered us to further investigate the idea of an aldehyde actually promoting the hydroacylation of alkenes. Thus, in our present work, a commercially available, cheap, substituted benzaldehyde is used as the promoter and studies on the desired selectivity have been conducted, affording unexpectedly good results with selectivity ratios exceeding 20:1 (Scheme 1**f**).



Scheme 1. Different pathways for the hydroacylation of Michael acceptors.

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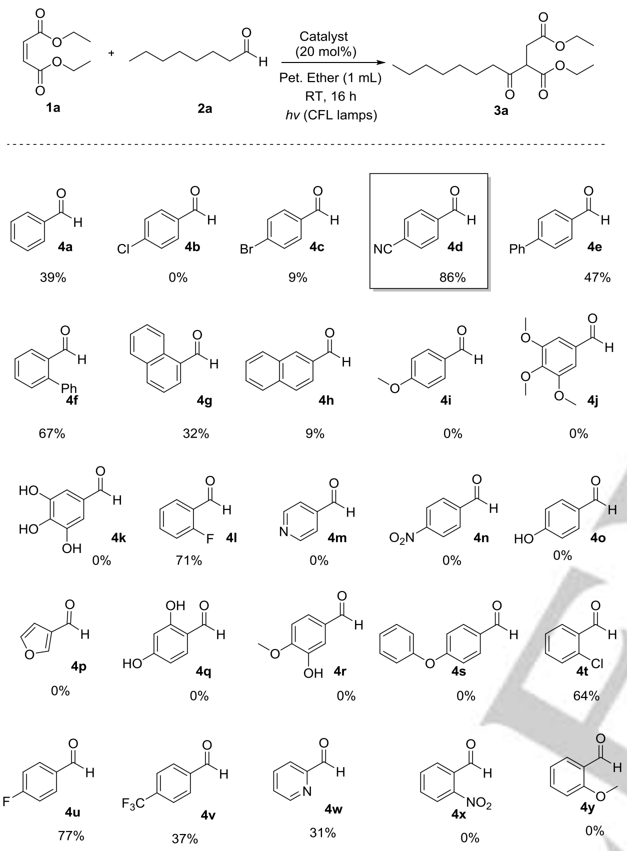
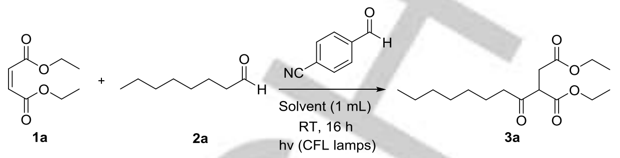
Results and Discussion

We initially investigated a wide range of substituted aromatic aldehydes as the potential photoinitiators in the reaction between diethyl maleate (**1a**) and octanal (**2a**) (Scheme 2).[11] In general, the *ortho*-substitution on the aromatic aldehyde provided better yields than the *para*-substitution (**4f** vs **4e** and **4t** vs **4b**), with the exception of fluoro-substituted aldehydes (**4l** vs **4u**). While various aromatic aldehydes were tested for their catalytic activity, only a few furnished the reaction. 4-Cyanobenzaldehyde (**4d**) proved to be the best initiator among the 25 benzaldehydes tested (Scheme 2). Then, the reaction conditions were optimized, testing different solvents, catalyst loadings and octanal equivalents (Table 1).[11] The reaction gave mediocre results in aqueous media (Table 1, entry 1), while in other solvents the yield was from low to mediocre (Table 1, entry 2). The reaction took place effectively in petroleum ether (40-60 ^oC) as the solvent, while decreasing the catalyst loading to 10 mol% (Table 1, entry 3 and 4).[11] Notably, the reaction does not proceed in the absence of light (Table 1, entry 5) or without catalyst (Table 1, entry 6). The reaction was also performed at 60 ^oC in the dark to exclude the heat as the driving force.[11]



Scheme 2. Substituted aromatic aldehydes tested as photoinitiators for the photocatalytic hydroacylation of **1a**.

Table 1. Optimization of the reaction conditions for the photochemical hydroacylation of diethyl maleate.

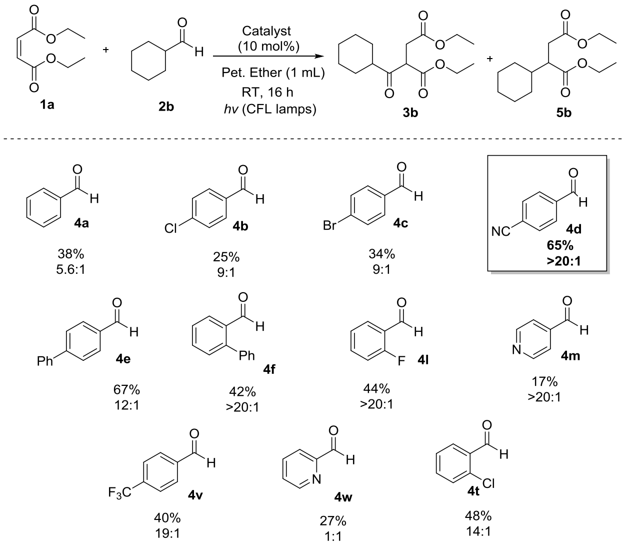


Entry	Solvent	Octanal (equiv.)	Catalyst loading (mol%)	Yield[a] (%)
1	H_2O	1.2	20	34
2[b]	solvent	1.2	20	0-54
3	Pet. Ether	1.2	20	57
4	**Pet. Ether**	**2.0**	**10**	**100 (86[c])**
5[d]	Pet. Ether	2.0	10	0
6	Pet. Ether	2.0	0	0
7[e]	Pet. Ether	2.0	10	0
8[f]	Pet. Ether	2.0	10	61
9[g]	Pet. Ether	2.0	10	0
10[h]	Pet. Ether	2.0	10	76

The reaction was performed with diethyl maleate (0.30 mmol), octanal (0.36-0.60 mmol), 4-cyanobenzaldehyde (10-20 mol%) in solvent (1 mL), under household bulb irradiation for 16 h. [a] Yield was determined by ^1H NMR. [b] CH_2Cl_2 or $CHCl_3$ or Et_2O or EtOAc or MeCN or MeOH or DMF or DMSO or benzene. [c] Isolated yield. [d] The reaction was performed in the dark. [e] 1 equiv. BHT or Tempo was added. [f] The reaction was performed in the absence of oxygen. [g] 1 equiv. anthracene was added. [h] 1 equiv. $CuCl_2$ was added.

Having identified the optimized reaction conditions, a study on the selectivity was also conducted in the reaction between diethyl maleate (**1a**) and cyclohexane carboxaldehyde (**2b**) (Scheme 3). In particular, when *α,α*-disubstituted aldehydes are used, the acyl radical that is formed can easily decarbonylate, due to the formation of a rather stable secondary alkyl radical, leading to products like **5b**. Again, we tested different aromatic aldehydes to find the perfect marriage of performance and selectivity (Scheme 3). Although other aromatic aldehydes showed selectivity ratio >20:1, such as 2-fluorobenzaldehyde (**4l**), isonicotinaldehyde (**4m**) and [1,1'-biphenyl]-2-carbaldehyde (**4f**), to our delight, 4-cyanobenzaldehyde (**4d**) proved to merge the best combination of yield and selectivity (65% and >20:1) (Scheme 3).

Having established the optimized photochemical protocol, our aim was to explore the substrate scope. Therefore, a series of aldehydes were tested. Primary alkyl aldehydes (**3a, 3c, 3d**) were excellent tolerated, giving high yields (Scheme 4).



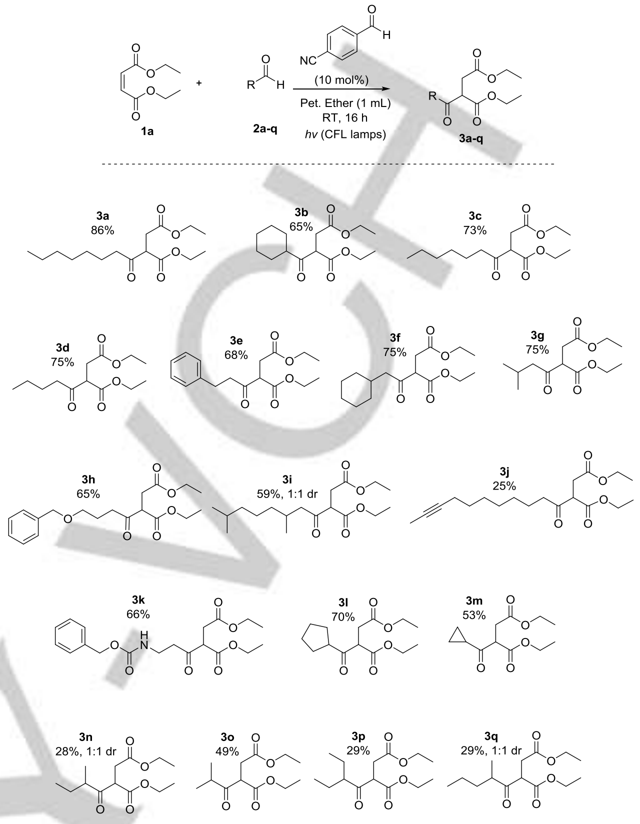
Scheme 3. Studies on the selectivity of photochemical hydroacylation of **1a** with *α,α*-disubstituted aldehydes.

Regarding the decarbonylation problem, *α,α*-disubstituted alkyl aldehydes were tested (**3n-q**), furnishing the desired products in good yields and also performing moderate to good selectivity, in favour of the carbonylated product (Scheme 4). Aldehydes bearing branched alkyl chains were successfully utilized (**3g**, **3i**), whereas aldehydes bearing cyclic aliphatic moieties (**3b**, **3l**, **3m**) afforded mediocre results (Scheme 4). Aldehydes bearing an amide bond, a triple bond or an ether moiety also performed well (**3h**, **3j**, **3k**).

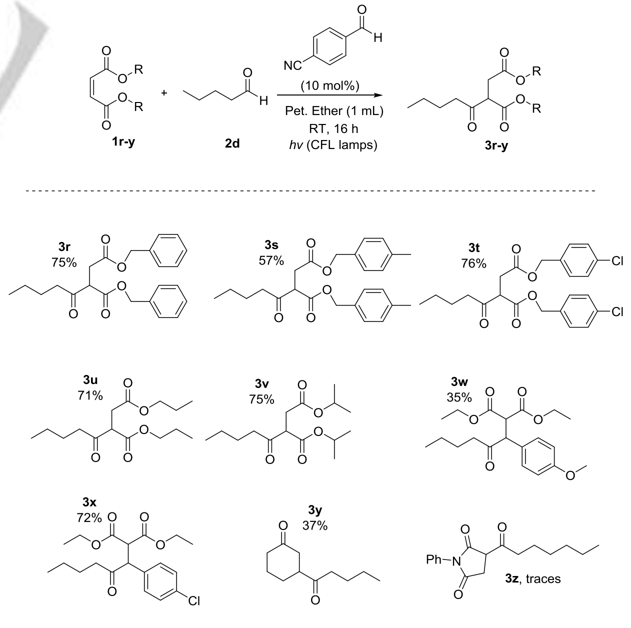
Then, we turned our attention to the alkene substrate scope (Scheme 5). Substituted benzyl diesters were well tolerated (**3r**, **3s**, **3t**). Aliphatic diesters were tested, giving the corresponding products in good yields (**3u**, **3v**). Also, other *α,β*- and electron-deficient olefins gave mediocre yields (**3w**, **3x**). To complete the scope, cyclohexenone was successfully utilized (**3y**) (Scheme 5).

In order to suggest a mechanistic pathway for 4-cyanobenzaldehyde, we carried out various mechanistic experiments. Thus, we started with fluorescence quenching studies.[11] A minimal quenching was observed with heptanal, while on the contrary, quenching was observed with diethyl maleate (Figure 1), which indicates a form of interaction between the excited 4-cyanobenzaldehyde and esters of maleic acid. Notably though, this mediocre quenching could also be attributed to *cis-trans* isomerization of diethyl maleate under irradiation.

In order to discover the interactions of 4-cyanobenzaldehyde in the reaction mixture, UV-Vis experiments were also conducted. The UV-Vis absorbance of each of the reactants and of their combinations was measured in petroleum ether (40-60 °C).[11] Mixing the reagents together, an insignificant increase in the UV absorbance band was observed (Figure 2), which is not representative of an EDA complex.[12-15]



Scheme 4. Substrate scope of the hydroacylation of diethyl maleate.



Scheme 5. Substrate scope of the hydroacylation of activated olefins.

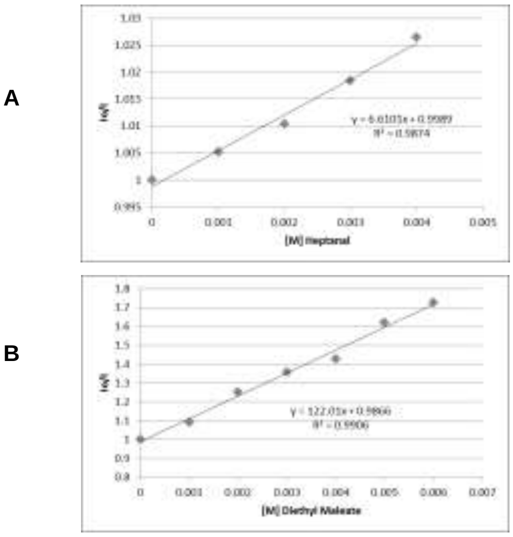


Figure 1 A: Stern-Volmer plot from fluorescence quenching of 4-cyanobenzaldehyde (1 mM in pet. ether) with heptanal. **B**: Stern-Volmer plot from fluorescence quenching of 4-cyanobenzaldehyde (1 mM in pet. ether) with diethyl maleate.

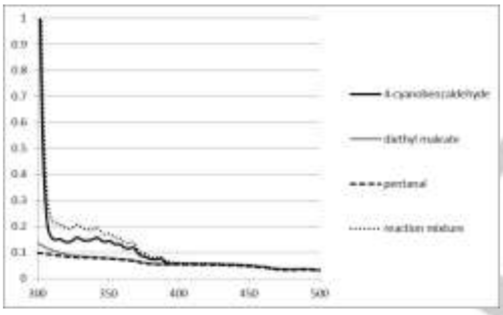


Figure 2. UV-Vis absorption of 4-cyanobenzaldehyde (10^{-2} M), diethyl maleate (10^{-2} M), pentanal (10^{-2} M) and the reaction mixture [4-cyanobenzaldehyde (10^{-2} M) with diethyl maleate (10^{-2} M) and pentanal (10^{-2} M)] in Pet. Ether.

An energy transfer mechanism, as suggested by Melchiorre for ATRA reactions,[16] is also ruled out, since in that case the solvent should not play any role for the yield of the product. This is not the case, since in different solvents various yields are obtained, which is also verified by the Stern-Volmer plots in different solvents.[11,17]

Another mechanistic tool in photocatalysis is the measurement of the quantum yield, which was reported by Yoon and Cismesia.[18] Based on that work, the quantum yield (Φ) of the photocatalytic reaction was calculated: [Φ = 67 (Φ>1)], indicating a chain propagation mechanism.[11,19] Moreover, a cut-off experiment below 400 nm was carried out, showing that the reaction proceeds only at this particular wavelength band.[11] As described above, the reaction demands light irradiation in order to take place, and as shown in Figure 3,

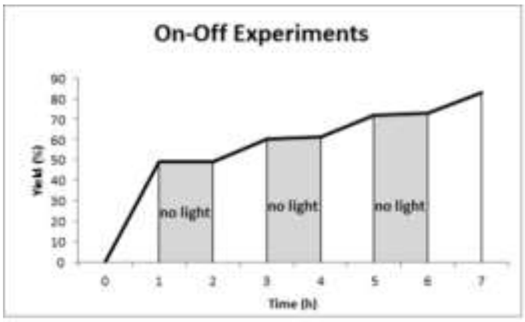
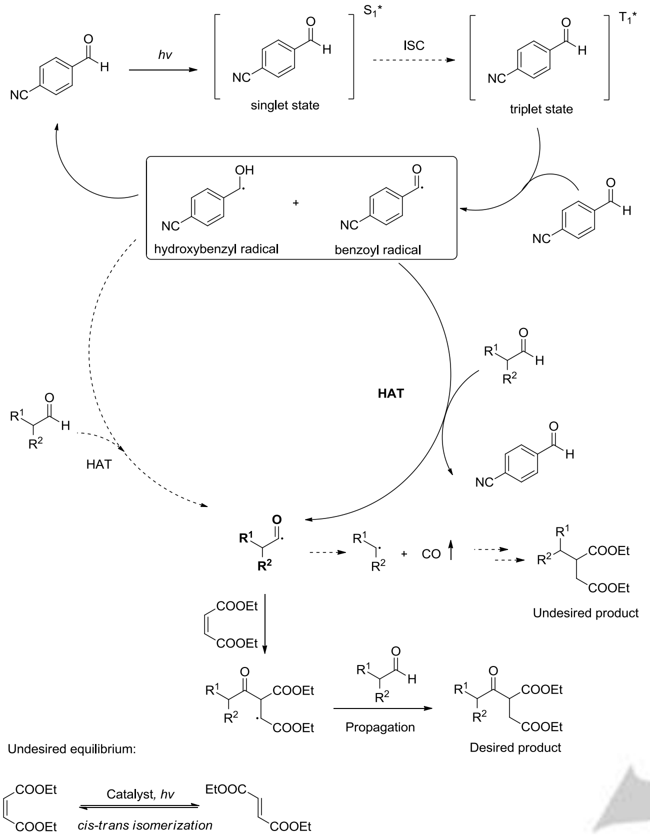


Figure 3. Hydroacylation of diethyl maleate utilizing 4-cyanobenzaldehyde: On-off experiment.

proceeds only under constant photoirradiation and ceases when the light is turned off.

Taking into consideration every possible mechanistic pathway, we investigated the role of the oxygen during the reaction. Thus, when the reaction was performed in the absence of oxygen, the yield dropped at 61% versus 86% in the presence of oxygen (Table 1, entry 8). These results indicate a minor role of oxygen for the hydroacylation and exclude its role as the driving force, as well as the formation of 4-cyanobenzaldehyde's benzoyl peroxy radical as the main promoting pathway. A minor yield drop was also noticed, when 1 equivalent of $CuCl_2$ was added to the reaction mixture (Table 1, entry 10), which is known in literature as an electron scavenger.[20] The 10% yield drop could be considered insignificant and therefore we believe that no SET process takes place. Also, when 1 equivalent of anthracene was added, no reaction took place (Table 1, entry 9). Anthracene is acting as a triplet state quencher (ET (anthracene) = 176 kJ/mol[21] vs ET (4-cyanobenzaldehyde) = 288 kJ/mol[22]) and effectively quenches 4-cyanobenzaldehyde. This constitutes evidence that 4-cyanobenzaldehyde's triplet state is involved in the mechanism. Finally, radical traps were added and the reaction did not take place, confirming that there is a radical propagation mechanism (Table 1, entry 7). Also, in the control experiment with TEMPO (when pentanal was employed as the aldehyde), the acyl radical formation of pentanal was confirmed by GC-MS analysis.[11] We also performed NMR mechanistic experiments to track the progress of the reaction during time, but no signals of new species were observed.[11]

Based on all the above mechanistic experiments, we propose a possible mechanistic pathway (Scheme 6). Initially, 4-cyanobenzaldehyde under irradiation transits to the excited singlet state and subsequently to the triplet via ISC (intersystem crossing).[23] The triplet state then, interacts with a ground state molecule of 4-cyanobenzaldehyde, furnishing two radicals: the hydroxybenzyl radical and the benzoyl radical.[23] This radical-pair mechanism has been first reported in 1970, when the photolysis of benzaldehyde was studied[23] and later verified via CIDNSP (Chemically Induced Dynamic Nuclear Spin Polarization) experiments.[24] These NMR experiments showed the existence of these two radicals and it is proposed



Scheme 6. Proposed mechanistic pathway.

by the authors that under irradiation, the two radicals can return back furnishing 2 ground state benzaldehyde molecules.[24] In our case, the formation of the two radicals is consistent with the structure of 4-cyanobenzaldehyde, which carries a nitrile group and can stabilize the radical in terms of resonance. The benzoyl radical (probably the ketyl radical is doing also this job in a lesser extend) in the presence of the reactant aldehyde generates the first acyl radical through a HAT process, regenerating a ground state 4-cyanobenzaldehyde ready to re-enter the mechanism. Then, this key acyl radical is added to diethyl maleate, furnishing a new radical species, which via a propagation mechanism (quantum yield measurement) affords the desired product (Scheme 6).

Based on examples in literature, the benzoyl radical seems to be the initiator, although examples using ketyl radicals to promote the HAT event are also known.[25,26] An energy transfer mechanism, an EDA complex mechanism or direct interaction of triplet benzaldehyde with one of the reagents seems unlikely to be the dominant mechanism of action, according to our experiments. The moderate quenching of 4-cyanobenzaldehyde by diethyl maleate is due to the parasitic reaction of *cis-trans* isomerization to fumarate. Also, a single electron transfer mechanism or a benzoyl peroxide radical-initiated processes (benzoyl radical coupled with oxygen) have also been ruled out as the dominant pathway of action. Nevertheless, further validation of the mechanism is still ongoing by our team.

Conclusions

In conclusion, a simple, cheap, metal-free and eco-friendly protocol is described for the hydroacylation of Michael acceptors, utilizing 4-cyanobenzaldehyde as the photoinitiator. This method is easy to set up, and only requires common household bulbs as the light source. 25 examples are reported, affording good yields and high selectivity ratios. 4-Cyanobenzaldehyde can be employed in low catalyst loading for this C-H activation photochemical protocol. Mechanistic studies reveal that it has an interesting photochemical behaviour and its capabilities are still under investigation in our lab.

Experimental Section

In a glass vial with a screw cap containing the Michael acceptor (0.30 mmol) and the aldehyde (0.60 mmol), 4-cyanobenzaldehyde (4 mg, 0.03 mmol) and Pet. Ether (1 mL) were added. The vial was sealed with a screw cap and left stirring under household bulb irradiation (2 x 80W household lamps) for 16 h. The desired product was isolated via purification of the crude mixture by flash column chromatography.

Acknowledgements

The authors gratefully acknowledge the John Latsis Foundation for financial support through the programme “ΕΠΙΣΤΗΜΟΝΙΚΕΣ ΜΕΛΕΤΕΣ 2015” (PhotoOrganocatalysis: Development of new environmentally-friendly methods for the synthesis of compounds for the pharmaceutical and chemical industry) and the Laboratory of Organic Chemistry of the Department of Chemistry of the National and Kapodistrian University of Athens for financial support. E.V. would like to thank the State Scholarship Foundation (IKY) for financial support through a doctoral fellowship. Also, COST Action C-H Activation in Organic Synthesis (CHAOS) CA15106 is acknowledged for helpful discussions.

Keywords: Photochemistry • Hydroacylation • Michael acceptors • 4-Cyanobenzaldehyde

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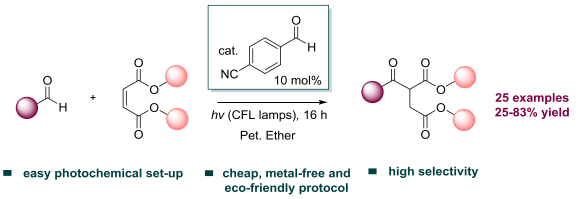

Photocatalysis. A facile and sustainable photochemical hydroacylation of Michael acceptors is described, affording products in good to high yields and selectivities utilizing 4-cyanobenzaldehyde as the photoinitiator and household lamps as the irradiation source.

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Photochemical Hydroacylation of Michael Acceptors Utilizing an Aldehyde as the Photoinitiator