Catalyst-free [2 + 2] photocycloadditions between benzils and olefins under visible light

Roberto Tinelli^{1,5} · Davide Ravelli¹ · Andrea Basso² · Serena C. Tarantino³ · Luca Capaldo⁴

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Abstract

The catalyst-free [2 + 2] photocycloaddition between benzils and simple olefins is reported. The adoption of visible light proved essential for the transformation, as shorter wavelengths led to uncontrolled decomposition. When cyclic olefins were used, the reaction occurred smoothly to afford the expected oxetanes regio- and stereoselectively after 24 h of irradiation. In contrast, in the case of acyclic olefins, longer reaction times were typically required and small amounts (ca. 20%) of [4 + 2] photocycloadducts and by-products deriving from competitive hydrogen atom abstraction were observed. The selectivity of the transformation could be consistently improved by decreasing the reaction temperature, thus restoring the desired [2 + 2] reactivity. An overall mechanistic picture is also offered based on the chemical and photophysical quenching experiments and the stereochemical output is rationalized based on Griesbeck models.

Graphical abstract

Keywords Paternò–Büchi · Cycloaddition · Benzils · Photochemistry · Oxetanes · Visible light irradiation

1 Introduction

The Paternò–Büchi (PB) reaction was first reported at the beginning of the twentieth century by the Italian chemist E. Paternò and consists in the [2 + 2] photocycloaddition of carbonyl compounds onto olefins to afford oxetanes [1]. However, the intimacies of the mechanism and the exact structures of the products were unveiled only 45 years later thanks to the contribution by the Swiss chemist Büchi [2]. Even today, the PB reaction keeps attracting synthesis practitioners since it allows to achieve a remarkable degree of molecular complexity literally with the flip of a switch (Scheme 1a). Moreover, it requires minimal (if any) pre-functionalization of starting materials and occurs with good levels of regio- and stereoselectivity [3–6]. In fact,

✉ Luca Capaldo
l.capaldo@uva.nl

¹ PhotoGreen Lab, Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy

² Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genoa, Italy

³ Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy

⁴ Flow Chemistry Group, Van't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

⁵ Present Address: Institute of Organic Chemistry, University of Vienna, 1090 Vienna, Austria

Scheme 1 Context, precedents and our work. *Bn*: benzyl

by shining light on commodity chemicals, such as ketones and olefins, densely functionalized oxetanes can be readily obtained. The latter compounds are an important core in drugs (e.g. in the antitumoral Taxol), since their presence can trigger profound changes in aqueous solubility, lipophilicity and metabolic stability [7]. Considering the above, it comes as no surprise that, even after more than a century, the study of the PB reaction still represents an active and vibrant research field [8–11].

Very recently, the PB reaction has been extended also to α -ketoesters as carbonyl surrogates by having recourse to sensitization. In these cases, a purposely added compound (i.e. the sensitizer) was added to absorb low-energy

visible light and activate the carbonyl compounds via triplet energy transfer. In 2020, Schindler and Yoon independently reported the use of Ir-polypyridyl complexes to perform the PB reaction between α -ketoesters and olefins under blue light irradiation (Scheme 1b) [8, 9]. Therein, blue light was absorbed by the very same photocatalyst,¹ which underwent triplet energy transfer with methyl phenylglyoxalate to generate the diradical triplet state of the latter. Eventually, this species was quenched by the olefin

¹ Schindler used $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$, while Yoon chose $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{BAR}^{\text{F}}$.

Scheme 2 [2+2] photocycloaddition of benzils onto cyclic olefins: optimization on 0.07 mmol scale (left) and scope on 1.75 mmol scale (right). ^aGC yield was calculated through calibration curves obtained with authentic samples; undecane as external standard. Consumption of the limiting reagent was > 90% except where otherwise noted.

to get the expected oxetane in high yields and regioselectivity. Notably, the photosensitized approach was also extended to oximes and quinaxolinones by Schindler and Bach, respectively, in what is known as aza-PB [12–18]. Despite the synthetic value of the approaches described so far, they require specialized sensitizers with high energy (> 60 kcal mol⁻¹) and long-lived triplet excited states, thus undermining the abovementioned operational simplicity.

α-Diketones absorb directly visible light, which allows to avoid the use of sensitizers. Different classes of α-diketones, such as isatin, isoquinoline-1,3,4-triones and phenanthrenediones have been investigated as carbonyl surrogates in the PB reaction in a catalyst-free approach [19]. More recently, Dell’Amico demonstrated the use of the PB reaction for the dearomatization of indoles (Scheme 1c) [10, 20, 21]: herein, a handful of benzils was also tested besides conventional ketones, however traditional reaction partners (i.e. alkenes) were not investigated.

Hereby, we report a detailed study of the catalyst-free PB reaction between benzils and simple olefins under blue light irradiation (Scheme 1d). In particular, the conditions were fully optimized towards the formation of the desired oxetanes and the scope of the photocycloaddition evaluated. Furthermore, we report on the marked dependency of the distribution of reaction products on reaction parameters (e.g. temperature and irradiation wavelength) and type of alkene employed.

^bConsumption of **1a**: 77%. ^c(±)-3 was not detected; instead, a messy crude was observed. Product (±)-S1 was the most relevant by-product (see Sect. 4.3 in the SI). ^dYields referring to isolated products are shown. ^eReaction time: 3 h. XRD structures of products (±)-3, (±)-S1 and (±)-6 are reported in Sect. 10 in the SI

2 Results

We set out by studying the [2+2] photocycloaddition of benzil (**1a**) onto 1,2-dihydronaphthalene (**2a**) as our benchmark process. After a routine survey of reaction conditions on a 0.07 mmol scale (see Sect. 4 in the Supplementary Information), we found that the irradiation of a cyclohexane solution of **1a** (0.07 M) and **2a** (2 equiv) with blue light (40 W LED, λ = 456 nm) afforded product (±)-3 in 83% GC yield after 24 h. If, on one side, solvent and concentration did not prove to be pivotal parameters (Scheme 2, entries 1–5 and SI), on the other hand, the choice of the irradiation wavelength turned out to be crucial. When the reaction was performed with UV light (entries 6–8), the uncontrolled decomposition of **1a** into a myriad of by-products occurred, the most relevant of which was compound (±)-S1 (Scheme 2, bottom left). On the contrary, when using blue light (entry 4), a clean conversion to (±)-3 was obtained. Thus, we questioned if this unexpected difference could be explained by calling into question the photostability of the latter compound at short irradiation wavelengths. However, when oxetane (±)-3 (0.07 M in cyclohexane) was exposed to UV light (40 W LED, λ = 390 nm), compound (±)-S1 was not observed despite GC-FID analysis did show decomposition already after 30 min.

Scheme 3 [2+2] photocycloaddition of benzils onto acyclic olefins: re-optimization of reaction conditions (0.07 mmol, left) and scope (1.75 mmol, right). ^aNMR yield was calculated using CH₂Br₂ as external standard. Consumption was > 90% in all cases. ^bYields referring to isolated products are shown. ^c15% of **8_{S2}** and 8% of **(±)-8_{S3}**

Next, we moved to evaluate the scope of the reaction on a 1.75 mmol. As reported in the right part of Scheme 2, **1a** reacted with **2a** to deliver **(±)-3** as the only product in 75% yield after isolation through column chromatography. Single-crystal XRD analysis showed that the product bears the phenyl ring in *anti* with respect to the two hydrogens on the rings junction (Scheme 2 and SI). Then, we decided to investigate the influence of the electronic nature of α -diketones by reacting commercially available **1b** and **1c** with **2a**. Although the former allowed to obtain oxetane **(±)-4** in good yield (~70%), the latter performed the worst in the series by delivering product **(±)-5** in 49% isolated yield. Interestingly, when replacing **2a** with indene (**2b**), the reaction proved to be much more efficient. Indeed, the reaction between **1a** and **2b** afforded **(±)-6** in 93% yield, while the use of **1b** allowed to obtain **(±)-7** in quantitative yield. Interestingly, compound **(±)-6** was synthesized also using a flow apparatus (residence time 1.5 h, see Sect. 3 in the SI) and obtained with similar selectivity and yield (92%), thus showing the versatility of our approach. The regio- and stereochemistry of the product was verified via HMBC NMR experiments and XRD analysis. It is perhaps worth mentioning that in our hands, diacetyl did not show any reactivity, in contrast with a report in the literature (therein, $\lambda > 320$ nm from a high-pressure Hg lamp and benzene as the solvent were employed) [22].

Next, we decided to investigate the reactivity of benzils **1a** and **1b** with acyclic olefins, for which some re-optimization

of reaction conditions was required: to this end, we selected the [2+2] photocycloaddition of **1a** onto tetramethylethylene (**2c**) as our benchmark reaction. We found that a polar solvent (MeCN) led to a better yield compared to cyclohexane (69 vs 42% GC yield, see Scheme 3, entries 1–3); however, the transformation required considerably longer time compared to the case of cyclic olefins. It is worth mentioning that, besides the expected oxetane, the formation of minor amounts (ca. 20%) of by-products **8_{S2}** and **(±)-8_{S3}** was observed. The concentration did not prove to be a crucial parameter for the reaction (entry 4).

As far as the scope is concerned (Scheme 3, right), when **2c** was reacted with **1a** on a 1.75 mmol scale, the expected oxetane **(±)-8** was obtained in 60% yield after 3 days of irradiation. Interestingly, the six-membered ring product 1,4-dioxene (**8_{S2}**, 15% yield) and traces (8%) of adduct **(±)-8_{S3}** were isolated as well. Also in this case, the use of flow conditions afforded comparable results (59% isolated yield), although with a residence time of 6 h. The use of **1b** allowed to obtain product **(±)-9** in 74% after 20 h of irradiation. When using amylene (**2d**) in combination with **1a**, the reaction required a remarkably longer irradiation time (7 days) to achieve 65% yield of regioisomers **(±)-10** and **(±)-10'** in a 3:1 ratio. The structures of the two regioisomers were determined via HMBC or XRD analysis and are shown in Scheme 3 (see also SI). Ethyl vinyl ether (**2e**) proved to be a competent olefin in the transformation, affording the expected oxetane **(±)-11** in an excellent yield (74%) after

Scheme 4 Mechanistic investigation: chemical quenching experiment with TEMPO (a), luminescence quenching experiments (b), mechanistic scenario (c) and Griesbeck models (d)

after 20 h), while the amount of compound **8_{S2}** did not vary (10% GC yield). Overall, decreasing the temperature to 0 °C allowed to increase the **(±)-8**: **8_{S2}** ratio to 7:1. Finally, we performed the reaction at −78 °C, which prevented the formation of compound **8_{S2}** (<5%), while **(±)-8** was obtained in 77% GC yield after only 6 h (Fig. 1). In all cases, **8_{S3}** was formed only in traces.

Since it is known that the PB reaction can proceed through different pathways, i.e. concerted [2 + 2] cycloaddition or radical pathway [5], we performed a series of experiments to ascertain which of these two is actually operating in the case of α -diketones. First, the model reaction between **1a** and **2a** was performed in the presence of the well-known radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (2 equiv), *aka* TEMPO: the reaction was completely inhibited (Scheme 4a). To exclude a competitive absorption by TEMPO preventing **1a** excitation, we also performed the experiment with a tube-in-tube setup (see Sect. 5 in the SI) where a solution of the radical scavenger functioned as a light filter for the actual reaction mixture. In the latter case, unaltered reactivity was observed (80% GC yield). Secondly, we set off to monitor the effect of the presence of **2a** on the fluorescence and phosphorescence of **1a** in cyclohexane solution (Scheme 4b). Consistently with a previous report [23], fluorescence emission ($\lambda_{max} = 510$ nm) could be observed when analyzing an air-equilibrated solution of **1a** (1 mM). Interestingly, this signal was not affected by addition of 1 or 2 equiv of **2a**. On the other hand, the phosphorescence emission contribution ($\lambda_{max} = 563$ nm) could be

detected in an Ar-sparged solution and, at contrast with the fluorescence signal, was visibly quenched upon addition of the same amounts of **2a** (see Sect. 6 in SI for further details). In the latter case, a k_{SV} of 150 M^{−1} was found, corresponding to a $k_Q = 1.5 \times 10^4$ M^{−1} s^{−1} [24].

3 Discussion

In this work, we have investigated the [2 + 2] photocycloaddition of benzils (**1a–c**) with cyclic (**2a** and **2b**) and acyclic (**2c–2f**) olefins under blue light irradiation and catalyst-free conditions. When the selected benzils were reacted with the former group of olefins, the hoped-for oxetanes ((±)-**3–7**) were readily formed after 24 h of irradiation. Quite interestingly, when the irradiation was carried out with shorter wavelengths (e.g. 390 nm) uncontrolled photodecomposition of benzil was observed [25]; on the other hand, light is essential for the reaction to occur and benzil **1a** is photostable when irradiated in neat cyclohexane at 456 nm (see Scheme S2 in the SI). It is important to mention here that **2a** does not absorb in the investigated window (> 310 nm) and it is not accountable for the observed photoreactivity [26]. The main product observed upon UV light irradiation was compound **(±)-S1**. Bunbury reported that one of the major decomposition pathways of benzil in cyclohexane under UV light irradiation is the carbonyl–carbonyl homolysis to afford benzoyl radicals [25]; thus, we speculate that the stepwise, double addition of such intermediates onto the C=C double bond of

2a leads to the formation of ($\pm$)-**S1**. Importantly, we safely excluded that the latter compound is formed upon UV light-promoted photolysis of the oxetane product (see Sect. 4.3 in the SI). From the above, we concluded that ($\pm$)-**S1** derives from direct absorption of UV light by benzil, which could be avoided by adopting visible light irradiation.

When it comes to acyclic olefins, the most remarkable difference was observed in reaction times; indeed, at least three days of irradiation were required in most cases. We attribute this difference to the increased flexibility of the first-formed 1,4-diradical adduct (intermediate **I** in Scheme 4c) as compared to cyclic olefins, which could undergo retro-addition. This phenomenon was most apparent when amylene (**2d**) was used in the role of the olefin to get product ($\pm$)-**10** and ($\pm$)-**10'**, which required 7 days of irradiation with blue light.

While evaluating the scope of the PB reaction between benzils and olefins **2c** and **2f**, compound **S2** and **S3** were also observed. As for 1,4-dioxene **S2**, it derives from a [4 + 2] cycloaddition, a reactivity manifold more typically encountered with rigid systems (e.g. 9,10-phenanthrenedione) and a 1,6-diradical intermediate is the preferred model to account for this reactivity (Scheme 4c) [19, 27, 28]. As for α -diketones, this reactivity has been documented only with specific olefinic substrates (i.e. silyl ketene acetals) and reported to occur via a benzil-triggered single-electron transfer [29]. Diacetyl did not lead to the formation of the desired oxetane derivatives, requiring harsher conditions (350 W high-pressure Hg lamp, 48 h) to engage in [2 + 2] photocycloadditions with **2b**. At any rate, in this case the reaction showed lower diastereoselectivity [22]. As far as compound **S3** is concerned, it is formed only in traces (never exceeding 10% yield) and its formation can be explained by taking into consideration a hydrogen atom transfer (HAT) reactivity [30, 31]. Indeed, the excited state of benzil has been reported to activate hydrocarbons by homolytic cleavage of a C(sp³)-H bond [25]. In the case of olefins **2c** and **2f**, the HAT step would afford a resonance-stabilized allyl radical through the cleavage of a rather labile C-H bond. A radical-radical coupling between the so-formed ketyl radical and such intermediate accounts for compound **S3** formation.

Remarkably, we found that the temperature was a pivotal parameter for the selectivity of the PB reaction with acyclic olefins: in fact, by decreasing the temperature to -78 °C, the formation of both by-products **S2** and **S3** could be inhibited.

Given the above, a general mechanism of the reaction can be proposed (Scheme 4c) and starts with the excitation of benzil (e.g. **1a**). After Intersystem Crossing (ISC), for which the quantum yield (QY) is 0.92 [25, 32], it delivers a diradical triplet state. The involvement of such species and not of the first-formed singlet state is corroborated by the selective quenching of the phosphorescence, not fluorescence, upon addition of **2a** (see Scheme 4b). The triplet state can then: (i) add onto olefins (**2**) to afford 1,4-diradical **I** and deliver

oxetanes after a second ISC and ring closure or (ii) undergo HAT reactivity with **2** to ultimately deliver product **S3**. Intermediate **I** is in resonance with a 1,6-diradical species that, upon ring closure, is responsible for the formation of by-product **S2** (Scheme 4c). The latter process is thermally activated. The radical nature of the process is corroborated by the inhibition effect of TEMPO on the overall transformation (Scheme 4a).

Coming to the selectivity of the reaction, the relative abundance of regioisomers can be explained by taking into account the relative stabilization of the 1,4-diradical intermediates that can be obtained after the radical addition of the benzil onto the C=C double bond. This is very well shown for product ($\pm$)-**10**, where the tertiary radical in intermediate **I** is more stable than the secondary radical; in sharp contrast, in the case of product ($\pm$)-**13**, the stability offered by the allyl or the tertiary radical is comparable and delivers the oxetane as a 1.1:1 mixture of regioisomers. As for the stereochemistry, this has been investigated with XRD analysis (when possible) and can be rationalized based on the “Griesbeck model” (see e.g. Scheme 4d) [33, 34]. According to the latter model, the triplet diradical intermediate **I** adopts a configuration where the axes of the orbitals of the unpaired electrons are orthogonal to minimize repulsive interaction (see Scheme 4d). In such an arrangement, the interactions between the substituents account for diastereoselectivity and can be attractive (e.g. hydrogen bonding) or repulsive (e.g. steric hindrance) [33]. Since with our substrates hydrogen bonding is unlikely to play a role, we propose that the marked steric hindrance [35] of the phenyl substituent is crucial to determine the stereochemical output of the reaction.

4 Conclusions

To sum up, the catalyst-free [2 + 2] photocycloaddition between benzils and simple olefins has been reported. We proved that visible light is crucial for the transformation, while more energetic photons promote uncontrolled decomposition. The mechanism has been ascertained on multiple levels: chemical quenching experiments suggested the radical nature of the process, while photophysical quenching experiments unequivocally showed that only the triplet excited state of benzil is competent in delivering the desired products by interacting with olefins. When cyclic olefins were used, the reaction occurred smoothly regio- and stereoselectively after 24 h of irradiation. In contrast, when acyclic olefins were used, longer reaction times were typically required and small amounts of by-products deriving from [4 + 2] photocycloaddition and HAT reactivity were observed. We also proved that the formation of these

by-products can be inhibited by lowering the reaction temperature; thus, maximizing the desired [2 + 2] reactivity.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43630-021-00129-4>.

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Author contributions RT: performed the experiments; LC and AB: performed preliminary experiments; and SCT: performed the crystallographic study. LC and DR: designed the experiments and prepared this manuscript with input from all co-authors.

Availability of data and materials Supplementary Information (SI) containing experimental details about the used materials, sample preparation, photophysical experiments and analytical data (NMR) is available free of charge at supplementary information. The primary NMR FID files for compounds (**±**)-**3**–**13**, (**±**)-**S1** are available in the FigShare repository, <https://doi.org/10.21942/uva.16821235>. CCDC contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/structures>

Declarations

Conflict of interest No conflict of interest to declare.

References

- Paternò, E., & Chieffi, G. (1909). Sintesi in Chimica Organica per Mezzo Della Luce. Nota II. Composti Degli Idrocarburi Non Saturi Con Aldeidi e Chetoni. *Gazzetta Chimica Italiana*, 39, 341–361.
- Büchi, G., Inman, C. G., & Lipinsky, E. S. (1954). Light-catalyzed organic reactions. I. The reaction of carbonyl compounds with 2-methyl-2-butene in the presence of ultraviolet light. *Journal of the American Chemical Society*, 76(17), 4327–4331. <https://doi.org/10.1021/ja01646a024>
- D'Auria, M., & Stoia, S. (2019). *The Paternò-Büchi reaction*. Cambridge Scholars Publishing.
- D'Auria, M. (2019). The Paternò-Büchi reaction—A comprehensive review. *Photochemical & Photobiological Sciences*, 18(10), 2297–2362. <https://doi.org/10.1039/c9pp00148d>
- Fréneau, M., & Hoffmann, N. (2017). The Paternò-Büchi reaction—Mechanisms and application to organic synthesis. *Journal of Photochemistry and Photobiology, C: Photochemistry Reviews*, 33, 83–108. <https://doi.org/10.1016/j.jphotochemrev.2017.10.002>
- Bach, T. (1998). Stereoselective intermolecular [2 + 2]-photocycloaddition reactions and their application in synthesis. *Synthesis*, 1998(05), 683–703. <https://doi.org/10.1055/s-1998-2054>
- Wuitschik, G., Carreira, E. M., Wagner, B., Fischer, H., Parrilla, I., Schuler, F., Rogers-Evans, M., & Müller, K. (2010). Oxetanes in drug discovery: Structural and synthetic insights. *Journal of Medicinal Chemistry*, 53(8), 3227–3246. <https://doi.org/10.1021/jm9018788>
- Rykaczewski, K. A., & Schindler, C. S. (2020). Visible-light-enabled Paternò-Büchi reaction via triplet energy transfer for the synthesis of oxetanes. *Organic Letters*, 22(16), 6516–6519. <https://doi.org/10.1021/acs.orglett.0c02316>
- Zheng, J., Dong, X., & Yoon, T. P. (2020). Divergent photocatalytic reactions of α -ketoesters under triplet sensitization and photoredox conditions. *Organic Letters*, 22(16), 6520–6525. <https://doi.org/10.1021/acs.orglett.0c02314>
- Franceschi, P., Mateos, J., Vega-Peñaloza, A., & Dell'Amico, L. (2020). Microfluidic visible-light Paternò-Büchi reaction of oxindole enol ethers. *European Journal of Organic Chemistry*, 2020(43), 6718–6722. <https://doi.org/10.1002/ejoc.202001057>
- Vogt, F., Jödicke, K., Schröder, J., & Bach, T. (2009). Paternò-Büchi reactions of silyl enol ethers and enamides. *Synthesis*, 24, 4268–4273. <https://doi.org/10.1055/s-0029-1217095>
- Großkopf, J., Kratz, T., Rigotti, T., & Bach, T. (2021). Enantioselective photochemical reactions enabled by triplet energy transfer. *Chemical Reviews*. <https://doi.org/10.1021/acs.chemrev.1c00272>.
- Richardson, A. D., Becker, M. R., & Schindler, C. S. (2020). Synthesis of azetidines by aza Paternò-Büchi reactions. *Chemical Science*, 11(29), 7553–7561. <https://doi.org/10.1039/D0SC01017K>.
- Kandappa, S. K., Valloli, L. K., Ahuja, S., Parthiban, J., & Sivaguru, J. (2021). Taming the excited state reactivity of imines—From non-radiative decay to aza Paternò-Büchi reaction. *Chemical Society Reviews*, 50(3), 1617–1641. <https://doi.org/10.1039/D0CS00717J>.
- Becker, M. R., Richardson, A. D., & Schindler, C. S. (2019). Functionalized azetidines via visible light-enabled aza Paternò-Büchi reactions. *Nature Communications*, 10(1), 5095. <https://doi.org/10.1038/s41467-019-13072-x>.
- Becker, M. R., Wearing, E. R., & Schindler, C. S. (2020). Synthesis of azetidines via visible-light-mediated intermolecular [2+2] photocycloadditions. *Nature Chemistry*, 12(10), 898–905. <https://doi.org/10.1038/s41557-020-0541-1>.
- Wearing, E. R., Blackmun, D. E., Becker, M. R., & Schindler, C. S. (2021). 1- and 2-azetidines via visible light-mediated [2+2]-cycloadditions of alkynes and oximes
- Li, X., Großkopf, J., Jandl, C., & Bach, T. (2021). Enantioselective, visible light mediated aza Paternò-Büchi reactions of quinoxalinones. *Angewandte Chemie International Edition*, 60(5), 2684–2688. <https://doi.org/10.1002/anie.202013276>.
- Huang, C., Zheng, M., Xu, J., & Zhang, Y. (2013). Photo-induced cycloaddition reactions of α -diketones and transformations of the photocycloadducts. *Molecules*, 18(3), 2942–2966. <https://doi.org/10.3390/MOLECULES18032942>
- Mateos, J., Vega-Peñaloza, A., Franceschi, P., Rigodanza, F., Andreetta, P., Companyó, X., Pelosi, G., Bonchio, M., & Dell'Amico, L. (2020). A visible-light Paternò-Büchi dearomatization process towards the construction of oxeto-indolinic polycycles. *Chemical Science*, 11(25), 6532–6538. <https://doi.org/10.1039/D0SC01569E>
- Mateos, J., Cuadros, S., Vega-Peñaloza, A., & Dell'Amico, L. (2021). Unlocking the synthetic potential of light-excited aryl ketones: Applications in direct photochemistry and photoredox catalysis. *Synlett*, 32, 70469. <https://doi.org/10.1055/a-1403-4613>
- Ryang, H.-S., Shima, K., & Sakurai, H. (1973). Photoaddition reaction of biacetyl. *Journal of Organic Chemistry*, 38(16), 2860–2865. <https://doi.org/10.1021/jo00956a028>
- Flamigni, L., Barigelletti, F., Dellonte, S., & Orlandi, G. (1983). Photophysical properties of benzil in solution: Triplet state deactivation pathways. *Journal of Photochemistry*, 21(2), 237–244. [https://doi.org/10.1016/0047-2670\(83\)80027-6](https://doi.org/10.1016/0047-2670(83)80027-6)
- Almgren, M. (1967). The natural phosphorescence lifetime of biacetyl and benzil in fluid solution. *Photochemistry and Photobiology*, 6(11), 829–840. <https://doi.org/10.1111/j.1751-1097.1967.tb08896.x>

25. Bunbury, D. L., & Wang, C. T. (1968). The photolysis of benzil in cyclohexane solution. *Canadian Journal of Chemistry*, 46(9), 1473–1479. <https://doi.org/10.1139/v68-243>
26. Lewis, F. D., & Zuo, X. (2003). Activated decay pathways for planar vs twisted singlet phenylalkenes. *Journal of the American Chemical Society*, 125(29), 8806–8813. <https://doi.org/10.1021/ja035066j>
27. Ho, J.-H., Ho, T.-I., Chen, T.-H., & Chow, Y. L. (2001). Efficient photocycloaddition of phenanthroquinones with simple olefins. *Journal of Photochemistry and Photobiology, A: Chemistry*, 138(2), 111–122. [https://doi.org/10.1016/S1010-6030\(00\)00402-0](https://doi.org/10.1016/S1010-6030(00)00402-0)
28. Chow, Y. L., Joseph, T. C., Quon, H. H., & Tam, J. N. S. (1970). Photoaddition of α -diketones to olefins. Stereospecificity of the addition reaction. *Canadian Journal of Chemistry*, 48(19), 3045–3052. <https://doi.org/10.1139/v70-514>
29. Cho, D. W., Lee, H.-Y., Oh, S. W., Choi, J. H., Park, H. J., Mariano, P. S., & Yoon, U. C. (2008). Photoaddition reactions of 1,2-diketones with silyl ketene acetals formation of β -hydroxy- γ -ketoesters. *Journal of Organic Chemistry*, 73(12), 4539–4547. <https://doi.org/10.1021/jo800473x>
30. Capaldo, L., & Ravelli, D. (2017). Hydrogen atom transfer (HAT): A versatile strategy for substrate activation in photocatalyzed organic synthesis. *European Journal of Organic Chemistry*, 2017(15), 2056–2071. <https://doi.org/10.1002/ejoc.201601485>
31. Capaldo, L., Ravelli, D., & Fagnoni, M. (2021). Direct photocatalyzed hydrogen atom transfer (HAT) for Aliphatic C–H bonds elaboration. *Chemical Reviews*. <https://doi.org/10.1021/acs.chemrev.1c00263>
32. Calvert, J. G., & Pitts, J. N., Jr. (1966). *Photochemistry* (1st ed.). Wiley.
33. Griesbeck, A. G., & Stadtmueller, S. (1990). Photocycloaddition of benzaldehyde to cyclic olefins: Electronic control of endo stereoselectivity. *Journal of the American Chemical Society*, 112(3), 1281–1283. <https://doi.org/10.1021/ja00159a079>
34. Kutateladze, A. G. (2001). Conformational analysis of singlet–triplet state mixing in Paternò–Büchi diradicals. *Journal of the American Chemical Society*, 123(38), 9279–9282. <https://doi.org/10.1021/ja016092p>
35. Hirsch, J. A. (2007). Table of conformational energies-1967. In *Topics in Stereochemistry* (199–222)