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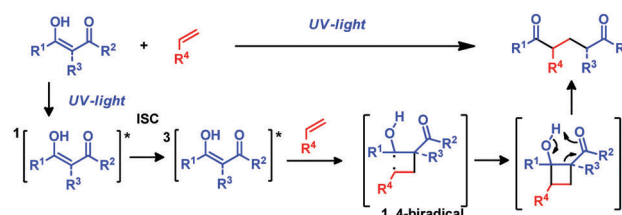
Reinventing the De Mayo reaction: synthesis of 1,5-diketones or 1,5-ketoesters *via* visible light [2+2] cycloaddition of β -diketones or β -ketoesters with styrenes†

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A visible light mediated De Mayo reaction between 1,3-diketones and styrenes following a [2+2] cycloaddition pathway *via* a photosensitization mechanism gives access to 1,5-diketones. The reaction has been applied to substituted styrenes and aryl- and alkyl-substituted ketones. Moreover, the method converts β -ketoesters, β -amido esters, and β -cyano ketones. Seven membered rings, a frequent structural motif of natural products, are also accessible using this methodology.

The photochemical reaction between β -diketones and double bonds under UV light irradiation is known as the De Mayo reaction.¹ In 1962 Paul Jose De Mayo reported that the enolic form of 1,3-diketones can undergo a [2+2] photocycloaddition with an olefin under UV irradiation affording a non-isolable cyclobutanol intermediate that evolves through a retro-aldol reaction yielding 1,5-diketones (Scheme 1). However, it was not until the late 1970s that its synthetic utility was fully realized when, *via* the intramolecular version, more complex macrocyclic structures became accessible.² Examples are the total syntheses of (\pm)-ingenol³ or the alkaloid mesembrine⁴ that employ the De Mayo reaction as the key step, or the formal synthesis of vindorosine,⁵ among others.⁶ In these reactions β -diketone is directly excited by UV irradiation to its singlet excited state, which undergoes intersystem crossing to the excited triplet (Scheme 1). Further complexation of the triplet state with the double bond forms an exciplex that evolves to form the most stable 1,4-biradical. This 1,4-biradical generates the cyclobutanol intermediate that affords the desired products (Scheme 1).^{7a} However, to the best of our knowledge a sensitized version of this reaction allowing the use of visible light has not been reported so far.⁷

Over the last few decades, visible light photocatalysis⁸ has developed into an important tool in synthesis. The lower cost



Scheme 1 De Mayo photocycloaddition.

and energy demand of the visible light sources, together with the selective excitation of the photocatalyst, thus avoiding undesired pathways, are some of the advantages. Photoredox catalysis has afforded several approaches for the [2+2] photocycloaddition between double bonds or Michael acceptors *via* photosensitization.⁹ In particular, Yoon reported the intramolecular [2+2] photocycloaddition of styrene derivatives by direct photosensitization using an iridium complex as a photosensitizer of the reaction under visible light irradiation.^{9a} Based on this precedent, we envisaged that a visible light De Mayo reaction may be possible *via* the photosensitization of the styrene using a photocatalyst through energy transfer, triggering the [2+2] photocycloaddition with the enol of 1,3-diketones to obtain the desired 1,5-diketones.

To prove this hypothesis, a solution of styrene **2a** and 1,3-diphenylpropane-1,3-dione **3a** in the presence of 2 mol% [Ir(dF(CF₃)ppy)₂(bpy)]PF₆ **1a**, in CH₃CN was subjected to blue LED irradiation over a period of 20 h, affording 1,5-diketone **4a** in 69% yield (entry 1, Table 1). Then, different catalysts with different oxidation powers (see the scheme in Table 1)¹⁰ were tested in the reaction. Ru(bpy)₃Cl₂ **1b**, Ir(ppy)₃ **1c** and Mes-Acr⁺ **1e** did not react, while the carbazol derivative **1d** afforded the desired product in 44% yield (entries 2–5, Table 1). Taking into account that the enol of **3a** is the reactive species, tributylmethylammonium dibutyl phosphate was tested in the reaction, in order to shift the keto–enol equilibria to the enol form, obtaining **4a** in 79% yield (entry 6, Table 1). Control reactions revealed that both the catalyst and light are necessary for the

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Table 1 Optimization of the reaction conditions for the photosensitized De Mayo reaction^a

Entry	Cat. (mol%)	Additive (25 mol%)	Solvent	Yield ^b (%)
1	1a (2)	—	CH ₃ CN	69
2	1b (3)	—	CH ₃ CN	0
3	1c (2)	—	CH ₃ CN	0
4	1d (4)	—	CH ₃ CN	44
5	1e (4)	—	CH ₃ CN	0
6	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	CH ₃ CN	79
7	1a (2) ^c	(BuO) ₂ P(O)ONBu ₃ Me	CH ₃ CN	0
8	—	(BuO) ₂ P(O)ONBu ₃ Me	CH ₃ CN	0
9	1a (2)	(BuO) ₂ P(O)ONBu ₃ Me	EtOH	96

^a The reactions were performed using 0.1 mmol of **3a**, 0.5 mmol of **2a**, and 1 mL of CH₃CN. ^b Isolated yields after 20 h. ^c Without light.

reaction (entries 7 and 8, Table 1). Finally, the use of the polar protic solvent EtOH improved the yield to 96% (entry 7, Table 1). Therefore, the optimized conditions are: **1a** (2 mol%), **2a** (5 equiv.), **3a** (1 equiv.), (BuO)₂P(O)ONBu₃Me (25 mol%), EtOH (1 mL), N₂, 25 °C, and 455 nm (for further details see Table S1, ESI†).

With the optimized conditions in hand, we proceed to study the scope of the reaction between β-diketone **3a** and different styrene derivatives **2** (Table 2). Styrenes bearing electron donating or electron withdrawing groups in the *ortho*, *meta* or *para* position yielded the final products in good to very good isolated yields (**4a–f**, Table 2). Therefore, the electronic nature of the substituents does not seem to have a big impact in the reaction. The reaction could also be performed on a 1 mmol scale of **3a** using a different set up (see the ESI,† Fig. S11), obtaining **4a** in 66% yield, thus proving the robustness of the methodology (Table 2). More hindered styrene derivatives also underwent this reaction satisfactorily. Thus, α-methyl styrene afforded **4g** in a moderate 56% yield, while dialin yielded **4h** as a single stereoisomer in a very good yield (Table 2). The reaction was also performed with the *E/Z*-mixture of isoeugenol that afforded **4h** as a single diastereoisomer. This stereoselectivity can be explained attending to the fast (*E*)/(*Z*) geometric isomerization of the triplet alkenes, and assuming that only (*E*)-isoeugenol would react in a stereoconvergent manner.^{9a} Alkyl substituted double bonds such as cyclohexene or 1-methyl-1-cyclohexene did not react (**4j** and **4k**, Table 2). This lack of reactivity is due to the higher triplet energy of these compounds (see the mechanistic proposal).¹¹ (Isopropenyloxy)trimethylsilane afforded the desired product in good yield (**4l**, 52% yield, Table 2). Next, we studied the scope of the reaction between β-diketones **3** and styrene **2a** (Table 2). First, differently substituted 1,3-diketones were studied. Under the optimized reaction conditions, aromatic diketones bearing

Table 2 Scope of the reaction between different styrene derivatives **2** and β-EGW-substituted ketones **3**^a

Entry	Substituent	Yield (%)	Notes
4a	H	66% ^b	Cond. A
4b	4-Me	87%	Cond. A
4c	2-Me	79%	Cond. A
4d	2-MeO	76%	Cond. A
4e	4-F	98%	Cond. A
4f	3-F	80%	Cond. A
4g	α-Me	56%	Cond. A
4h	isoeugenol	82%	(<i>rac</i>)-(1 <i>R</i> ,2 <i>S</i>)- 4h , Cond. A
4i	OTMS	52%	Cond. A
4j	cyclohexene	0%	R = H
4k	1-methyl-1-cyclohexene	0%	R = Me
4l	isopropenyloxy-TMS	52%	Cond. A
4m	4-Me	84%	Cond. A
4n	4-OMe	74%	Cond. A
4o	4-Cl	66%	Cond. A
4p	4-CN	71%	Cond. A
4q	2-Me, 3-Me	87%	Cond. B
4r	<i>t</i> -Bu	0%	Cond. A, B, or C
4s	Me	0%	Cond. A, B, or C
4t	H	78%	Cond. C
4u	4-OMe	60%	Cond. C
4v	Ph	46%	Cond. A
4w	Ph	78%	Cond. C
4x	Ph	65%	Cond. B, <i>anti</i> / <i>syn</i> = 1.3/1
4y	Ph	57%	Cond. B

^a All reactions were carried out using 0.1 mmol **3**, 0.5 mmol **2a** and the reaction conditions indicated in each case. Reaction conditions A: 0.002 mmol Ir[dFCF₃ppy]₂(bpy)PF₆ **1a**, 0.025 mmol *n*-Bu₂PO₄NMe(*n*-Bu)₃, EtOH, N₂, 25 °C, 455 nm; reaction conditions B: 0.004 mmol 4CzIPN **1d**, 0.025 mmol *n*-Bu₂PO₄NMe(*n*-Bu)₃, CH₃CN, N₂, 25 °C, 455 nm; reaction conditions C: 0.004 mmol 4CzIPN **1d**, 0.1 mmol K₂CO₃, CH₃CN, N₂, 25 °C, 455 nm. ^b Reaction carried out with 1 mmol **3a**, 5 mmol **2a**, 0.02 mmol Ir[dFCF₃ppy]₂(bpy)PF₆ **1a**, 0.25 mmol *n*-Bu₂PO₄NMe(*n*-Bu)₃, EtOH (10 mL), N₂, 25 °C and 455 nm LED.

electron withdrawing or electron donating substituents in the aromatic ring reacted smoothly, affording the desired products **4m–p** in good to excellent yields (Table 2). Alkyl substituents are also tolerated in the reaction, but in this case slightly different reaction conditions are required: compound **4q** is obtained in an excellent yield when 4 mol% of **1d** is used as a catalyst in CH₃CN as a solvent (conditions B, Table 2). The steric hindrance afforded by the *t*-Bu or the methyl group in the reactive methylene completely suppresses the reactivity (**4r** and **4s**, Table 2).

We extended the reaction scope to other ketones bearing different electron withdrawing substituents in the β-position. β-Keto esters also underwent this reaction, but a combination of 1 equivalent of a stronger base (K₂CO₃) and 4 mol% **1d** in CH₃CN was necessary to obtain **4t** and **4u** in good yields (conditions C, Table 2). β-Cyano ketones reacted under the standard conditions giving **4v** in a moderate 46% yield, while from a β-amido ester, **4w** was isolated in 78% yield using reaction conditions C (Table 2). To prove that the reaction could be applied for the synthesis of larger ring systems, such as compounds bearing 7 membered rings,¹² the reaction was performed with cyclic β-keto esters. Thus, under reaction conditions B, **4x** was obtained as a diastereomeric mixture 1.3 : 1 of the (*rac*)-(6*S*,8*R*)

and (*rac*)-(6*R*,8*R*) δ -keto esters in good yield, while **4y** was isolated as a single regioisomer in good yield (Table 2).

Then, the elucidation of the reaction mechanism was attempted, considering either an electron transfer or an energy transfer as the initial step of the reaction. Tobita *et al.* reported that, in solution, **3a** exists mainly as the enol form,¹³ therefore, this will be the initial reactive species considered for the reaction mechanism. Regarding the radical mechanism an initial oxidation step was considered. The oxidation potentials of the three initial species are 1.43 V for **3a** (see Fig. S5, ESI[†]), 1.97 V for **2a**,¹⁴ and 0.6 V vs. SCE for the enolate of **3a** (H-NMR experiments revealed the presence of the enolate in solution in the presence of the base, see the ESI,† Section 5 and Fig. S7 for CV). Reported redox potentials for the photocatalysts, which afford the final products, are 1.32 V and 1.35 V vs. SCE for **1a** and **1d**, respectively (see Table 1).¹⁰ Thus, in principle, an electron transfer reaction (photoredox) between any of the photocatalysts and the enolate of the β -diketone could be thermodynamically favoured, but it would not be favoured in the case of an electron transfer with the styrene (see the ESI,† Table S2). With this assumption, photocatalyst **1e**, with a redox potential of 2.18 V vs. SCE,^{10f,g} should even work better than the active ones. However no product formation was observed when **1e** was used (Table 1, entry 5). Besides, previous studies by Sharp¹⁵ revealed that the radical reaction between β -diketones and double bonds under oxidative conditions affords linear α -substituted β -diketones,¹⁶ while the De Mayo reaction (photochemical conditions) yields the 1,5-diketone derivative.¹⁷ Under these precedents, a photocycloaddition pathway promoted by photosensitization is more likely than a radical pathway promoted by oxidation of the β -diketone.

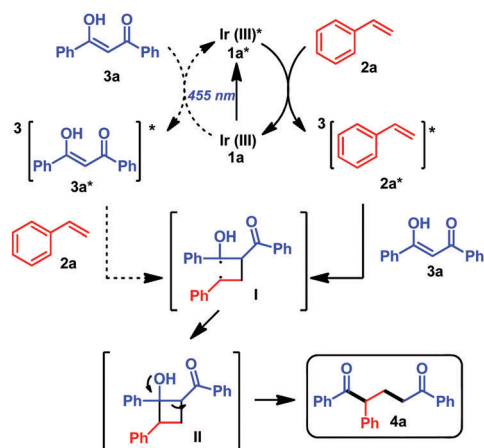
Regarding the photosensitization mechanism, the excited photocatalyst can transfer the energy either to **2a** or to **3a** (Scheme 2). According to the triplet energy values ($E_{T(\text{enol-3a})} = 59 \text{ kcal mol}^{-1}$,¹⁸ $E_{T(2a)} = 60 \text{ kcal mol}^{-1}$,^{9a} $E_{T(1a)} = 62 \text{ kcal mol}^{-1}$,^{10a} $E_{T(1d)} = 60 \text{ kcal mol}^{-1}$ ^{10c}), sensitization¹⁹ of enol-**3a** or styrene **2a**, with triplet energies in the range of **1a**, is feasible. This statement was corroborated by the efficient quenching

observed in the time resolved luminescence quenching experiments of **1a*** with **2a** and **3a** (see the ESI,† Fig. S2 and S3). In addition, the lack of reactivity in the reactions with photocatalysts that are well known photosensitizers²⁰ such as Ru(ppy)₃Cl₂ **1b** ($E_T = 46.5 \text{ kcal mol}^{-1}$ ^{10b,c}), Ir(ppy)₃ **1c** ($E_T = 55 \text{ kcal mol}^{-1}$ ^{10d}) or **1e** ($E_T = 55 \text{ kcal mol}^{-1}$ ^{10f}), but whose triplet energies are below the triplet energies of **2a** and **3a** support an energy transfer as the most likely mechanism (see the ESI,† Section 4). Therefore, our proposed mechanism starts with the excitation of the photocatalyst by irradiation with blue light, followed by energy transfer to **2a** or **3a**, reaching the triplet excited state $3(2a)^*$ or $3(3a)^*$. Then, $3(2a)^*$ reacts with **3a**, while $3(3a)^*$ would react with **2a**, leading to a common 1,4-biradical intermediate **I**, with the radicals in the most stable positions (α to the OH and in the benzylic position), explaining the observed regioselectivity of the final products. From this biradical intermediate, cyclobutanol **II** is generated, followed by retro aldol condensation affording the final product **4a** (Scheme 2).

According to the time resolved luminescence quenching experiments it is difficult to elucidate whether the energy transfer to styrene **2a** or **3a** would be predominant. However, **2a** is 5 times more concentrated in the reaction mixture than **3a**, thus energy transfer to **2a** seems more likely. In addition, GC-MS analysis (see the ESI,† Fig. S10) of the reaction between **3a** and **2a** under the optimized conditions (entry 9, Table 1) revealed the formation of the dimerization product of styrene^{9c} as side product of the reaction. On the other hand, the lack of reactivity with cyclohexene derivatives (**4j**, **4k**, Table 2) that present triplet energies around 80 kcal mol^{-1} suggested that photosensitization of **3a** is not enough to trigger the reaction (a time resolved luminescence quenching experiment of **1a** with cyclohexene shows no interaction between **1a*** and the olefin, see the ESI,† Fig. S4). Therefore, although photosensitization of **3a** cannot be discarded as a possible mechanistic pathway, all this indirectly proves the indicated photosensitization of styrene **2a** as the predominant pathway under these reaction conditions. Finally, the quantum yield of the reaction was determined to be $\Phi = 1.1\%$, suggesting that the mechanism does not contain significant radical chains.²¹

In conclusion, the first visible light mediated De Mayo reaction through a photosensitization mechanism has been developed. α or β -substituted styrenes undergo this reaction smoothly, but the higher triplet state energy of alkyl substituted olefins made them unreactive under this condition. β -Diketone, β -ketoester, β -cyano ketone and β -amido ester derivatives could be successfully functionalized and 7 membered rings are readily accessible using this method. Mechanistic studies support photosensitization as the key step of the reaction, and experimental observations suggested photosensitization of styrenes as the most likely mechanistic pathway.

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Scheme 2 Visible light mediated photosensitized approach of the De Mayo photocycloaddition.

Conflicts of interest

There are no conflicts to declare.

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