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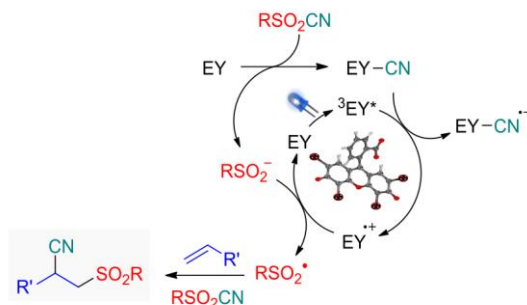
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Eosin-mediated Alkylsulfonyl-cyanation of Olefins.

V. Pirenne, G. Kurtay, S. Voci, L. Bouffier, N. Sojic, F. Robert, D. M. Bassani, Y. Landais*

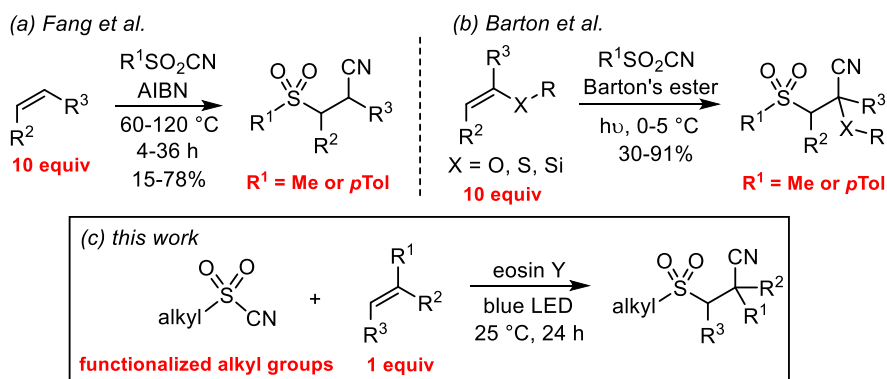
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ABSTRACT: Eosin-Y (EY)-mediated alkylsulfonyl-cyanation of olefins was shown to afford alkylsulfonyl nitriles in good yields. On the basis of transient absorption spectroscopy, the reaction was shown to proceed via a photoinduced electron transfer from $^3\text{EY}^*$ to an O-cyanated derivative of the photocatalyst, formed in situ, with generation of the corresponding sulfinate, finally oxidized by EY^+ into a sulfonyl radical. Addition of the latter on the olefin, followed by a radical cyano group transfer then furnished the nitrile along with a RSO_2 radical sustaining the radical chain.

Sulfones represent an important subclass in the family of organosulfur compounds, exhibiting a wide range of biological activities.¹ They serve as key synthetic intermediates² for the construction of important building blocks in the total synthesis of natural products,³ and the development of methodologies to access structurally complex sulfones is currently flourishing.⁴ These are mostly based on the use of SO_2 ,^{5,6} or the free-radical addition of RSO_2X ($\text{X} = \text{Cl}$, I , Br , CN , oxime, vinyl, alkynyl, ...) to alkenes or alkynes.⁷ The sulfonyl-cyanation of alkenes was reported by Fang *et al.* using AIBN as an initiator,⁹ and later by Barton *et al.* using the photolysis of PTOC esters (Scheme 1).¹⁰ These processes however require a large excess of olefin (10 equiv) and are limited to electron-rich olefins in the latter case.

Scheme 1. Sulfonyl cyanation of olefins.

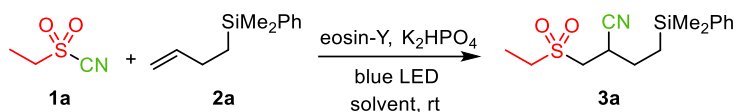


We envisioned extending the scope and application of the sulfonyl-cyanation reaction using conditions which would avoid desulfonylation and allow the incorporation of functionalized alkyl groups. Visible-light photocatalyzed processes are attracting a growing interest,¹¹ and appear well-suited to generate the required sulfonyl radical at room temperature from sulfonyl cyanide.¹² We now show that eosin-Y (EY) is able to promote the photoinduced sulfonyl-cyanation of alkenes from *alkyl*/sulfonyl cyanides in spite of energetically unfavorable electron transfer, thanks to an unexpected mechanism involving the cyanation of the photocatalyst which generates a co-catalytic intermediate

(Scheme 1). This mechanism contrasts with the related addition of *p*-TsCN onto olefins proposed to occur by direct electron transfer.¹³ To the best of our knowledge, the participation of EY adducts in photocatalyzed transformations has not been previously reported and provides an important new aspect to EY photocatalyzed processes. These results provide a general protocol for the formation of β -sulfonyl nitriles under mild reaction conditions.

Preliminary studies starting from cyanide **1a** and olefin **2a** as model substrates in the presence of various organic and organometallic photocatalysts (Table S1-S2), showed that the conjunction of eosin-Y, visible light and K₂HPO₄ is required for optimal efficiency of the sulfonyl-cyanation process. The reaction was slow in CH₂Cl₂, whereas DMF leads to full conversion and an excellent yield after 20 h of irradiation (Table 1, entries 1-3). Decreasing the stoichiometry of the sulfonyl cyanide below 1.5 equiv (Table 1, entries 4-5), increasing the amount of EY to 10 mol % (Table 1, entry 6), or the presence of oxygen (Table 1, entry 7) lead to a lower yield. Scaling up of the process (1 mmol) using the optimal conditions led to high yields and similar reaction time (Table 1, entry 8). Finally, it was found that polar solvents such as acetonitrile or *i*PrOH were also effective for this reaction (Table 1, entries 9-11).

Table 1. Optimization of the alkylsulfonyl-cyanation conditions.

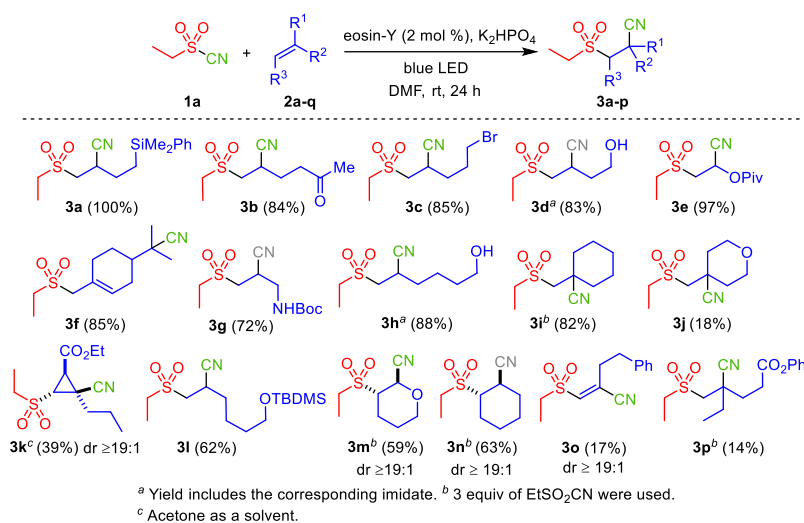


entry ^a	1a (equiv)	solvent	time/h	yield/% ^b
1	2	DCE	24	53
2	2	DCE	112	81
3	2	DMF	20	98
4	1.5	DMF	18	quant
5	1	DMF	18	68
6 ^c	1.5	DMF	20	86
7 ^d	1.5	DMF	20	48
8 ^e	1.5	DMF	20	quant
9	1.5	acetone	19	94
10	1.5	CH ₃ CN	19	97
11	1.5	<i>i</i> PrOH	23	86

a Conditions: Eosin-Y (2 mol %), **1a** (1.5-2.0 equiv), **2a** (1 equiv), K₂HPO₄ (0.2 equiv), solvent (0.5 mL, [C] = 1 mol/L), blue LED, rt. b Isolated yield of **3a** after purification through silica gel. c Eosin-Y (10 mol %). d The reaction mixture was not degassed prior to irradiation. e **2a** (1 mmol).

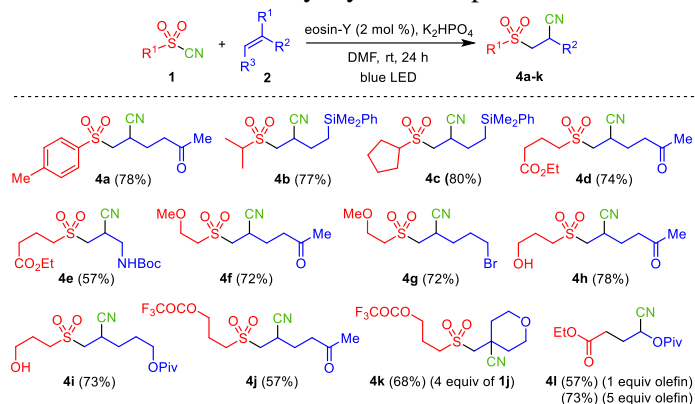
The optimized reaction conditions were applied to a series of olefins using sulfonyl cyanide **1a** (Scheme 2).¹⁴ The EY-mediated sulfonyl-cyanation showed a broad scope with the corresponding alkylsulfonyl nitriles formed in high and reproducible yields. α -Pinene led to nitrile **3f** in excellent yield, in agreement with a radical-based reaction mechanism.¹⁴ Lower yields were, however, obtained from 1,1-disubstituted olefins (i.e. **3i-j-3p**), but this could be circumvented using a larger amount of sulfonyl cyanide (e.g. **3i**). The reaction was also found to be compatible with various functional groups including ketones (**3b**), bromides (**3c**), ester (**3e**), carbamate (**3g**) and silyl protecting groups (**3l**). With alkenes bearing free hydroxyl groups, the corresponding imidate was also formed. Treatment of the crude mixture of **3d** with *p*-TsOH led to the corresponding lactone in one-pot operation and 54% over 2 steps (Supporting Information (SI)). The sulfonyl-cyanation also proceeds well with cyclic olefins such as 3,4-dihydro-2H-pyran (**3m**), cyclohexene (**3n**) and cyclopropene (**3k**), affording the corresponding nitriles as *trans*-diastereomers with high dr. Alkynes were found to be poorly reactive, although the stereoselectivity was high (**3o**). Finally, styrene did not react under our standard conditions.

Scheme 2. Alkylsulfonyl-cyanation of olefins. Olefin scope.



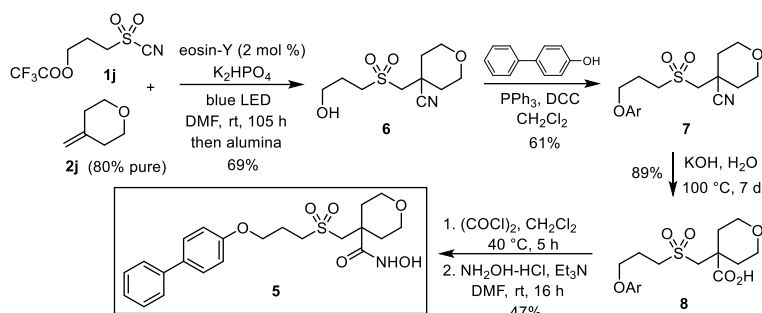
Sulfonyl cyanation may be carried out with sulfonyl cyanides **1** (SI) bearing ester, ether, trifluoroacetate or aromatic groups attached to the sulfur atom (Scheme 3). The process is also efficient with secondary sulfonyl groups (**4b-c**), which showed no desulfonylation under the reaction conditions. A reaction of sulfonyl cyanide **1j** with olefins **2b** and **2j** led to the corresponding trifluoroacetates **4j** and **4k** when purification was carried out through silica gel and free alcohols **4h** and **4i** when alumina was used. With 1,1-disubstituted olefins (e.g. 4-methylenepyrene), an excess of sulfonyl cyanide **1j** was however necessary (e.g. **4k**). The reaction of vinyl pivalate with sulfonyl cyanide **1e** led to the carbocyanation product **4l** in good yield.¹⁴ Here, loss of SO_2 is fast as a result of the formation of a stabilized C-centered radical resulting from the α -scission.

Scheme 3. Alkylsulfonyl-cyanation of olefins. Sulfonyl cyanide scope.



A further illustration of the utility of this process is provided with the synthesis of metalloproteinase inhibitor **5**¹⁵ (Scheme 4). EY-mediated sulfonyl-cyanation of alkene **2j** led to the desired nitrile **4k**, affording alcohol **6** in 69% yield after trifluoroacetate deprotection over alumina. The latter was then subjected to the Mitsunobu reaction, leading to ether **7** in 61% yield. Direct nitrile aminolysis of **7** in the presence of hydroxylamine ($AcONa$, $EtOH-H_2O$, 80 °C) proved to be difficult, leading essentially to the corresponding amide (SI). Nitrile **7** was thus first hydrolyzed under basic aqueous conditions, leading to carboxylic acid **8**, which was then converted into the desired hydroxamic acid **5**¹⁵ via the corresponding acyl chloride and NH_2OH .

Scheme 4. Synthesis of metalloproteinase inhibitor **5**.



In order to evidence radical chain processes, we carried out light-dark experiments using olefin **2a** and **1a** over a 50 h period (Figure S4). Although the reaction appears to stop when the light was switched off, we noticed that the formation of **3a** continues at a much slower rate in the dark. This suggests that an inefficient radical chain mechanism is operating, in contrast with what was previously reported for the addition of *p*-TsCN.¹³ When the reaction was performed in the presence of 2 equiv of TEMPO, no trace of **3a** was detected, supporting the radical nature of the addition process. Eosin-Y possesses a short-lived singlet and a long-lived triplet excited state that can undergo oxidative or reductive photoinduced electron transfer (PET) quenching, depending on the nature of the substrate.¹⁶ Fluorescence lifetime quenching measurements rule out a reaction from the singlet excited state (Figure S22), whereas time-resolved absorption experiments revealed the formation of a species possessing a transition at 420 nm, typically assigned to the formation of EY⁺ (Figure S5). In the absence of **1a**, only the transient absorption of ³EY* ($\lambda_{\text{max}} = 440$ nm) could be detected. The lack of electrochemical data for RSO₂CN¹⁷ led us to estimate the redox potential of several sulfonyl cyanides using cyclic voltammetry (Figure S7-8, Table S3). Alkylsulfonyl cyanides exhibit highly negative irreversible reduction potentials, rendering direct electron transfer from EY* very unlikely. For comparison, we find PET from ³EY* to *p*-TsCN to be slightly endothermic ($\Delta G_{\text{PET}} = +5.3$ Kcal/mol, SI).¹⁸ In the case of sulfonyl cyanide **1a**, we estimate $\Delta G_{\text{PET}} = +5.1$ or $+14.1$ Kcal/mol from ¹EY* or ³EY*, respectively, assuming the energies of the singlet and triplet states of EY to be 2.28 and 1.89 eV, respectively, and $E_{1/2}(\text{EY}/\text{EY}^+) = +0.78$ V vs SCE (SI).^{16a-c} Energy transfer from ³EY* to the substrate followed by homolytic bond cleavage¹⁹ is also unlikely since bond dissociation energies (Table S5) are systematically above those available from the triplet sensitizer (43 Kcal/mol).

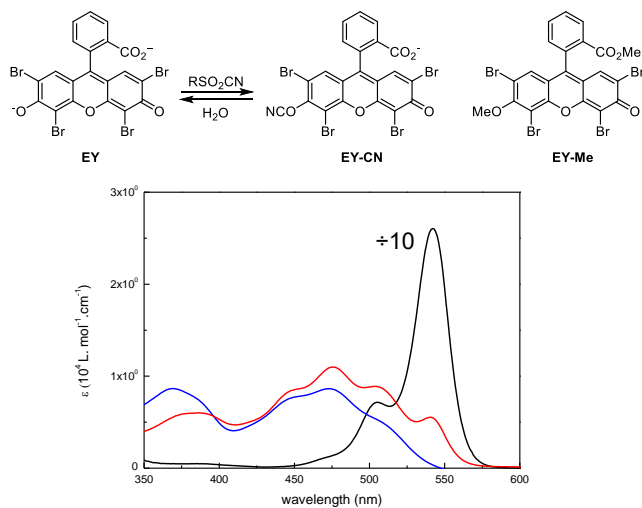


Figure 1. Proposed structure of the adduct formed between EY and RSO₂CN (EY-CN) and electronic absorption spectrum of EY in DMF (black curve, divided by 10) and of the O-methylated derivative (EY-Me, blue curve). The red curve shows the absorption spectrum of the EY-CN adduct obtained by the addition of 10 mM **1a to a 20 μ M solution of EY. The exact concentration of the adduct is unknown.**

Greater complexity in the reaction mechanism is obvious from the electronic absorption spectra collected in parallel with these studies. In DMF solutions, the EY dianion absorbs strongly in the visible with an absorption maximum at 544 nm.¹⁶ We observed a fast discoloration of the solution when mixing EY with **1a**, accompanied by the appearance of a new, structured absorption with $\lambda_{\text{max}} = 475$ nm (Figure S17). Although slower, the same process was also observed

with *p*-TsCN. ^1H and ^{13}C NMR spectra as well as ROESY experiments did not reveal weak or through-space interactions between EY and the sulfonyl cyanides.²⁰ Based on tabulated data for substituted EY derivatives,²¹ we assign this new species to the formation of the cyanate derivative of EY (EY-CN, Figure 1). Indeed, the reaction of phenoxides with *p*-TsCN to yield the corresponding cyanate is reported to occur rapidly, even at low temperature through an addition-elimination reaction releasing the sulfinate anion.²² To verify this hypothesis, we compared the absorption spectrum of the intermediate with that of the *O*-methylated derivative of EY. In agreement with the proposed structure, the two spectra are nearly identical (Figure 1). Furthermore, we find that the adduct is rapidly hydrolyzed by the addition of water (see Figure S17), and that the addition of K_2HPO_4 , which may contain traces of water, partly converts the adduct to release EY. From the absorption spectrum, we estimate the proportion of EY that is converted to EY-CN to be *ca.* 75%.

The absorption envelope of the EY-CN adduct is broad and overlaps well with the emission profile of the light source. To verify whether the adduct exhibits photocatalytic activity, we compared the photoreaction yields using sulfonyl cyanide **1a** and olefin **2a**, with those obtained upon monochromatic irradiation at 436 nm (where EY does not absorb) or in the presence of EY-Me. In all cases, only a low yield of the corresponding sulfonyl-cyanation product **3a** was obtained, suggesting that the EY-CN adduct generated upon EY bleaching is not, or only weakly, photoactive. In contrast with **1a**, the greater electrophilicity of $\text{EtO}_2\text{CCH}_2\text{SO}_2\text{CN}$ (**1e**) or $\text{ClCH}_2\text{SO}_2\text{CN}$ (**1i**) led to the complete conversion of EY to the adduct, thereby explaining the absence of sulfonyl cyanation products in these cases (SI). Although the EY-CN adduct was not found to be photoactive under the reaction conditions, it is formed in concentrations that are sufficiently high (*ca.* 15 mM) to undergo a bimolecular reaction with $^3\text{EY}^*$. In agreement with this hypothesis, laser flash photolysis studies of DMF solutions of EY in the presence of EY-Me showed the formation of a transient species strongly resembling that of the semi-oxidized form of EY ($\text{EY}^{+\bullet}$), despite overlap with the bleaching of EY-Me, which partly absorbs the 532 nm excitation. EY-Me possesses a reversible reduction at $E_{1/2}(\text{EY-Me}/\text{EY-Me}^-) = -0.65$ V vs SCE (Figure S9, Table S4) and we may expect that $^3\text{EY}^*$ can undergo efficient oxidative PET to EY-Me ($\Delta G_{\text{PET}} = -10.6$ Kcal/mol).

On the basis of the above observations, we propose a mechanism that reconciles the apparently contradictory results involving PET (Figure 2). In the presence of sulfonyl cyanides, EY undergoes cyanation to afford the EY-CN adduct and the corresponding sulfinate RSO_2^- . The latter was shown by König and co-workers to react efficiently with $\text{EY}^{+\bullet}$ to generate the sulfonyl radical.²³ Therefore, we expect that $^3\text{EY}^*$ undergoes oxidative PET with the EY-CN adduct, and that the ensuing $\text{EY}^{+\bullet}$ then oxidizes sulfinate into the sulfonyl radical **II**. Reversible addition of the latter onto the olefin affords a nucleophilic C-centered radical **III**, which may evolve through two different pathways: (1) a cyano group radical transfer to afford product **V**,¹⁴ or (2) the oxidation of **III** into a carbocation **IV**, eventually trapped by a cyanide anion. In the latter case, $\text{EY}^{+\bullet}$ is reduced back to EY. The proposed mechanism also explains the excess of sulfonyl cyanides (1.5 equiv) needed to obtain optimal yields. Estimation of the oxidation potential of model α -sulfonyl radicals **III** in DMF, through DFT calculations (SI), indicates that oxidation of **III** into **IV** is slightly exergonic ($\Delta G_{\text{ET}} \sim -2$ Kcal/mol), or favored with for more substituted olefins (**IIIc**, $\Delta G_{\text{ET}} = -14.1$ Kcal/mol, SI). The absence of elimination products, alcohols or ethers, when water or *i*PrOH were used as co-solvents is however in sharp contrast with literature reports on radical-polar cross-over processes.^{13,23,24} Our experimental evidence thus rules out the involvement of a cation such as **IV** as an intermediate and a back electron transfer (BET) from **III** to $\text{EY}^{+\bullet}$ cation-radical. Direct conversion of **III** into product **V**, through a cyano group transfer process, would then constitute a viable alternative pathway, as shown by the light ON/OFF experiment (Figure S4). Quantum yields for the formation of **V** measured in DMF and acetone upon monochromatic excitation at 546 nm led respectively to values of $\Phi_{\text{DMF}} = 0.2$ and $\Phi_{\text{Acetone}} = 1.17$ (SI). Considering the intersystem crossing efficiency of EY ($\Phi_{\text{ISC}} = 0.32$ in methanol),²⁵ these values suggest that a moderately efficient radical chain is operating.

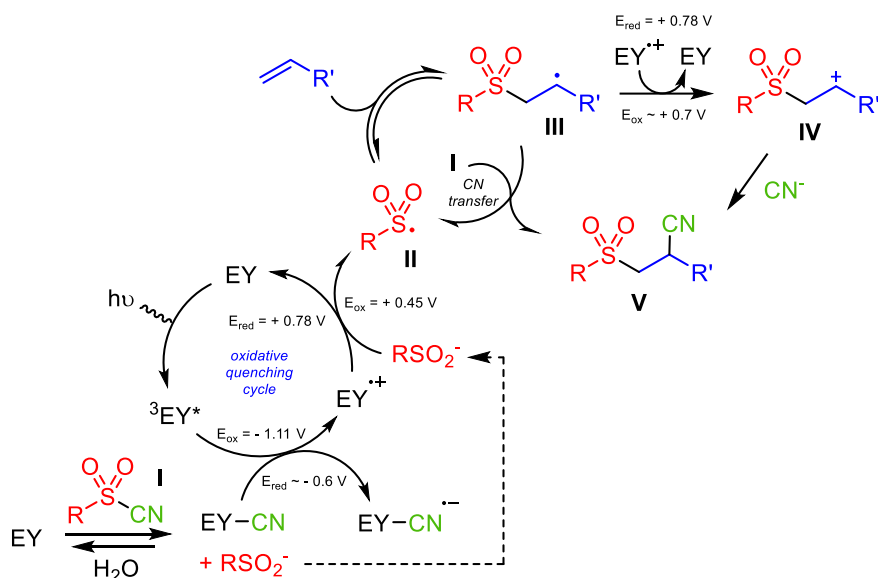


Figure 2. Proposed mechanism for EY-mediated sulfonyl-cyanation of olefins involving PET to an O-CN adduct of EY.

In summary, we have shown that the photocatalyzed alkylsulfonyl-cyanation of a variety of olefins affords the corresponding β -sulfonyl nitriles in good yield. Combined with a safe protocol for the preparation of sulfonyl cyanides, this methodology provides a convenient access to β -sulfonyl nitriles, useful synthetic intermediates, as shown by the synthesis of a metalloproteinase inhibitor. We find that the reaction proceeds through a photoinduced electron transfer mechanism involving a cyanated derivative of EY formed *in situ*. This mechanism circumvents the energetically unfavored direct electron transfer from the excited EY triplet state to the alkylsulfonyl cyanide and instead relies on the oxidation of the sulfinate anion by the ground state oxidized $\text{EY}^{\bullet+}$.^{23a} The present mechanistic studies provide an in-depth and more general picture of the unique reactivity of alkyl- and arylsulfonyl cyanides in the presence of eosin,¹³ which adds to the direct ET or energy transfer mechanisms usually proposed in EY-mediated processes. Further work will be necessary to establish whether this mechanism is also present in other photocatalyzed transformations involving xanthene dyes.

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