



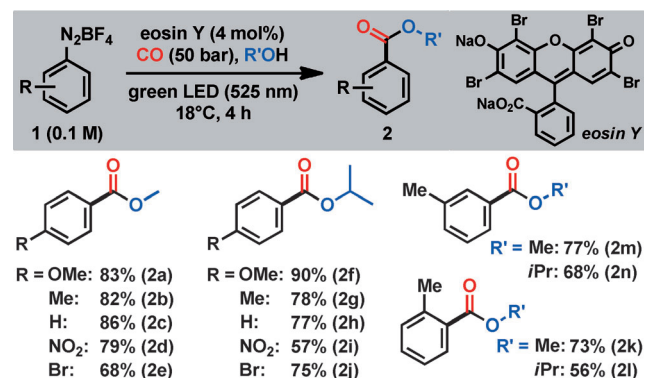
**Table 1:** Selected optimization experiments.<sup>[a]</sup>

Entry	Deviation from the optimized conditions	Yield of <b>2a</b> [%]
1	—	83
2 <sup>[b]</sup>	Rose bengal	8
3 <sup>[b]</sup>	eosin B	29
4 <sup>[b]</sup>	fluorescein	24
5 <sup>[b]</sup>	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	30
6	without dye	2
7	dark reaction at 60 °C	< 1

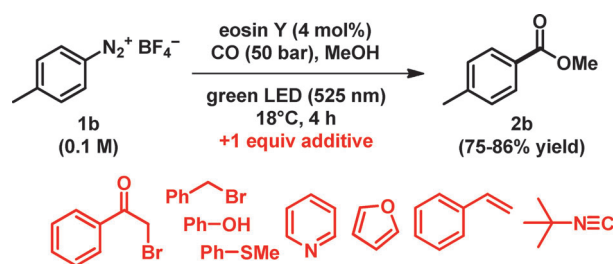
[a] Conditions: **1a** (0.1 mmol), eosin Y (0.04 mmol), methanol (1 mL), CO (50 bar), irradiation (LEDs,  $\lambda_{\text{max}} = 525$  nm, 3.8 W), 18 °C, 4 h. [b] In methanol/acetonitrile (1/1). bpy = bipyridine.

that were reported for related photoredox Meerwein reactions.<sup>[17]</sup> Under irradiation with green light (LED,  $\lambda_{\text{max}} = 525$  nm, 3.8 W), solutions of **1a** in methanol were treated under an atmosphere of CO at room temperature to give methyl 4-methoxybenzoate (**2a**, Table 1).<sup>[18]</sup>

Commercial eosin Y (4 mol %, employed as the disodium salt) was used as the metal-free photoredox catalyst. Unwanted dimerization (Ar<sub>2</sub>) and reduction (Ar-H) was suppressed at higher dilutions by the higher relative concentrations of CO and the alcohol. Other dyes were less active (entries 2–5). Lower pressures of CO resulted in low conversion and competing hydrodediazotization (10–25 %) and biaryl coupling (ca. 5 %). Eosin-free (entry 6) as well as dark and thermal reactions (entry 7) produced only minimal amounts of **2a**. The optimized conditions were applied to the synthesis of various alkyl benzoates (Scheme 2). Several

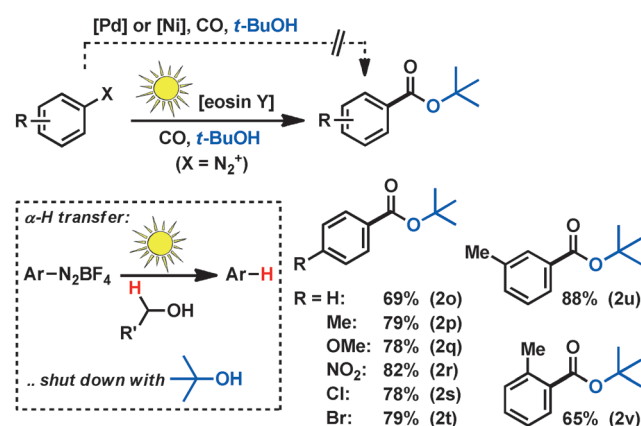

**Scheme 2.** General conditions and scope of the photoredox carbonylation.

functional groups and electron-poor and -rich substituents (nitro, chloro, bromo, esters, benzylic protons) were tolerated in the substrates. A screening of various additives (Scheme 3) showed significant tolerance of halogen-containing electrophiles, acidic protons,  $\pi$ -nucleophiles, and electron-deficient arenes, without erosion of the ester yield or consumption of the additive.<sup>[18]</sup> The presence of 1 equiv phenol ( $\text{p}K_{\text{a}} \approx 9$ ) was

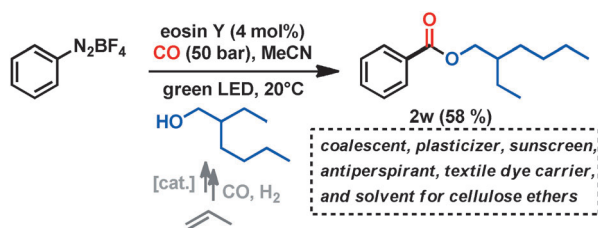

**Scheme 3.** Compatibility with various functionalized additives that resulted in unaffected ester formation without competing conversion of the additive.

tolerated well, which is in contrast to the employment of phenol (in large excess) as a reaction partner under otherwise identical conditions, where complex product mixtures were formed. Methylthio-bearing compounds did not affect the ester formation, in agreement with a previous report,<sup>[19]</sup> where *S*-alkylated compounds were produced under similar conditions. Interestingly, *tert*-butylisocyanide—a competent radical trap in some reactions<sup>[20]</sup>—was tolerated. Iodobenzene only resulted in little interference, presumably by radical cleavage of the weak Ar–I bond. The addition of thiophenol led to a large decrease in the yield, which is known from reports of diazosulfide formation/photocatalytic cleavage under similar conditions.<sup>[21]</sup> Biaryl sulfide (Ar–S–Ar) coupling was observed in this case. The presence of aniline or *N,N*-dimethylaniline resulted in the quenching of the excited state of the dye. Azobenzenes were detected in small amounts. The addition of triphenylphosphine led to inhibition as a result of quenching of the excited dye. Accordingly, triphenylphosphine oxide was formed.<sup>[18]</sup>

*tert*-Butyl esters are notoriously difficult to obtain by conventional esterification procedures because of their steric bulk.<sup>[1,2,22]</sup> Palladium-catalyzed carbonylation procedures also fail to generate *tert*-butyl esters. The photocatalytic carbonylation, however, produced *tert*-butyl benzoates in very good yields, exceeding those of the less hindered methyl and isopropyl esters. This is due to the lack of  $\alpha$ -hydrogen atoms within *tert*-butanol, which excludes undesired radical hydrogen abstraction and subsequent reductive reactions (Scheme 4).


**Scheme 4.** Photocarbonylation to *tert*-butyl benzoates.

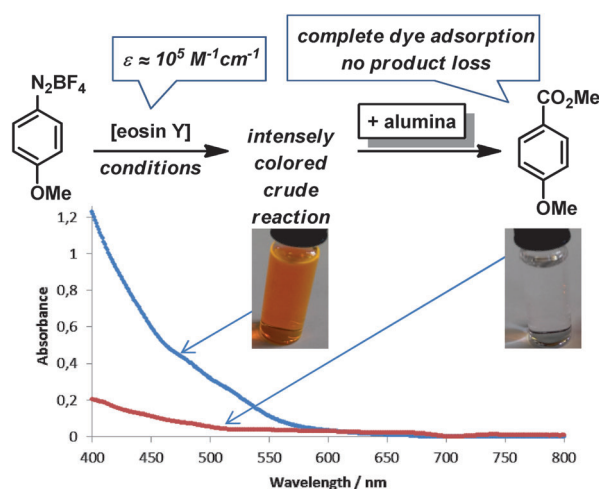
We have probed the effectiveness of the metal-free photocarbonylation in the context of the synthesis of **2w**, a low-odor, low-volatility, and low-viscosity ester produced on multiton scales for applications as a coalescent in the formulation of latex paints (Velate 368), a plasticizer in the manufacture of key polymers, as a sunscreen, and an antiperspirant ingredient in cosmetics (Finsolv EB), as a textile dye carrier for the treatment of synthetic fibers, and as a solvent for cellulose ethers.<sup>[23]</sup> Under standard conditions, 2-ethylhexyl benzoate (**2w**) was obtained in 58 % yield from the reaction of  $\text{PhN}_2\text{BF}_4$  with 2-ethylhexanol and CO under irradiation with green light (Scheme 5). Acetonitrile was used



**Scheme 5.** Synthesis of the technical ester **2w**.

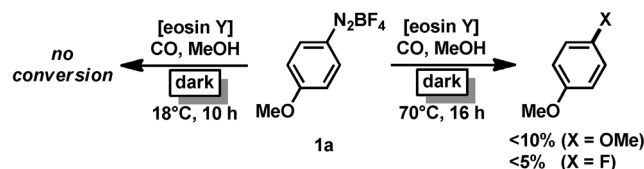
as a cosolvent to solubilize the diazonium salt in the fatty alcohol. Methyl 4-anisate (**2a**) is another technical product with applications as a food and flavor ingredient. Technical applications of catalytic reactions are always associated with the search for an effective technique for catalyst separation. The intensely colored eosin Y ( $\epsilon \approx 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ , 530 nm, ethanol)<sup>[24]</sup> was removed from the reaction mixture by adsorption on basic alumina.<sup>[25]</sup> UV/Vis spectra documented the complete removal of the dye, while < 1 % of the product was lost in this operation (Scheme 6).

The mechanistic proposal of a visible-light-driven dye-catalyzed process was supported by the following experiments: The product yields severely dropped when no photocatalyst was present in the reaction and/or under dark conditions. Reactions in the dark and at increased temper-



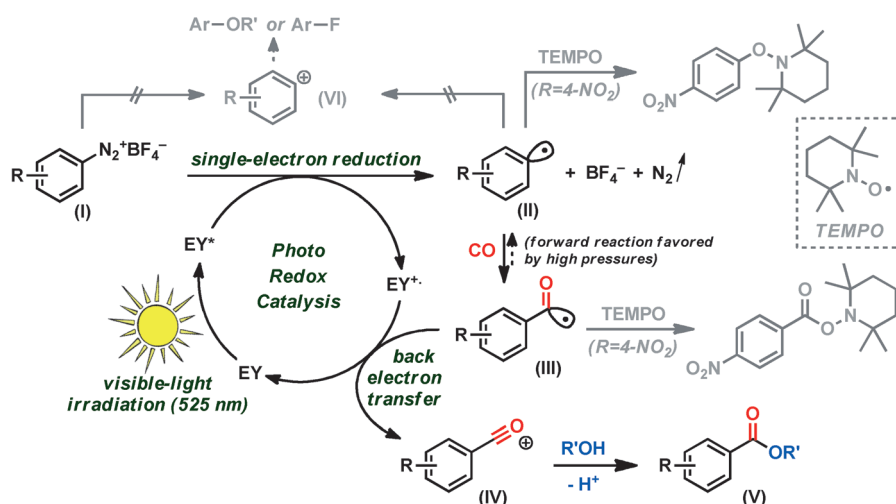
**Scheme 6.** Dye removal with basic alumina. Bottom: corresponding absorption spectra before (blue) and after (red) work-up.

ature (up to 70°C) gave no carbonylation product, which excludes homolytic bond cleavage of the starting material to an aryl radical under these conditions. Instead, the thermal dark reaction of **1a** in methanol at 70°C produced small amounts of the corresponding methyl ether and aryl fluoride (Scheme 7). This observation is consistent with previous reports of unsuccessful attempts to thermolytically carbonylate diazonium salts.<sup>[26]</sup>

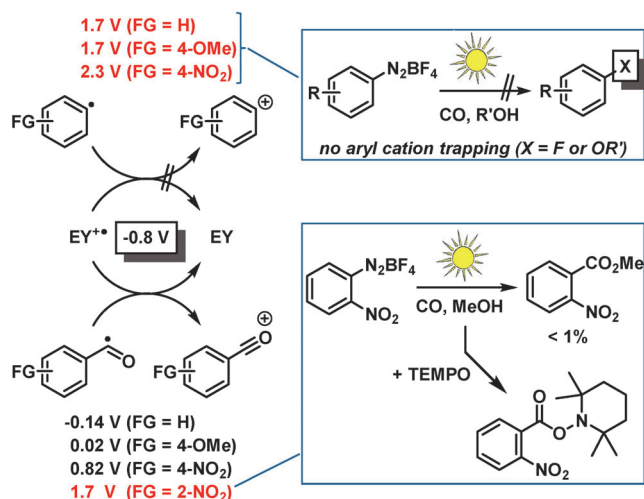


**Scheme 7.** Dark reactions of 4-anisyl diazonium salt (**1a**).

We have performed detailed mechanistic studies to prove the postulate of a light-driven reduction/oxidation cascade which is devoid of any sacrificial redox partner. On the basis of related literature reports<sup>[11,17,27]</sup> and our own findings we propose the following operating mechanism (Scheme 8): The electron-deficient arene diazonium salt (**I**) accepts one electron from the electron-rich, dianionic, photoexcited state of eosin Y (**EY\***). This single-electron transfer (SET) results in the release of dinitrogen ( $\text{N}_2$ ) and generation of aryl radical **II**. This initiation step is thermodynamically favored due to the more positive redox potential of the **I**→**II** reduction (ca. 0 V versus SCE)<sup>[9]</sup> compared with the **EY\***→**EY** reduction (−1.1 V versus SCE). The aryl radical **II** then rapidly reacts with CO to afford acyl radical **III**.<sup>[28]</sup> The addition of the radical trap TEMPO (2,2,6,6-tetramethylpiperidinyloxy) results in the formation of adducts with both radical species (**II**, **III**) being observed.<sup>[18]</sup> We further propose that **III** undergoes rapid one-electron oxidation to give the highly electrophilic acylium ion **IV**. Reaction thereof with the alcohol affords the benzoate ester **V**. The back electron transfer (BET) is presumed to be fast, as no adduct of acyl radical **III** with electron-rich  $\pi$ -donors (anisole, furan, styrene) was detected. This assumption can be instructively substantiated by thermodynamic data: The redox potential of the **EY\***→**EY** reduction is −0.8 V (versus SCE). The potential of the **III**→**IV** redox couple is not available experimentally, since both species are short lived. However, an estimation of this redox potential could be derived from DFT calculations,<sup>[18,29]</sup> which provided values between −0.14 V and 0.82 V (versus SCE) depending on the substitution pattern on the aromatic ring (Scheme 9). Therefore, the BET step is thermodynamically feasible. Calculation of the redox potential of the back electron transfer for the 2-nitroaryl radical species gave a prohibitive value of 1.7 V (versus SCE). Indeed, 2-nitrobenzenediazonium tetrafluoroborate did not afford the desired ester under carbonylation conditions. The addition of TEMPO to the reaction resulted in the formation of the benzoyl–TEMPO adduct. Both experiments provide further evidence of the postulated mechanism involving the carbonylation of the intermediate



**Scheme 8.** Mechanism of the visible-light-driven eosin-catalyzed carbonylation of arene diazonium salts.



**Scheme 9.** The back electron transfer (BET): DFT calculations on the prohibitive redox process to aryl cations (top left), the operating BET to give acylium ions (bottom left), and supportive preparative experiments (right).

2-nitroaryl radical, but the BET to  $\text{EY}^{+}$  is thermodynamically prohibited.<sup>[21]</sup>

The reaction of aryl cations with CO is known from acid-catalyzed Gatterman-Koch carbonylations,<sup>[30]</sup> but can be excluded on the basis of DFT calculations. The carbonylation of aryl cations (**VI**, from thermal heterolysis of the arene diazonium) was already disproven (Scheme 7). A potential back electron transfer with  $\text{EY}^{+}$  at the aryl radical stage (**II**) can likewise be refuted. The DFT-derived reduction potentials of the **VI/II** couples of our substrates are 1.7–2.3 V (versus SCE).<sup>[18]</sup> These values are prohibitively high in comparison with the oxidizing power of  $\text{EY}^{+}$  (−0.8 V versus SCE) and thus exclude the intermediacy of aryl cations.

This new procedure enables metal-free and base-free carbonylations through an photoredox mechanism catalyzed

by an organic dye. Alkyl benzoates can be prepared from arene diazonium salts, CO, and alcohols at room temperature under irradiation with visible light. The reaction uses catalytic eosin Y as a cheap photosensitizer. Mechanistic studies support the sequential operation of SET reduction, carbonylation, and back electron transfer to give aroylium cations, which undergo rapid addition to alcohols. Unlike with metal-catalyzed carbonylations, *tert*-butyl esters can be prepared in good yields. The general method has been applied to the synthesis of industrial intermediates.

## Experimental Section

**General procedure:** A vial (3 mL) was charged with a magnetic stir bar, the arene diazonium salt (0.1 mmol), and eosin Y (0.04 mmol) under  $\text{N}_2$ , and capped with a rubber septum. Dry solvent (1 mL, alcohol or mixture with MeCN if the solubility of the diazonium salt was poor) was added. The vial was purged with  $\text{N}_2$  (5 min) in the dark and transferred to a reactor containing a Quartz window bottom (Parr Instr.; Figure 1). The septum was punctured with a needle. The



**Figure 1.** High-pressure photoreactor.

reactor was sealed, placed on a magnetic stirrer, and slowly filled with CO (50 bar). The reaction was irradiated with external LEDs ( $\lambda_{\text{max}} = 525 \text{ nm}$ , 3.8 W). After 4 h at 18°C, the gas was released and the vial retrieved. Water (5 mL) was added to give an emulsion, which was extracted with ethyl acetate (2 × 5 mL). The organic phases were washed (5 mL brine) and dried ( $\text{Na}_2\text{SO}_4$ ). Volatiles were evaporated and the residues purified by chromatography on  $\text{SiO}_2$  gel.

Received: August 28, 2014

Revised: September 23, 2014

Published online: November 20, 2014

**Keywords:** carbonylation · esters · organocatalysis · photoredox catalysis · redox reaction · visible light



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