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# Photocatalytic Synthesis of Acetals and Ketals from Aldehydes and Silylenolethers without the Use of Acids

Desirée Steuernagel<sup>[a]</sup> and Hans-Achim Wagenknecht<sup>\*[a]</sup>

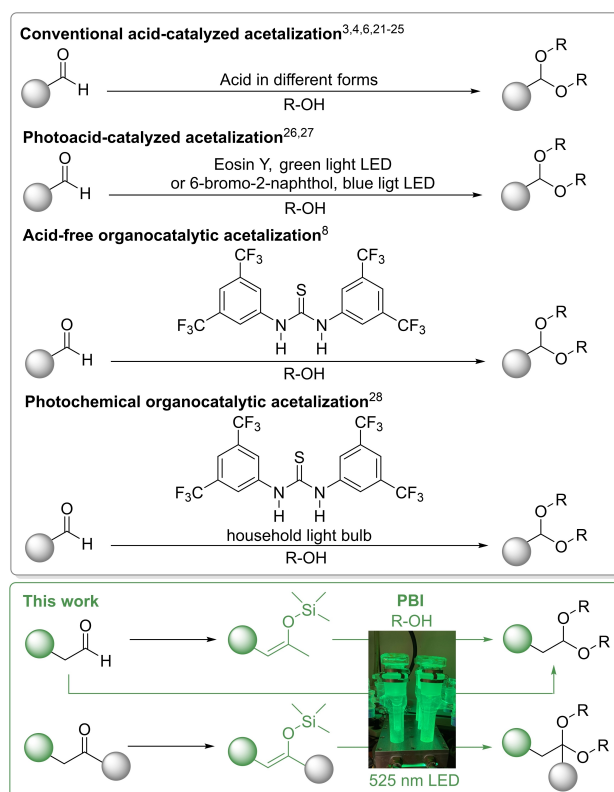
**Abstract:** Acetals and ketals are among the most important protecting groups for carbonyl compounds. A new method for acetalization and ketalization by means of photoredox catalysis has been developed. A biscyanolated perylene bisimide is used as an electron-poor photocatalyst, together with green light (525 nm LED). Silylenolethers derived from aldehydes react efficiently to give acetals in good to excellent yields. A broad substrate range was shown with respect to both the aldehydes and the alcohols. The functional group

tolerance is high; in particular, acid- and hydrogen-labile protecting groups are tolerated. Aldehydes can also be directly and selectively converted into the respective acetals. Only ketones must be converted to their silylenolethers before ketalization. This photocatalytic method works without any use of acids or photoacids, and does not need any additives or H-atom transfer reagents. Hence, it broadens the substrate scope and repertoire of photoredox catalysis with respect to carbonyl chemistry.

## Introduction

Organic compounds with a carbonyl group, in particular aldehydes, are of great synthetic interest as small building blocks for C–C bond formation, and aldehydes are among the most frequently used starting compounds in organic synthesis.<sup>[1,2]</sup> However, their high reactivity also poses a challenge for multistep syntheses, why such groups are often protected. Acetals and ketals are broadly applied protective groups for carbonyls which tolerate neutral and basic reaction conditions, but not acids.<sup>[3–6]</sup> Nevertheless, total synthesis is a multifaceted complex problem,<sup>[7]</sup> and synthesis methods are often catalyzed by acid, which is problematic for total synthesis if acid-labile groups are already present in the molecule. In order to circumvent this problem, alternative synthetic methods are necessary, like the acid-free organocatalytic acetalization.<sup>[8]</sup> Photoredox catalysis<sup>[9–13]</sup> proved to be predestined for this purpose, because it allows late-state functionalizations in natural product synthesis.<sup>[14,15]</sup> Photoredox catalysis also is a sustainable method by the use of light as primary energy source in combination with organophotoredox catalysts.<sup>[16–19]</sup> It can be merged with carbonyl chemistry.<sup>[20]</sup> Conventional

methods for acetalization of carbonyl compounds utilize all different types of acids, including HCl,<sup>[3–6]</sup> solid acids,<sup>[21]</sup> ionic liquids,<sup>[22]</sup> polymeric acids,<sup>[23]</sup> and organic acids.<sup>[24,25]</sup> Recent reports show the photochemical conversion of aldehydes into acetals by means of eosin Y,<sup>[26]</sup> 6-bromo-2-naphthol<sup>[27]</sup> or Schreiner's thiourea<sup>[28]</sup> (Figure 1). However, the latter three



**Figure 1.** Conventional and photochemical synthetic routes from aldehydes and ketones to acetals in comparison to the photoredox catalytic approach (for the structure of PBI, see Figure 2).

[a] M.Sc. D. Steuernagel, Prof. Dr. H.-A. Wagenknecht  
Institute of Organic Chemistry  
Karlsruhe Institute of Technology (KIT)  
Fritz-Haber-Weg 6, 76131 Karlsruhe (Germany)  
E-mail: Wagenknecht@kit.edu

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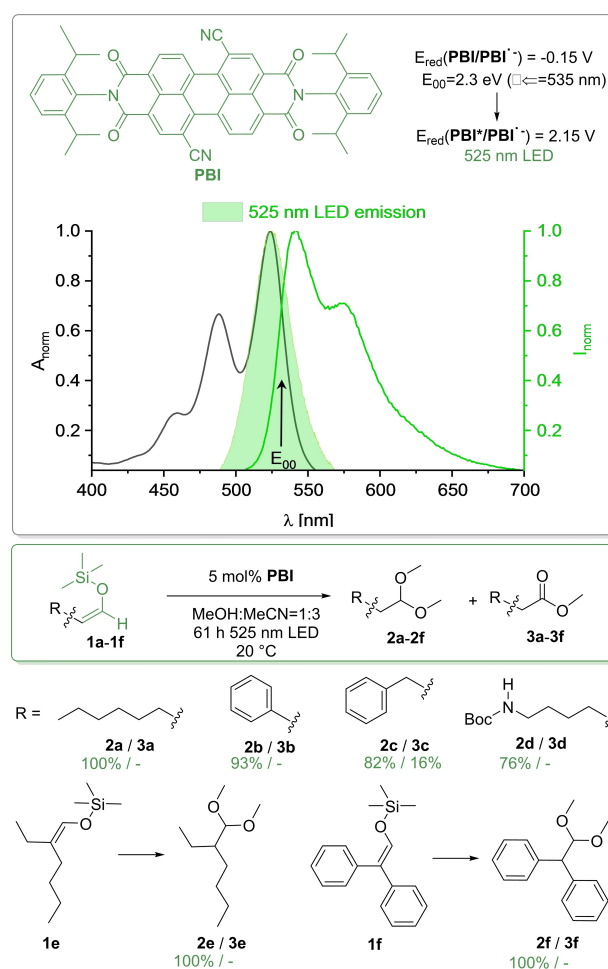
This article belongs to a Joint Special Collection dedicated to Ulf Diederichsen.

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methods are in fact photochemical versions of aldehyde protonation by photoacids leading to the acetals and would not tolerate acid-labile functional groups. Furthermore they are not described for the conversion of ketones. Herein, we report a new acetalization and ketalization method by means of photo-redox catalysis using an electron-deficient perylene bisimide as catalyst which allows not only to convert aldehydes but also ketones as their silylenolethers into their corresponding acetals or ketals, without any acid, photoacid or additional reagent.

## Results and Discussion

Perylene-3,4:9,10-tetracarboxylic acid bisimides belong to the rylene dyes<sup>[29,30]</sup> and have only been rarely used in synthetic photocatalysis although they have unique photochemical properties and a high photostability.<sup>[31]</sup> They form stable radical anions and dianions that can also be applied in photochemistry.<sup>[32,33]</sup> We synthetically modified the perylene bisimide chromophore by two cyano substituents at the core to make it even more electron-deficient. This bis-cyanolated PBI (Figure 2) was successfully applied in the nucleophilic addition of alcohols to styrene derivatives,<sup>[34]</sup> and PBI-modified peptides as “photozymes”.<sup>[35]</sup> PBI shows a reduction potential of  $E_{\text{red}}(\text{PBI}/\text{PBI}^{\bullet-}) = -0.15 \text{ V}$  (vs. SCE).<sup>[35]</sup> With  $E_{00} = 2.3 \text{ eV}$  (from the crossing point of the normalized absorbance and the normalized emission,  $\lambda = 535 \text{ nm}$ ) the excited state reduction potential of PBI can be estimated,  $E_{\text{red}}(\text{PBI}^*/\text{PBI}^{\bullet-}) = 2.15 \text{ V}$ , which shows that this chromophore is a potent photo-oxidant. The cyclic voltammetric measurements of the silylenolether as substrates **S** revealed oxidation potentials of  $E_{\text{ox}}(\text{S}^{\bullet+}/\text{S}) = 2.0\text{--}2.1 \text{ V}$  (Figures S107 and S108). These values are higher compared to the literature reported values of 1.2 and 1.5 V (vs. SCE).<sup>[36,37]</sup> According to the Rehm-Weller equation omitting the Coulomb interactions (that are negligible in an MeOH/MeCN solvent mixture),  $\Delta G = E_{\text{ox}} - E_{\text{red}} - E_{00}$ , the driving force is estimated to be  $\Delta G = -0.1 \text{ eV}$ . This supports the idea that PBI is the right organophotoredox catalyst for the oxidation of silylenolethers. Aldehydes show much higher oxidation potentials in the range from 2.9 to 3.0 V.<sup>[38]</sup> Only their conversion into silylenolethers or the equilibrium with enols make aldehydes convertible by means of photocatalysis. In fact, the initial experiments showed that PBI as catalyst enables the conversion of the unfunctionalized silylenolether **1a** to the acetal **2a** (Figure 2) in good yield. Several optimizations of the photocatalysis were carried out. i) Various solvent compositions were tested with substrate **1a** and the best results were achieved with a composition of MeOH/MeCN = 1:3. While the yields are generally lower with a lower proportion of methanol, more by-products are produced with pure methanol as the solvent. ii) The temperature was also varied between 20 and 40 °C to evaluate how the product mixture might change. In fact, an increased formation of a by-product was observed at higher temperatures, which could be identified as the respective ester **3a**. While at 20 and 30 °C only the acetal **2a** is formed quantitatively, at 40 °C about 6% of the ester **3a** is formed as side product. iii) The reaction time was also optimized with respect to the yields. After 48 h 20% acetal



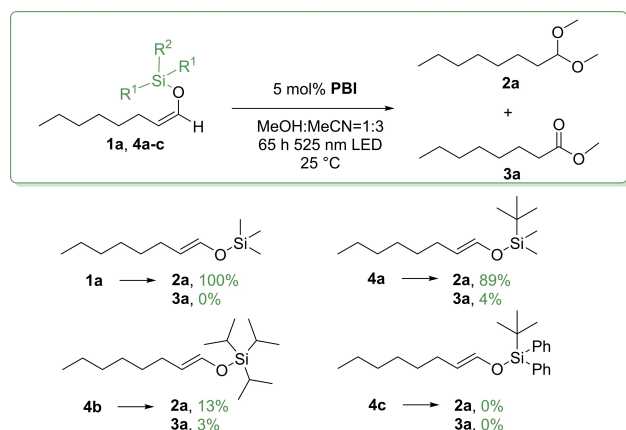
**Figure 2.** Top: Structure, redox properties and absorption/emission of the photoredox catalyst PBI, including  $E_{00}$  and the emission of the 525 nm LED. Bottom: substrate scope and yields for the acetalization of the silylenolethers **1a–f** derived from aldehydes. Yields of main products **2a–f** and side products **3a–f** determined by NMR spectroscopy.

**2a** is formed; quantitative conversion could be observed after 65 h. We have no clear evidence what accelerates the reaction after 48 h irradiation. Possibly, based on the mechanism discussed below, the formation of the silane  $\text{R}_3\text{SiH}$  accelerates the reaction as H-atom transfer reagent for back electron and proton transfer. Hence, all following photocatalytic reactions were carried out in a mixture of MeOH/MeCN = 1:3, at 25 °C and by irradiating for 65 h with the 525 nm LED. The yields were determined by means of  $^1\text{H}$  NMR spectroscopy, all products were additionally isolated and characterized (see the Supporting Information). The initially tested substrate scope for silylenolethers **1a–f** derived from the corresponding aldehydes is broad. Various substrates were successfully irradiated, including alkyl (**1a**, **1e**) and phenylalkyl (**1b**, **1c**, **1f**) silylenolethers and give the corresponding products in yields of 76–100%. Most importantly, substrate **1d** contains the acid-labile Boc-protecting group. Its conversion into product **2d** in 76% yield clearly excludes that acids are formed as intermediates during the photocatalysis because the protecting group remains intact.

There are only very few examples in literature of conventional acid-catalyzed acetalizations in the presence of a Boc group.<sup>[39,40]</sup> Our photocatalytic acetalization is complementary to those conventional methods with acids or photoacids as catalysts. This is important for future total synthesis strategies as it allows an alternative way to insert the Boc group *before* the formation of an acetal at a different position of the molecule.

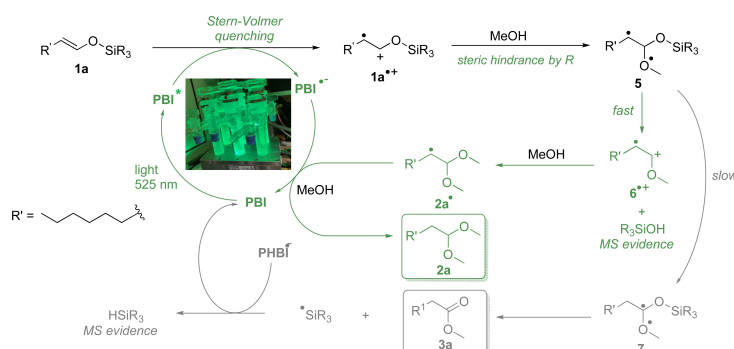
The next obvious step is the variation of the silyl substituents to sterically more demanding ones (Figure 3). A clear dependence on the steric hindrance was observed in comparison of substrate **1a** with substrates **4a–c**. Sterically less demanding silyl groups, such as the TMS (trimethylsilyl) or even the TBDMS (*tert*-butyldimethyl silyl) groups in the substrates **1a** and **4a**, respectively, can be converted almost quantitatively to the corresponding acetal **2a**, whereas the introduction of the sterically hindered TIPS (*tri-iso*-propyl silyl) group in **4b** reduces the yield of **2a** to 13%. The TBDPS (*tert*-butyldiphenyl silyl) group in **4c** completely blocks its conversion. This supports a mechanism of nucleophilic attack by the alcohol which depends on the steric demand of the silyl group.

The reaction quantum yield, exemplarily determined for the photocatalytic conversion of substrate **1a** to product **2a**, is  $\Phi = 0.11 \pm 0.03$ . This value clearly excludes a chain propagation mechanism, for which the reaction quantum yield would be



**Figure 3.** Silylenolethers **1a**, **4a–c** as substrates with different steric hindrance at the silyl group and their influence on the photocatalytic acetalization to products **2a** and **3a**.

higher than 1. Therefore, the following mechanism was postulated for the conversion of silylenolethers based on our experimental evidence (representatively shown for substrate **1a** in Figure 4). The first photoinduced electron transfer between **PBI** and the silylenolether to the ion pair **1a<sup>•+</sup>/PBI<sup>•-</sup>** is slightly exergonic based on the electrochemical potentials discussed above. Moreover, the silylenolether **1a** shows quenching of the **PBI** fluorescence with a Stern-Volmer constant of  $K_{SV} = 20.4 \text{ M}^{-1}$  (Figures S103 and S104). We are able to observe the radical anion **PBI<sup>•-</sup>** in the reaction mixture by its characteristic red-shifted absorption at approximately 700 nm in the visible range (Figure S120). Methanol is added as nucleophile to the resulting radical cation **1a<sup>•+</sup>**, as briefly mentioned above. Alternatively, methanolate could attack the radical cation **1a<sup>•+</sup>**. The resulting radical **5<sup>•</sup>** releases  $\text{R}_3\text{SiO}^-$  to yield the resulting radical cation **6<sup>•+</sup>**.  $\text{SiR}_3\text{OH}$  was detected by mass spectroscopy in the irradiated sample with substrate **1a** (Figure S101). A second methanol addition forms radical **2a<sup>•</sup>** and a final H-atom transfer gives the acetal **2a** as product and closes the photoredox catalytic cycle. It is important to mention here, that despite this H-atom transfer PhSH or any other additive typically used for H-atom transfer in photoredox catalysis is not needed. This is very likely due to the fact that the radical anion of the photocatalyst **PBI<sup>•-</sup>** is extremely long lasting in the range of minutes to hours (under exclusion of oxygen)<sup>[34,35]</sup> which is a significant advantage of this organo-photocatalyst. The formation of the ester as side product can be controlled by several experimental parameters, as already discussed above. In particular, the formation of the ester **3a** is increased as side product at higher temperature. This suggests an additional, slower pathway for the formation of the ester **3a**. As an alternative to the release of  $\text{R}_3\text{SiO}^-$ , the radical **5<sup>•</sup>** can slowly rearrange to the radical **7<sup>•</sup>** which releases  $\text{R}_3\text{Si}^{\bullet}$  to form **3a** as side product. The ester formation is already completed at this point and the resulting radical  $\text{R}_3\text{Si}^{\bullet}$  closes the photoredox catalytic cycle by back electron transfer/protonation (H-atom transfer). The resulting side product  $\text{HSiR}_3$  was detected by mass spectroscopy in irradiated samples (Figure S102). Although protonation steps by methanol are included in this mechanism, it is not likely that the formation of acids is involved. Photocatalytic experiments in the presence of  $\text{K}_2\text{CO}_3$  show only deprotection of silyl group from substrate **1a** but not further conversion. This allows to use

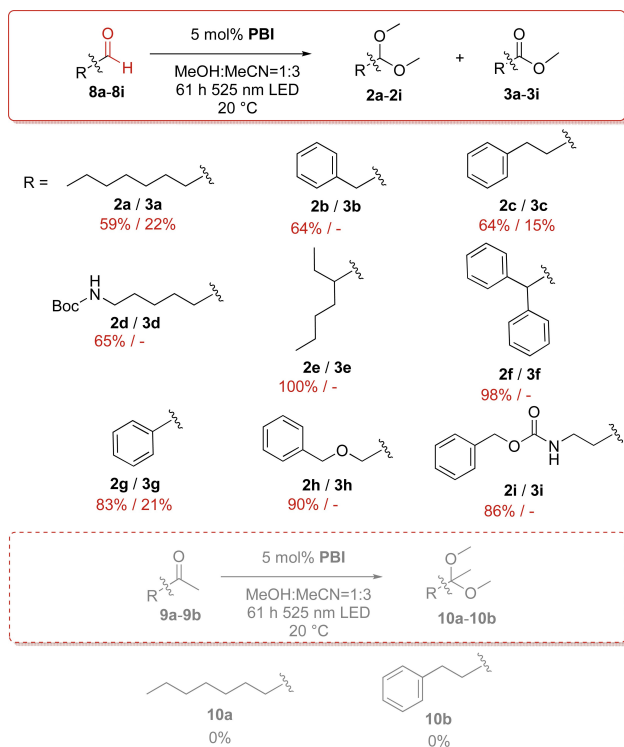


**Figure 4.** Postulated mechanism of the photocatalytic conversion of silylenolether **1a** to acetal **2a** (main product, green) and ester **3a** (side product, gray).

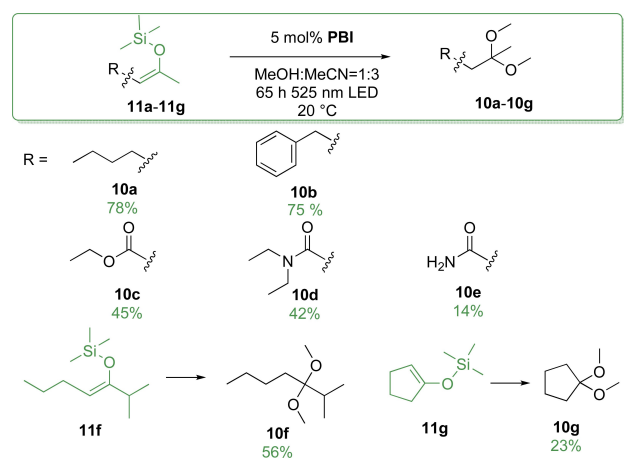


acid-labile groups as part of the substrates, like the Boc group in **1 d** (see above).

Motivated by these results, the aldehydes **8 a–i** were irradiated as substrates under the same experimental conditions as the silylenolethers before. Unexpectedly, in all cases the acetals **2 a–2 i** were formed in good to excellent yields (Figure 5). Some substrates (**8 a**, **8 c**, **8 g**) also give the esters **3 a–3 i** in small quantities as side products. Most importantly, substrate



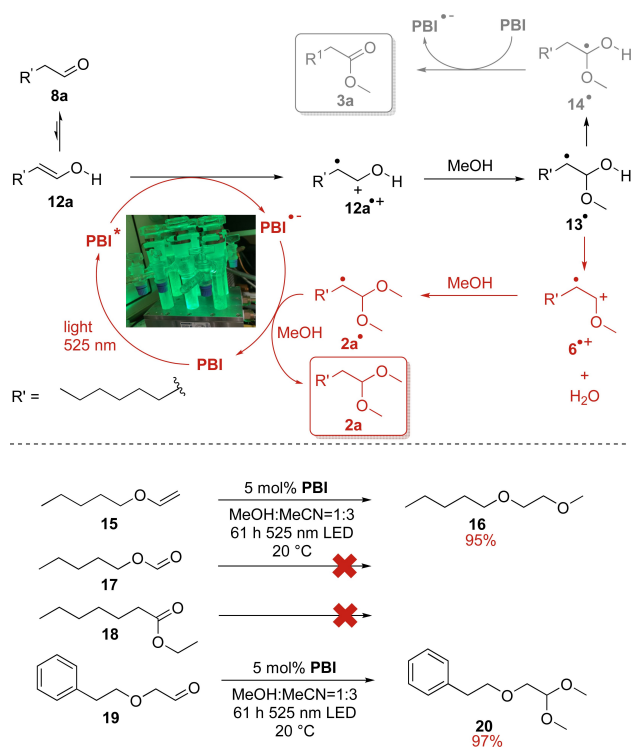
**Figure 5.** Substrate scope and yields for the acetalization of the aldehydes **8 a–i**. The yields of products **2 a–i** and **3 a–i** were determined by NMR spectroscopy. The ketones **9 a** and **9 b** are not converted to **10 a** and **10 b** by the same method.



**Figure 6.** Substrate scope and yields for the ketalization of the silylenolethers **11 a–e** derived from ketones. Yields of products **10 a–e** determined by NMR spectroscopy.

**8 d** contains the acid-labile Boc-protecting group, **8 i** the hydrogenolytic Cbz-protecting group and **8 g** the hydrogenolytic benzyl group as typical protecting groups applied in organic synthesis. Their conversion clearly shows that neither acidic conditions are present nor nascent hydrogen (by H-atom transfer) is formed during the photocatalysis, because products **2 d**, **2 g** and **2 i** are obtained in 76–96% yield. All three protecting groups remain intact under the conditions of this photocatalysis which underscores again the potential of this photocatalytic method in the context of a multistep synthesis.

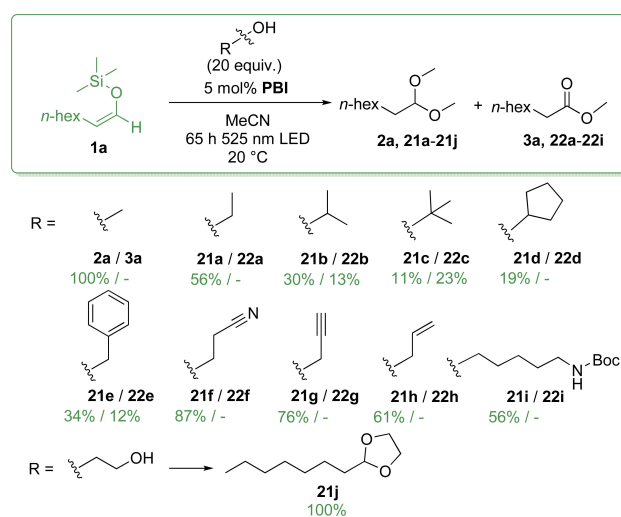
Interestingly, ketones are not substrates of this photocatalytic acetalization. We tested the ketones **9 a** and **9 b**, structurally very similar to the aldehydes **8 a** and **8 c**, which are not at all converted under these experimental conditions. In contrast, the silylenolethers **11 a** and **11 b**, derived from the ketones **9 a** and **9 b**, respectively, are converted to the ketals **10 a** and **10 b** in good yields (Figure 6). Admittedly, the yields were lower than those of the structurally comparable silylenolethers **1 a** and **1 c** from aldehydes **8 a** and **8 c**. Various functional groups were also tested for their tolerance and stability in this. In particular the ester in **11 c** and the amide substrates **11 d** and **11 e** were stable under these experimental conditions. This shows that our photocatalytic method for the synthesis of ketals works under mild conditions. The conversion of the aldehydes **8 a–i** is astonishing because the energetic situation based on the excited state potential of  $E_{red}(PBI^*/PBI^{\cdot-}) = 2.15$  V is endergonic with respect to the oxidation of aldehydes (oxidation potentials in the range from 2.9 to 3.0 V<sup>[38]</sup>). The lack of fluorescence quenching at the fluorescence in the Stern-Volmer plot supports that there is no electron transfer between **PBI** and **8 a** (Figure S117). This assumption is valid for the one-photon excitation. The discrepancy between the energetic scenario and the experimental results makes the direct photo-oxidation of the aldehyde function very unlikely (representatively shown for substrate **8 a** in Figure 7). It seemed more reasonable to assume that the enol **12 a** is oxidized by the photoexcited **PBI** in the first step. Firstly, a small substrate screening supports this assumption. The vinyl ether **15** and the aldehyde **19** are converted to their products **16** and **20** (that can form enols), respectively, in excellent yield, whereas substrates **17** and **18** (that cannot form enols) are not at all converted. Secondly, the fact that the ketones **9 a** and **9 b** are not converted at all although they are structurally very similar to the aldehydes **8 a** and **8 b** also supports a mechanism via enols. It is known from literature that there are significantly less enols from ketones in the equilibrium than enols from aldehydes.<sup>[41]</sup> This implies that the steady-state concentrations of the enols from ketones **9 a** and **9 b** are too low for their efficient photoredox catalytic conversion. The other steps of the photocatalytic cycle follow the proposed mechanism for the conversion of silylenolether, as discussed above. After oxidation of the enol **12 a** the addition of methanol gives radical **13\*** that releases water and the remaining steps to the product **2 a** are identical to the previous mechanism for silylenolether **1 a**. Alternatively, radical **13\*** can rearrange to radical **14\*** similar to the reaction to radical **7\***. However, the cleavage of the strong O–H bond seems to be very unlikely in comparison to the O–Si



**Figure 7.** Postulated mechanism for the photoredox catalytic acetalization of aldehyde **8a** via its enol **12a**. Substrate scope of **15**, **17**–**19** to support the hypothesis of enols as intermediates, only products **16** and **20** are formed.

bond. Radical **14\*** is the protonated ketyl radical; hence its oxidation gives product **2a**, probably by concomitant reduction of PBI to the radical anion PBI<sup>•-</sup>. Unexpectedly, benzaldehyde (**8g**) is also converted to products **2g** and **3g** although it cannot form enols. We assume a direct oxidation of this aromatic substrate to radicals similar to **14\*** and **2a\***, possibly by a two-photon excitation which is feasible due to the very long lifetime of the radical anion PBI<sup>•-</sup>.

Finally, the use of different alcohols as reacting partner in this photocatalytic method is a promising possibility to broaden the reaction scope furthermore (Figure 8). Alcohols with different alkyl substituents were reacted with the silylenolether **1a** as representative substrate. Here again, the yields depend on the steric demand and give higher yields for sterically less demanding alcohols in the product series **2a**, **21a**–**c**. Concomitantly, an increased formation of the esters **3a**, **22a**–**c** is obtained in this series as more demanding the alcohol residues are. Also, the reaction of **1a** with cyclopentanol gives product **21d** only in low yield. More importantly, alcohols with a cyanide, an alkyne and an alkene as additional functional groups react with substrate **1a** to the corresponding products **21f**–**h** in yields of 61–87%. Obviously, these functional groups are tolerated by this photocatalytic method. Even the  $\epsilon$ -amino-protected alcohol with the acid-labile Boc group gives product **21i**; the Boc group obviously withstands this reaction condition. The reaction of **1a** with glycol gives the product **21j** with the cyclic acetal in quantitative yield. These are notable results and - taken together - prove our photocatalytic acetalization to be



**Figure 8.** Use of different functionalized alcohols for acetalization of reference substrate **1a** into acetals **2a**, **21a**–**j** as the main products and esters **3a**, **22a**–**i** as side products.

mild and comparable in yield, but orthogonal to the conventional acid-catalyst methods.

## Conclusion

In conclusion, a new photocatalytic method with the biscyanated PBI as electron-poor photocatalyst, and therefore potent photooxidant, has been developed to convert silylenolethers and carbonyl compounds into acetals or ketals. Silylenolethers of aldehydes react efficiently with the acetals in good to excellent yield, with the corresponding esters as side products in a few cases. Remarkably, aldehydes can also be directly and selectively converted into the respective acetals, whereas ketones do not react. Therefore, ketones must be converted to silylenolethers before their photocatalytic ketalization. The functional group tolerance is high, which could be a reason why the detour via the silylenolether might be necessary for ketalizations of carbonyls. This might be feasible if protecting groups prevent direct ketalization. For both variants, a broad substrate range was shown as well as variety in the choice of alcohols, including those with other functional groups, like amides and cyanides. In particular, the tolerance of this photocatalytic method towards acid- and hydrogen-labile groups is remarkable because it allows these protection groups to be present during acetalization. This photocatalytic method works completely free of acids or photoacids, does not need any additives or H-atom transfer reagents, and hence broadens the substrate scope and repertoire of photoredox catalysis with respect to carbonyl chemistry.

## Experimental Section

All experimental procedures and data are given in the Supporting Information.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** photocatalysis · carbonyl compounds · enols · perylene bisimide · photochemistry

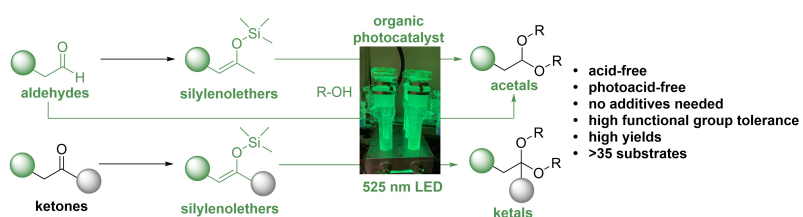
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# RESEARCH ARTICLE



**Use light instead of acids:** Silylenolethers derived from aldehydes and ketones as well as aldehydes themselves react efficiently to give acetals in good to excellent yields. The

substrate range with respect to both aldehydes and alcohols is broad, and acid- and hydrogen-labile protecting groups are tolerated.

*M.Sc. D. Steuernagel, Prof. Dr. H.-A. Wagenknecht\**

1 – 7

**Photocatalytic Synthesis of Acetals and Ketals from Aldehydes and Silylenolethers without the Use of Acids**

