

# Oral Presentation

## Generation of Silyl Radicals via Photocatalyzed Si-H Bond Activation

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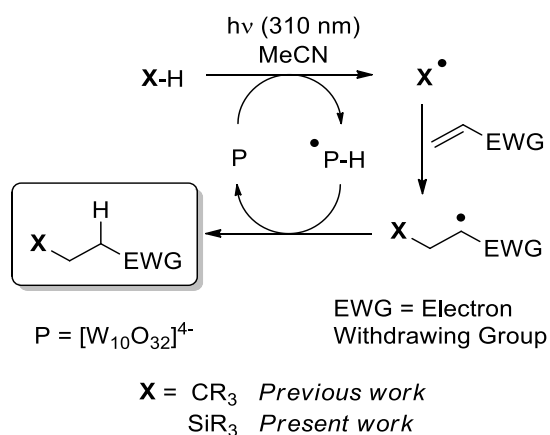
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### Abstract

Photocatalytic reactions are those processes that take place by using a catalyst activated by light.<sup>1</sup> Photocatalysis by polyoxoanions, in particular by tetrabutyl ammonium decatungstate ( $(n\text{-Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$ ) (TBADT)<sup>2</sup> is emerging as a powerful method for the formation of valuable chemical bonds under environmental friendly conditions. This is based on the capability of TBADT to activate a variety of aliphatic derivatives including amides, aldehydes, oxygenated compounds (ethers, acetals) and even alkanes, via direct C-H activation ( $X = \text{CR}_3$ , see Scheme).<sup>2,3</sup> The corresponding radicals ( $X^\bullet$ ) are then trapped by electron-poor olefins to give a radical adduct that accepts a hydrogen atom from the reduced photocatalyst ( $^{\bullet}\text{P-H}$ ), to afford the end product with the concomitant P regeneration.



In this work we shifted our attention to Si-H bonds since none of the methods so far described for the generation of silyl radicals is of general applicability. Indeed, the direct silylation of electrophilic alkenes ( $\alpha,\beta$ -unsaturated nitriles, esters, sulfones and even ketones) has been achieved in the presence of 2% mol TBADT.

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The reaction was limited to trisubstituted alkyl or aryl silanes ( $X = \text{SiR}_3$ ). The presence of at least one phenyl group was mandatory to achieve a clean reaction (36%-90%). By contrast, the reaction on trialkylsilanes gave a mixture of products in moderate yields (40-60%) arising from the competitive Si-H/ C-H bonds activation.<sup>4</sup>

### References:

1. D. Ravelli, D. Dondi, M. Fagnoni, A. Albini. *Chem. Soc. Rev.*, **2009**, *38*, 1999.
2. M. D. Tzirakis, I. N. Lykakis, M. Orfanopoulos *Chem. Soc. Rev.*, **2009**, *38*, 2609.
- 3 For recent examples by our group, see: H. Qrareya, D. Ravelli, M. Fagnoni, A. Albini. *Adv. Synth. Catal.*, **2013**, *355*, 2891 and references therein.
4. H. Qrareya, D. Ravelli, M. Fagnoni, A. Albini, *manuscript in preparation*.