

[A0052]

Towards a Selective Activation of Functional Groups Using Monochromatic Light.

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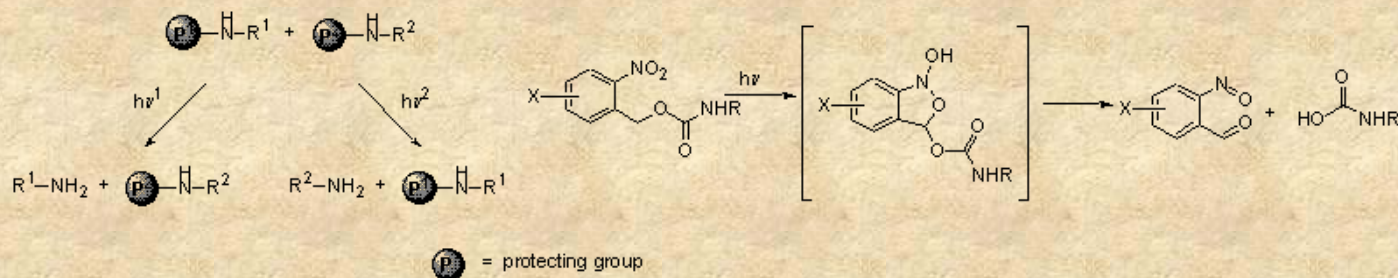
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1. Introduction

Selectivity has always been a major goal in any chemical processes, and particularly in organic synthesis. It is thus not surprising that more and more selective reagents have been developed in the last few decades. In photochemical reactions, the light can be considered as one of the reactants. Among the parameters characterizing the light, the wavelength is undoubtedly the most easily tunable one. This project aims at developing a set of functional groups that can be selectively activated by monochromatic light at various wavelengths, either to form bonds (eg. photoacylation) or to break bonds (eg. photodeprotection).

2. The goals

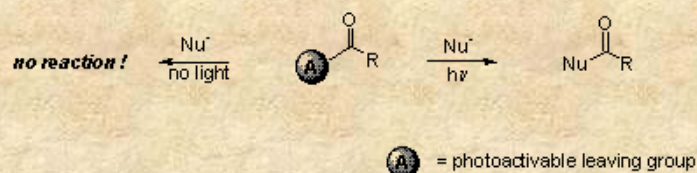
Preparation and evaluation of selective photolabile groups



We anticipate the substituents on the aromatic ring to have a strong influence on the position λ of the absorption, its intensity ϵ and the cleavage quantum yield F . By the proper tuning of these parameters, mutually orthogonal photolabile protecting groups should be available.

Optimisation of a clean and mild photoacylation reaction

Our next endeavour aims at developing a wavelength-selective acylation reaction by binding a photoactivable leaving group to a carbonyl. This function is expected to be stable towards nucleophiles under dark conditions, but to be highly reactive under irradiation at the proper wavelength. The parameters λ , ϵ and F will be adjusted to achieve selectivity.



3. The challenges

The following requirements have to be fulfilled:

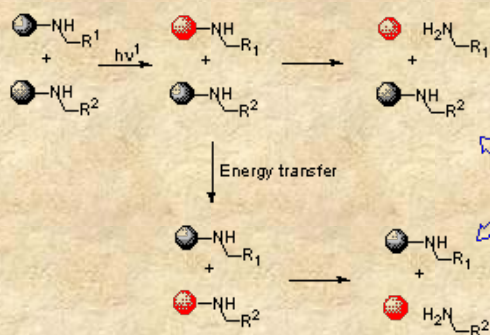
- Easy preparation
- Efficient coupling

Orthogonality

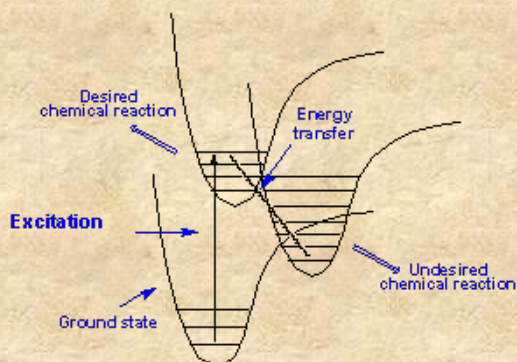
- Efficient deprotection

The energy transfer, either **inter-** or **intramolecular**, is of crucial importance. The initial excited state can indeed relax into a lower energy state. The information embedded into the original excitation energy is then lost. Relaxation can operate through several mechanisms, also at long distances and/or high dilution. In some cases, it can even totally inhibit the reaction.

Intermolecular energy transfer

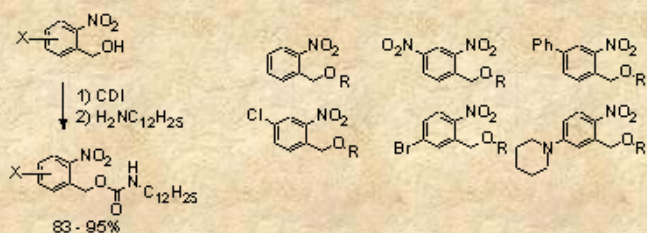


Intramolecular energy transfer

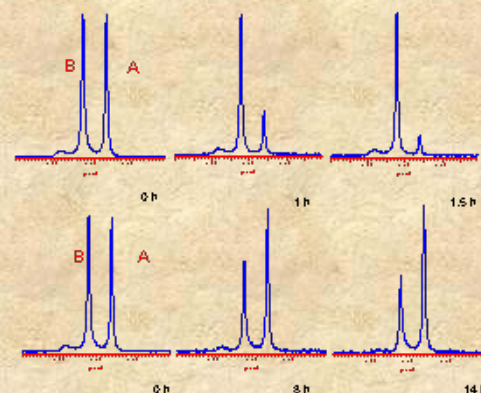


4. The results

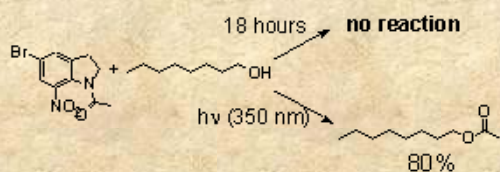
Preparation of the photolabile groups



Checking the relative reaction rates



Studies on the photochemical acylation



- Clean acylation
- Neutral medium
- Recycling of the indoline
- Wavelength-dependence

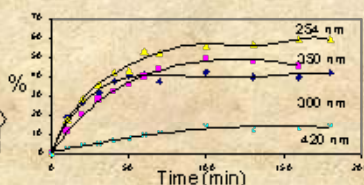


Figure 1: Wavelength-dependence of the acylation of 1-octanol with the nitroindoline

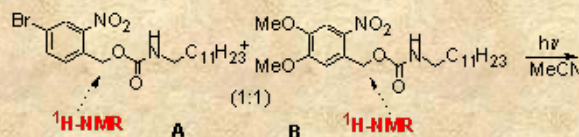


Figure 2: $^1\text{H-NMR}$ spectra of an equimolar mixture of the two chromophores A and B at increasing irradiation time, with 254 nm and 420 nm UV-light.

Checking the energy transfer

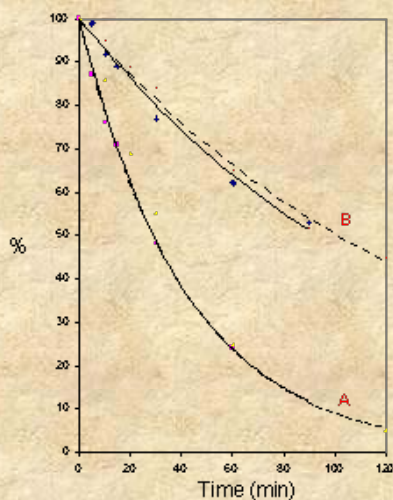
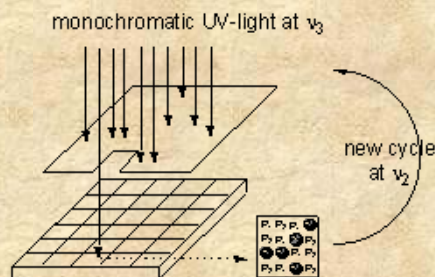
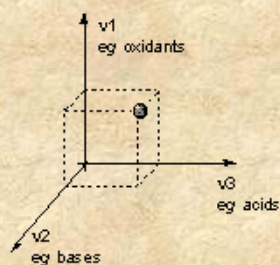
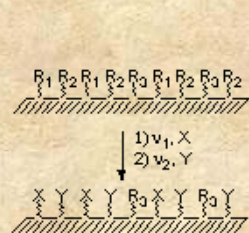


Figure 3: Photolysis of the equimolar mixture **A** and **B** (plain line) and pure components (dashed lines) at 254 nm. The identical rates show that intermolecular energy transfer is not operating.

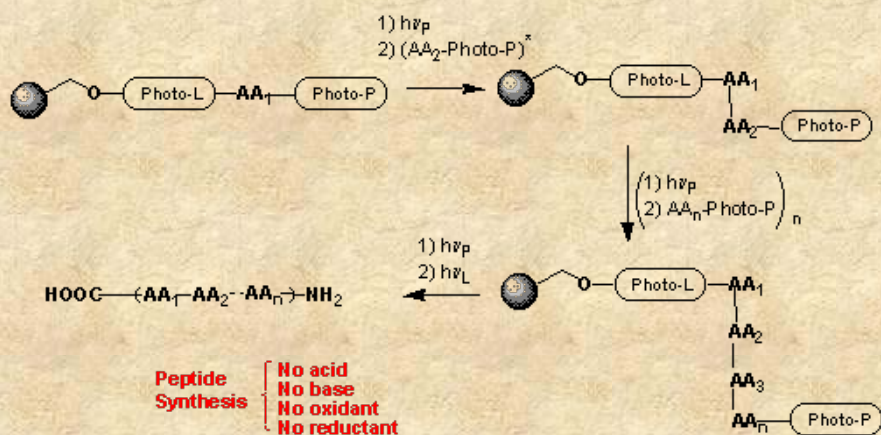
5. The Applications



Color-sensitive materials

Orthogonal protecting groups

Spatially addressable combinatorial libraries



'Reagentless' Solid-phase peptide synthesis

6. References

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7. Acknowledgements

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