STUDY OF A NEW PHOTOREMOVABLE PROTECTING GROUP ABSORBING ABOVE 500 nm

Lovely Angel P.A, Peter Šebej, Tomáš Slanina, Jürgen Wintner, Pavel Müller, Jamaludin Al Anshori, , Petr Klán, and Jakob Wirz

A new water soluble photoremovable protecting group (PPG)^{1,2} for phosphates and carboxylic acids with high molar absorption coefficient in the visible region has been designed, synthesized and tested. The structure of this PPG was obtained by extending the 7-hydroxycoumarin-4-yl-methyl (HCM) chromophore³ by an additional aromatic ring to form derivatives of 6-hydroxy-3*H*-xanthen-3-one. The introduction of an additional aromatic core to the coumarinyl unit resulted in a substantial shift of absorption towards longer wavelengths and also caused a drop in pKa of the phenolic proton to about 6. The three derivatives (bromide, acetate and diethylphosphate) were isolated as complexes with DDQ. They have a molar absorption coefficient ε of ~ 4 x 10⁴ m⁻¹ cm⁻¹ at ~ 520nm and shown to release the ligands with quantum yields $\leq 2.4\%$ in aqueous solution.⁴



 $X = Br, CH_3COO, (EtO)_2PO$

The quantum yields of photodeprotection of model compounds were relatively low but still comparable to those of coumarinyl cages. In the dark, the model compounds were stable for several hours in aqueous solutions at room temperature. The photoproduct 6-hydroxy-3-oxo-3*H*-xanthene-9-carboxylic acid was isolated and its photoreactivity was studied in different solvents.

References

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