

Highly diastereoselective [2+2] photocycloaddition of homochiral 2(5*H*)-furanones to vinylene carbonate

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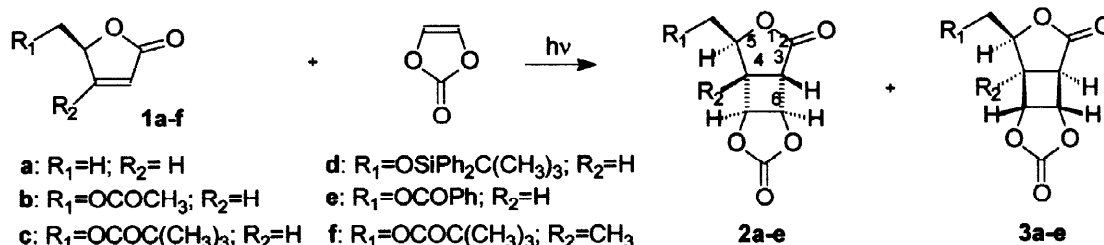
Abstract

The [2+2] photocycloaddition of homochiral 5-alkyl-2(5*H*)-furanones to vinylene carbonate was studied in order to enhance the induced facial diastereoselectivity created by the stereogenic centre. Diastereomeric excesses of up to 92% were found. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclobutanes; photochemistry; lactones; diastereoselection.

1. Results and discussion

In our aim to obtain cyclobutane containing natural products through [2+2] photocycloaddition of α,β -unsaturated lactones to alkenes [1, 2] we have studied extensively the behaviour of homochiral α,β -butenolides type **1** with ethylene and tetramethylethylene [3-5]. Steric and stereoelectronic effects (mainly $n-\pi$ overlapping between the lone electron pairs of the oxygen of the ester group, when present, and the π electrons of the α,β -butenolide) were invoked to govern the approach of the olefin to the unsaturated lactone creating the diastereofacial differentiation. Diastereomeric excesses of up to 64 % were found with pivalate esters, e.g. **1f**. Vinylene carbonate was also used as an electron poor, functionalized and more sterically demanding olefin with the pivalate ester **1c**, d.e. increasing then to 72 % [5]. We have found now that the presence of a phenyl group in the R_1 moiety can highly increase the d.e. of the *anti* cycloadduct and, since the starting butenolides are homochiral, enantiopure products are obtained in good yields from these photocycloadditions. Laser flash photolysis techniques allowed us to detect the radical intermediates involved in these photochemical reactions.

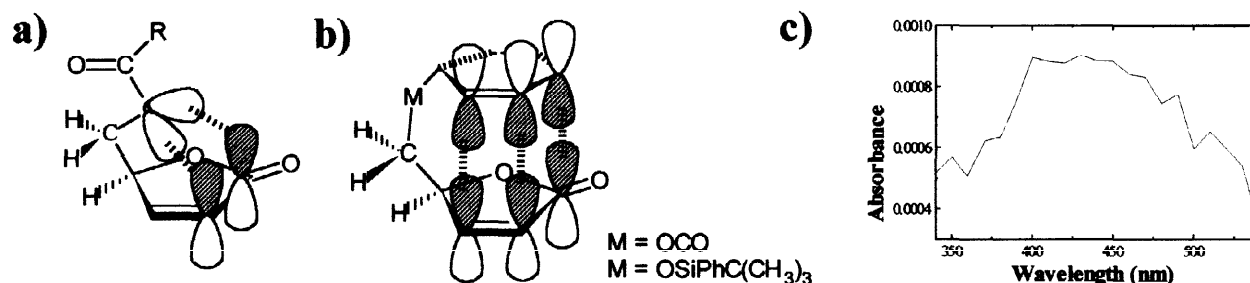


Irradiation of furanones **1a**, **1b**, **1c**, **1d** and **1e** in the presence of vinylene carbonate in a small pyrex reactor using a medium pressure 125 W mercury lamp and acetone as solvent and photosensitizer was performed as already described [3-5]. Only adducts **2** and **3**, derived from an *exo* approach ($J_{3,6} = 1\text{Hz}$) of the olefin in the transition states, were obtained in moderate to good yields. The diastereomeric ratio and yields were determined after separation of the products by

column chromatography (except for **1e** where g.l.c. was used). Specific rotations: **2b**: $[\alpha]_D^{20} = -56.9$ (*c*:0.86, acetone); **3b**: $[\alpha]_D^{20} = +47.3$ (*c*:0.55, acetone); **2d**: $[\alpha]_D^{20} = -28.2$ (*c*:0.78, CHCl_3); **2e**: $[\alpha]_D^{20} = -62.8$ (*c*:0.86, CHCl_3). The relative *anti* and *syn* configuration for **2** and **3** respectively was determined, among other features, by means of the $J_{4,5}$ value measured in their 400 MHz spectra. Major adducts showed small $J_{4,5}$ (around 1.5 Hz), while minor isomers with larger $J_{4,5}$ (around 5.5 Hz) were assigned the *syn* configuration. The low d.e. of 40 % obtained when $R_1 = \text{H}$ (furanone **1a**) increases up to 60 and 72 % with the presence of an ester group in the γ -position of the lactone (furanones **1b** and **1c** respectively), see above and Fig.1a. Much better results came out when a phenyl group was introduced in the ester or ether moiety. The silyl ether **1d** gave 84 % *anti* d.e., and this value was increased to 92 % for the benzoate **1e**. A π - π interaction between the aromatic ring and the π system of the α,β -butenolide could enhance predominant conformations (Fig. 1b) causing the hindrance of the *syn* face of the latter compound. We think that this is the first time that a kind of π -stacking has been shown to operate in photochemical cycloadditions of enones to alkenes.

Figure 1:

a) n- π interactions; b) π - π interactions; c) Transient absorption spectrum of a N_2 -purged solution of furanone **1b**.



The generally accepted mechanism for the photocycloaddition of enones to alkenes [6] states that the triplet state of the enone and 1,4-biradicals are involved along the reaction pathway. In order to detect such radicals we have studied some of our substrates with the Laser Flash Photolysis technique. The difference transient absorption spectrum of an N_2 -purged solution of furanone **1b** has been recorded using a 355-nm laser pulse of a Q-switched Nd:YAG laser for excitation. The spectrum (see Figure 1c, similar for **1c** and **1d**), shows a single broad band centred at 380-440 nm. The transient absorption has a lifetime of 550 ± 50 ns and is assigned to the mixture of the radicals involved in the photoreaction. The described lifetimes [7] for other 1,4-biradicals range from 90 ns to 900 ns. The 550 ns, being the upper extreme of the range, suggests that our diradicals are sensitive to the mesomeric effect of the carbonate group [8].

The use of these homochiral cyclobutanes in a short synthesis of sugar templates is shown in the next paper.

2. Acknowledgements

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3. References

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