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Diastereoselective |2+2| Photocycloaddition of Alkenes to 2(*5H*)-Furanones

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É descrita a fotocicloadição de diferentes alquenos a 2(*5H*)-furanonas. É proposto um mecanismo para explicar a forte dependência dos rendimentos dos cicloadutos em relação ao solvente.

The photocycloaddition of different alkenes to 2(*5H*)-furanones is described. A mechanism is proposed to explain the strong dependence of the cycloadducts yields with the solvent.

Keywords: *diastereoselective |2+2| photocycloaddition, (+)-grandisol*

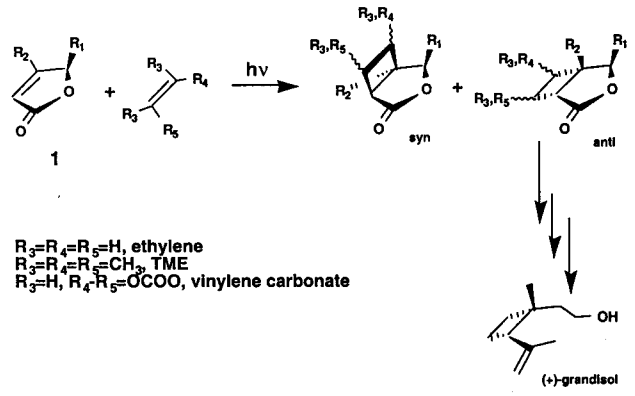
Introduction

The [2+2] photocycloaddition of alkenes to 2(*5H*)-furanones is a well-known approach to obtain cyclobutanic compounds[1]. We have already published that using the easily available homochiral 2(*5H*)-furanones, **1**, their stereogenic center perform an asymmetric induction that ensures the creation of new chiral centers in the cyclobutane ring[2,3]. Our target was to obtain a large excess of the *anti*-cycloadduct that eventually would yield a natural product like the pheromone (+)-grandisol (28% overall yield when $R_1 = (CH_3)_3CCOOCH_2$, $R_2 = CH_3$, alkene = TME, (see Scheme)[3]. We have also shown that the steric and stereoelectronic effects of R_1 force the alkene to approach the furanone preferentially by the α face[2]. Now we wish to report here the strong dependence of the cycloadduct yields with the solvent used and a mechanism that can account for such a dependence.

Experimental

The general experimental procedure for photocycloadditions of TME and ethylene to 2(*5H*)-furanones has been already described[2]. Irradiations were performed in a small conventional photochemical reactor, consisting of a two-necked 50 mL reaction vessel and a water-jacketed Quartz (or Pyrex) immersion well, using a medium pressure 125 W mercury lamp (Philips HPK-125), usually under an argon atmosphere and with magnetic stirring. Ethylene saturated solutions at -78 °C were used in the cycloaddition experiments of this olefin. Water was used for refrigeration of the immersion well jacket. The progress of the reaction was generally monitored by glc or tlc taking aliquots of *ca* 50 μL. Gas chromatographic analyses were performed on a Hewlett-Packard model 5930 instrument with a Hewlett-Packard Ultra 1 (crosslinked methyl silicone gum, 12 m x 0.2 mm x 0.3 μm) capillary column. The GC-MS analyses (70 eV for electron impact) were recorded on a Hewlett-Packard 5989A GC-MS system with the previously described capillary column. NMR spectra were recorded on a Bruker WP80SY or a Bruker AM400Wb. A typical cycloaddition experiment was carried out as follows:

Cycloaddition of TME to (-)-(*R*)-5-methyl-2(*5H*)-furanone (Exp. 1). A solution of (-)-(*R*)-5-methyl-2(*5H*)-furanone (300 mg, 3.06 mmol) and tetramethyl ethylene (TME) (3.6 mL, 30.37 mmol) in dry ether (45 mL) was irradiated at room temperature for 3 h through quartz after degassing with argon (45 min). Elimination of the solvent at reduced pressure gave a residue which was chromatographed on silica gel using initially hexane alone and then a mixture of hexane and ether, gradually increasing the amount of ether, as eluent (0 → 30% ether in hexane). The first fraction gave (-)-(1*S*,4*R*,5*R*)-4-methyl-6,6,7,7-tetramethyl-3-oxabicyclo [3.2.0]heptan-2-one, *anti*-cycloadduct, (184 mg, 1.01 mmol, 33% yield) as a colourless crystalline solid (chemical properties as described)[2]. The second fraction gave (1*R*,4*R*,5*S*)-4-methyl-6,6,7,7-tetramethyl-3-oxabicyclo[3. 2.0] heptan-2-one, *syn*-cycloadduct, (61 mg, 0.33 mmol 11% yield) as a liquid (chemical properties as described)[2]. The third fraction gave 74 mg of unreacted lactone.



Scheme 1.

Discussion

In the Table 1, we show 16 experiments where the major obtained cycloadduct is always the *anti*-cycloadduct for any furanone or alkene used, thus following the already explained approach of the alkene to the α face of the furanone. The yields of the cycloaddition are high when TME is dissolved in ether but they drop dramatically when the solvent is acetone. On the contrary, yields are high when ethylene or vinylene carbonate are dissolved in acetone but drop to < 2% when the solvent changes to ether. This behaviour can be explained if we assume that a charge transfer *furanone* ↔ *alkene* (See Fig. 1) is formed for electron-rich alkenes like TME, but is not formed for electron-poor alkenes like ethylene or vinylene carbonate. As it is well-known, cycloaddition between lactones like **1** and olefins are sensitized by acetone and proceed *via* a triplet excited state[4]. For an efficient triplet-triplet energy transfer, acetone has to collide with the furanone. This is not possible if the furanone has its two faces hindered, one by the bulky R_1 group and the other by the olefin complex. That would be the situation for the TME: the acetone can not sensitize the cycloaddition but the chemical reaction can progress under direct irradiation in ether; since the TME and the excited furanone are very close, they can react immediately to yield the diradical species and eventually the cycloadducts[5]. On the contrary, direct irradiation of mixtures of furanone and ethylene or vinylene carbonate in ether gives excited states of the furanone that deactivate quickly in processes others than cycloaddition; these processes lead to by-products. If acetone is the solvent, the lactone can be excited to its long lived triplet by sensitization (there is not charge transfer complex in this case) and will approach the olefin to form the diradical and the cycloadduct. In spite of the indirect evidences, we have not been successful to record any spectroscopic and direct evidence of the charge transfer. Experiments with acetone as sensitizer were performed using a pyrex filter instead of a quartz filter to avoid the decrease of the cycloaddition

Table 1. Solvent influence in the yield of the cycloadducts.

Exp.	R_1	R_2	alkene	solvent	filter	yield %	ratio *anti:syn*
1	CH_3	H	TME	ether	quartz	59	74:26
2	CH_3	H	"	acetone	pyrex	< 2	-
3	$(CH_3)_3CCOOCH_2$	H	"	ether	quartz	60	82:18
4	$(CH_3)_3CCOOCH_2$	H	"	acetone	pyrex	18	83:17
5	$(CH_3)_3CCOOCH_2$	CH_3	"	ether	quartz	32	78:22
6	$(CH_3)_3CCOOCH_2$	CH_3	"	acetone	pyrex	6	83:17
7	CH_3COOCH_2	H	ethylene	acetone	pyrex	82	74:26
8	CH_3COOCH_2	H	"	ether	quartz	< 2	-
9	$(CH_3)_3CCOOCH_2$	H	"	acetone	pyrex	59	76:24
10	$(CH_3)_3CCOOCH_2$	H	"	ether	quartz	< 2	-
11	$(CH_3)_3CCOOCH_2$	CH_3	"	acetone	pyrex	70	62:38
12	$(CH_3)_3CCOOCH_2$	CH_3	"	acetone	quartz	10	60:40
13	$(CH_3)_3CCOOCH_2$	H	vinylene carbonate	acetone	pyrex	47	85:15
14	$(CH_3)_3CCOOCH_2$	H	"	ether	quartz	< 2	-
15	$(CH_3)_3CCOOCH_2$	CH_3	"	acetone	pyrex	54	88:12
16	$(CH_3)_3CCOOCH_2$	CH_3	"	ether	quartz	< 2	-

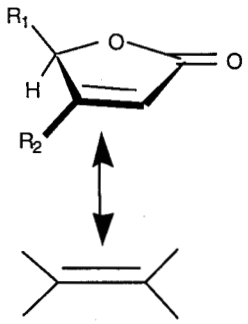


Figure 1. charge transfer *furanone* ↔ alkene.

yields (compare experiments 11 and 12): acetone still operates as a triplet sensitizer when excited with $\lambda > 300$ nm[4b] while the direct irradiation of the free furanones (and the subsequent formation of by-products) is avoided.

In summary, the cycloaddition of furanones like **1** to electron-rich olefins like TME is inefficient in acetone and efficient in ether, while the cycloaddition to electron-poor olefins like ethylene or vinylene carbonate is efficient in acetone but not in ether.

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