Organische Chemie IV: Organische Photochemie

Sommersemester 2005 – Technische Universität München

Klausur am 22.07.2005

Name; Vorname .... Matrikel-Nr. ....
(Druckbuchstaben)

geboren am .... in ....

....
(Eigenhändige Unterschrift)

☐ The questions will be answered in english.
☐ Die Fragen werden auf Deutsch beantwortet.

| 1	2	3	4	5	6	7	8	9	Σ

Hinweise zur Klausur:

1. Die Klausur besteht aus insgesamt 9 Blättern (Deckblatt plus 8 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
2. Es dürfen nur die vorgedruckten Bögen (einschließlich Rückseite) genutzt werden. Antworten sind zu kennzeichnen, sonst werden sie nicht bewertet. Bitte kurze Antworten!
3. Es sind keine Hilfsmittel erlaubt. Täuschungen und Täuschungsversuche führen zum Nichtbestehen der Klausur.
4. Bitte schreiben Sie mit einem Kugelschreiber oder Füller. Verwenden Sie keinen Bleistift und keine rote Tinte!
5. Jede richtig und vollständig beantwortete Aufgabe wird mit der jeweils angegebenen Anzahl von Punkten bewertet. Es können Teilpunkte gegeben werden. Die Klausur ist bestanden, wenn mindestens 50 Punkte erreicht worden sind.

Information

1. The exam is comprised of 9 sheets (cover page, plus 8 question pages). Please check immediately that the exam paper is complete.
2. You may use both sides of the distributed paper to give your answers, but no additional sheets will be allowed. Make sure you indicate clearly which question you are answering, otherwise it will not be counted. Short answers please!
3. No additional sources of information are allowed. Cheating, and cheating attempts will result in the candidate failing the exam.
4. Please write clearly in ink or ballpoint pen. Do not use pencil or red colours!
5. Every correct and fully answered question will be awarded the number of points shown. It is possible to obtain only some of the points if the answer is not completely satisfactory. A pass is obtained if at least 50 points are awarded.
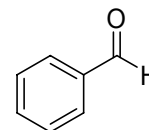
1. Complete the text by adding the words or terms from the box to the correct places of the text! (Each word or term from the box should be used once at most!)   (18)
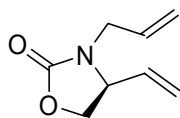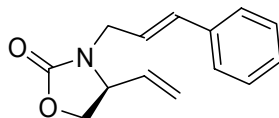
1   **2**   **3**

Isolated double bonds as in alkene **1** have short-wavelength absorption maxima around _____nm. Their excitation and subsequent photocycloaddition is possible by the use of _____ as a catalyst and irradiation at a wavelength of _____ nm.

Styrene **2** on the other hand has a low lying triplet $\pi\pi^*$ state. Its photocycloaddition can be performed by employing _____ as a sensitiser and by irradiation at a wavelength of _____ nm. In order to allow for a sensitised reaction, the triplet energy $E(T_1)$ of the sensitiser must be _____ than the triplet energy $E(T_1)$ of the olefinic double bond. Before the intermediately formed biradical can collapse to the cyclobutane ring, an_____ must occur.

Irradiation of carbonyl compounds like benzaldehyde (**3**) initiates a $n\pi^*$ transition and population of the _____ state. Especially in aromatic carbonyl compounds, inter system crossing to the _____ state is fast. This transformation is a _____ process. According to the rules of *El Sayed*, only the transformations _____ and _____ are allowed.

500	300	254	180	75
Pd(PPh)$_3$		Cu	PtCl$_2$(NH$_3$)	CuOTf
ethyl acetate		acetophenone	tetrahydrofuran	
internal conversion		isomerisation	inter system crossing	fluorescence
$^1n\pi^* \to {}^3\pi\pi^*$		$^1\pi\pi^* \to {}^3\pi\pi^*$	$^1n\pi^* \to {}^3n\pi^*$	$^1\pi\pi^* \to {}^3n\pi^*$
	more stable		lower	higher
R$_1$	R$_2$	S$_1$	S$_2$	T$_1$	T$_2$
thermodynamic		radiative		non radiative	kinetic

2. Fill in the products in the following photochemical reactions, and give the name of the reaction where indicated. Mind any necessary regio- and stereochemistry.
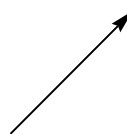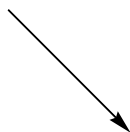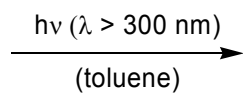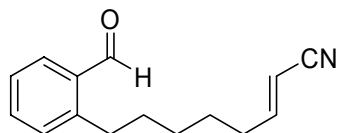
a)

hν (λ = 300 nm)

(Et₂O)
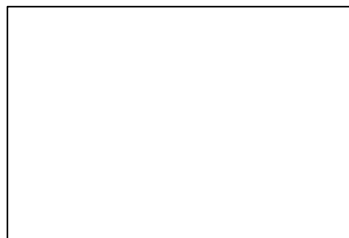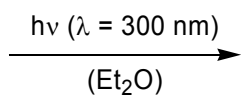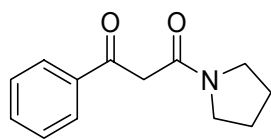
(2)

Name of the reaction: [   ]
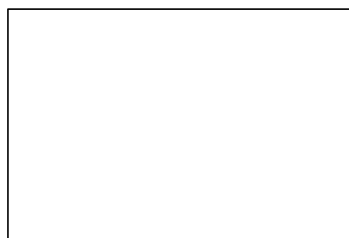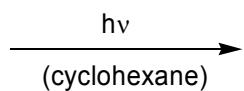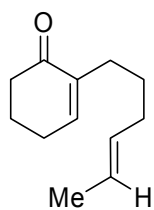
(2)

b)   Give the intermediate as well as the final product! (Hint: a hydrogen abstraction is involved)

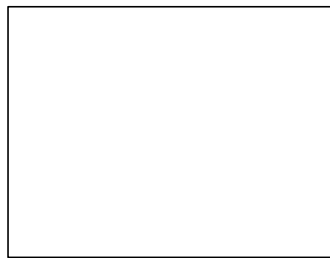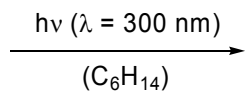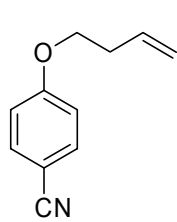hν (λ > 300 nm)

(toluene)

(6)

c)

hν

(cyclohexane)

(3)

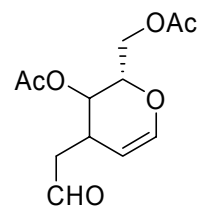Which rule governs product formation in c) ? [   ]

(2)

d)

hν (λ = 300 nm)
(C₆H₁₄) → $h\nu\ (\lambda = 300\ \text{nm})$ over (C_6H_{14})
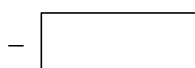
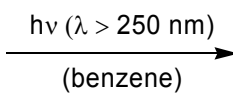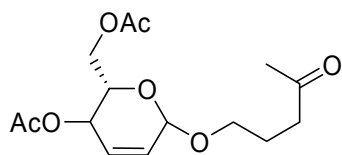(3)

Name of the reaction: [   ]   (2)

3. Explain the formation of the product in the following sequence by giving the photochemical intermediate. Hint: the second step is a Claisen rearrangement.
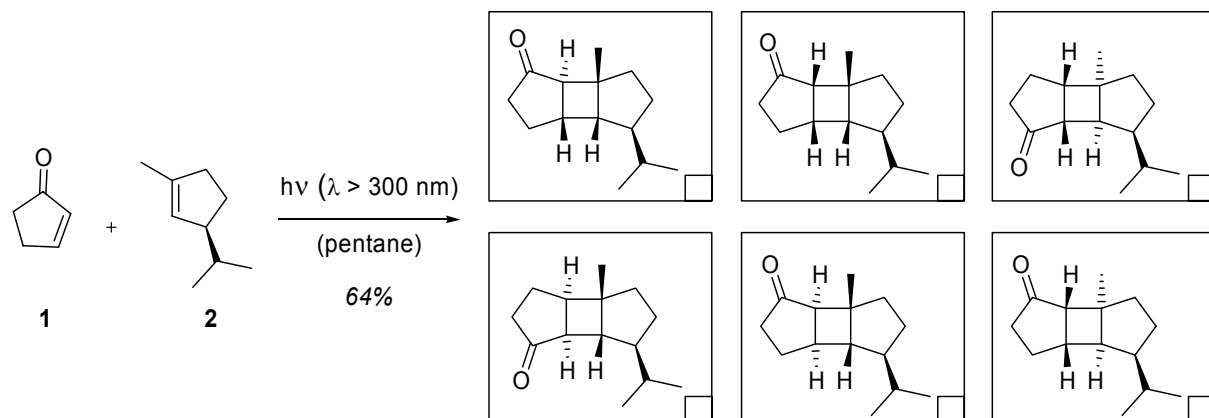
$h\nu\ (\lambda > 250\ \text{nm})$
(benzene)

−[   ]

ΔT

(4)

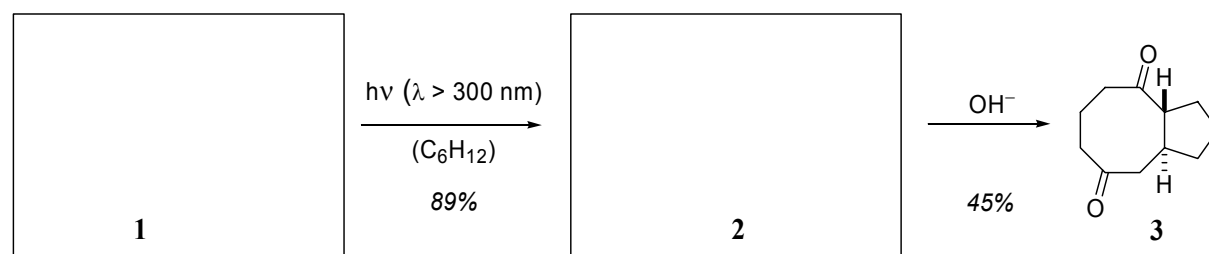Name of the photochemical reaction: [   ]   (2)

4.   Enone-alkene photocycloaddition

a)   In the [2+2]-photocycloaddition of cyclopentenone (**1**) with chiral cyclopentene **2**, the stereogenic center present in **2** is responsible for the *perfect* facial diastereoselectivity observed. Two regioisomers are formed in a ratio of 1:1. Select the two products you expect!
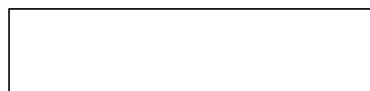

(4)

b)   1,5-Dione **3** is accessible via a well-known two-step sequence including an *intramolecular* [2+2]-photocycloaddition. Give a possible starting material **1** and the resulting photoproduct **2**. What is this two-step process called?
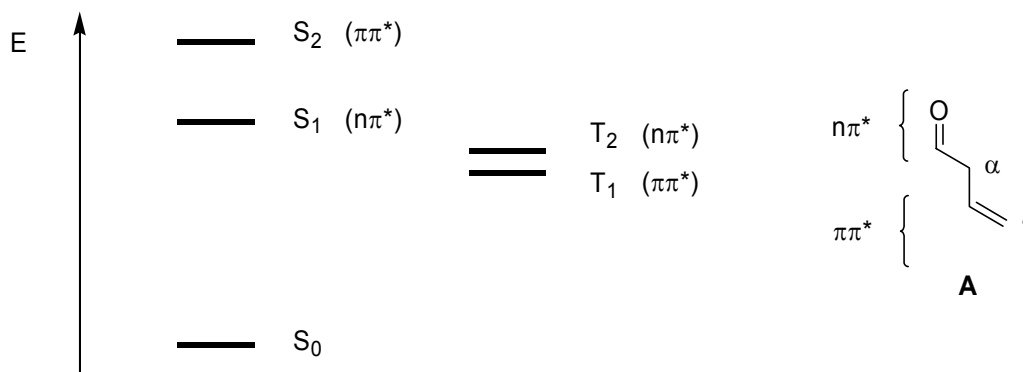

(6)

Name of the two-step sequence:

(2)

5. After photochemical excitation of β,γ-unsaturated compounds (**A**) two different mechanistic pathways are accessible: oxadi-π-methane rearrangement or 1,3 acyl shift. (The simplified MO scheme of β,γ-unsaturated compounds is depicted below and may help you to answer the following questions).

a) Which electronic state is first populated by direct irradiation of β,γ-unsaturated compounds? (2)

  □ S_1 □ S_2 □ T_1 □ T_2

b) From which electronic state does the oxa-di-π-methane rearrangement occur? (2)

  □ S_1 □ S_2 □ T_1 □ T_2

c) A possible side reaction is the 1,3 acyl shift. From which electronic state does this mechanistic pathway occur? (2)

  □ S_1 □ S_2 □ T_1 □ T_2

d) The oxadi-π-methane rearrangement can be used for the construction of diquinane skeletons. What does the starting material **1** leading to diquinanes **2** and **3** look like? (as a drawing help, its [2.2.2]bicyclooctane skeleton is already given!)

(4)
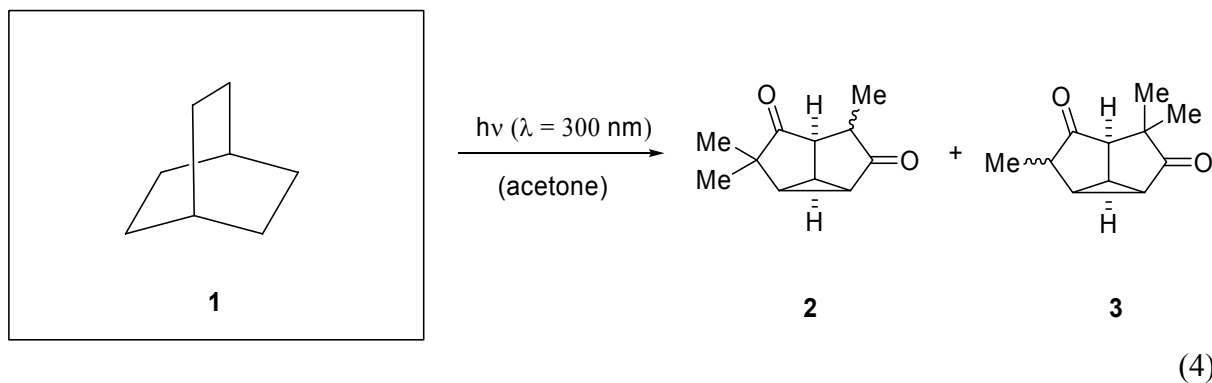
e) Explain the function of the solvent acetone in this reaction! (2)

6. For pericyclic reactions a general rule can be applied for the determination whether a reaction is thermally or photochemically allowed.

a) What is it called? [   ] (2)

b) Which equation belongs to the rule above?
(s = suprafacial, a = antarafacial, q,r = variables)

☐ $\Sigma\,(4q+2)_s + \Sigma\,(4r)_a$ = even (photochemically allowed)
uneven (thermally allowed)

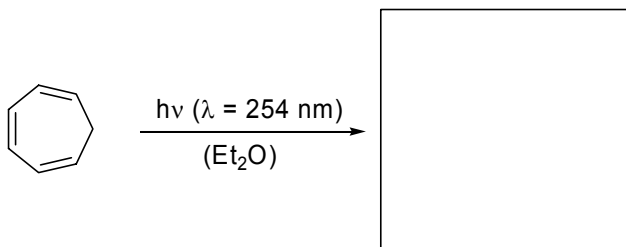☐ $\Sigma\,(4q+2)_a + \Sigma\,(4r)_s$ = even (thermally allowed)
uneven (photochemically allowed)

☐ $\Sigma\,(4q+2)_s + \Sigma\,(4r)_a$ = even (thermally allowed)
uneven (photochemically allowed)

☐ $\Sigma\,(4q+2)_a + \Sigma\,(4r)_s$ = even (photochemically allowed)
uneven (thermally allowed)

(2)

c) Fill in the product and tick the box, which belongs to the correct answer!

$$\xrightarrow[\text{(Et}_2\text{O)}]{h\nu\ (\lambda = 254\ \text{nm})}$$

(2)

This cyclisation is a ..

... 4π conrotatory ... ☐

... 6π conrotatory ... ☐

... 4π disrotatory ... ☐

... 6π disrotatory ... ☐

... process.

(2)

7. The substrate depicted below is *not* directly suited for a pericyclic ring-closure. Under irradiation only the *central* double bond is isomerised and then a photochemical 6π cyclisation takes place. The primary photoproduct can undergo a further photochemical cyclisation reaction. Fill in the missing structures!
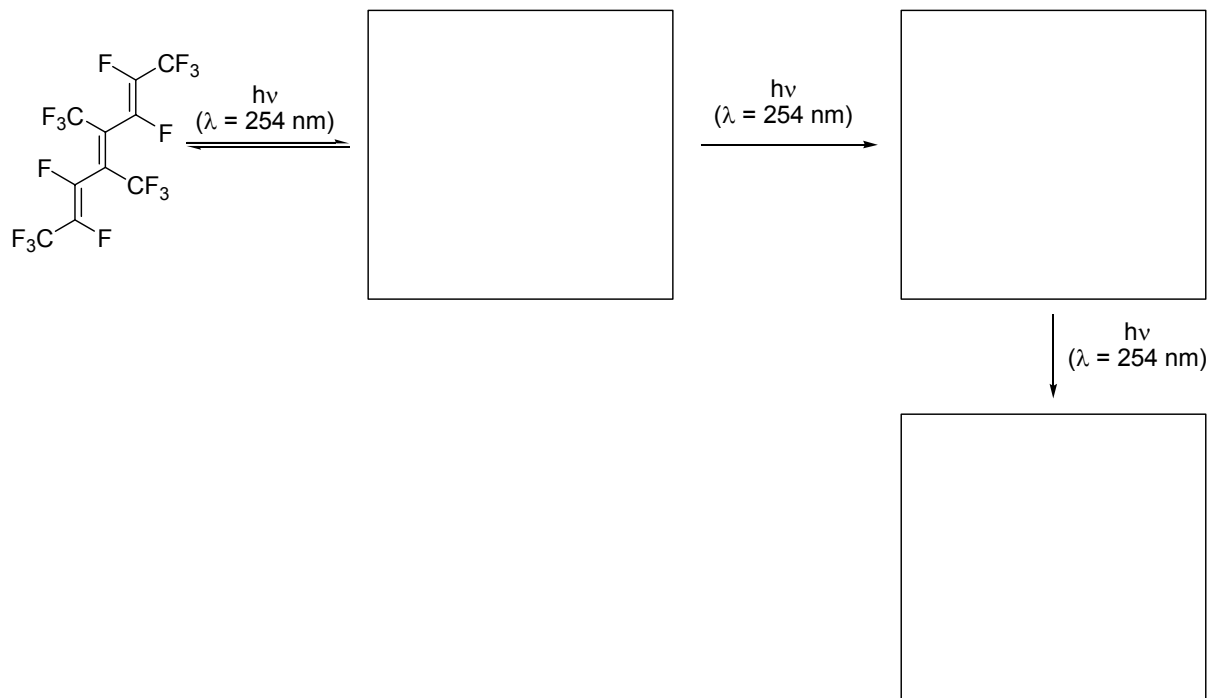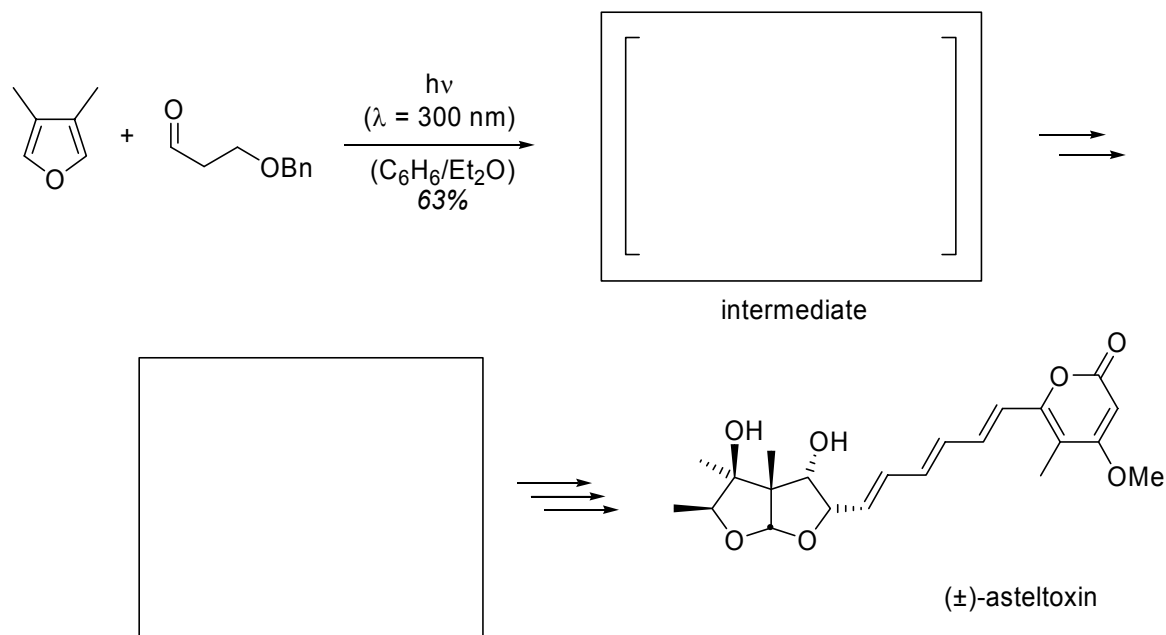

(8)

8. Discuss the mechanism of the following Paternò-Büchi reaction briefly and explain the regio- and stereoselectivity! What energy state does the intermediate have? Wich two processes are involved in the oxetane formation?
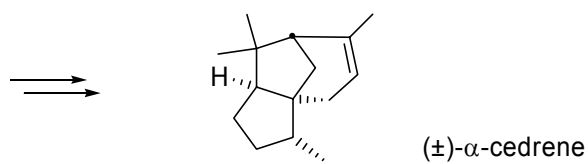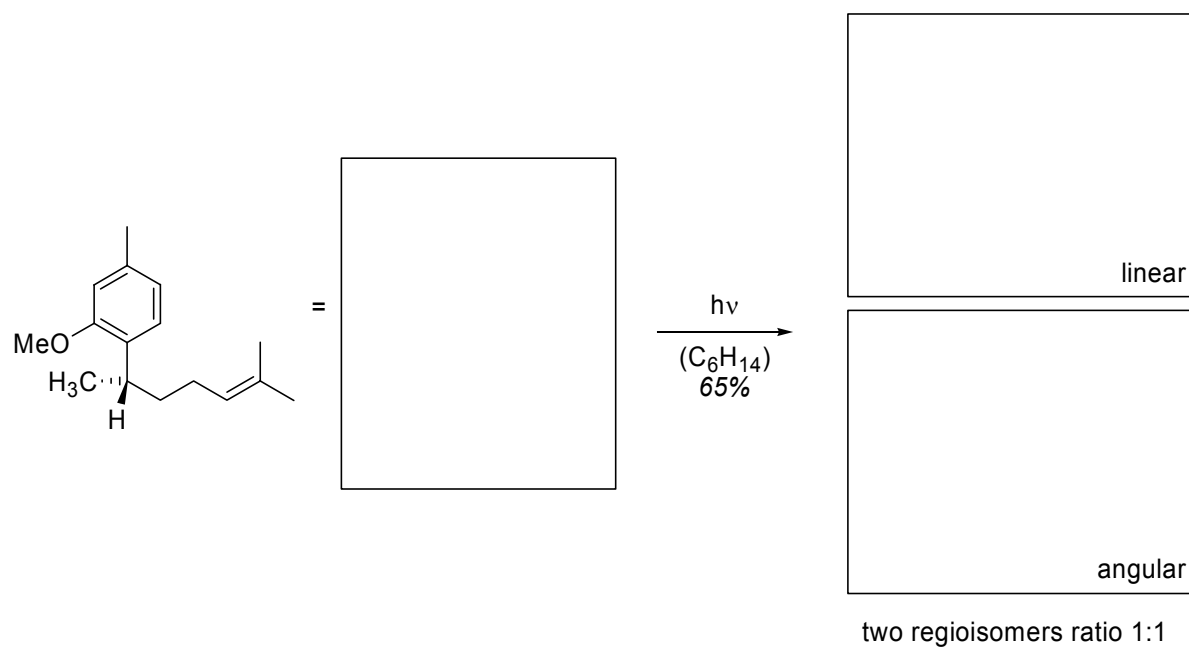
_____

_____

_____ (3)

intermediate

(±)-asteltoxin
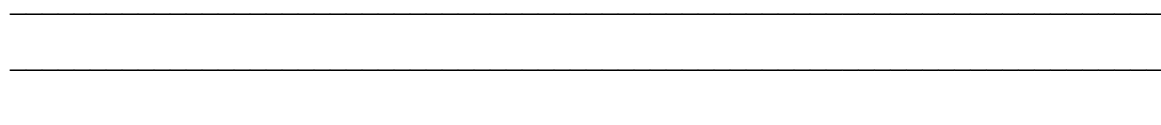
(5)

9. Give the expected photoproducts in this key step of the total synthesis of (±)-α-cedrene. Use the 1,3-allylic strain model in the starting material to predict the side from which the reaction occurs.

two regioisomers ratio 1:1

(±)-α-cedrene

(8)