II.12 Organic Photochemistry

Civil Services 2016–2026: **29** parts, **285** marks · IFoS 2016–2025: **32** parts, **220** marks

Syllabus. Photochemical reactions of simple organic compounds, excited and ground states, singlet and triplet states, Norrish Type I and Type II reactions.

Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	20	20	40	20	15	25	25	25	25	30	40
IFoS	25	25	5	35	25	25	20	20	20	20	

How to use this chapter. Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

2026

CSE 2026 · Q5(c) Photoenolisation of 2-methylbenzophenone [10 marks]

Explain why 2-methyl benzophenone undergoes rapid and reversible photo-enolisation reaction. Discuss the stereoisomerism of the photo-enol formed.

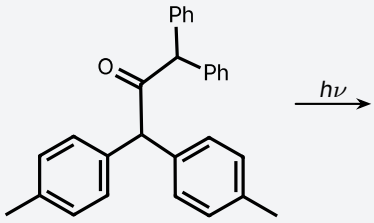
CSE 2026 · Q7(a) Stokes shift; why phosphorescence is slow [10 marks]

(i) What are the phenomena that result in the emission wavelength being longer than the excitation wavelength in photochemical reactions?

(ii) Why is phosphorescence slower than fluorescence? Explain.

CSE 2026 · Q7(b) Norrish type I products; spin state in Norrish type II [20 marks]

(i) Complete the following Norrish Type I reaction:



(ii) Do Norrish Type II reactions proceed through singlet state and/or triplet state? Justify your answer with two different examples.

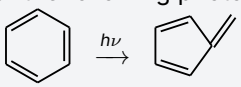
2025

CSE 2025 · Q5(c) 290 nm or 450 nm for a reaction through T_1? [10 marks]

A photochemical reaction takes place through T_1 state. S_0–S_1 and S_0–T_1 energy gaps correspond to 290 nm and 450 nm, respectively. To get an efficient photochemical reaction should we use light of 290 nm or 450 nm? Give your answer presenting the relevant Jablonski diagram.

CSE 2025 · Q6(c) Benzene to fulvene by light; Quantum yield of photobromination; Photolysis of 4,5-dimethylhexan-2-one; A, B and C from the mixed ketones [20 marks]

(i) Write the mechanism for the following photochemical transformation: 5



(ii) Photobromination of cinnamic acid was carried out by using light of wavelength 480 nm with a light intensity of $1{\cdot}5 \times 10^{-3}$ J-s^{-1}. An exposure of 10 minutes showed a decrease of 0·05 millimole of Br_2. Calculate the quantum yield assuming that 80% of radiation is absorbed by cinnamic acid. (Planck's constant $h = 6{\cdot}627 \times 10^{-34}$ J-s and velocity of light $c = 3 \times 10^8$ m-s^{-1}) 5

(iii) Predict the major and minor products for the following photoreaction. Give the logic: 5

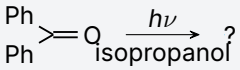
$$(CH_3)_2CH-CH(CH_3)-CH_2-CO-CH_3 \xrightarrow{h\nu} ?$$

(iv) Assign *A*, *B* and *C* in the following reaction: 5

$$Ph_2CH-CO-CHPh_2 + PhCH_2-CO-CH_2Ph \xrightarrow{hv} A + B + C \text{ (Major)} + CO$$

IFoS 2025 · Q5(c) Photoreduction of benzophenone [5 marks]

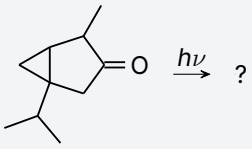
Complete the following reaction and identify the electronic states involved in the reaction by showing the proper mechanism for formation of the product(s).



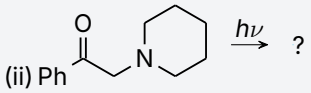
IFoS 2025 · Q6(a) Photodecarbonylation of thujone; Photochemistry of an amino ketone; Di-pi-methane rearrangement [15 marks]

Write the products formed in the following reactions and give suitable mechanism/explanation. 5 × 3 = 15

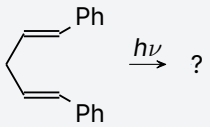
(i)



(ii)



(iii)



2024

CSE 2024 · Q5(c) α-Keto esters irradiated in alcohols [10 marks]

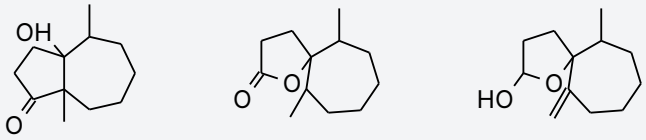
Write down the product(s) in the following reactions:

(i) $C_6H_5COCOOC_2H_5 + CH_3CHOHC_2H_5 \xrightarrow{hv}$

(ii) $CH_3COCOOC_2H_5 + CH_3OH \xrightarrow{hv}$

CSE 2024 · Q6(b) Photochemistry of a β-hydroxy bicyclic ketone [15 marks]

Write down the mechanism for the formation of compounds *B* and *C* from compound *A* on photoirradiation:



A *B* *C*

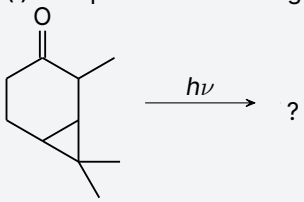
IFoS 2024 · Q5(e) Norrish-II cleavage of a branched aldehyde [5 marks]

Indicating the major/minor product(s), complete the following reaction:

$$CH_3CH_2-CH(CH_3)-CH_2-CHO \xrightarrow{h\nu} \ ?$$

IFoS 2024 · Q6(c) Photorearrangement of 4-caranone; Substituent effects on Norrish-II reaction [15 marks]

(i) Complete the following photochemical reaction giving the most probable mechanism: 10



(ii) Arrange the following compounds in order of their decreasing Norrish type II potential. Give the proper reason for the order you have given: 5

4-X$-C_6H_4-COCH_2CH_2CH_3$ with X = Cl (I), CH_3O (II), CF_3 (III), CH_3 (IV), HO (V).

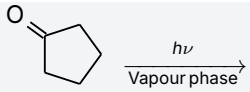
2023

CSE 2023 · Q5(e) Photolysis of acetone: vapour phase and room temperature [10 marks]

(i) $CH_3-CO-CH_3 \xrightarrow[\text{Vapour phase}]{h\nu}$ (ii) $CH_3-CO-CH_3 \xrightarrow[\text{Room temperature}]{h\nu}$

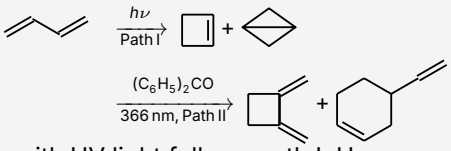
Identify the products in the above reactions with plausible mechanism.

CSE 2023 · Q7(b) Vapour-phase photolysis of cyclopentanone; Direct and benzophenone-sensitised photolysis of 1,3-butadiene [15 marks]

(i) 

Identify all the possible products in the above reaction showing the sequential pathways of their formation: *10*

(ii)



1,3-Butadiene solution on irradiation with UV light follows path I. However, irradiating 1,3-butadiene in the presence of benzophenone at 366 nm follows path II. Give a suitable explanation. *5*

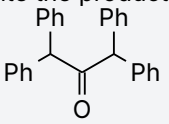
IFoS 2023 · Q5(c) Photocyclization of isomesityl oxide [5 marks]

Giving the mechanism complete the following reaction:

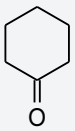
$$CH_3-C(=O)-CH_2-C(CH_3)=CH_2 \xrightarrow[\text{hexane}]{hv} \ ?$$

IFoS 2023 · Q6(b) Photochemical alpha cleavage [10 marks]

Write the products in the following reactions with their mechanisms:

(i) 

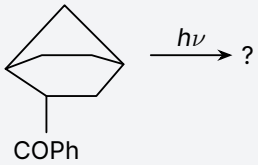
$\xrightarrow{h\nu}$?

(ii) 

$\xrightarrow[\text{ROH}]{h\nu}$?

IFoS 2023 · Q7(a) Photochemistry of a rigid aryl ketone [5 marks]

Write the product(s) in the following photochemical reaction:



2022

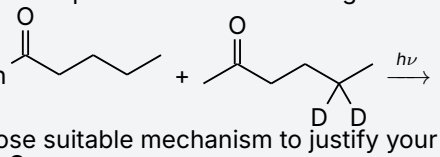
CSE 2022 · Q5(b) Photolysis of 2-methylcyclohexanone in solution [10 marks]

Write down the products obtained after photolysis of 2-methylcyclohexanone in solution phase. Explain the formation of products.

CSE 2022 · Q6(a) Photolysis of a mixture of valerophenone and 5,5-dideuteriohexan-2-one; Photolysis of 4,5-dimethylheptan-2-one [15 marks]

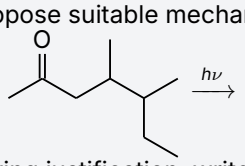
Predict the products in the following reactions:

(i)



Propose suitable mechanism to justify your answer.

(ii)



Giving justification, write the major and minor product(s). Comment upon the chirality of recovered reactant (if any).

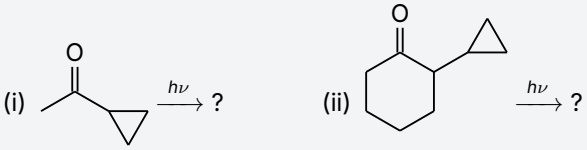
IFoS 2022 · Q6(d) Norrish-II hydrogen abstraction [5 marks]

The compound *A* undergoes H-abstraction under photochemical conditions. Give the major/minor products and their mechanism of formation along with proper explanation:

$$\underset{A}{R{-}C(=O){-}CH_2{-}CHR{-}CHPh_2}$$

IFoS 2022 · Q6(e) Photolysis of methyl cyclopropyl ketone; Three-carbon photochemical ring expansion [15 marks]

Giving their plausible mechanisms, complete the following reactions:

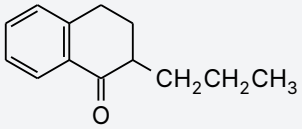


2021

CSE 2021 · Q5(d) Ease of Norrish type II hydrogen abstraction in two groups of ketones [10 marks]

(i) $Ph{-}CO{-}CH_2CH_2CH_3$ (I) $Ph{-}CO{-}CH_2CH_2CH_2CH_3$ (II) $Ph{-}CO{-}CH_2CH_2{-}CH(CH_3)_2$ (III)

(ii) $Ph{-}CO{-}CH_2CH_2CH_3$ (I)

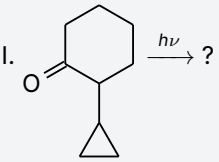
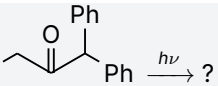


(II) 2-benzoylnorbornane (III)

Arrange the compounds in the above groups for ease of Norrish type-II H-abstraction in decreasing order

giving the plausible explanations.

CSE 2021 · Q6(c) Photolysis of 2-cyclopropylcyclohexanone and of 1,1,3-triphenylpropan-2-one [15 marks]

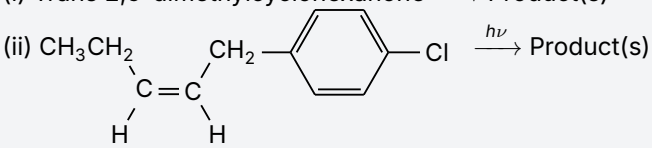
I.  II. 

Complete the above reactions by giving the suitable mechanisms.

IFoS 2021 · Q1(g) Photochemical cleavage and alkene isomerization [5 marks]

Complete the following reactions and indicate the intermediates involved in their formation (if any):

(i) Trans 2,6-dimethylcyclohexanone $\xrightarrow{h\nu}$ Product(s)

(ii)  Product(s)

IFoS 2021 · Q5(h) Photoproducts of ketone excitation [5 marks]

Identify the following photo products A to F in the given reactions:

(i) 2-pentanone $\xrightarrow{h\nu}$ A + B + C and 2-pentanone $\xrightarrow{h\nu}$ A + D + E

(ii) Benzophenone + Isobutylene $\xrightarrow{h\nu}$ F (major) products

IFoS 2021 · Q7(e) State-dependent diene chemistry and photo-Fries rearrangement [5 marks]

(i) Complete the following photochemical reaction and indicate S_1 and T_1 state products:

$CH_2=CH-CH=CH_2 \xrightarrow{h\nu}$?

(ii) Complete the following reactions: p-cresol $\xrightarrow[\text{Aq NaOH}]{\text{PhCOCl}}$? $\xrightarrow{h\nu}$?

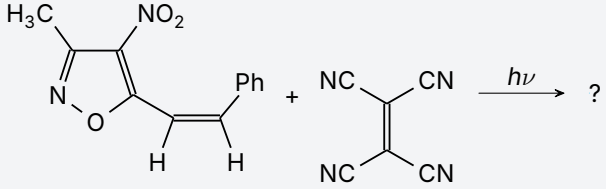
IFoS 2021 · Q8(c)(ii) Cyclopentenone photocycloadditions [5 marks]

(ii) Complete the following reaction: 5

cyclopent-2-en-1-one $\xrightarrow{h\nu}$ A + B $\xrightarrow[\text{MeOH}]{\text{Excess } NaBH_4}$ C + D; cyclopent-2-en-1-one + cyclopentene $\xrightarrow{h\nu}$ E

IFoS 2021 · Q8(d) Photochemical cycloaddition and cleavage [5 marks]

Complete the following reactions:

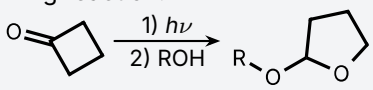
(i) 

(ii) $CH_3-CO-CH_2-CH_2-CH_2-CH_3 \xrightarrow{h\nu}$? + ?

2020

CSE 2020 · Q6(a) Photochemical ring expansion of cyclobutanone (Norrish type I) [15 marks]

Describe the steps involved in the following reaction:



IFoS 2020 · Q5(d) Why Norrish type I is unimportant for diaryl ketones [5 marks]

The Norrish type-I process is not important for the photolysis of diaryl ketones. Suggest a reason.

IFoS 2020 · Q7(b) Mechanism of the photo-Claisen rearrangement [10 marks]

Write down the mechanism of the Claisen rearrangement on photolysis.

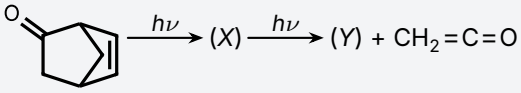
IFoS 2020 · Q8(d) Photo-Fries rearrangement of aryl acetates [10 marks]

How does the aryl acetate undergo photochemical rearrangement? Give the products and mechanism.

2019

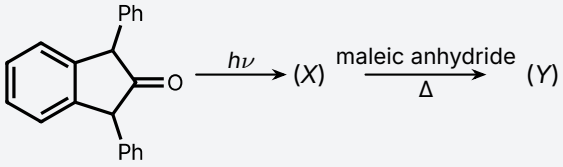
CSE 2019 · Q5(c) Photochemistry of norbornenone: 1,3-acyl shift and ketene loss [10 marks]

Identify (*X*) and (*Y*) in the following reaction. Name the type of photochemical reaction involved:



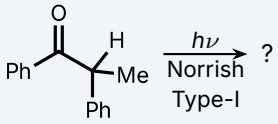
CSE 2019 · Q8(c)(ii) Photodecarbonylation; trapping the o-xylylene [10 marks]

Identify (*X*) and (*Y*) in the following reaction:



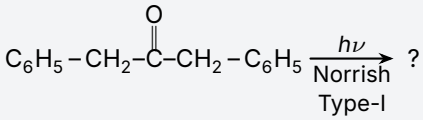
IFoS 2019 · Q5(d) Racemisation of a chiral ketone by Norrish type I photolysis [5 marks]

The following ketone-containing chiral centre undergoes racemization on photolysis. Write down the mechanism:



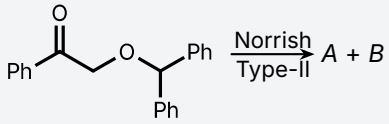
IFoS 2019 · Q6(b) Norrish type I of dibenzyl ketone [10 marks]

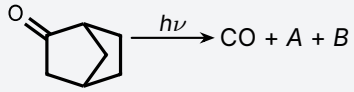
Complete the following reaction and give its mechanism:



IFoS 2019 · Q6(c) Norrish type II of a benzyl ether ketone; photolysis of norcamphor [10 marks]

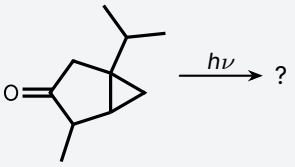
Identify the products *A* and *B* of the following reactions: 5×2=10

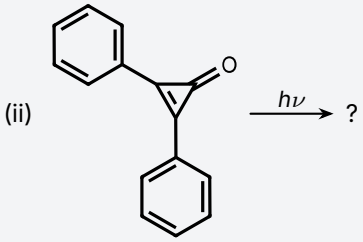
(i) 

(ii) 

IFoS 2019 · Q7(c) Photochemistry of a cyclohexenone and of diphenylcyclopropenone [10 marks]

Identify the product(s) in the following transformations: 5×2=10

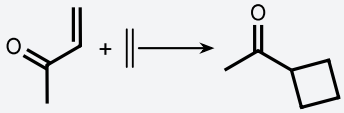
(i) 

(ii) 

2018

CSE 2018 · Q1(e) Photochemical [2+2] cycloaddition of methyl vinyl ketone and ethene [10 marks]

Explain the conditions for the following reaction, very briefly describe the steps involved and comment if the reaction is reversible :



CSE 2018 · Q8(a) Fluorescence and phosphorescence [10 marks]

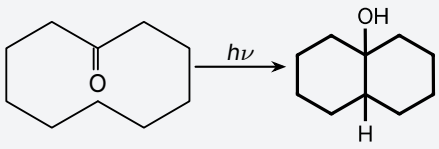
Distinguish between fluorescence emission and phosphorescence emission giving suitable examples.

CSE 2018 · Q8(b) Photostationary state of cis- and trans-stilbene [10 marks]

The direct irradiation of either *cis*- or *trans*-stilbene at 313 nm results in the formation of a mixture of 93% *cis*- and 7% *trans*-olefin, no matter how long, within reason, the irradiation is continued. Give a suitable explanation for that.

CSE 2018 · Q8(c) Photocyclisation of cyclodecanone to 9-decalol [10 marks]

Classify the following reaction and propose a suitable mechanism for it :



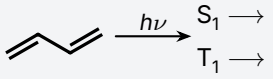
IFoS 2018 · Q1(h) Photocycloaddition of tetrafluoroethene with 1-buten-3-yne [5 marks]

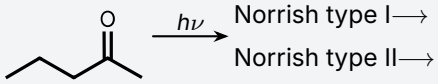
When irradiated, tetrafluoroethene undergoes a cycloaddition reaction with 1-buten-3-yne to yield two products in almost equal amounts. What are the structures of these products?

2017

CSE 2017 · Q6(c) Photochemistry of butadiene (S_1, T_1) and of pentan-2-one (Norrish I, II) [10 marks]

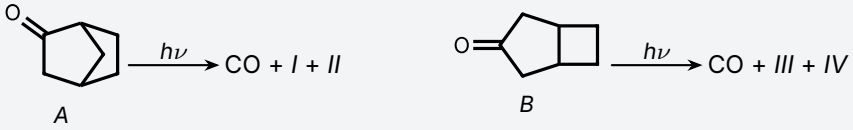
Write the products for the following reactions.

(i) 

(ii) 

CSE 2017 · Q6(d) Photodecarbonylation of norcamphor and bicyclo[3.2.0]heptan-3-one [10 marks]

Compounds *A* and *B* undergo photodecarbonylation resulting in the formation of *I* and *II* (From *A*) and *III* and *IV* (From *B*). Give their structures.

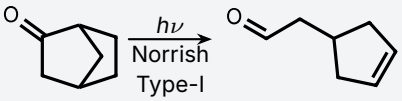


IFoS 2017 · Q1(c) Norrish type II cleavage [5 marks]

With a suitable example show 'Norrish Type-II' cleavage reaction.

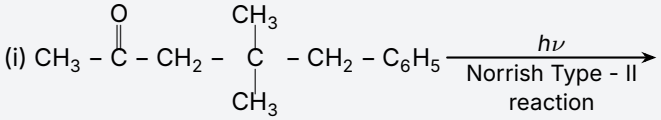
IFoS 2017 · Q4(b) Norrish type I photolysis of norcamphor [10 marks]

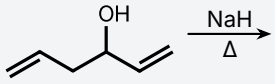
Write down the mechanism of the following reaction:



IFoS 2017 · Q8(c) Norrish type II of a phenyl ketone; anionic oxy-Cope [10 marks]

Complete the given reactions and give its mechanism:

(i) 
 5

(ii) 
 5

2016

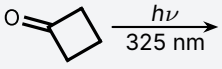
CSE 2016 · Q6(a) Which ketone undergoes the Norrish type II reaction [10 marks]

Among the following, identify the compound which can undergo Norrish type II reaction. Write the mechanism:

(i) $CH_3COCH_2CH_3$ (ii) $CH_3COCH_2CH_2CH(CH_3)_2$ (iii) $CH_3COCH_2CH_2C(CH_3)_3$ (iv) $C_6H_5COCH_2CH_3$

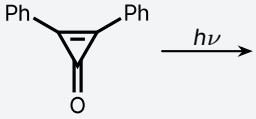
CSE 2016 · Q6(b) Photolysis of cyclobutanone [10 marks]

Write the intermediate and possible products for the following reaction:



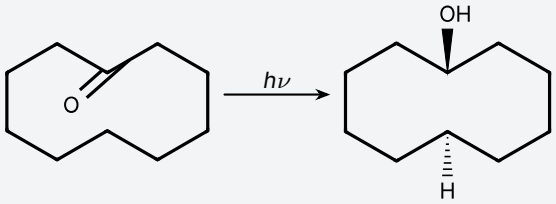
IFoS 2016 · Q5(d) Photodecarbonylation of diphenylcyclopropenone [5 marks]

Formulate the product(s) and give the mechanism for the following reaction :



IFoS 2016 · Q8(a)(ii) Photocyclisation of cyclodecanone to 9-decalol [10 marks]

Complete the reactions and give appropriate mechanisms of the following :



IFoS 2016 · Q8(a)(iii) Norrish type II reaction of 2-benzoylnorbornane [10 marks]

Complete the reactions and give appropriate mechanisms of the following :

