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ORGANIC

CH 03

Baeyer–Villiger & Diels–Alder

03

Peracid migration rules, stereospecificity, endo/exo selectivity, electron-demand criteria and reagent cluster mapping.

WHAT YOU WILL BE ABLE TO DO

- Place the new oxygen in any Baeyer–Villiger product in seconds using the migration order
- Draw the Criegee mechanism and the concerted Diels–Alder with correct arrows
- Predict cis/trans, endo/exo and ortho/para outcomes of Diels–Alder reactions
- Group reagents like mCPBA and maleic anhydride by function across chapters

INSIDE

A Baeyer–Villiger: the reaction
B The Criegee mechanism
C Peracid migration rules
D Diels–Alder: the [4+2]
E Stereospecificity & endo/exo
F Electron demand & regiochemistry
G Reagent cluster mapping
H Traps · MCQs · revision

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HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

Baeyer–Villiger oxidation: the reaction

A

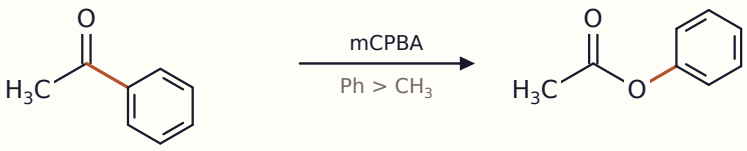
A peracid slips one oxygen atom in between the carbonyl carbon and one of its neighbours. Ketones become esters; cyclic ketones become lactones with one more ring atom.

IN ONE LINE Ketone + peracid ⟶ ester. The new O goes next to the better-migrating group.

$$R\text{-}CO\text{-}R' + R''CO_3H \longrightarrow R\text{-}CO\text{-}O\text{-}R' + R''CO_2H$$

Common peracids: mCPBA (meta-chloroperbenzoic acid), CF_3CO_3H, CH_3CO_3H, perbenzoic acid; also H_2O_2 with a Lewis acid.

THE CLASSIC EXAMPLE



ACETOPHENONE PHENYL ACETATE

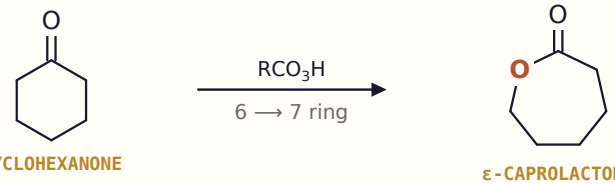
O inserted on the phenyl side

Acetophenone ⟶ phenyl acetate. Phenyl migrates in preference to methyl, so O lands on the phenyl side.

THINK OF IT LIKE THIS

Imagine the carbonyl carbon holding two hands — one on each group. The peracid offers an oxygen; the group that is better at handling positive charge lets go of carbon and grabs that oxygen. Methyl is the worst at this, so it almost never moves.

CYCLIC KETONES GIVE LACTONES



CYCLOHEXANONE ε-CAPROLACTONE

ring O sits next to C=O

Cyclohexanone ⟶ ε-caprolactone. The ring grows by one atom: the inserted oxygen.

SECTION B

The Criegee mechanism

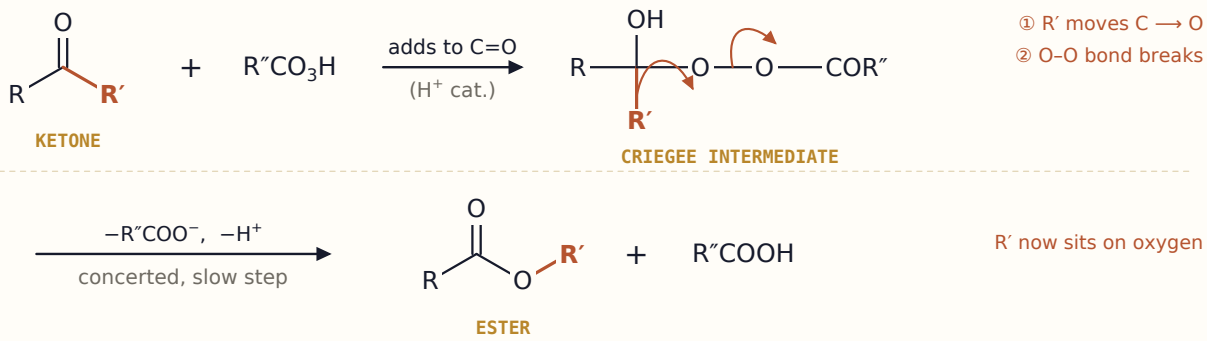
B

The reaction has two stages: the peracid adds to C=O, then a group migrates in one concerted step. The migration is the slow step and it decides the product.

IN ONE LINE

Peracid adds ⟶ Criegee intermediate ⟶ group moves C ⟶ O as carboxylate leaves ⟶ ester.

BAEYER–VILLIGER MECHANISM



Red arrows: R′ shifts to the nearer oxygen while the weak O–O bond breaks. Then OH loses H+ to give C=O.

01 **Activate C=O.** Acid (or the peracid's own O–H) makes the carbonyl carbon more electrophilic.

02 **Peracid adds.** Its terminal oxygen attacks C=O, giving a tetrahedral peroxy-hemiketal — the **Criegee intermediate**, $R_2C(OH)–O–O–COR''$.

03 **Concerted migration (slow).** One group moves from carbon to the nearer peroxide oxygen *as* the O–O bond breaks and carboxylate leaves. The migrating group must be **antiperiplanar** to the O–O bond.

04 **Lose H^+** from the OH ⟶ the ester (or lactone).

KEY IDEA

Retention of configuration: a chiral migrating carbon keeps its configuration in the product.

Better leaving group = faster reaction. Peracid strength follows the acidity of the parent acid: CF_3CO_3H > p-$NO_2C_6H_4CO_3H$ > mCPBA > CH_3CO_3H > H_2O_2.

CHECK YOURSELF

C1 Name the tetrahedral intermediate in Baeyer–Villiger oxidation.

C2 Which bond breaks as the group migrates?

Answers at the end of the chapter.

SECTION C

Peracid migration rules

C

The migrating group carries partial positive charge in the transition state, so groups that stabilise positive charge move best.

IN ONE LINE H > 3° > 2° ≈ phenyl > 1° > methyl. Methyl ketones always give acetates.

$$\text{H} > \text{3° alkyl} > \text{cyclohexyl} \approx \text{2° alkyl} \approx \text{benzyl} \approx \text{phenyl} > \text{1° alkyl} > CH_3$$

$$\text{p-}CH_3O\text{-}C_6H_4 > C_6H_5 > \text{p-}NO_2\text{-}C_6H_4$$

Electron-rich groups migrate faster; electron-poor aryl groups slower.

FOUR-SECOND METHOD

1. Name the two groups on C=O.
2. Rank them with the order above.
3. Insert O between C=O and the **higher-ranked** group.
4. Sanity check: a methyl ketone always gives an **acetate**, $CH_3CO–O–R$.

Ketone	Group that migrates	Product
Acetophenone, Ph–CO–CH_3	Phenyl	Phenyl acetate, $CH_3CO–O–Ph$
Pinacolone, $(CH_3)_3C–CO–CH_3$	tert-Butyl	tert-Butyl acetate
3-Methylbutan-2-one, $(CH_3)_2CH–CO–CH_3$	Isopropyl	Isopropyl acetate
Cyclopentanone	Ring CH_2	δ-Valerolactone (6-membered)
2-Methylcyclohexanone	More substituted ring C	7-Methyloxepan-2-one (O next to $CH–CH_3$)
Benzaldehyde, Ph–CHO	H	Benzoic acid

SOLVED EXAMPLE 01 RING + REGIOSELECTIVITY

Predict the product of 2-methylcyclohexanone with mCPBA.

SOLUTION

1. The two groups on C=O are both ring carbons: C2 is 3° (CH bonded to C1, C3 and CH_3); C6 is 2° (a ring CH_2).
2. 3° outranks 2°, so C2 migrates.
3. O is inserted between C=O and C2. Ring grows from 6 to 7 atoms.

ANSWER 7-Methyloxepan-2-one — the lactone O sits next to the $CH(CH_3)$ carbon.

SOLVED EXAMPLE 02 3° VS METHYL

Pinacolone, $(CH_3)_3C–CO–CH_3$, is treated with CF_3CO_3H. Product?

SOLUTION

1. Groups: tert-butyl (3°) and methyl.
2. 3° migrates; methyl stays on the carbonyl.
3. $CH_3–CO–O–C(CH_3)_3$.

ANSWER tert-Butyl acetate.

EXAM TRAP

- **Aldehydes:** H migrates ⟶ carboxylic acid. But electron-rich aryl aldehydes (o/p-OH, p-OMe) can give aryl formates ⟶ phenols (the Dakin pathway).
- **Alkenes compete:** mCPBA epoxidises isolated C=C quickly. If a molecule has both, epoxidation usually wins unless the alkene is electron-poor.
- **Lactone ring size** is always one more than the ketone ring.

SECTION D

Diels–Alder: the [4+2] cycloaddition

D

A conjugated diene and an alkene (the dienophile) join in a single step to make a six-membered ring. No intermediate, no ions, no radicals.

IN ONE LINE 4 π-carbons + 2 π-carbons ⟶ cyclohexene, in one concerted step.

THE DIELS–ALDER REACTION



DIENE (s-cis) DIENOPHILE CYCLOHEXENE

3 π bonds broken
2 σ + 1 π bond formed
6 electrons in a ring

Three arrows move together: three π bonds break, two new σ bonds and one new π bond form.

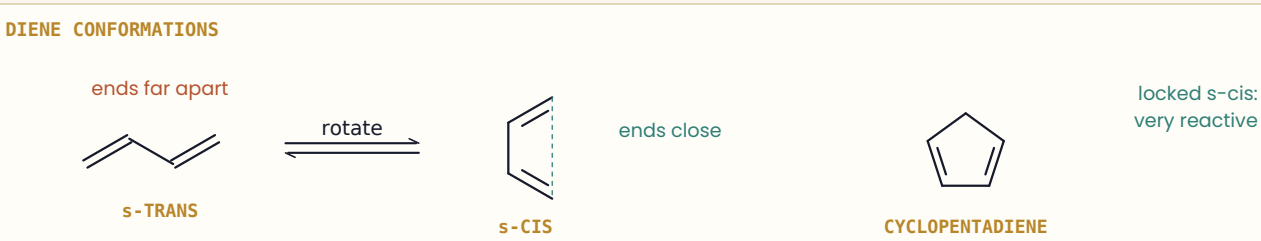
Buta-1,3-diene + ethene ⟶ cyclohexene

Buta-1,3-diene + maleic anhydride ⟶ cis-1,2,3,6-tetrahydrophthalic anhydride

Ethene is a poor dienophile and needs high temperature; maleic anhydride reacts readily.

Feature	What it means in questions
Concerted, one transition state	No carbocation, so no rearranged products
Suprafacial on both partners	Cis/trans relationships are carried straight into the ring
Thermally allowed [4s+2s]	6 π electrons in a cyclic array (aromatic TS). [2+2] needs light
Reversible at high T	Retro-Diels–Alder: dicyclopentadiene ⟶ cyclopentadiene (~170 °C)
Needs s-cis diene	Both ends of the diene must face the dienophile

Which dienes react? The s-cis requirement



Only the s-cis form can bond at both ends. Cyclopentadiene is locked s-cis, so it is extremely reactive.

- **Cyclopentadiene** — locked s-cis, so reactive that it dimerises at room temperature.
- **(E)-1,3-Pentadiene** reacts well; **(Z)-1,3-pentadiene** is slow — its cis methyl clashes in the s-cis form.
- **Not dienes:** non-conjugated dienes (1,4-pentadiene), dienes locked s-trans, and benzene (aromatic).
- **Furan** reacts but reversibly; **anthracene** reacts across C-9 and C-10 (middle ring).

CHECK YOURSELF

C3 Why is (Z)-penta-1,3-diene less reactive than its (E) isomer?

C4 How many new σ bonds form in a Diels–Alder reaction?

Answers at the end of the chapter.

SECTION E

Stereospecificity and endo/exo selectivity

E

Two separate questions. Stereospecificity is about cis/trans relationships. Endo/exo is about which way a substituent points in a bicyclic product.

IN ONE LINE Cis stays cis, trans stays trans. With cyclic dienes, endo forms faster; exo is more stable.

Stereospecificity: the cis principle

Dienophile or diene	In the product
cis dienophile (dimethyl maleate, maleic anhydride)	Substituents cis on the ring
trans dienophile (dimethyl fumarate)	Substituents trans on the ring
(E,E)-1,4-disubstituted diene	The two 'outside' groups end up cis to each other

SOLVED EXAMPLE 03 STEREOSPECIFICITY

Buta-1,3-diene reacts with dimethyl fumarate. Are the two ester groups cis or trans in the product?

SOLUTION

1. Dimethyl fumarate is the trans isomer (E).
2. Diels–Alder is suprafacial — the dienophile's geometry is kept.
3. So the esters end up trans on adjacent ring carbons.

ANSWER Trans (a racemic pair of trans-diesters).

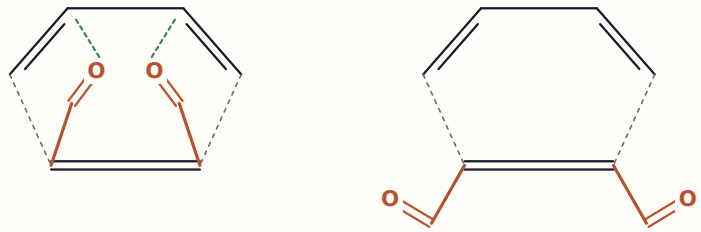
Endo rule: kinetic vs thermodynamic

With a cyclic diene such as cyclopentadiene, the dienophile's electron-withdrawing group can point **under** the diene as the bonds form (endo) or **away** from it (exo).

	Endo	Exo
Where the EWG points	Toward the diene's π system	Away from the diene
Rate	Faster — **kinetic** product	Slower
Stability	Less stable (more crowded)	More stable — **thermodynamic** product
Reason	Secondary orbital overlap between EWG π and diene C2/C3	Less steric repulsion
Favoured by	Low temperature, Lewis acid catalysts	High temperature, long times (reversible cases)

SHARE FREELY · DO NOT SELL

ENDO VS EXO APPROACH



ENDO · KINETIC
C=O tucked under the diene

EXO · THERMODYNAMIC
C=O points away from the diene

teal dashes = secondary orbital overlap (endo only)

grey dashes = the two new σ bonds forming

Endo: the C=O groups sit under the diene and overlap with C2/C3. Exo: they point away.

KEY IDEA

Cyclopentadiene + maleic anhydride ⟶ **endo** adduct (kinetic; the textbook example).

Furan + maleic anhydride ⟶ **exo** adduct isolated: the reaction is reversible, so it ends at the thermodynamic product.

SECTION F

Electron demand and regiochemistry

F

Fast Diels–Alder reactions pair an electron-rich partner with an electron-poor one. That pairing also tells you which way round an unsymmetrical reaction goes.

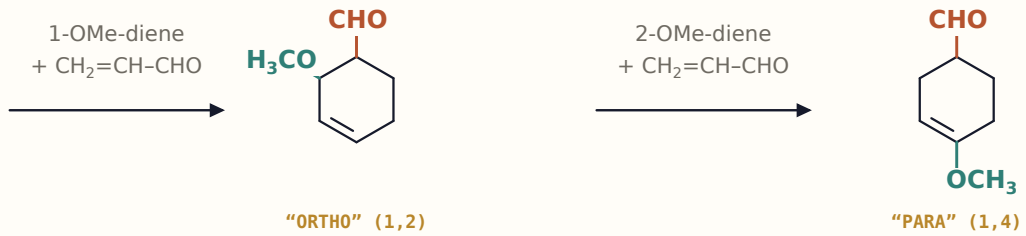
IN ONE LINE

Normal demand: rich diene + poor dienophile. 1-substituted diene ⟶ 'ortho'; 2-substituted ⟶ 'para'.

Type	Diene	Dienophile	Key orbital interaction
Normal demand	Electron-rich (–OR, $–NR_2$, alkyl)	Electron-poor (–CHO, –COR, –COOR, –CN, $–NO_2$)	HOMO(diene) – LUMO(dienophile)
Inverse demand	Electron-poor (e.g. tetrazines, EWG-dienes)	Electron-rich (enol ethers, enamines)	LUMO(diene) – HOMO(dienophile)

Dienophile reactivity: $(NC)_2C=C(CN)_2$ > maleic anhydride > acrolein ≈ acrylate > ethene

THE ORTHO/PARA RULE



"ORTHO" (1,2) "PARA" (1,4)

Donor at diene C1 ⟶ substituents end up 1,2 ('ortho'). Donor at diene C2 ⟶ 1,4 ('para'). Never 'meta'.

WHY IT HAPPENS

Draw the resonance form of the donor-substituted diene: the negative charge sits on the carbon that becomes bonded to the β-carbon of the dienophile (the electrophilic end). Matching these two ends gives ortho for 1-substituted and para for 2-substituted dienes.

SOLVED EXAMPLE 04 REGIOCHEMISTRY

2-Methylbuta-1,3-diene (isoprene) reacts with methyl acrylate. Which regioisomer is major?

SOLUTION

1. Methyl is a weak donor at diene C2 ⟶ use the 'para' rule.
2. The ester carbon and the methyl-bearing carbon end up 1,4 on the cyclohexene ring.

ANSWER The 'para' (1,4) product: methyl 4-methylcyclohex-3-ene-1-carboxylate.

SECTION G

Reagent cluster mapping

G

Revise reagents by what they do, not by chapter. One card per reagent covers several reactions at once.

IN ONE LINE	mCPBA, H_2O_2/NaOH, maleic anhydride and Lewis acids each turn up in several chapters — learn them once.

Reagent	On C=C	On C=O	Also
mCPBA (peracid)	Epoxide (syn addition)	Baeyer–Villiger ester/lactone	3° amine ⟶ N-oxide
CF_3CO_3H	Epoxide	BV of sluggish ketones	Strongest common peracid
H_2O_2 / NaOH	Epoxidises enones (nucleophilic)	Dakin: o/p-HO-ArCHO ⟶ phenol	Oxidation step of hydroboration
Maleic anhydride	Dienophile in Diels–Alder	—	Test for an s-cis conjugated diene
Cyclopentadiene	Most reactive common diene	—	Stored as dimer; cracked by retro-DA
Lewis acid ($AlCl_3$, BF_3)	Speeds DA; raises endo- and regio-selectivity	Activates C=O	Friedel–Crafts catalyst

Cluster: a group moves to…	Members
…oxygen	Baeyer–Villiger, Dakin, cumene hydroperoxide ⟶ phenol
…nitrogen	Beckmann, Hofmann, Curtius, Lossen, Schmidt (Chapter 02)
…carbon (C^+)	Pinacol, Wagner–Meerwein (Chapter 02)

SECTION H

Exam trap gallery

H

Cover the right column; check you would have caught each one.

✗ TRAP 01 · WHAT STUDENTS WRITE

Acetophenone + mCPBA ⟶ methyl benzoate.

✓ WHAT IS ACTUALLY CORRECT

Gives **phenyl acetate**, $CH_3CO–O–Ph$.

WHY Phenyl migrates, not methyl. Methyl is always last.

✗ TRAP 02 · WHAT STUDENTS WRITE

Cyclohexanone + peracid ⟶ 6-membered lactone.

✓ WHAT IS ACTUALLY CORRECT

Gives a **7-membered** lactone (ε-caprolactone).

WHY The inserted O adds one ring atom.

✗ TRAP 03 · WHAT STUDENTS WRITE

2-Methylcyclohexanone: O goes next to the CH_2 side.

✓ WHAT IS ACTUALLY CORRECT

O goes next to the **more substituted** $CH(CH_3)$ carbon.

WHY The 3° ring carbon ($CH–CH_3$) outranks the 2° ring CH_2.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Diels–Alder goes through a carbocation.	It is **concerted** — one step, no intermediate.

WHY So there are no rearranged products and stereochemistry is retained.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Dimethyl fumarate gives a cis diester.	Fumarate (trans) gives a **trans** diester; maleate gives cis.

WHY Suprafacial addition keeps the dienophile's geometry.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Endo is the more stable product.	Endo is the **faster** (kinetic) product; exo is more stable.

WHY Secondary orbital overlap lowers the endo transition state, not the product energy.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
1-Methoxybutadiene + acrolein ⟶ 'meta' product.	Gives the **'ortho'** (1,2) product.

WHY C1 donor ⟶ ortho; C2 donor ⟶ para. Diels–Alder does not give 'meta' as the major product.

MEMORY HOOK

BV — "Tertiary travels, methyl minds the shop." 3° moves first; methyl stays on the carbonyl.

DA — "Endo is early." Kinetic, low temperature, secondary orbital overlap.

DA regiochemistry — "One-two, two-four." Donor at C1 ⟶ 1,2-product; at C2 ⟶ 1,4-product.

SECTION I

Practice MCQs

I

Easy = recall · Moderate = one reasoning step · Tough = two ideas combined.

Q01 Acetophenone with mCPBA gives: [EASY]

(a) Methyl benzoate
(b) Phenyl acetate
(c) Benzoic acid
(d) Styrene oxide

Q02 The key intermediate of the Baeyer–Villiger oxidation is called: [EASY]

(a) Wheland intermediate
(b) Criegee intermediate
(c) Meisenheimer complex
(d) Tetrahedral carbanion

Q03 Diels–Alder reaction is classified as a: [EASY]

(a) [2+2] cycloaddition
(b) [4+2] cycloaddition
(c) 1,3-dipolar addition
(d) Electrocyclic ring opening

Q04 Cyclohexanone with a peracid gives a lactone of ring size: [MODERATE]

(a) 5
(b) 6
(c) 7
(d) 8

Q05 Pinacolone on Baeyer–Villiger oxidation gives: [MODERATE]

(a) Methyl pivalate
(b) tert-Butyl acetate
(c) Acetone + acetic acid
(d) Pivalic acid

Q06 The most reactive peracid among these: [MODERATE]

(a) CH_3CO_3H
(b) mCPBA
(c) CF_3CO_3H
(d) H_2O_2

Q07 Cyclopentadiene + maleic anhydride at room temperature gives mainly: [MODERATE]

(a) Exo adduct
(b) Endo adduct
(c) 1:1 endo/exo
(d) No reaction

Q08 Most reactive diene in a Diels–Alder reaction: [MODERATE]

(a) (Z)-Penta-1,3-diene
(b) Penta-1,4-diene
(c) Cyclopentadiene
(d) (E)-Penta-1,3-diene

Q09 Butadiene + dimethyl fumarate gives the cyclohexene diester with ester groups: [TOUGH]

(a) cis
(b) trans
(c) geminal
(d) 1,4-related

Q10 2-Methoxybuta-1,3-diene + acrolein gives mainly: [TOUGH]

(a) 2-Methoxycyclohex-3-ene-1-carbaldehyde
(b) 3-Methoxycyclohex-3-ene-1-carbaldehyde
(c) 4-Methoxycyclohex-3-ene-1-carbaldehyde
(d) No reaction

Q11 2-Methylcyclohexanone with mCPBA gives: [TOUGH]

(a) 3-Methyloxepan-2-one
(b) 7-Methyloxepan-2-one
(c) 2-Methylcyclohexanol
(d) 6-Methylcaprolactam

Q12 An inverse-electron-demand Diels–Alder reaction pairs: [TOUGH]

(a) Electron-rich diene + electron-poor dienophile
(b) Electron-poor diene + electron-rich dienophile
(c) Two electron-rich partners
(d) Two electron-poor partners

Answer key with explanations

Q01 (b) **Phenyl acetate** — phenyl outranks methyl, so O goes on the phenyl side.

Q02 (b) **Criegee intermediate** — the tetrahedral peroxy-hemiketal.

Q03 (b) **[4+2]** — 4 diene π-carbons + 2 dienophile π-carbons.

Q04 (c) **7** — ε-caprolactone; O adds one ring atom.

Q05 (b) **tert-Butyl acetate** — 3° alkyl migrates; methyl never does.

Q06 (c) **CF_3CO_3H** — CF_3COO^- is the best leaving group.

Q07 (b) **Endo** — kinetic product, secondary orbital overlap.

Q08 (c) **Cyclopentadiene** — locked s-cis.

Q09 (b) **trans** — suprafacial addition keeps the trans geometry.

Q10 (c) **4-Methoxy…** — donor at C2 gives the 'para' (1,4) product.

Q11 (b) **7-Methyloxepan-2-one** — the more substituted (3°) ring carbon migrates; O sits next to $CH(CH_3)$.

Q12 (b) — LUMO(diene)–HOMO(dienophile) controls the reaction.

SECTION J

Previous-year questions

J

HONEST NOTE

Baeyer–Villiger and Diels–Alder are outside NCERT, so JEE Main and NEET rarely test them directly. They appear in JEE Advanced, MHT CET, GATE Chemistry, CSIR-NET and TGT/PGT papers.

Example: GATE Chemistry (CY) 2021 asked for the major product of a Diels–Alder reaction that turned on the endo rule (Section E). Like most such questions it is built on structure drawings, which I could not reproduce faithfully, so it is described here rather than copied.

I have not tagged any question with a year I could not verify. Send past papers from your students' exams and I will add the matching questions.

SECTION K

Advanced problems

K

Problems at JEE Advanced / PGT / GATE level. They combine regiochemistry, ring size and retro-analysis.

IN ONE LINE Each problem combines two ideas from this chapter. Try it before reading the solution.

SOLVED EXAMPLE 05 SYMMETRY

Predict the product of 4-tert-butylcyclohexanone with mCPBA.

SOLUTION

1. Both α-carbons are ring CH_2 groups (2°) and equivalent by symmetry — either can migrate.
2. O is inserted next to C=O; the ring grows from 6 to 7 atoms.
3. Numbering the lactone (O1, C2 = carbonyl), the tert-butyl carbon ends up at C5.

ANSWER 5-tert-Butyloxepan-2-one (a substituted ε-caprolactone).

SOLVED EXAMPLE 06 2° VS METHYL

Cyclohexyl methyl ketone is treated with CF_3CO_3H. Which ester forms?

SOLUTION

1. Groups on C=O: cyclohexyl (a 2° carbon) and methyl.
2. 2° outranks methyl, so cyclohexyl migrates to O.
3. $CH_3–CO–O–C_6H_{11}$.

ANSWER Cyclohexyl acetate.

SOLVED EXAMPLE 07 WORKING BACKWARDS

Identify the diene and dienophile needed to make cyclohex-3-ene-1-carbonitrile by a Diels–Alder reaction.

SOLUTION

1. Retro-Diels–Alder method: find the ring C=C (C3=C4). Its two neighbours (C2, C5) were the diene termini; the remaining two carbons (C1, C6) were the dienophile.
2. Break C1–C2 and C5–C6: C2–C3=C4–C5 becomes buta-1,3-diene; C1=C6 with the CN becomes acrylonitrile.

ANSWER Buta-1,3-diene + acrylonitrile (CH_2=CH–CN).

SOLVED EXAMPLE 08 REGIOCHEMISTRY

Isoprene (2-methylbuta-1,3-diene) reacts with methyl vinyl ketone. Give the major regioisomer.

SOLUTION

1. Methyl is a donor at diene C2 ⟹ 'para' (1,4) rule.
2. The acetyl group and the methyl end up 1,4 on the cyclohexene ring.

ANSWER 1-(4-Methylcyclohex-3-en-1-yl)ethan-1-one (the 'para' adduct).

Check-yourself answers

C1 The Criegee intermediate.

C2 The weak O–O bond of the peroxide (carboxylate leaves).

C3 In the s-cis form its terminal methyl points inward and clashes with the C1 hydrogen, so s-cis is disfavoured.

C4 Two (plus one new π bond).

QUICK REVISION

One-page revision

Read this page the night before the exam. Every line points back to a section in these notes.

Baeyer–Villiger

- Ketone + RCO_3H ⟶ ester; cyclic ketone ⟶ lactone (+1 ring atom)
- Criegee intermediate; concerted migration is slow step
- Migrating group retains configuration

Migration order

- H > 3° > 2° ≈ Ph ≈ benzyl > 1° > CH_3
- Methyl ketone ⟶ always an acetate
- Peracid power: CF_3CO_3H > mCPBA > CH_3CO_3H > H_2O_2

Diels–Alder basics

- Diene (s-cis) + dienophile ⟶ cyclohexene, one step
- 2 σ + 1 π formed; thermal [4s+2s]
- Cyclopentadiene best diene; benzene does not react
- Retro-DA at high T

Stereochemistry

- Cis dienophile ⟶ cis product; trans ⟶ trans
- Endo = kinetic (secondary orbital overlap)
- Exo = thermodynamic; furan gives exo

Electron demand

- Normal: rich diene + poor dienophile ($HOMO_{diene}$–$LUMO_{dienophile}$)
- Inverse: poor diene + rich dienophile
- Donor at C1 ⟶ ortho; at C2 ⟶ para

Memory hooks

- Tertiary travels, methyl minds the shop
- Endo is early
- One-two, two-four