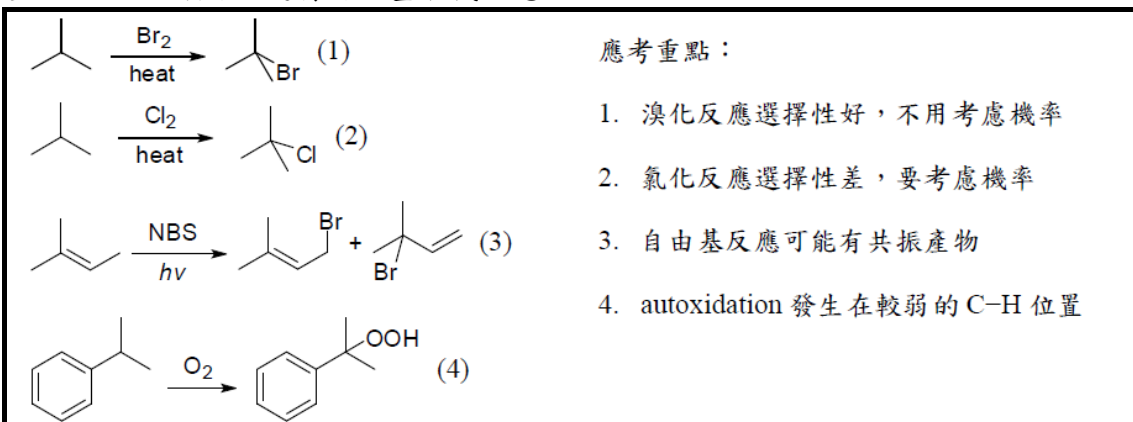


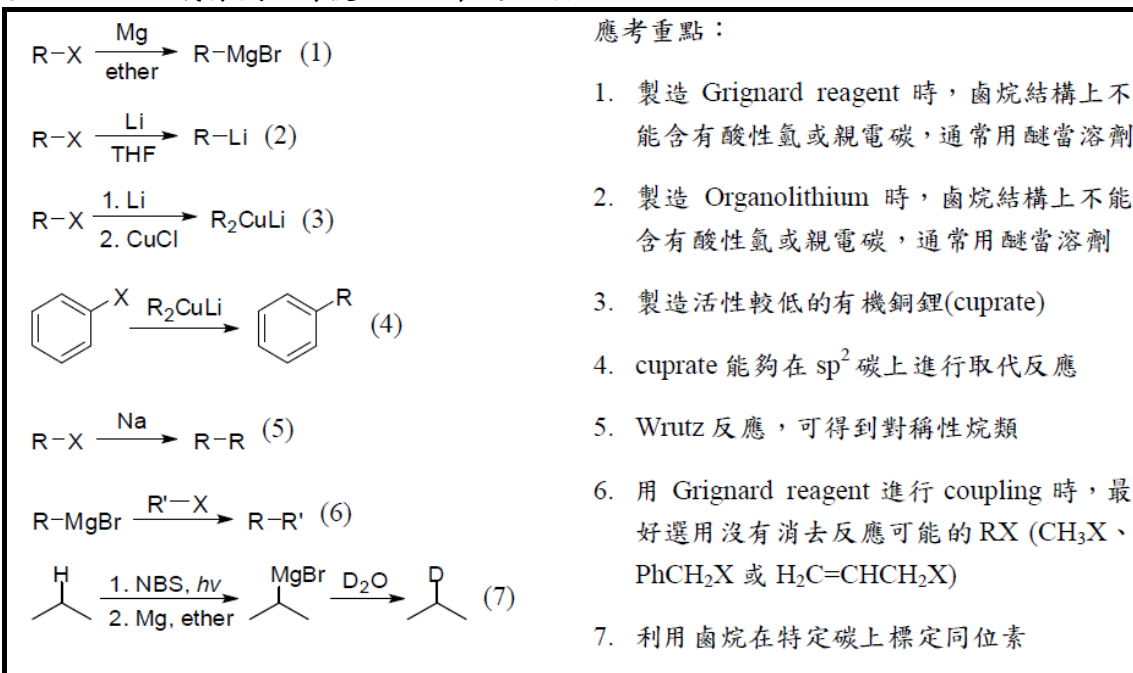
有機

Chapter 01 烷 Alkanes

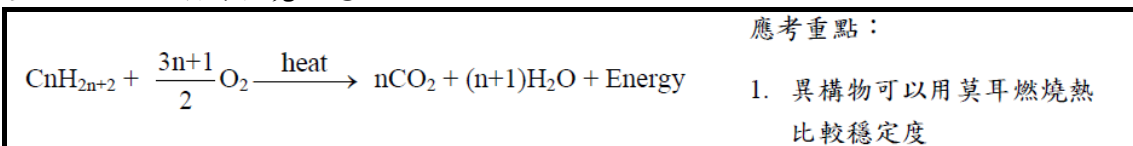
重點 1.1：烷類可以進行自由基取代反應



重點 1.2：合成有機金屬後，可以製造烷類

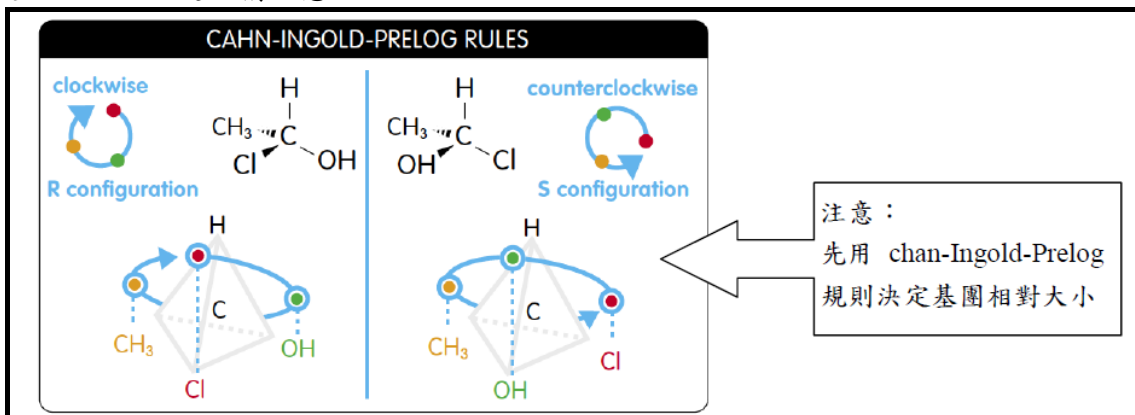


重點 1.3：烷類的燃燒反應



Chapter 02 立體化學 Stereochemistry

重點 2.1：決定結構組態



重點 2.2：比旋光

- 0.300 g sucrose dissolved in 10.0 mL of water
- Sample cell = 10.0 cm
- Observed rotation = +1.99°

$$[\alpha] = \frac{\alpha}{c \times l} = \frac{+1.99^\circ}{\frac{0.03\text{g}}{\text{mL}} \times 1.00 \text{ dm}} = +66.3$$

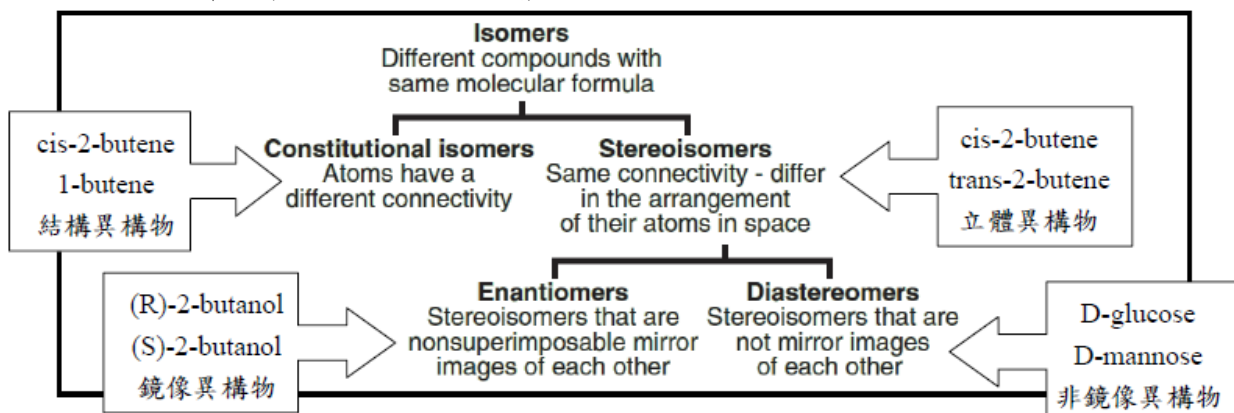
重點 2.3：鏡像過量

- The specific rotation of optically pure adrenaline is -53. A mixture of (R)- and (S)-adrenaline was found to have a specific rotation of -45. Calculate the % ee of the mixture.

$$\% \text{ ee} = \frac{\text{observed } [\alpha]}{[\alpha] \text{ of pure enantiomer}} \times 100\%$$

$$\% \text{ ee} = \frac{-45}{-53} \times 100\% = 85\%$$

重點 2.4：常用來描述化合物之間關係的名詞



Chapter 04 鹵烷 Alkyl Halides

• Summary of Nucleophilic Substitutions

	S_N1	S_N2
影響因素		
親核劑	通常使用弱親核劑	使用強親核劑
鹵烷結構 (RX)	$3^\circ > 2^\circ$	$CH_3X > 1^\circ > 2^\circ$
溶劑	介電常數較大的溶劑	通常使用非質子溶劑
離去基	好離去基	好離去基
其他因素	加入 $AgNO_3$ 可幫助 RX 解離	
特色		
反應動力學	first order, $k_r[RX]$	second order, $k_r[RX][Nuc:^-]$
立體化學	翻轉和保持組態皆有(翻轉稍多)	完全翻轉
結構重排的可能性	很可能重排	不會重排

• Summary of Eliminations

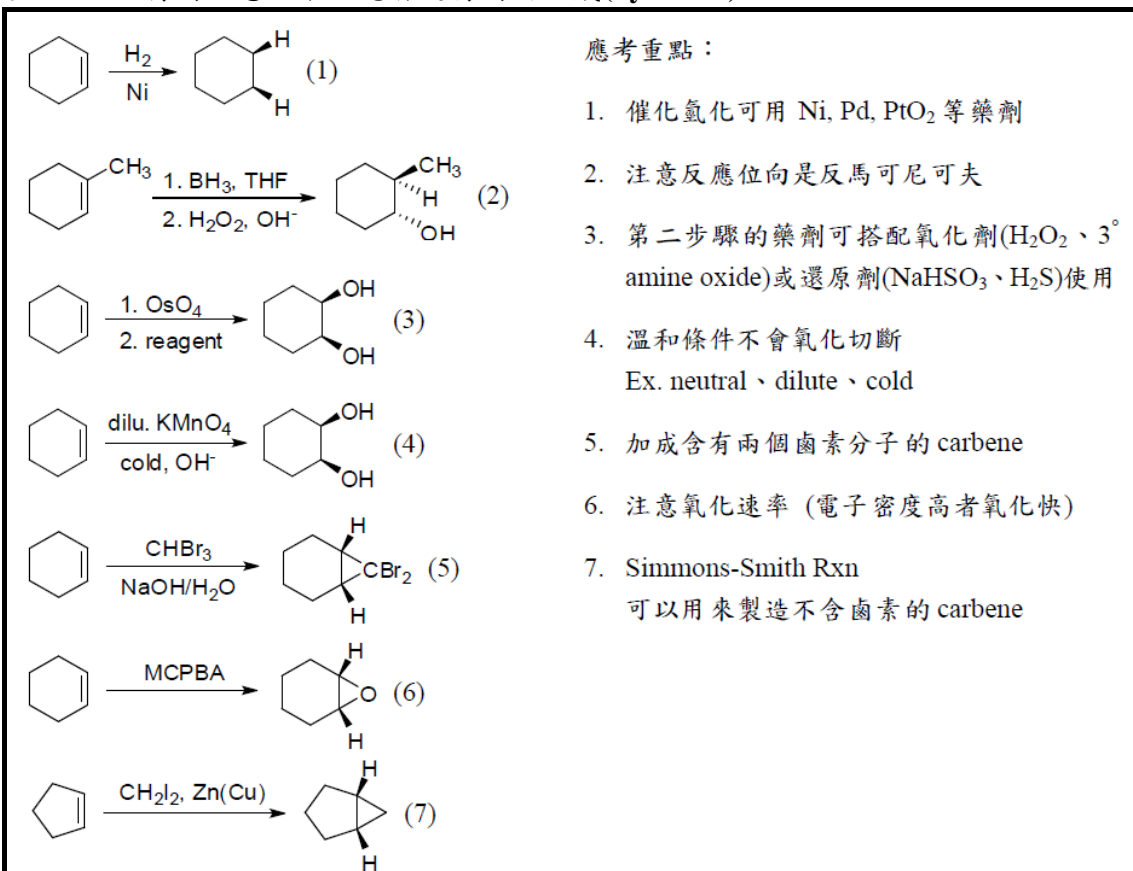
	E1	E2
影響因素		
鹼	通常使用弱鹼	使用強鹼
鹵烷結構 (RX)	$3^\circ > 2^\circ$	$3^\circ > 2^\circ > 1^\circ$
溶劑	介電常數較大的溶劑	可使用的溶劑很多 (通常用極性較小的)
離去基	好離去基	好離去基
其他因素		高溫條件會導致消去產物比例增加
特色		
反應動力學	first order, $k_r[RX]$	second order, $k_r[RX][B:^-]$
產物位向	Zaitsev's rule	Zaitsev's rule (立障小的鹼) Hofmann's rule (立障大的鹼)
立體化學	沒有特別的立體要求	能產生軌域共平面的過渡狀態
結構重排的可能性	很可能重排	不會重排

Table: Predicting substitution v.s. elimination at $C(sp^3)-X$ under basic conditions

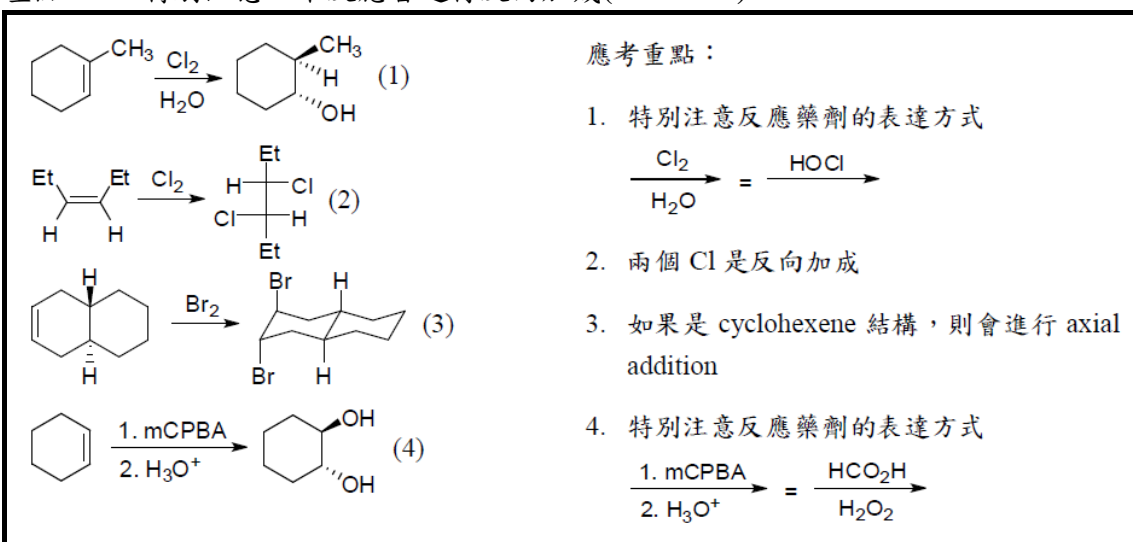
	Poor Base Good Nu	Good Base Good Nu	Good Base Poor Nu	Poor Base Poor Nu
methyl or benzyl	S_N2	S_N2	S_N2	-
1°	S_N2	$S_N2 > E2$	E2	$S_N1/E1$
2°	$S_N2 > E2$	$E2 > S_N2$	E2	$S_N1/E1$
3°	$E2$ or $S_N1/E1$	E2	E2	$S_N1/E1$

Chapter 05 烯 Alkenes

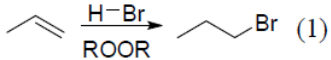
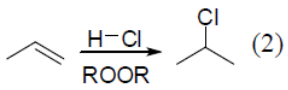
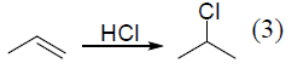
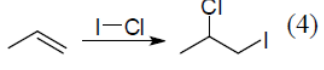
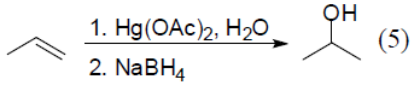
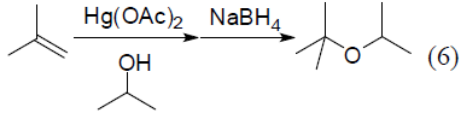
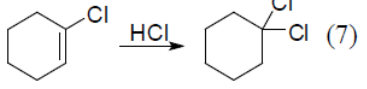
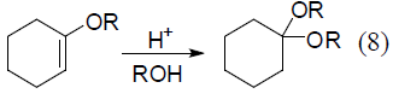
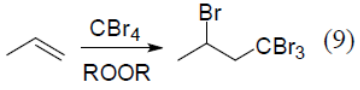
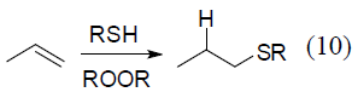
重點 5.1：特別注意以下反應皆進行同向加成(Syn-Add)



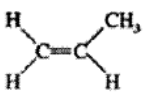
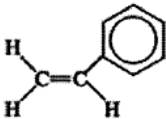
重點 5.2：特別注意以下反應皆進行反向加成(Anti-Add)



重點 5.3：特別注意以下反應的產物位向(1)

	應考重點：
	1. 自由基加成 HBr 有 peroxide 效應
	2. 加成 HCl 沒有 peroxide 效應
	3. 加成 HCl 得到馬可尼可夫位向
	4. 高陰電性的 Cl 當 LVG 而最後攻擊高級碳的位置
	5. 汞離子催化水合得到馬可尼可夫產物
	6. 如果用 ROH 當溶劑，得產物得到醚
	7. Cl 接在因為共振穩定而較穩定的碳陽離子位置
	8. ROH 接在因為共振穩定而較穩定的碳陽離子位置
	9. 自由基加成優先把立障大的基團放在低級碳
	10. 自由基加成優先把立障大的基團放在低級碳

重點 5.4：常見的加成聚合物(addition polymer)

Some of the Most Important Addition Polymers			
Polymer	Polymer Uses	Monomer Formula	Polymer Repeating Unit
polyethylene	bottles, bags, films	$\text{H}_2\text{C}=\text{CH}_2$	$[-\text{CH}_2-\text{CH}_2-]_n$
polypropylene	plastics, olefin fibers		$[-\text{CH}_2-\text{CH}(\text{CH}_3)-]_n$
polystyrene	plastics, foam insulation		$[-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-]_n$

poly(isobutylene)	specialized rubbers		$\left[\text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} \right]_n$
poly(vinyl chloride)	vinyl plastics, films, water pipes		$\left[\text{CH}_2 - \underset{\text{Cl}}{\text{CH}} \right]_n$
poly(acrylonitrile)	Orlon®, Acrilan® fibers		$\left[\text{CH}_2 - \underset{\text{CN}}{\text{CH}} \right]_n$
poly(methyl α-methacrylate)	acrylic fibers, Plexiglas®, Lucite® paints		$\left[\text{CH}_2 - \underset{\text{COOCH}_3}{\overset{\text{CH}_3}{\text{C}}} \right]_n$
poly(methyl α-cyanoacrylate)	"super" glues		$\left[\text{CH}_2 - \underset{\text{COOCH}_3}{\overset{\text{CN}}{\text{C}}} \right]_n$
poly(tetrafluoroethylene)	Teflon® coatings, PTFE plastics		$\left[\text{CF}_2 - \text{CF}_2 \right]_n$

注意：加成聚合物的聚合方式：陽離子聚合、陰離子聚合、自由基聚合、過渡金屬催化聚合

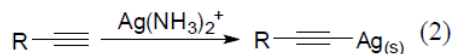
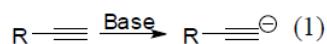
1. 可形成穩定陽離子的單體結構，如：isobutylene，適合用cationic polymerization
2. 可形成穩定陰離子的單體結構，如：methyl α -cyanoacrylate，適合用anionic polymerization
3. 可形成穩定自由基的單體結構，如：styrene，適合用free-radical polymerization
4. 如果需要形成isotactic form或syndiotactic form或no branching的高強度聚合物，可以使用Ziegler-Natta催化劑 (TiCl_4 , AlEt_3)

Chapter 06 共軛烯 Conjugated Polyenes

重點 6.1：1,2-Addition & 1,4-Addition

	應考重點：
	1. 動力控制通常在低溫條件，得到動力產物
	2. 熱力控制通常在高溫條件，得到熱力產物
	3. 某些結構的動力和熱力產物相同

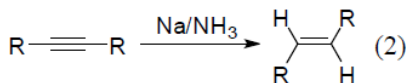
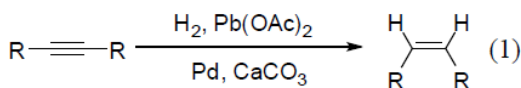
重點 7.2 : Terminal Alkynes



應考重點：

1. 強鹼如 NaH、NaNH₂、RMgBr 等可拔氫
2. 可用重金屬反應而沉澱
注意：Cu(NH₃)₂ 也有類似效果

重點 7.3 : Lindlar Catalyst & Metal-ammonia Reduction



應考重點：

1. Lindlar's catalyst 為 Pd 中加入 Pb²⁺ 毒劑
可以合成 cis-alkene
也可以使用 $\xrightarrow[\text{Pd, BaSO}_4]{\text{H}_2, \text{quinoline}}$
2. Metal-Ammonia Reduction
反應機構經過 radical anion、radical、anion
可以合成 trans-alkene


Chapter 08 Aromatic Compounds

重點 8.1 : 常見的芳香化合物親電取代反應

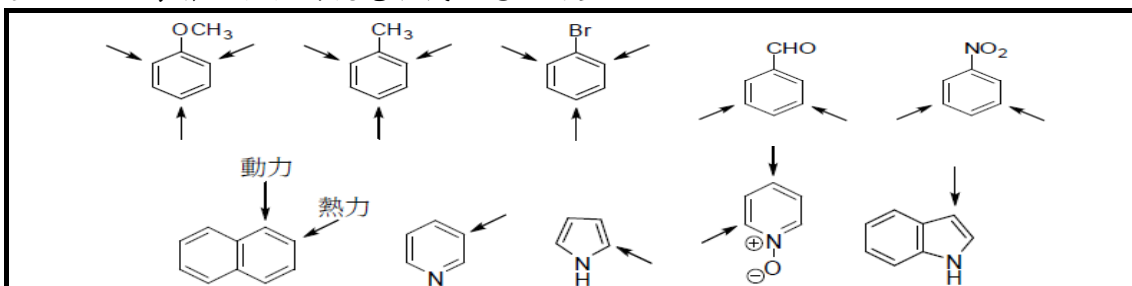
反應性	反應條件	備註
大 ↓ 小	$\text{C}_6\text{H}_6 \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{C}_6\text{H}_5\text{NO}_2$	單獨使用 HNO ₃ 不加 H ₂ SO ₄ 也可以反應
	$\text{C}_6\text{H}_6 \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_6\text{H}_5\text{SO}_3\text{H}$	磺化反應可逆，可當保護基
	$\text{C}_6\text{H}_6 \xrightarrow[\text{Lewis acid}]{\text{X}_2} \text{C}_6\text{H}_5\text{X}$	① X ₂ = Cl ₂ or Br ₂ ② E ⁺ 是 complex 而非 X ⁺
	$\text{C}_6\text{H}_6 \xrightarrow[\text{Lewis acid}]{\text{R-Cl}} \text{C}_6\text{H}_5\text{R}$	① 可能重排或多取代 ② 碰到中、強去活化基不反應 ③ 可以用 ROH/BF ₃ 或 Alkene/HF 當親電劑
	$\text{C}_6\text{H}_6 \xrightarrow[\text{Lewis acid}]{\text{R-CO-Cl}} \text{C}_6\text{H}_5\text{COR}$	① 不會重排，沒有多取代 ② 碰到中、強去活化基不反應 ③ 可以用 anhydride 當親電劑

注意：苯環上面有取代基的話，取代基的種類會影響反應速率和產物的位向。

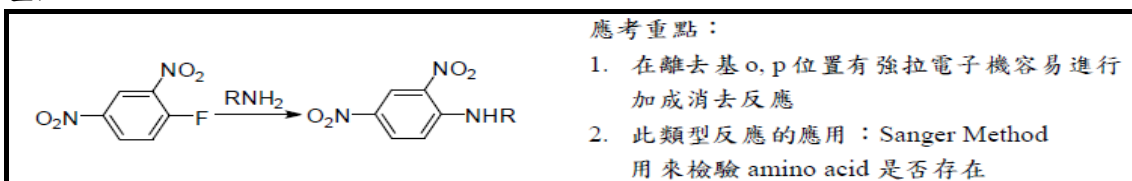
重點 8.2：不同取代基的反應活性表

Electron Donating Group (EDG)			Electron Withdrawing Group (EWG)		
強活化	中活化	弱活化	弱去活化	中去活化	強去活化
-O ⁻		-R	-F	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H}(\text{R}) \end{array}$	-CF ₃
-NH ₂	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{N}-\text{C}-\text{R} \end{array}$		-Cl	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR}(\text{H}) \end{array}$	-CCl ₃
-NHR		$\begin{array}{c} \text{H} \\ \\ -\text{C}=\text{CH}_2 \end{array}$	-Br	-C≡N	-NR ₃ ⁺
-NR ₂	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{O}-\text{C}-\text{R} \end{array}$		-I	-SO ₃ H	-NO ₂
-OH					
-OR					

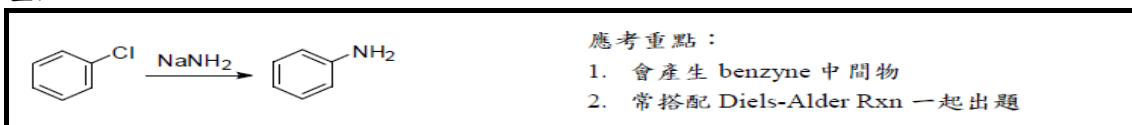
重點 8.3：芳香化合物的親電取代反應位向整理



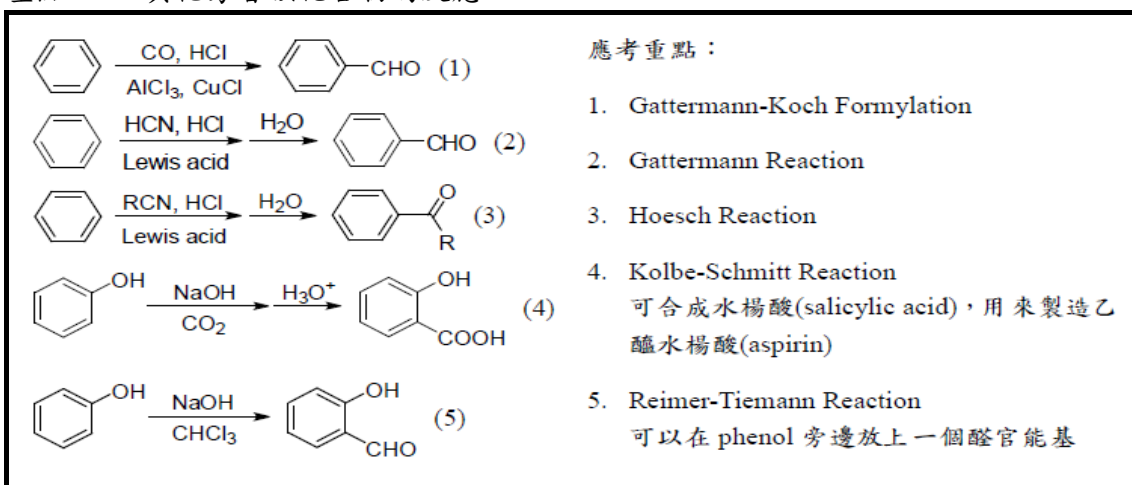
重點 8.4：Addition-Elimination Mechanism



重點 8.5：Elimination-Addition Mechanism



重點 8.6：其他芳香族化合物的反應



Chapter 09 醇、醚、環氧化物、酚 Alcohol, Ether, Epoxide, Phenol

重點 9.1：醇類的反應

(1) C1CCCCC1O $\xrightarrow[\text{Dioxane}]{\text{SOCl}_2}$ C1CCCCC1Cl

(2) C1CCCCC1O $\xrightarrow[\text{Pyridine}]{\text{SOCl}_2}$ C1CCCCC1Cl

(3) C1CCCCC1O $\xrightarrow{\text{PCl}_3}$ C1CCCCC1Cl

(4) C1CCCCC1O $\xrightarrow[2. \text{LiAlH}_4]{1. \text{TsCl, pyridine}}$ C1CCCCC1

(5) CC1(O)CCCC1 $\xrightarrow[\text{ZnCl}_2]{\text{HCl}}$ CC1(Cl)CCCC1

(6) CC(C)=C + CC(O)C $\xrightarrow[\text{NaBH}_4]{\text{Hg(OAc)}_2}$ CC(C)OC(C)C

(7) CC(O)CCCCl $\xrightarrow{\text{NaH}}$ CC1(O)CCCC1

(8) C1CCCCC1O $\xrightarrow[\text{or H}_3\text{PO}_4]{\text{H}_2\text{SO}_4}$ C1=CCCCC1

(9) C1CCCC1O $\xrightarrow[\text{base}]{\text{POCl}_3}$ C1=CCCC1

(10) CC(C)(O)C(C)(O)C $\xrightarrow{\text{H}^+}$ CC(C)(=O)C(C)C

應考重點：

1. 用 SOCl_2 把 OH 轉成 Cl，通常用沒有親和性的溶劑，則產物為 retention
2. 用 SOCl_2 把 OH 轉成 Cl，通常用有親和性的溶劑，則產物為 inversion
3. 用 PBr_3 或 I_2/P 也會得到類似效果
4. 用 TsCl 把 OH 轉成 OTs 後，被 LAH 還原通常可用來還原 1° 或 2° 醇
5. Lucas Test
可以用來做醇類的分級檢驗
6. 汞離子催化但用醇當溶劑可得醚
7. Williamson Ether Synthesis
RX 立障受限制
8. 醇類在有硫酸或磷酸作用下可脫水
脫水速率： $3^\circ > 2^\circ > 1^\circ \text{ROH}$
9. POCl_3 也可使醇脫水
10. Pinacol Rearrangement
結構特色：OH 旁邊出現碳陽離子

重點 9.2：醇類的氧化反應

(1) C1CCCCC1CO $\xrightarrow{\text{PCC}}$ C1CCCCC1C=O

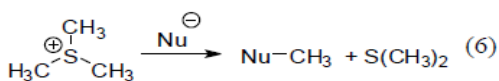
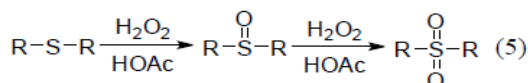
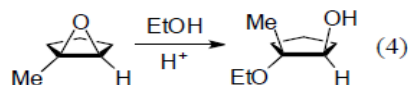
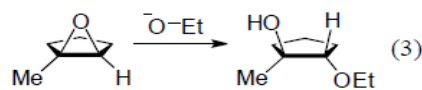
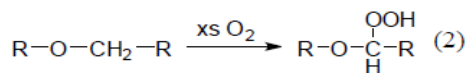
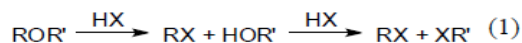
(2) C1CCCCC1CO $\xrightarrow[\text{H}_2\text{SO}_4]{\text{CrO}_3}$ C1CCCCC1C(=O)O

(3) C1CCC(O)C1O $\xrightarrow{\text{HIO}_4}$ C1CCC(=O)C1=O

應考重點：

1. 1° 醇被不含水氧化劑氧化可得醛
PCC、Collins reagent、Swern Oxidation
2. 1° 醇被含水的氧化劑氧化可得酸
Jones reagent、 $\text{KMnO}_4(\text{aq})$
3. 可形成五環中間物的 diol 可以氧化切斷
注意： $\text{Pb}(\text{OAc})_4$ 也有類似效果

重點 9.3：醚類、環氧化物、硫化物的反應

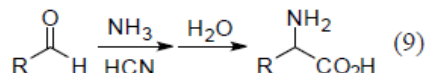
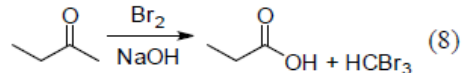
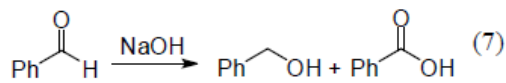
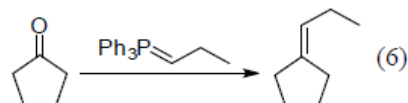
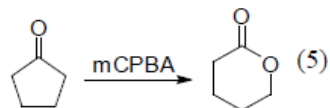
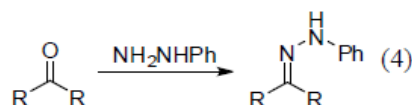
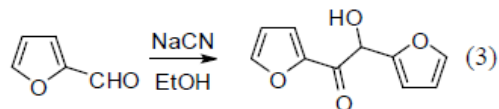
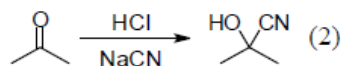
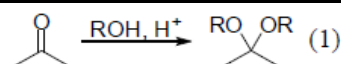


應考重點：

1. 醚類在 HBr 或 HI 作用下可形成 RX
注意：HI > HBr >> HCl
2. 醚類通常不易氧化，但可進行 autoxidation
3. 環氧化物鹼性條件開環：
反向開環 + Nu 接低級碳
4. 環氧化物酸性條件開環：
反向開環 + Nu 接高級碳
5. sulfide 能氧化成 sulfoxide 或 sulfone
6. sulfonium salt 可用來當甲基化藥劑
SAM = biological methylating agent

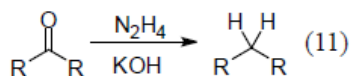
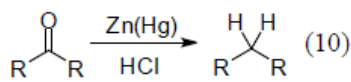
Chapter 10 醛、酮 Aldehyde, Ketone

重點 10.1：醛、酮的反應(1)



應考重點：

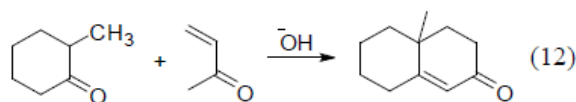
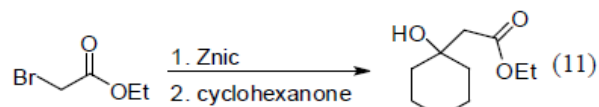
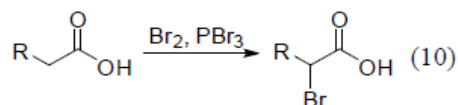
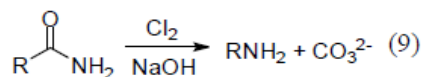
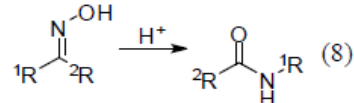
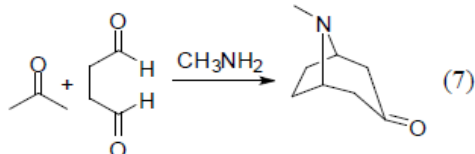
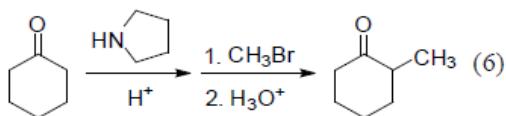
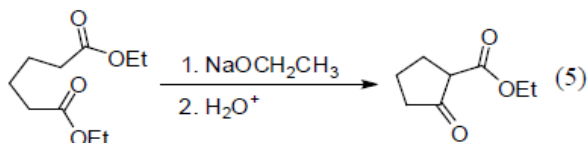
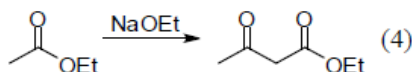
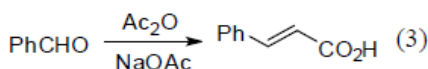
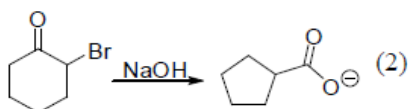
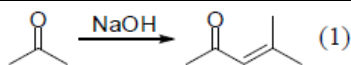
1. Nucleophilic Addition Reaction
可以用來當醛、酮的保護劑基
2. 得到 cyanohydrin
3. Benzoin Condensation
芳香醛在沒有 H⁺ 的條件下容易進行
4. 與 Hydrazine 反應得到 hydrazone
5. Baeyer Villiger Oxidation
注意電子密度高者氧化速率較快
6. Wittig Reaction
注意 stabilized ylide(得到 E-form)和 unstabilized ylide(得到 Z-form)
7. Cannizzaro Reaction
沒有 alpha 氫的醛或酮容易進行的反應
8. Haloform Test
檢驗甲基酮、甲基醇的方法
9. Strecker Amino acid Synthesis



10. Clemmensen Reduction (酸性條件)

11. Wolff-Kishner Reaction (鹼性條件)

重點 10.2：醛、酮的反應(2)



應考重點：

1. Aldol Condensation

如果產物不能脫水，則可能進行 Retro Aldol Rxn

2. Favorskii Reaction

3. Perkin Condensation

4. Claisen Condensation

如果起始的 ester 只有 1 個 H α ，則可能會進行 Retro Claisen Rxn

5. Dieckmann Condensation

分子內的 Claisen condensation

6. Stork Rxn

E⁺ = CH₃X, benzyl RX, allyl RX
 α,β -unsaturated carbonyl cpd
acyl halide.

7. Mannich Rxn

反應特色：醛 + 胺 + 親核劑

8. Beckmann Rearrangement

轉位基團在離去基的背面

9. Hofmann Rearrangement

1° amide 才能進行 Hofmann 重排

10. Hell-Volhard-Zelinsky Reaction

若再加入 NH₃(xs)可合成 amino acid

11. Reformatsky Rxn

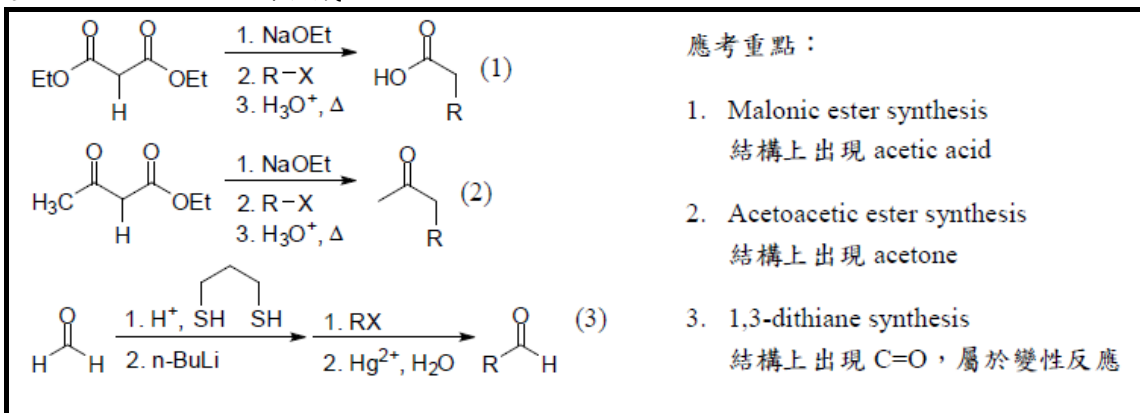
產生有機金屬攻擊醛或酮的 C=O

12. Robinson Annulation

先進行共軛加成後再 aldol 縮合

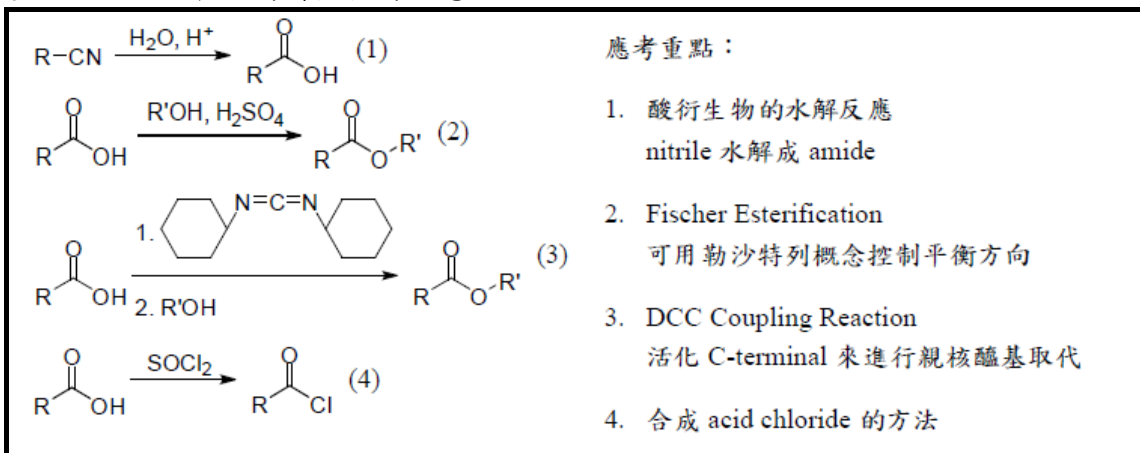
☞ 注意：生物合成 fatty acid 是利用 malonyl thioester 和 acetyl thioester 進行 Claisen Condensation

重點 10.3：醛、酮的合成

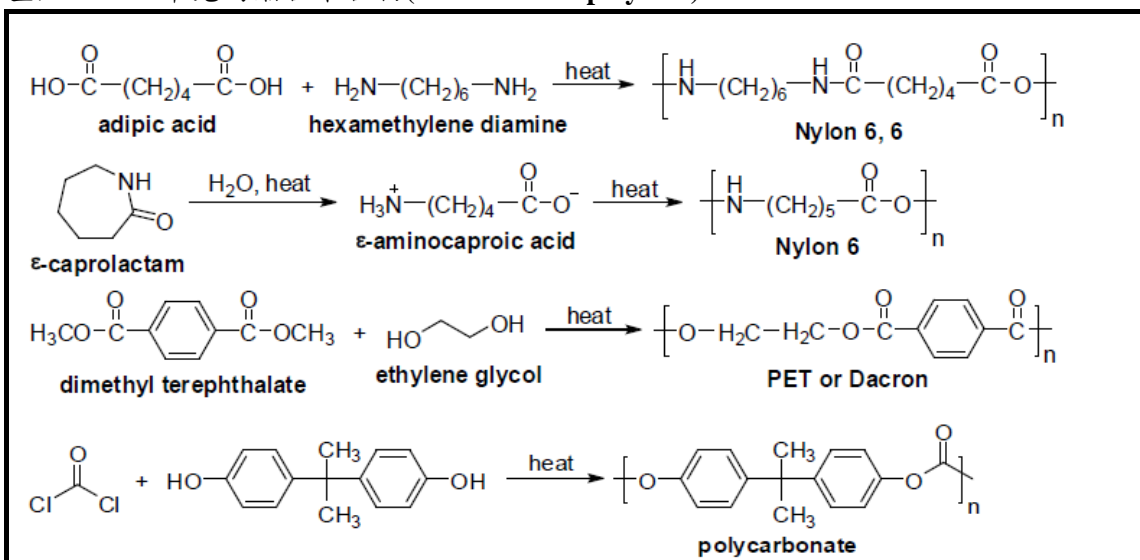


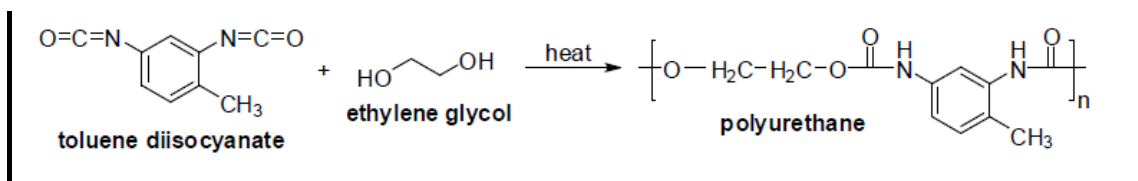
Chapter 11 酸和酸的衍生物 Acid, Acid Derivatives

重點 11.1：酸和酸的衍生物的反應



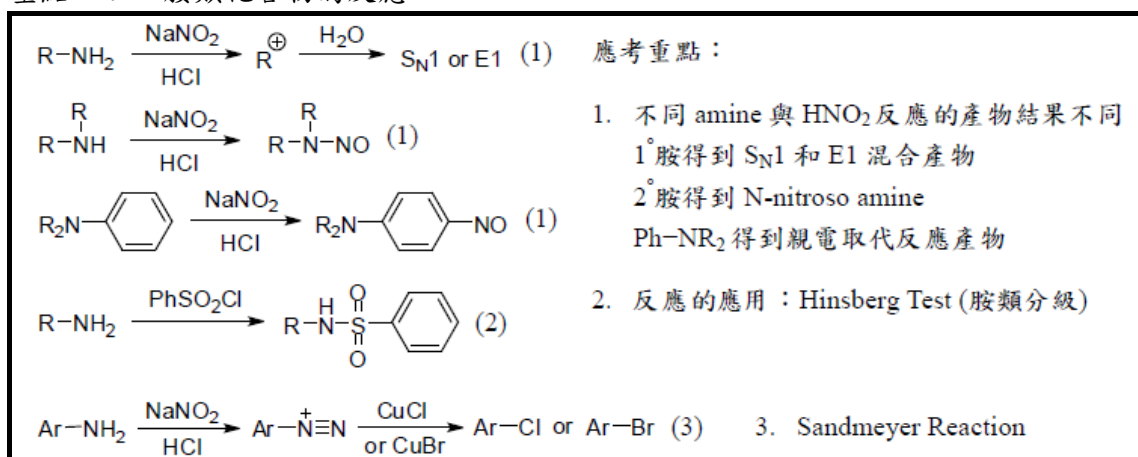
重點 11.2：常見的縮合聚合物(condensation polymer)



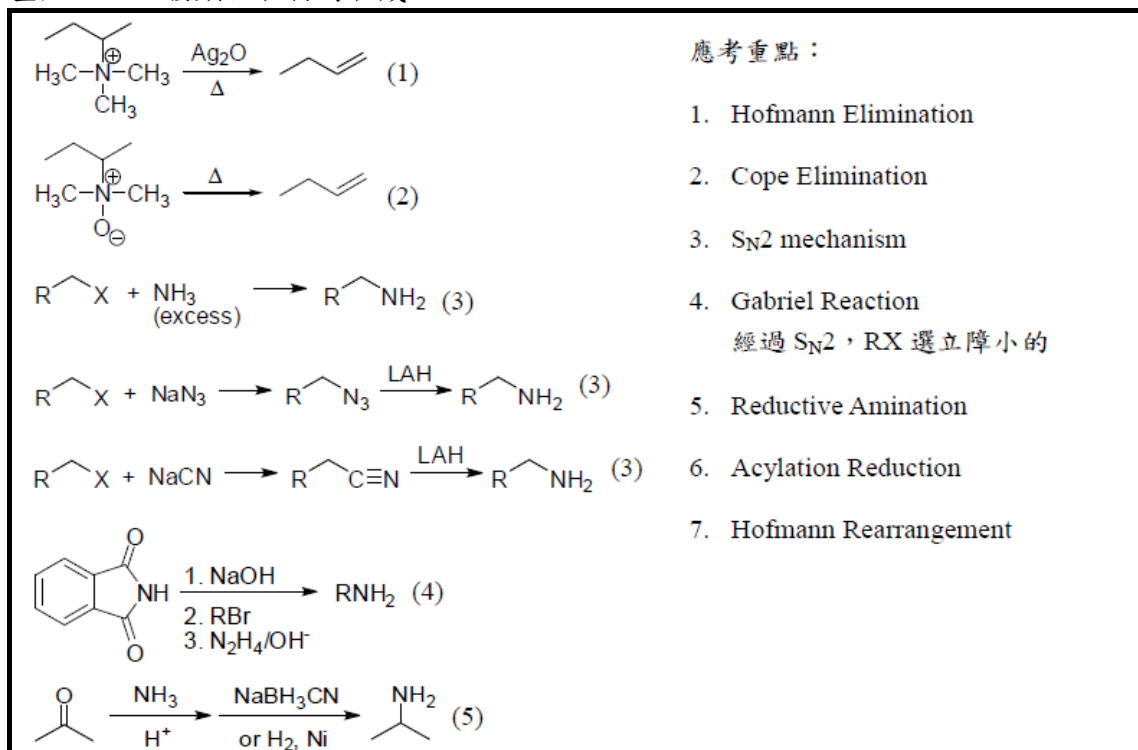


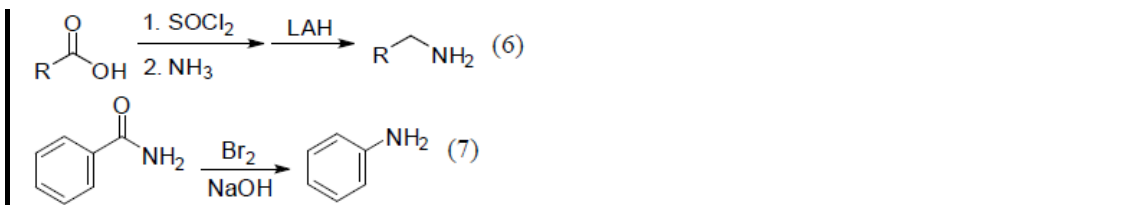
Chapter 12 胺 Amines

重點 12.1：胺類化合物的反應



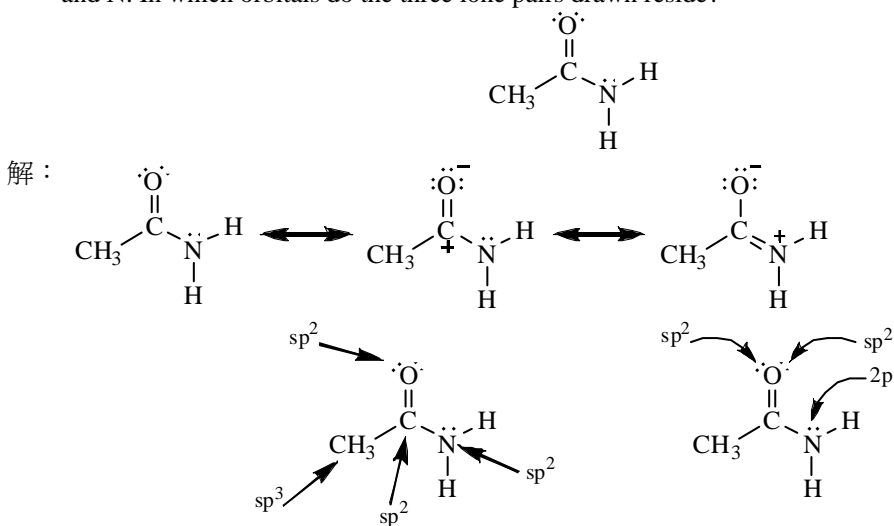
重點 12.2：胺類化合物的合成



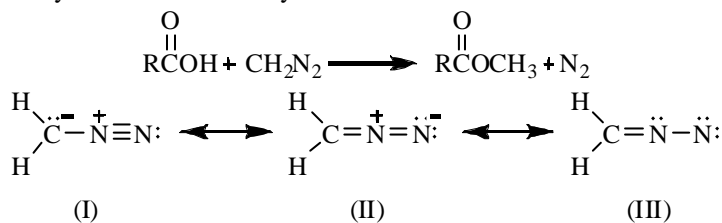


[綜合演練]

1. Draw three contributing structures of the following amide and state the hybridization of the O, C, and N. In which orbitals do the three lone pairs drawn reside?



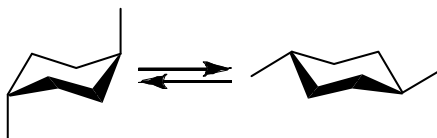
2. Following are three contributing structures for diazomethane, CH_2N_2 . This molecule is used to make methyl esters from carboxylic acids.



Which contributing structure makes the largest contribution to the hybrid?

解：(II)

3. Calculate the ratio of the diequatorial to diaxial conformation of *trans*-1,4-dimethylcyclohexane at 25°C. (CH_3/H 1,3-diaxial interactions = 3.64 kJ/mol)



解： $\Delta G^\circ = -RT \ln K_{eq}$

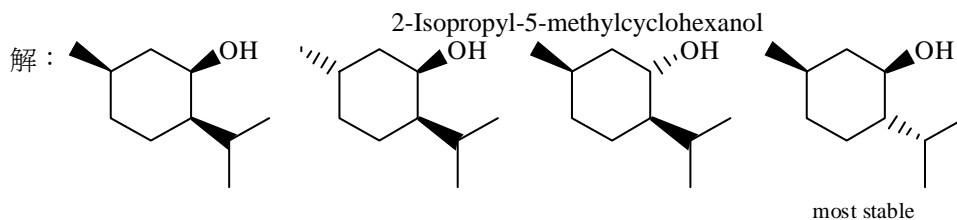
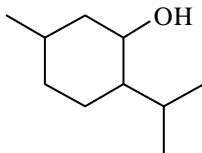
$$-3.64 \times 4 = -(8.314 \times 10^{-3})(298) \ln K_{eq}$$

$$K_{eq} = 357$$

$$K_{eq} = \frac{\left[\text{chair conformation} \right]}{\left[\text{chair conformation} \right]} = \frac{357}{1}$$

$$\text{chair conformation} : \frac{357}{357+1} \times 100\% = 99.7\%$$

4. There are four *cis*, *trans* isomers of 2-isopropyl-5-methylcyclohexanol, which is the most stable?

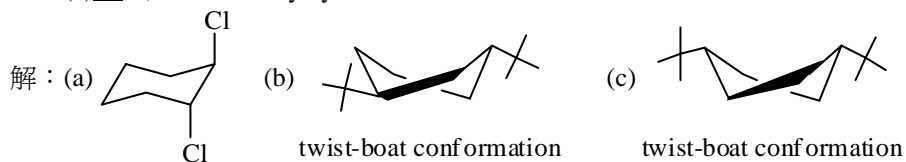


5. The more stable conformation is

(a) *trans*-1,2-Dichlorocyclohexane

(b) *trans*-1,3-Di-*tert*-butylcyclohexane

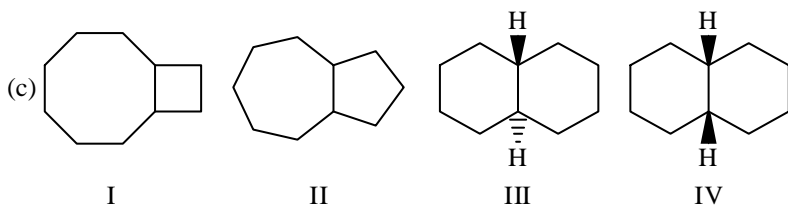
(c) *cis*-1,4-Di-*tert*-butylcyclohexane



6. Arrange these compounds in order of decreasing (less negative) heat of combustion:

(a) hexane, 2-methylpentane, and 2,2-dimethylbutane

(b) *cis*-1,2-, *trans*-1,2-, *trans*-1,3-, and *cis*-1,3-dimethylcyclohexane

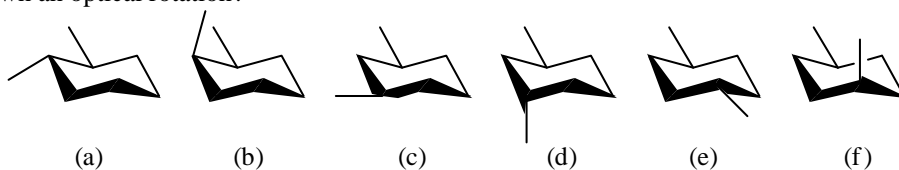


解：(a) hexane > 2-methylpentane > 2,2-dimethylbutane

(b) *cis*-1,2- > *trans*-1,3- > *trans*-1,2- > *cis*-1,3-

(c) I > II > IV > III

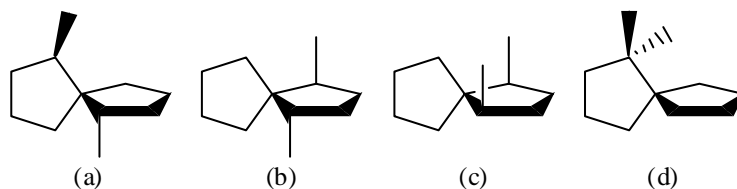
7. Are the following structures chiral as drawn? When placed in a solution at 298K, which structure will show an optical rotation?



解：chiral: (a) (b) (d)

optical rotation: (a) (d)

8. Which of the following compounds are chiral? Which, if any, are meso? Which, if any, does not have a possible diastereomer?



解：chiral: (a) (b) ; meso: (c) ; diastereomers: (d)

9. To the following statements, answer True or False.

(a) All chiral centers are also stereocenters.

(b) All stereocenters are also chiral centers.

(c) All chiral molecules are optically active when pure.

(d) All mixtures of chiral molecules are optically active.

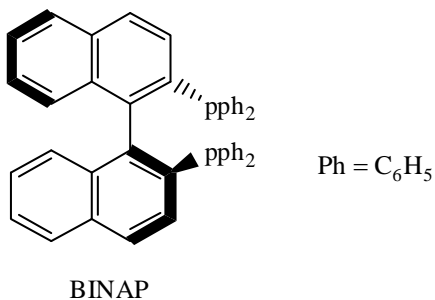
(e) To be optically active, a molecule must have a chiral center.

(f) To be meso, a molecule must have at least two chiral centers.

解：True: (a) (c) (f)

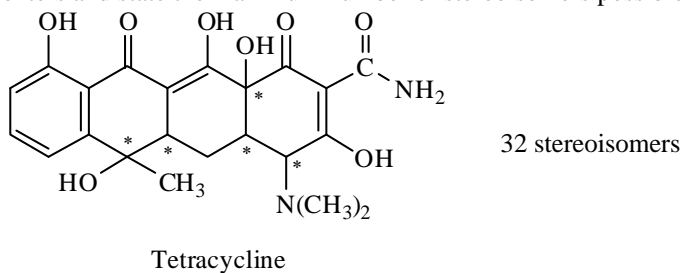
False: (b) (d) (e)

10. What kind of isomers are the enantiomers of BINAP?



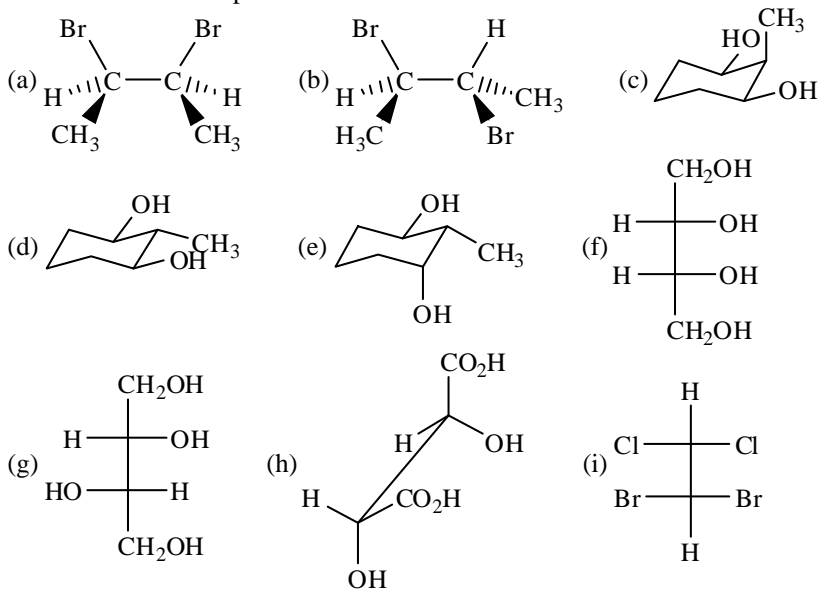
解：Atropisomers

11. Mark all stereocenters and state the maximum number of stereoisomers possible for tetracycline.



解：

12. Which are meso compounds?



解：(a) (c) (d) (f)

13. A solution is prepared by dissolving 400mg of testosterone, a male sex hormone, in 10.0mL of

ethanol and placing it in a sample tube 10.0cm in length. The observed rotation of this sample at 25°C using the D line of sodium is +4.36°. Calculate the specific rotation of testosterone.

$$\text{解： } [\alpha]_{\text{D}}^{25} = \frac{+4.36^{\circ}}{(1.00) \left(\frac{0.0400\text{g}}{10.0\text{mL}} \right)} = +109^{\circ}$$

14. The specific rotation of optically pure (S)-(-)-mandelic acid is -158° , the sample is a mixture of mandelic acid enantiomers with a specific rotation of -134° . For this sample, calculate the following.

(a) The enantiomeric excess of this sample of (S)-(-)-mandelic acid.

(b) The percentage of (S)-(-)-mandelic acid and of (R)-(+)-mandelic acid in the sample.

$$\text{解： (a) e.e.} = \frac{-134^{\circ}}{-158^{\circ}} \times 100 = 84.8\%$$

(b) 92.4% (S)-(-)- and 7.6% (R)-(+)-mandelic acid

15. Alcohols are weak organic acids, pka 16~18. The pka of ethanol- $\text{CH}_3\text{CH}_2\text{OH}$, is 15.9. Which of the following bases reacts with ethanol equilibria lie considerably toward the right?

(A) NaHCO_3 (B) NaOH (C) NaNH_2 (D) NH_3

解：(C)

16. Benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$, is insoluble in water, but its sodium salts, $\text{C}_6\text{H}_5\text{CO}_2\text{Na}$, is quite soluble in water. Will benzoic dissolve in

(A) $\text{NaOH}_{(\text{aq})}$ (B) $\text{NaHCO}_{3(\text{aq})}$ (C) $\text{Na}_2\text{CO}_{3(\text{aq})}$

解：(A) (B) (C)

17. Phenol, $\text{C}_6\text{H}_5\text{OH}$, is only slight soluble in water, but its sodium salts, $\text{C}_6\text{H}_5\text{ONa}$, is quite soluble in water. Will phenol dissolve in

(A) $\text{NaOH}_{(\text{aq})}$ (B) $\text{NaHCO}_{3(\text{aq})}$ (C) $\text{Na}_2\text{CO}_{3(\text{aq})}$

解：(A) (C)

18. Which of the following bicycloalkanes would you expect to show *cis-trans* isomerism?

(A) Bicyclo[2,2,2] octane

(B) Bicyclo[4,3,0] nonane

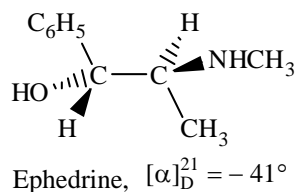
(C) 2-Methylbicyclo[2,2,1] heptane

(D) 1-Chlorobicyclo[2,2,1] heptane

(E) 7-Chlorobicyclo[2,2,1] heptane

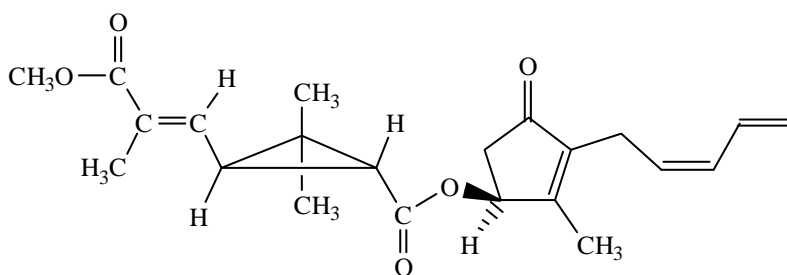
解：(B)(C)

19. The naturally occurring ephedrine is levorotatory and has the following structure. Assign R or S configuration to each stereo-center.



解：(1*R*,2*S*)-(-)-ephedrine

20.



Pyrethrin II

- (a) How many stereoisomers are possible for Pyrethrin II?
 (b) Calculate the index of hydrogen deficiency for Pyrethrin II?

解：(a) 64 (b) 9

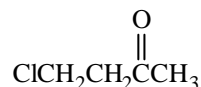
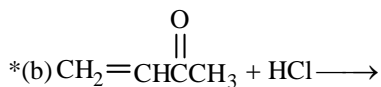
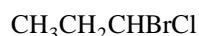
21. Following are lengths for a series of C-C single bonds

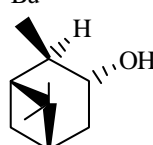
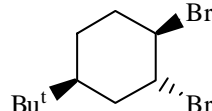
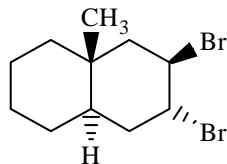
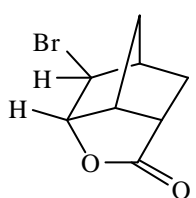
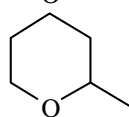
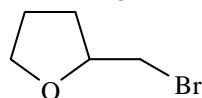
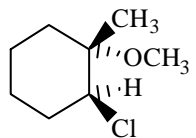
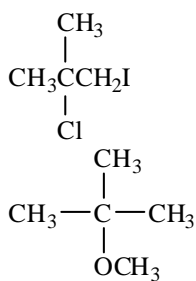
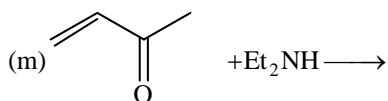
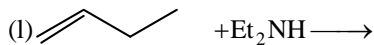
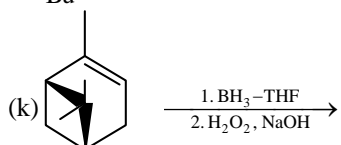
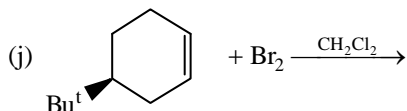
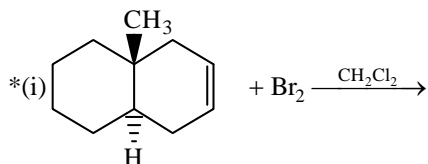
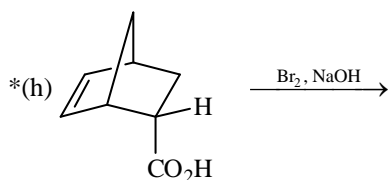
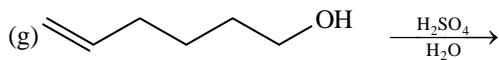
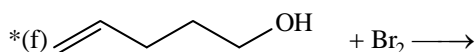
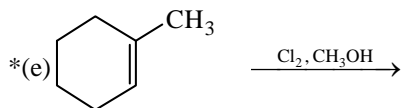
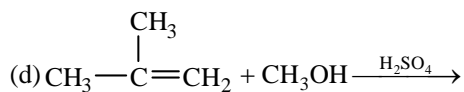
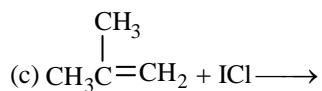
解：

$\text{H}_3\text{C}-\text{CH}_3$	$\text{H}_2\text{C}=\text{CH}-\text{CH}_3$	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	$\text{HC}\equiv\text{C}-\text{CH}_3$
↑	↑	↑	↑
153.7 pm	151.0 pm	146.5 pm	145.9 pm
(sp^3-sp^3)	(sp^2-sp^3)	(sp^2-sp^2)	($\text{sp}-\text{sp}^3$)
50% S	58% S	66% S	75% S

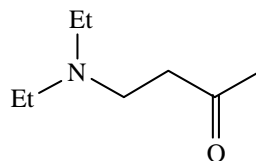
22. What major product would you expect to obtain from each of the following reactions?

解：



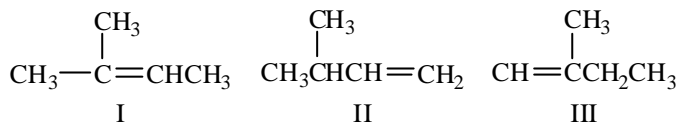


N.R.



23. Arrange the alkenes in order of increasing rate of reaction with

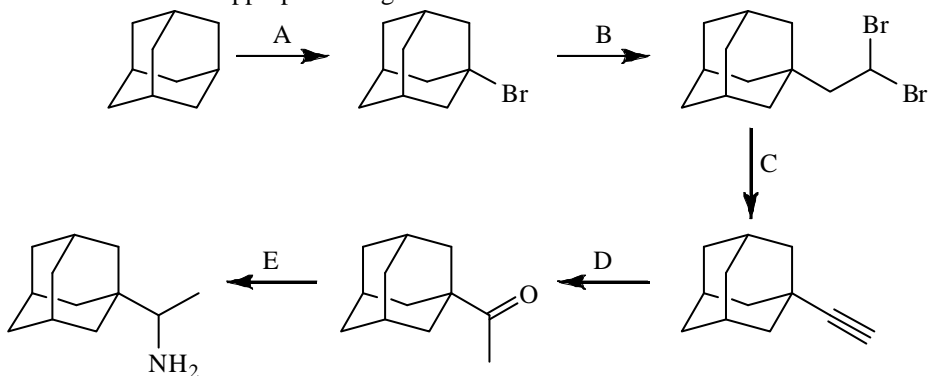
(a) HI (b) Br₂, CH₂Cl₂ (c) H₂O, H₂SO₄ (d) O₃ (e) mCPBA



解：(a) (b) (c) (d) (e)

II < III < I

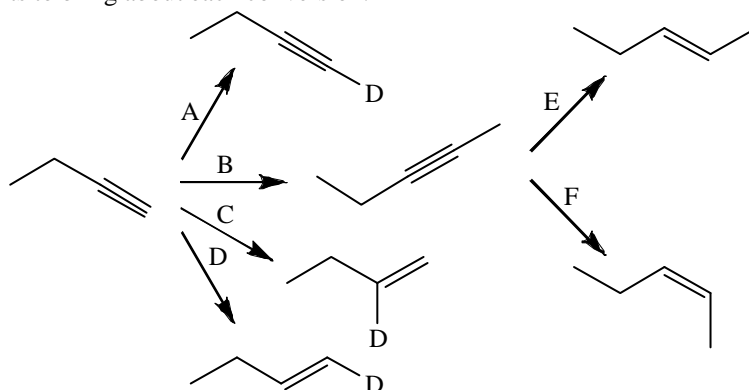
24. Fill in each box with the appropriate reagent:



解：A = Br₂, light ; B = CH₂=CHBr, AlBr₃ ; C = NaNH₂, NH₃(l) ;

D = H₂SO₄, H₂O, HgSO₄ ; E = NH₃, H₂, Ni

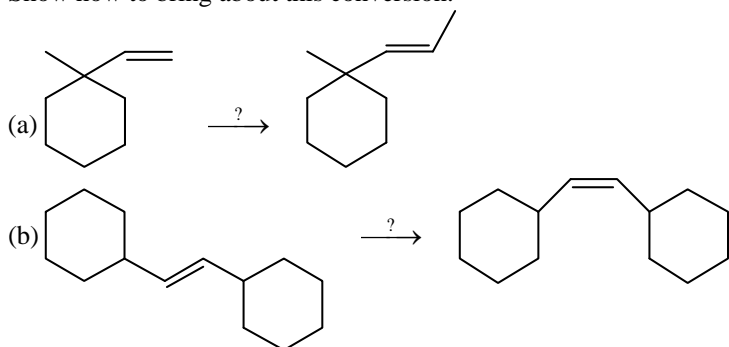
25. Show reagents to bring about each conversion.



解：A = LiND₂, ND₃ ; B = 1. NaNH₂, NH₃ 2. CH₃I ; C = B₂D₆, CH₃CO₂H ;

D = 1. B₂H₆ 2. CH₃CO₂D ; E = Na, NH₃(l) ; F = H₂, Lindlar's catalyst

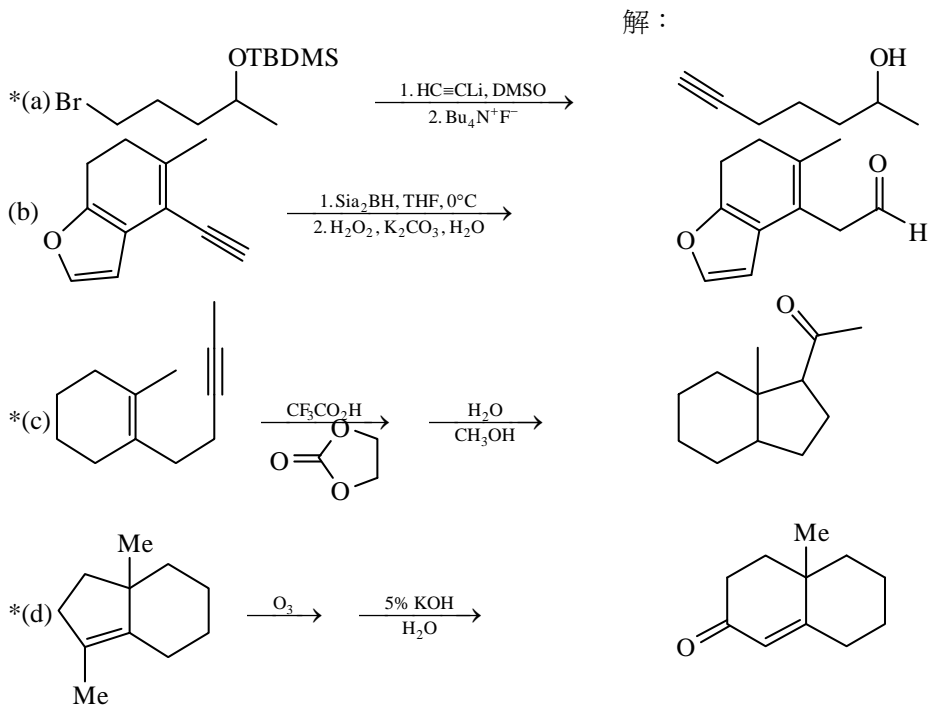
26. Show how to bring about this conversion.



解：(a) 1. $\text{Br}_2, \text{CCl}_4$ 2. $3\text{NaNH}_2, \text{NH}_3(\ell)$ 3. CH_3I 4. $\text{Na}, \text{NH}_3(\ell)$

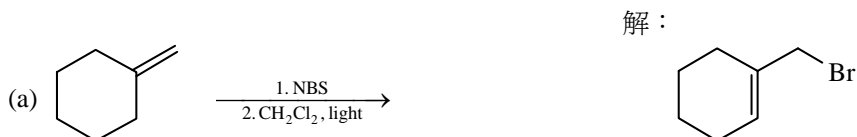
(b) 1. $\text{Br}_2, \text{CCl}_4$ 2. $2\text{NaNH}_2, \text{NH}_3(\ell)$ 3. H_2 , Lindlar's catalyst

27. Draw the expected products for the following reactions.

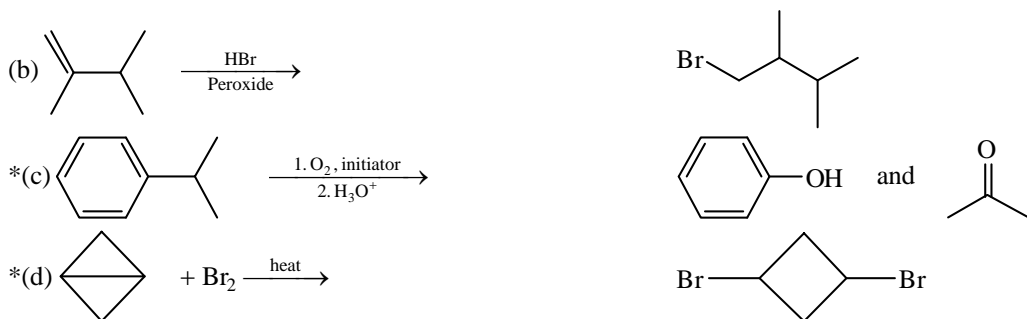


解：

28. Give the major product of the following reactions.

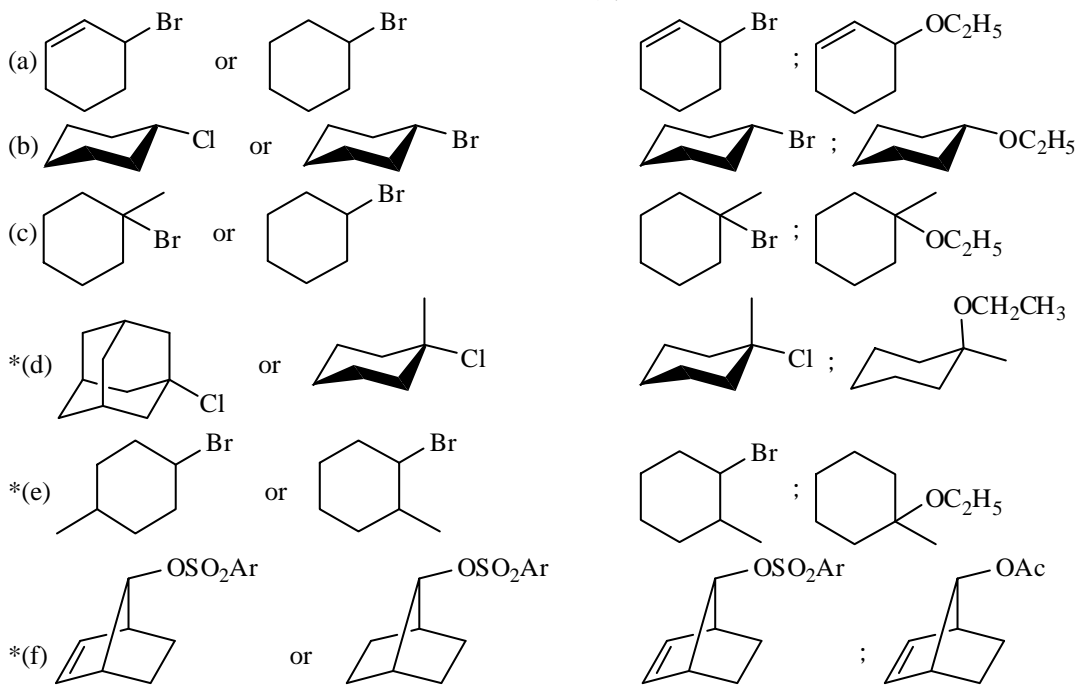


解：



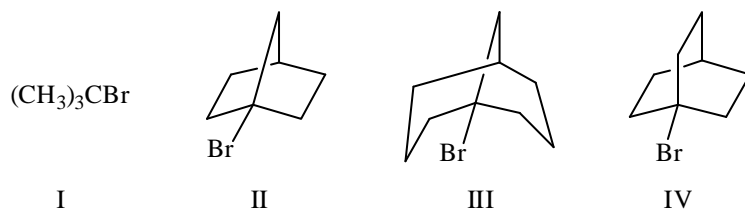
29. Which compound in each set undergoes more rapid solvolysis when refluxed in ethanol? Show the major product formed from the more reactive compound.

解：



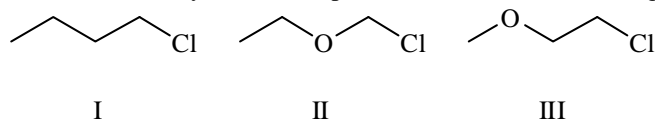
(solvolysis in acetic acid)

*30. Arrange the relative rates of solvolysis of these compounds in aqueous acetic acid.



解：I > III > IV > II

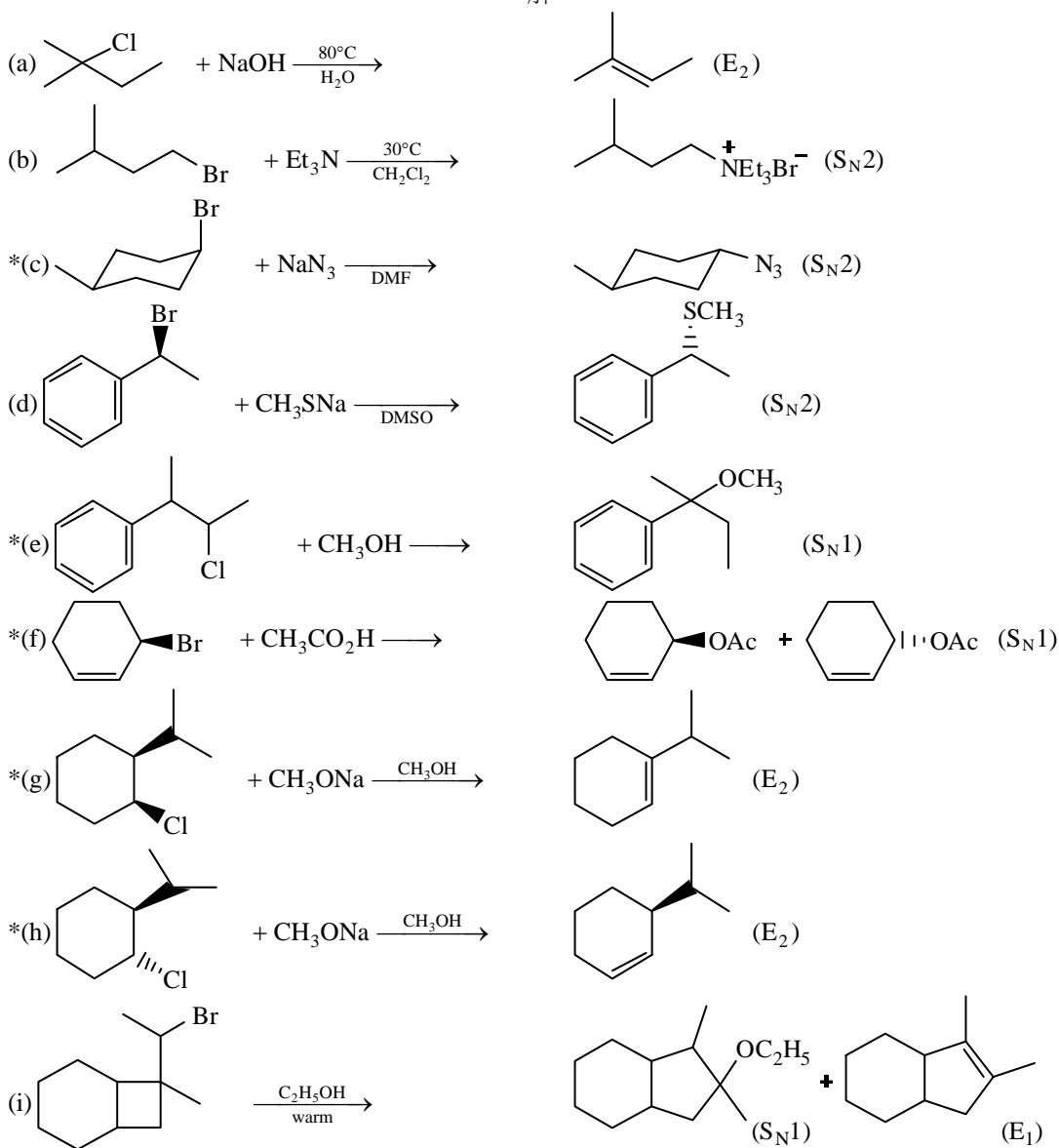
*31. Arrange the relative rates of solvolysis under experimental conditions favoring SN1 reaction.

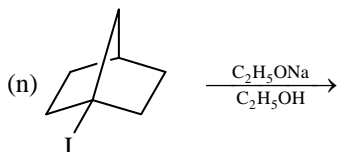
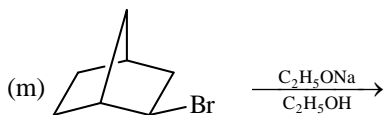
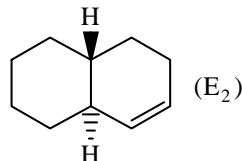
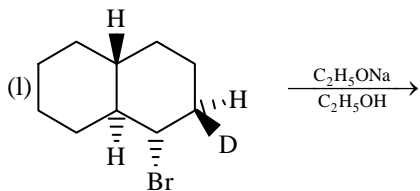
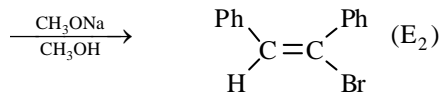
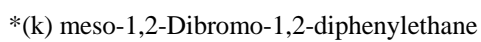
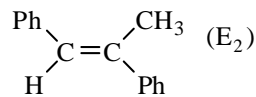
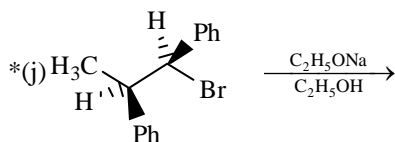


解：II > I > III

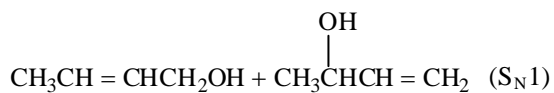
32. Predict whether each reaction proceeds predominantly by substitution (SN1 or SN2) or elimination (E1 or E2) or whether the two compete. Write structural formula for the major organic product(s).

解：



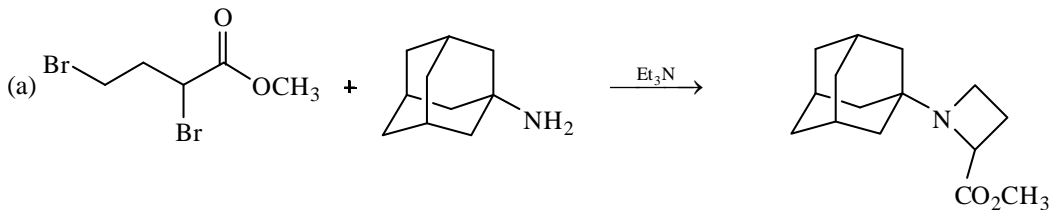


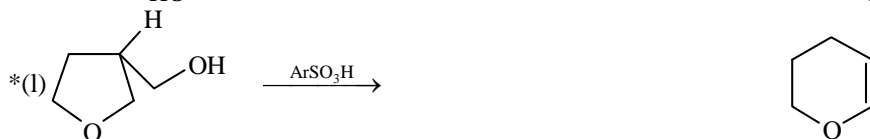
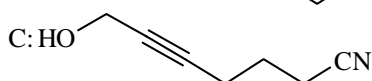
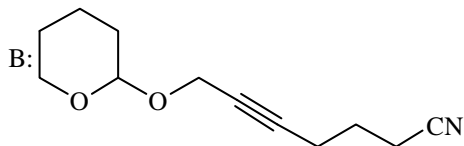
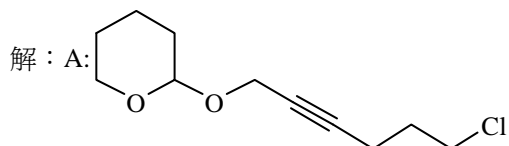
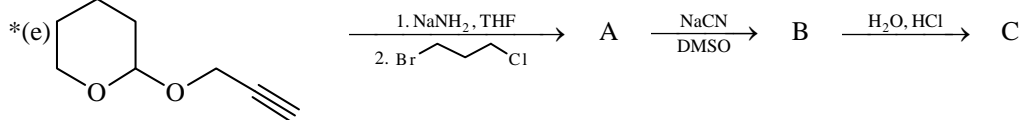
N.R.

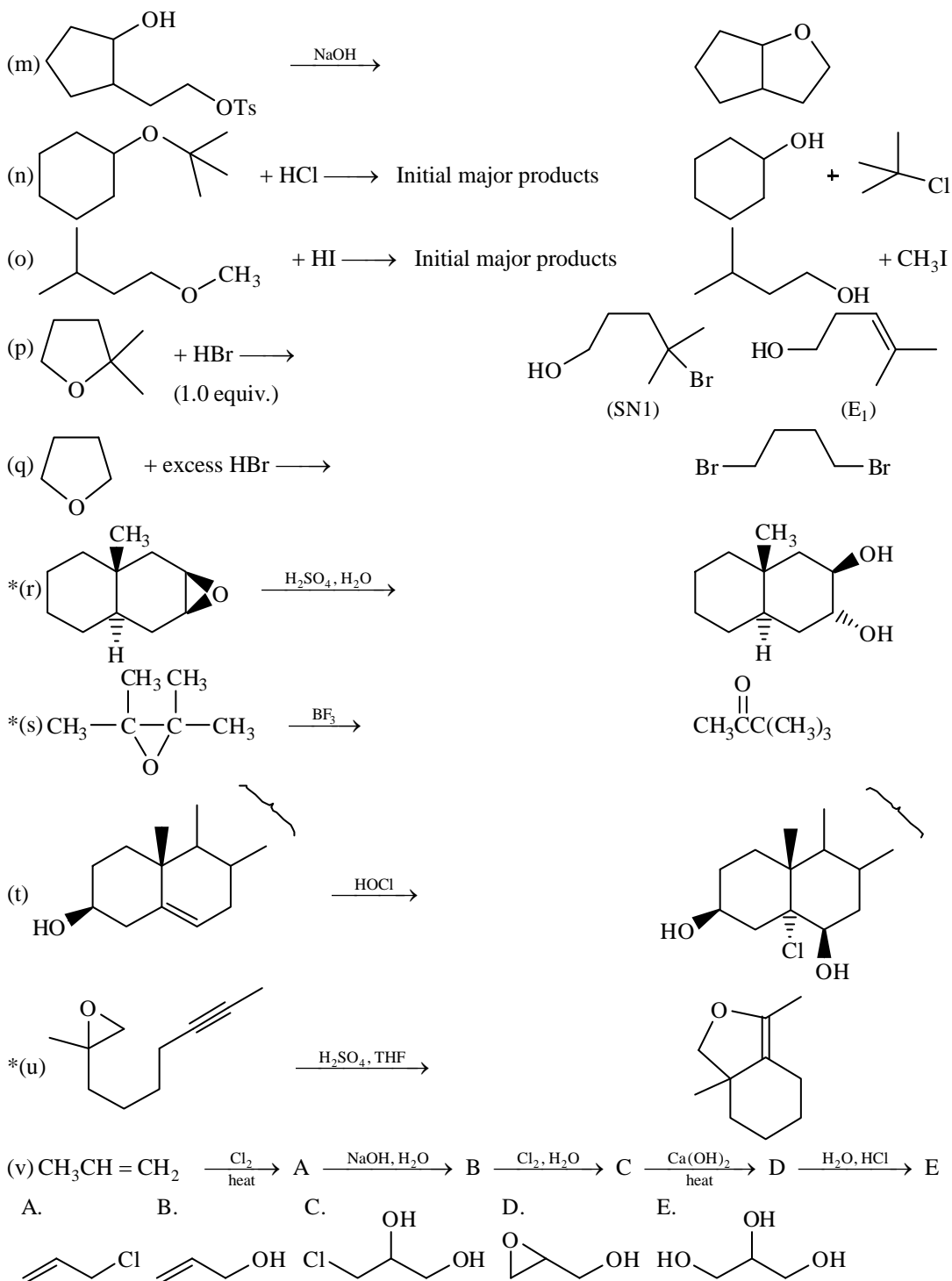


33. Give the major product of the following reactions.

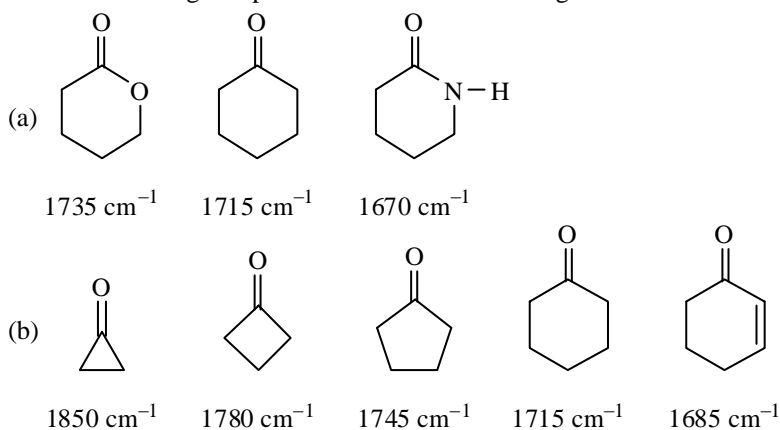
解：



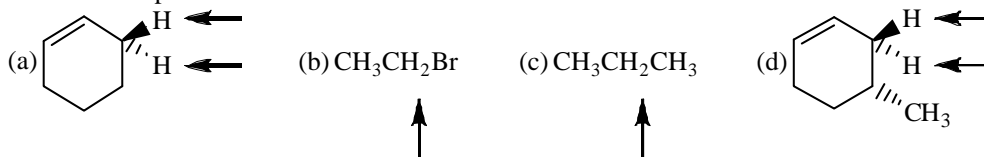




34. List the following compounds in order of decreasing wavenumber of the C = O absorption band:

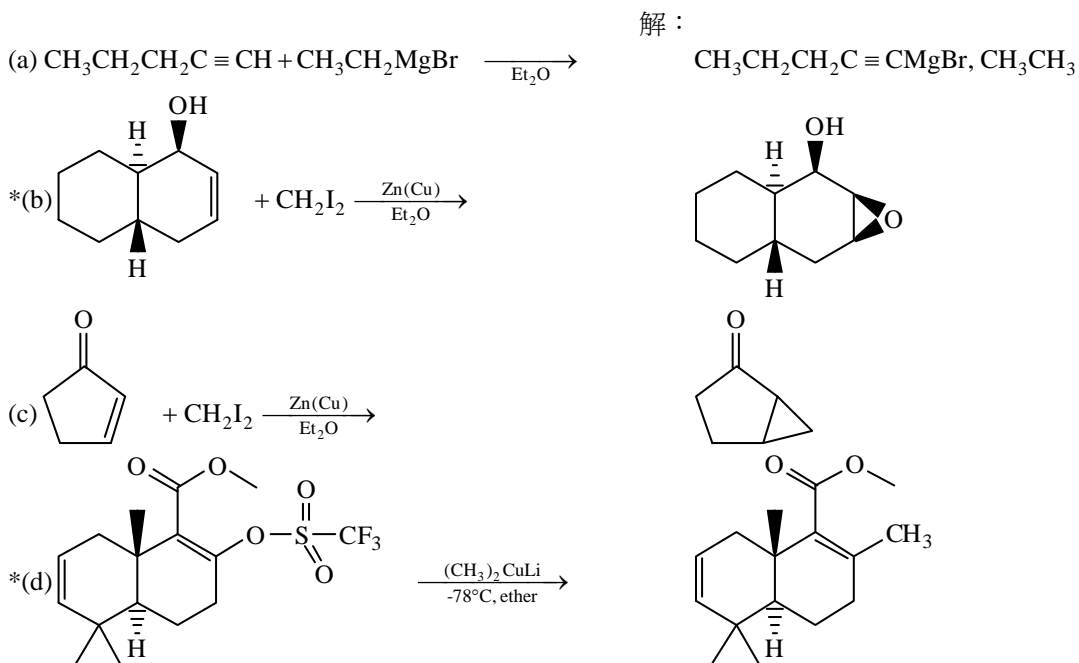


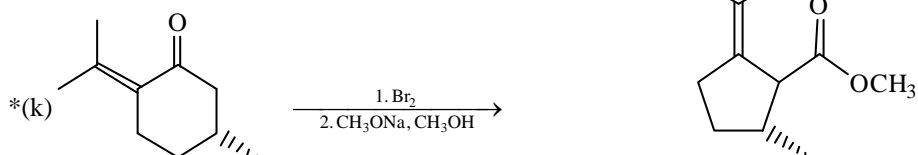
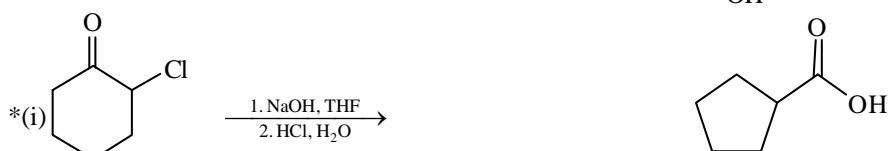
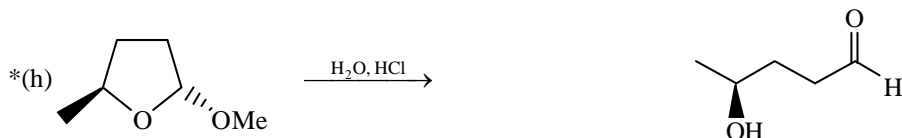
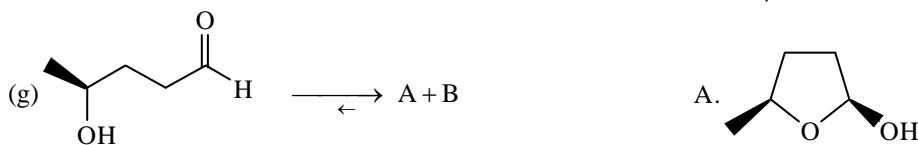
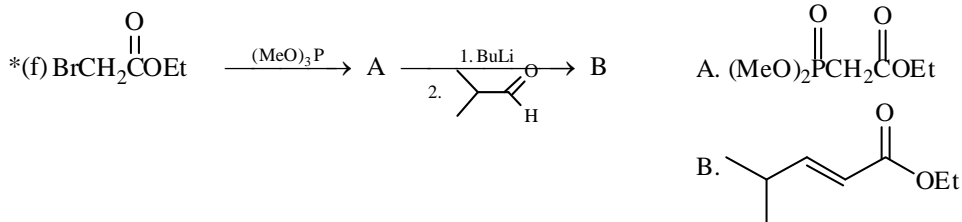
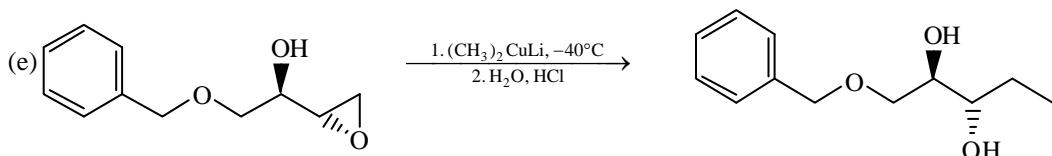
35. Indicate whether the arrowhead hydrogens in the following compounds are homotopic, enantiotopic, or diastereotopic.

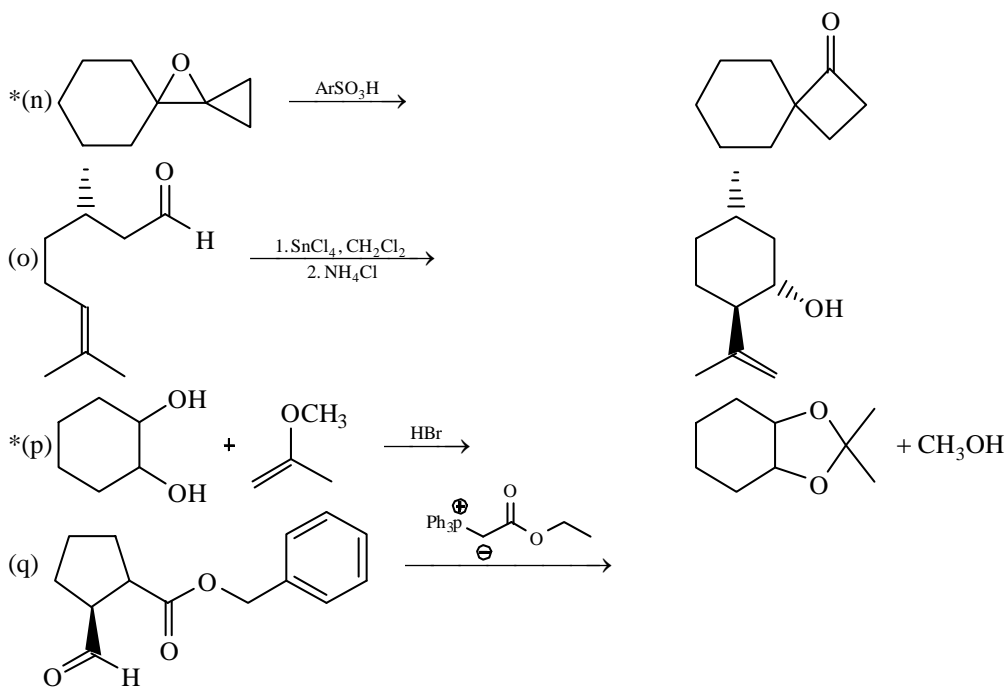


解：(a) Enantiotopic (b) Enantiotopic (c) Homotopic (d) Diastereotopic

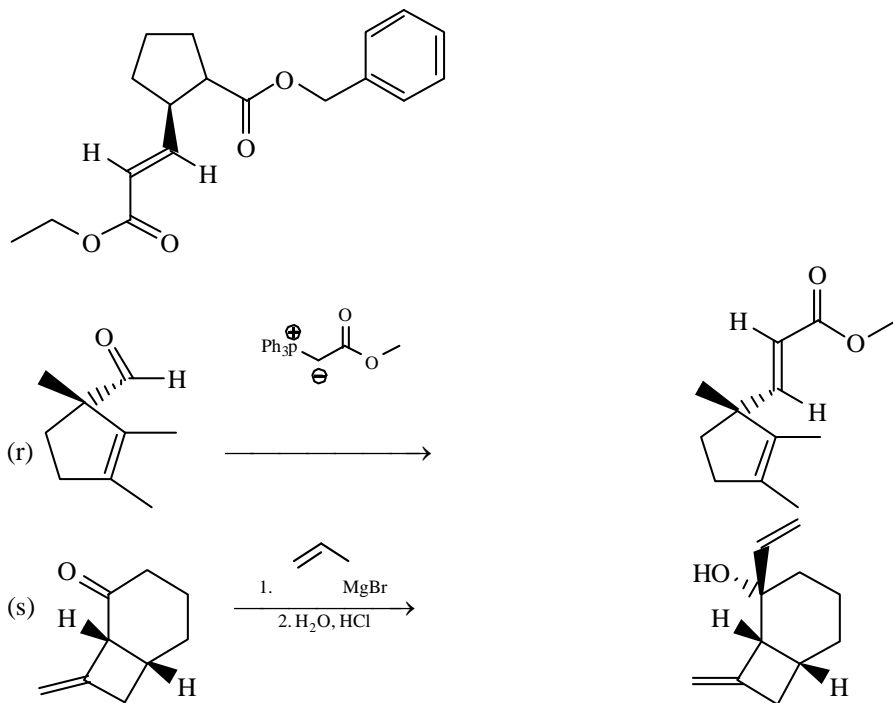
36. Give the major product of the following reactions.



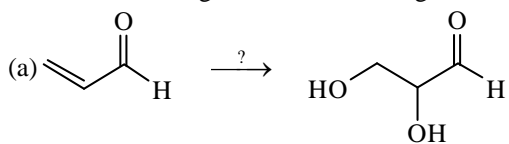


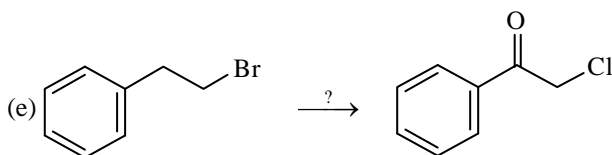
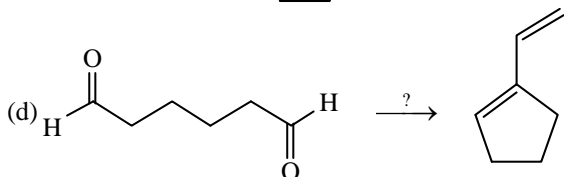
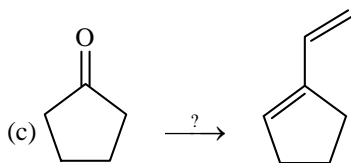
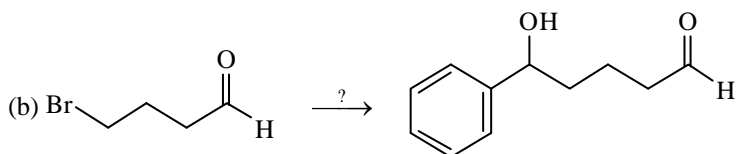


解：

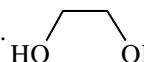


37. Show how to bring about the following conversions.





解：(a) 1. $2 \text{CH}_3\text{OH}$, H_2SO_4 2. Dilu, KMnO_4 , OH^- , cold 3. H_2O , HCl

(b) 1. , H^+ 2. Mg , ether 3. $\text{C}_6\text{H}_5\text{CHO}$ 4. H_2O , HCl

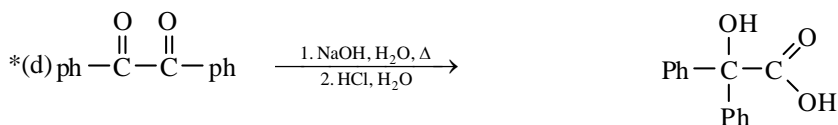
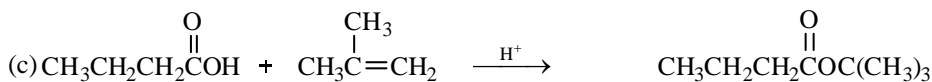
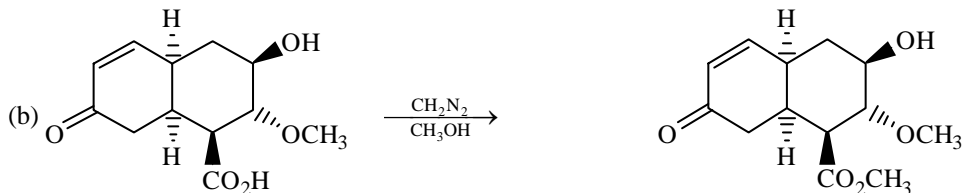
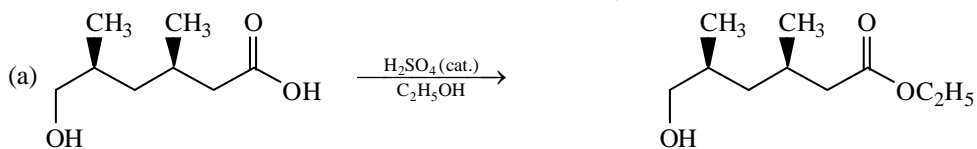
(c) 1. $\text{HC}\equiv\text{CH}$, NaNH_2 2. H_2O 3. H_2 , Lindlar catalyst 4. KHSO_4 , heat

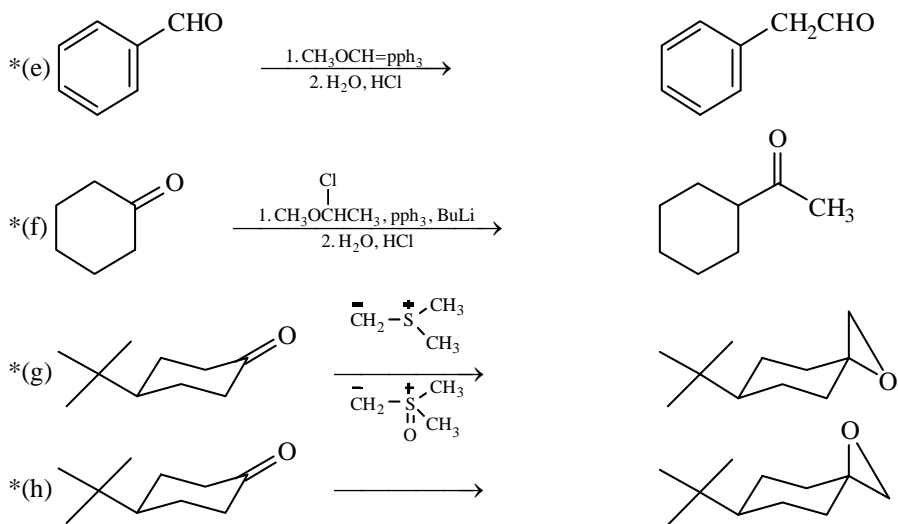
(d) 1. OH^- , H_2O , Δ 2. $\text{CH}_2=\text{pPh}_3$

(e) 1. t-BuOK 2. H_2SO_4 , H_2O 3. H_2CrO_4 4. Cl_2 , H^+

38. Give the major product of the following reactions.

解：





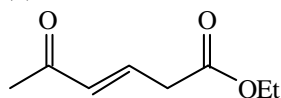
39. Show the product expected when the following unsaturated δ -ketoester is treated with

(a) H_2 (1 mol), Pd, EtOH

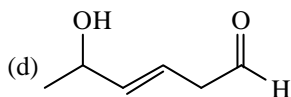
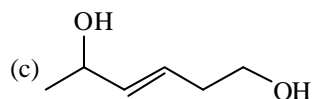
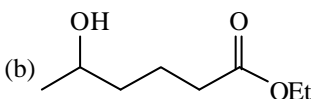
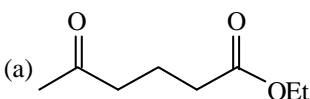
(b) NaBH_4 , CH_3OH

(c) 1. LiAlH_4 , THF 2. H_2O

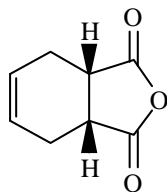
(d) 1. DIBAL-H, -78°C 2. H_2O



解：



40. Show the product of treating this anhydride with



(a) H_2O , HCl, heat

(b) H_2O , NaOH, heat

(c) 1. LiAlH_4 2. H_2O

(d) CH_3OH

(e) NH_3 (2 mol)

