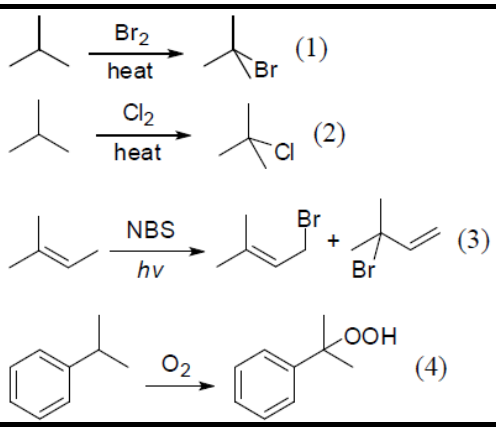
化學

Chapter 01 烷 Alkanes

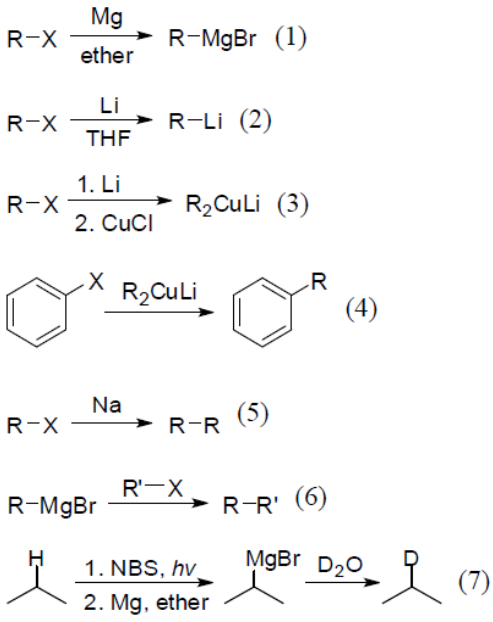
重點 1.1：烷類可以進行自由基取代反應



應考重點：

1. 溴化反應選擇性好，不用考慮機率
2. 氯化反應選擇性差，要考慮機率
3. 自由基反應可能有共振產物
4. autoxidation 發生在較弱的 C−H 位置

重點 1.2：合成有機金屬後，可以製造烷類



應考重點：

1. 製造 Grignard reagent 時，鹵烷結構上不能含有酸性氫或親電碳，通常用醚當溶劑
2. 製造 Organolithium 時，鹵烷結構上不能含有酸性氫或親電碳，通常用醚當溶劑
3. 製造活性較低的有機銅鋰(cuprate)
4. cuprate 能夠在 sp^2 碳上進行取代反應
5. Wrutz 反應，可得到對稱性烷類
6. 用 Grignard reagent 進行 coupling 時，最好選用沒有消去反應可能的 RX (CH_3X、$PhCH_2X$ 或 $H_2C{=}CHCH_2X$)
7. 利用鹵烷在特定碳上標定同位素

重點 1.3：烷類的燃燒反應

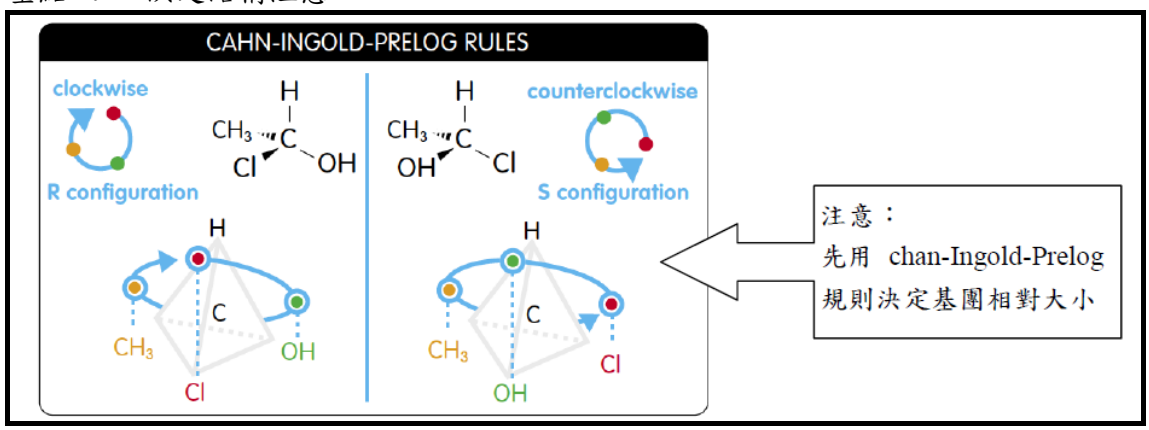
$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \xrightarrow{heat} nCO_2 + (n+1)H_2O + Energy$$

應考重點：

1. 異構物可以用莫耳燃燒熱比較穩定度

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°

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

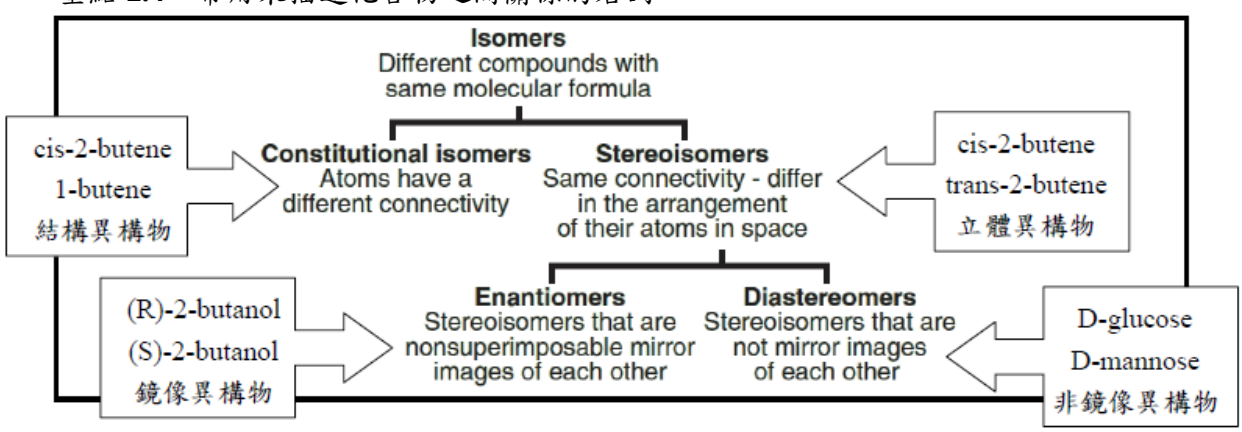
重點 2.3：鏡像過量

- 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.

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

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

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° > 2°	CH_3X > 1° > 2°
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

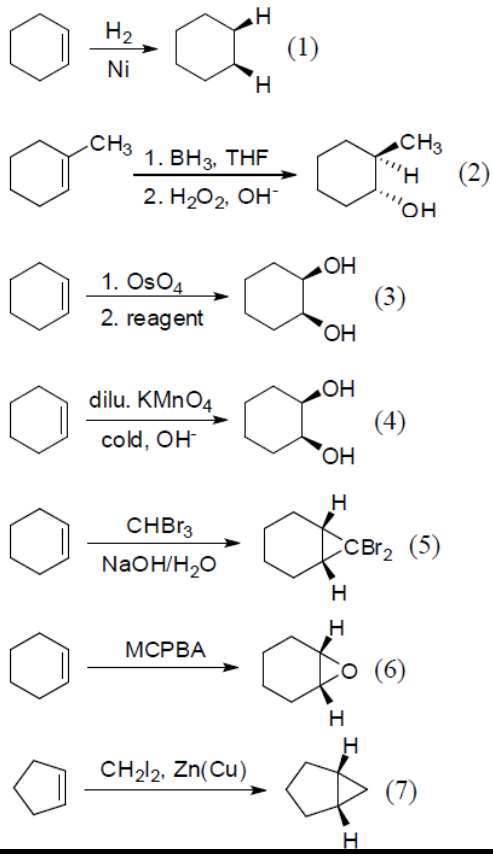
	E1	E2
影響因素		
鹼	通常使用弱鹼	使用強鹼
鹵烷結構 (RX)	3° > 2°	3° > 2° > 1°
溶劑	介電常數較大的溶劑	可使用的溶劑很多 (通常用極性較小的)
離去基	好離去基	好離去基
其他因素	高溫條件會導致消去產物比例增加	
特色		
反應動力學	first order, k_r[RX]	second order, k_r[RX][B:$^-$]
產物位向	Zaitsev's rule	Zaitsev's rule (立障小的鹼) Hofmann' rule (立障大的鹼)
立體化學	沒有特別的立體要求	能產生軌域共平面的過渡狀態
結構重排的可能性	很可能重排	不會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

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

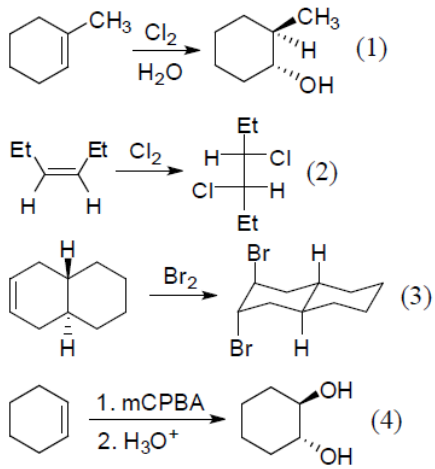
重點 **5.1**：特別注意以下反應皆進行同向加成**(Syn-Add)**



應考重點：

1. 催化氫化可用 Ni, Pd, PtO_2 等藥劑
2. 注意反應位向是反馬可尼可夫
3. 第二步驟的藥劑可搭配氧化劑(H_2O_2、3° amine oxide)或還原劑($NaHSO_3$、H_2S)使用
4. 溫和條件不會氧化切斷
   Ex. neutral、dilute、cold
5. 加成含有兩個鹵素分子的 carbene
6. 注意氧化速率（電子密度高者氧化快）
7. Simmons-Smith Rxn
   可以用來製造不含鹵素的 carbene

重點 **5.2**：特別注意以下反應皆進行反向加成**(Anti-Add)**



應考重點：

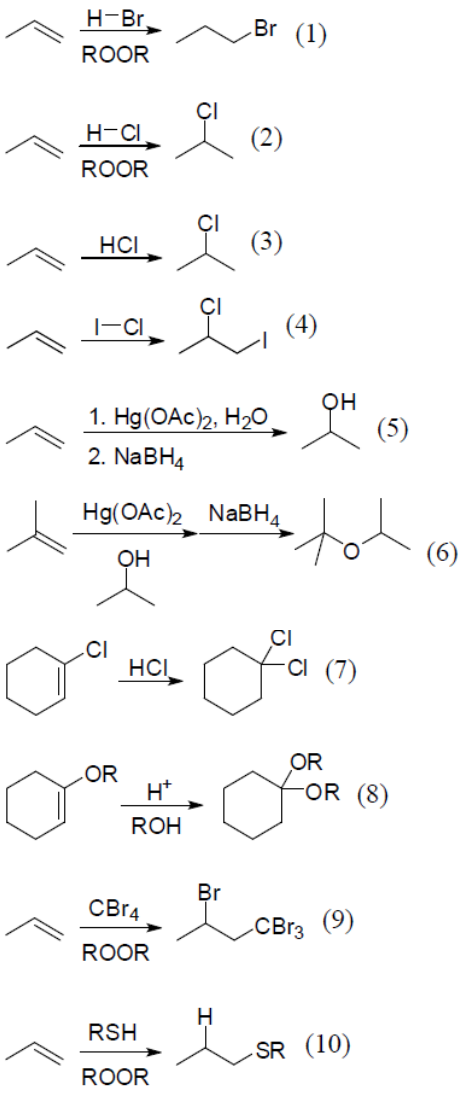
1. 特別注意反應藥劑的表達方式

   $\xrightarrow[H_2O]{Cl_2}$ = $\xrightarrow{HOCl}$

2. 兩個 Cl 是反向加成
3. 如果是 cyclohexene 結構，則會進行 axial addition
4. 特別注意反應藥劑的表達方式

   $\xrightarrow[2.\ H_3O^+]{1.\ mCPBA}$ = $\xrightarrow[H_2O_2]{HCO_2H}$

重點 **5.3**：特別注意以下反應的產物位向**(1)**

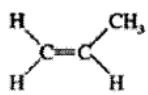
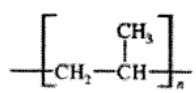
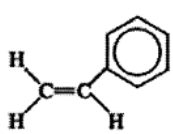
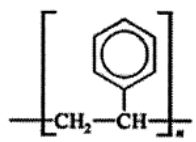


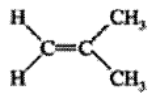
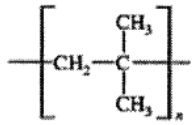
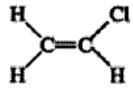
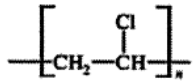
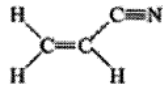
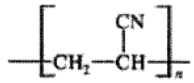
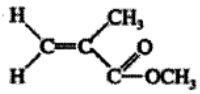
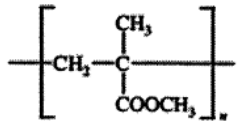
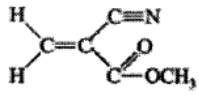
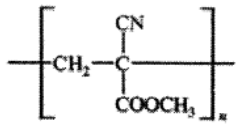
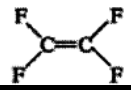
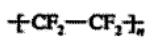
應考重點：

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	$H_2C{=}CH_2$	$+CH_2{-}CH_2+_n$
polypropylene	plastics, olefin fibers		
polystyrene	plastics, foam insulation		

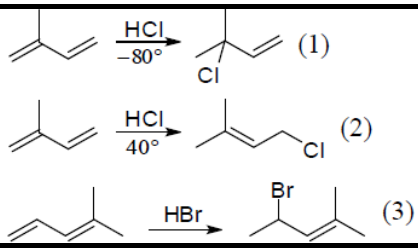
poly(isobutylene)	specialized rubbers		
poly(vinyl chloride)	vinyl plastics, films, water pipes		
poly(acrylonitrile)	Orlon®, Acrilan® fibers		
poly(methyl α-methacrylate)	acrylic fibers, Plexiglas®, Lucite® paints		
poly(methyl α-cyanoacrylate)	"super" glues		
poly(tetrafluoroethylene)	Teflon® coatings, PTFE plastics		

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

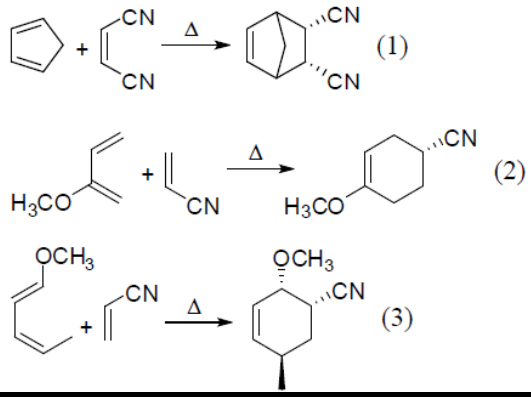
重點 6.1：1,2-Addition & 1,4-Addition



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

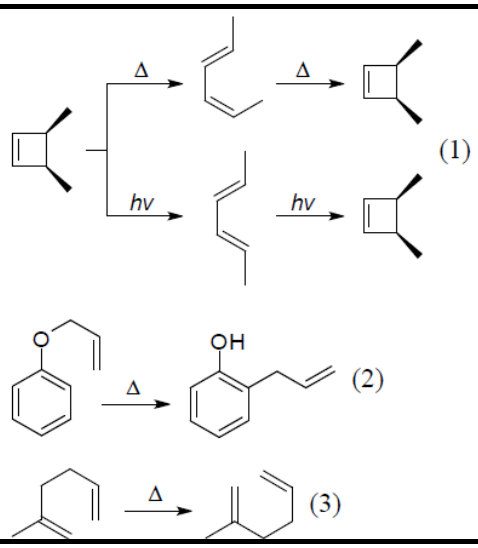
重點 6.2：Diels-Alder Reaction



應考重點：

1. Diels-Alder Rxn [4+2] 加熱才反應，照光不反應
2. Diels-Alder Rxn 有位向選擇性(-o, -p 位向)
3. Diels-Alder Rxn 有立體選擇性(Endo rule)

重點 6.3：Pericyclic Reaction

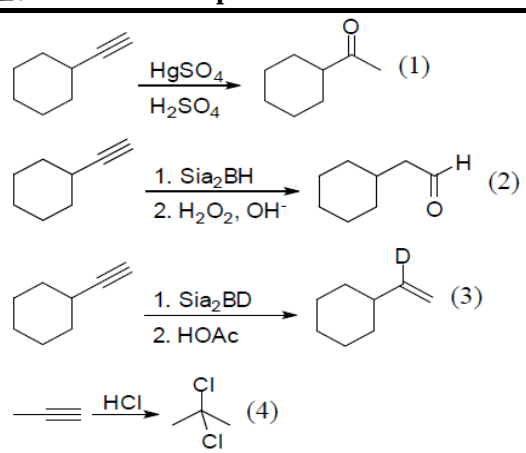


應考重點：

1. 照光和加熱會造成 HOMO 或 LUMO 有所變化
2. Claisen 重排
3. Cope 重排

Chapter 07 炔 Alkynes

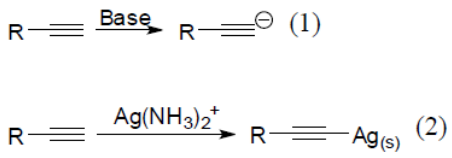
重點 7.1：Electrophilic Addition Reaction



應考重點：

1. 末端炔有位向選擇性，可得到單一主產物使用汞離子催化水合得到 ketone
2. 末端炔有位向選擇性，可得到單一主產物使用硼氫化氧化反應得到 aldehyde
3. 硼氫化還原可以在特定位置標定同位素
4. 注意兩個 nucleophile 都接在高級碳

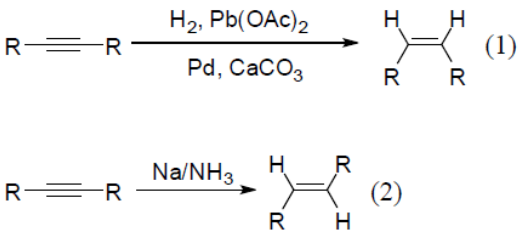
重點 7.2：Terminal Alkynes



應考重點：

1. 強鹼如 NaH、$NaNH_2$、RMgBr 等可拔氫
2. 可用重金屬反應而沉澱
   注意：$Cu(NH_3)_2$ 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 Pb^{2+}毒劑
   可以合成 cis-alkene
   也可以使用 $\xrightarrow[Pd,\ BaSO_4]{H_2,\ quinoline}$
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

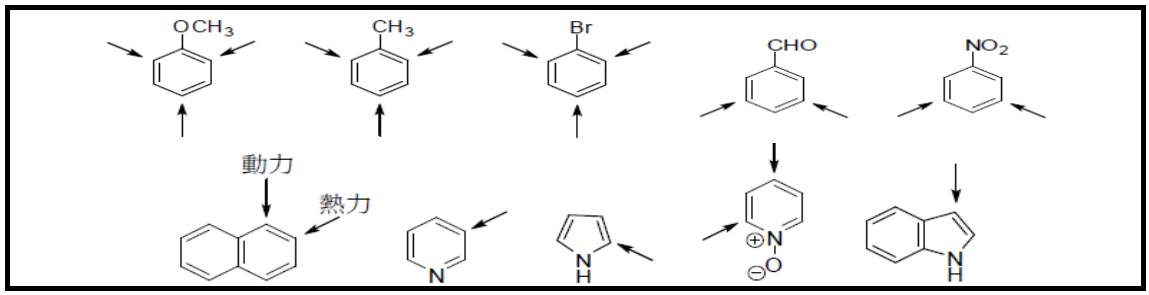
反應性	反應條件	備註
大 ↓ 小	$\xrightarrow[H_2SO_4]{HNO_3}$ NO_2	單獨使用 HNO_3 不加 H_2SO_4 也可以反應
	$\xrightarrow{H_2SO_4}$ SO_3H	磺化反應可逆，可當保護基
	$\xrightarrow[Lewis\ acid]{X_2}$ X	① $X_2 = Cl_2$ or Br_2 ② E^+是 complex 而非 X^+
	$\xrightarrow[Lewis\ acid]{R-Cl}$ R	① 可能重排或多取代 ② 碰到中、強去活化基不反應 ③ 可以用 ROH/BF_3 或 Alkene/HF 當親電劑
	$\xrightarrow[Lewis\ acid]{R-C(=O)-Cl}$ C(=O)R	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。

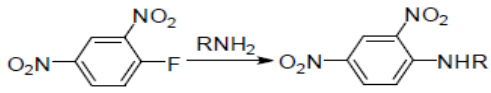
重點 **8.2**：不同取代基的反應活性表

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
$-O^-$ $-NH_2$ $-NHR$ $-NR_2$ $-OH$ $-OR$	$-\overset{H}{\underset{}{N}}-\overset{O}{\overset{\|}{C}}-R$ $-O-\overset{O}{\overset{\|}{C}}-R$	$-R$ $-\overset{H}{\underset{}{C}}=CH_2$	$-F$ $-Cl$ $-Br$ $-I$	$-\overset{O}{\overset{\|}{C}}-H(R)$ $-\overset{O}{\overset{\|}{C}}-OR(H)$ $-C\equiv N$ $-SO_3H$	$-CF_3$ $-CCl_3$ $-\overset{+}{N}R_3$ $-NO_2$

重點 **8.3**：芳香化合物的親電取代反應位向整理



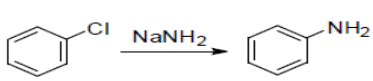
重點 **8.4**：**Addition-Elimination Mechanism**



應考重點：

1. 在離去基 o, p 位置有強拉電子機容易進行加成消去反應
2. 此類型反應的應用：Sanger Method 用來檢驗 amino acid 是否存在

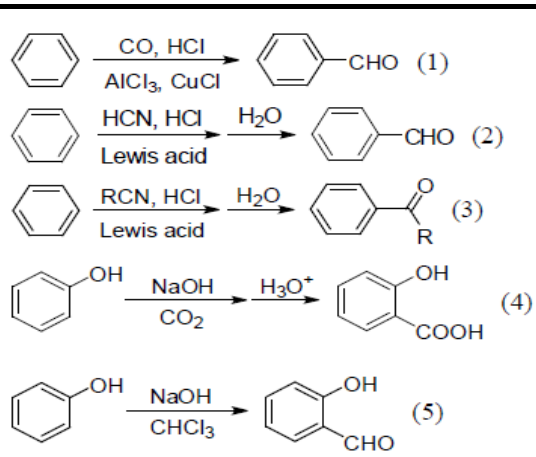
重點 **8.5**：**Elimination-Addition Mechanism**



應考重點：

1. 會產生 benzyne 中間物
2. 常搭配 Diels-Alder Rxn 一起出題

重點 **8.6**：其他芳香族化合物的反應

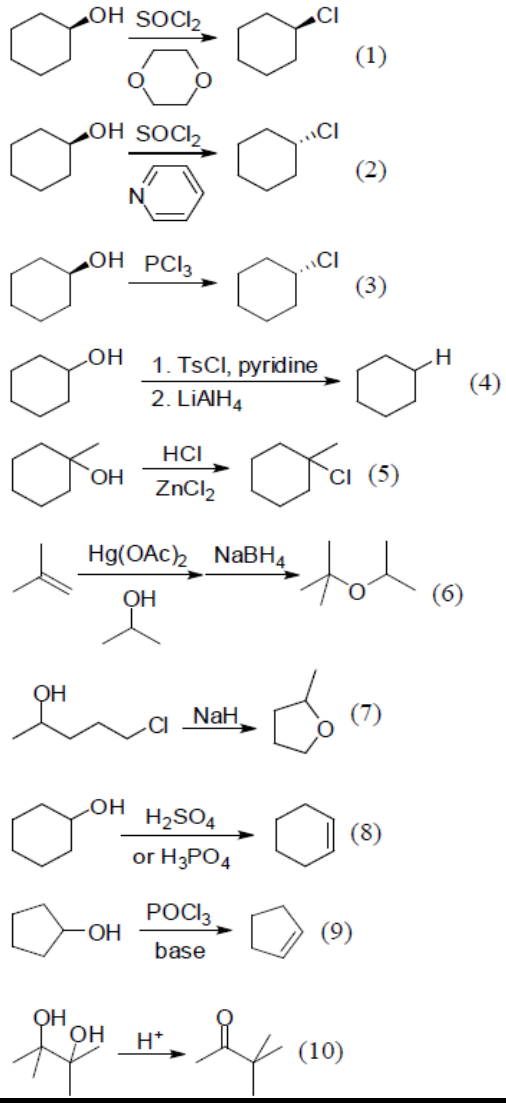


應考重點：

1. Gattermann-Koch Formylation
2. Gattermann Reaction
3. Hoesch Reaction
4. Kolbe-Schmitt Reaction
   可合成水楊酸(salicylic acid)，用來製造乙醯水楊酸(aspirin)
5. Reimer-Tiemann Reaction
   可以在 phenol 旁邊放上一個醛官能基

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

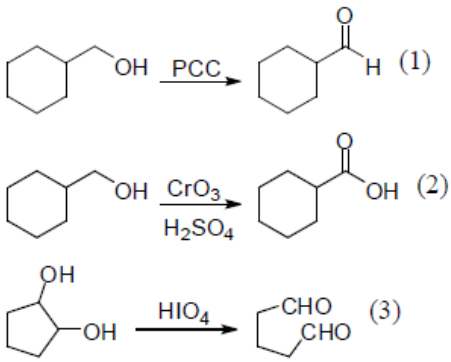
重點 9.1：醇類的反應



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° > 2° > 1° 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

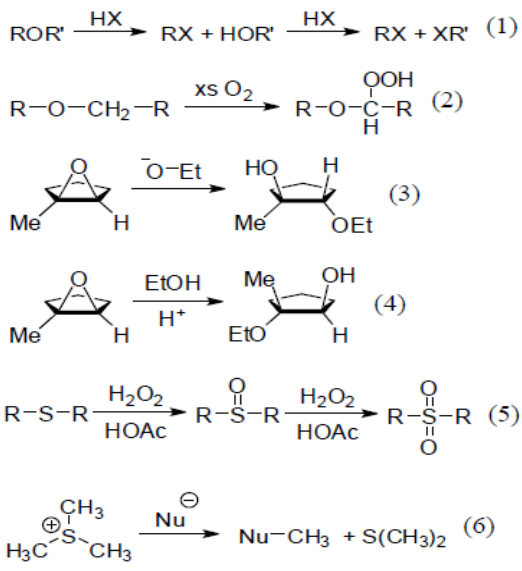
重點 9.2：醇類的氧化反應



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、$KMnO_4$(aq)
3. 可形成五環中間物的 diol 可以氧化切斷
   注意：$Pb(OAc)_4$ 也有類似效果

重點 **9.3**：醚類、環氧化物、硫化物的反應

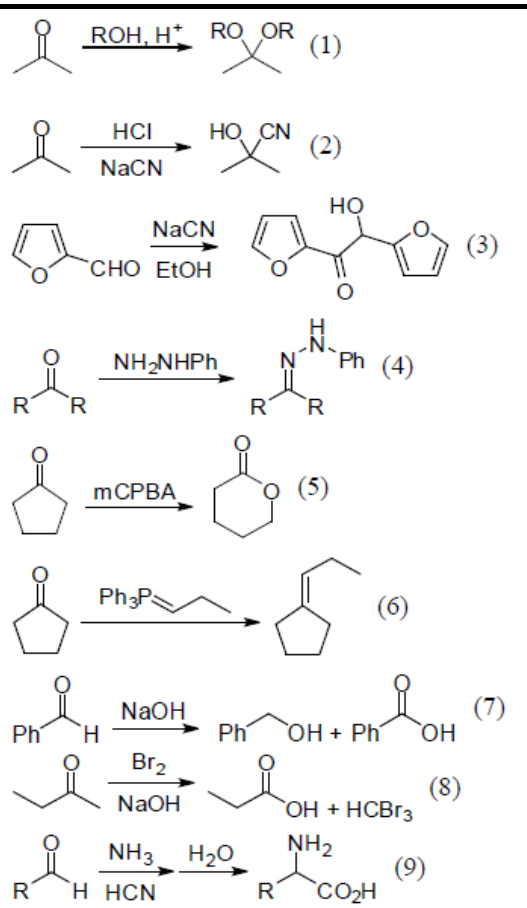


應考重點：

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

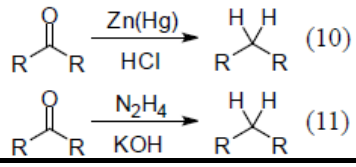
Chapter 10 醛、酮 Aldehyde, Ketone

重點 **10.1**：醛、酮的反應(1)



應考重點：

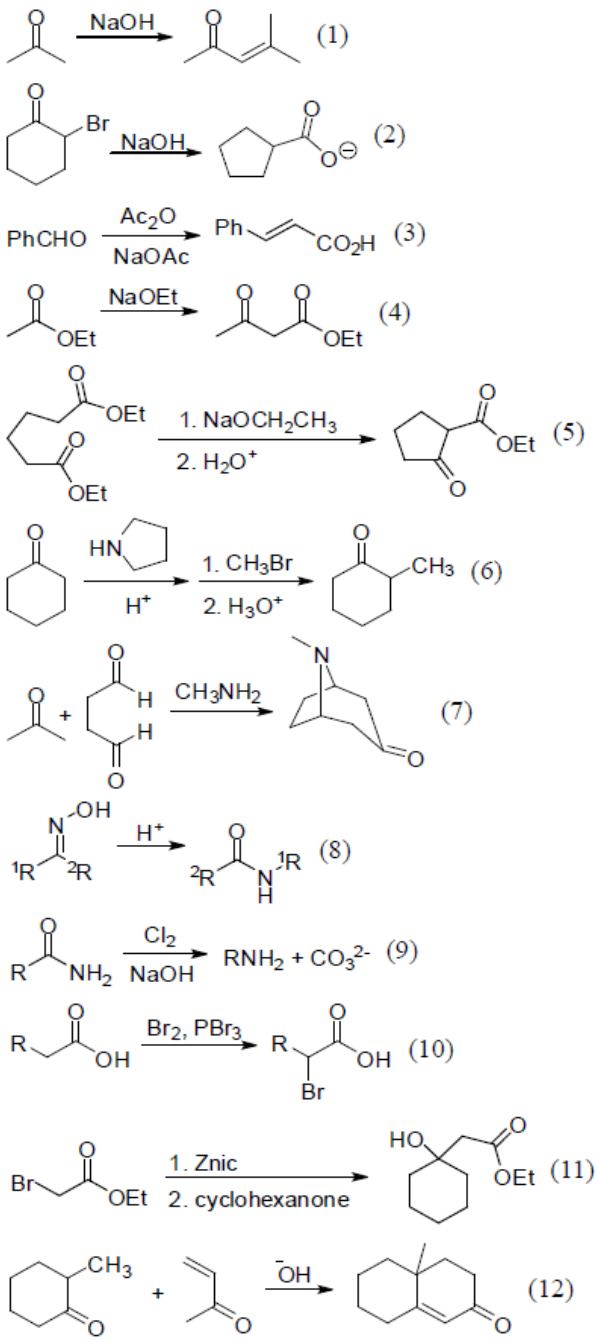
1. Nucleophilic Addition Reaction
   可以用來當醛、酮的保護劑基
2. 得到 cyanohydrin
3. Benzoin Condensation
   芳香醛在沒有 H^+的條件下容易進行
4. 與 Hydrazine 反應得到 hydrazone
5. Baeyler Villiger Oxidation
   注意電子密度高者氧化速率較快
6. Wittig Reaction
   注意 stabilized ylide(得到 E-form)和
   unstabilized ylide(得到 Z-form)
7. Cannizzaro Reaction
   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-Kishnner Reaction (鹼性條件)

重點 **10.2**：醛、酮的反應(2)

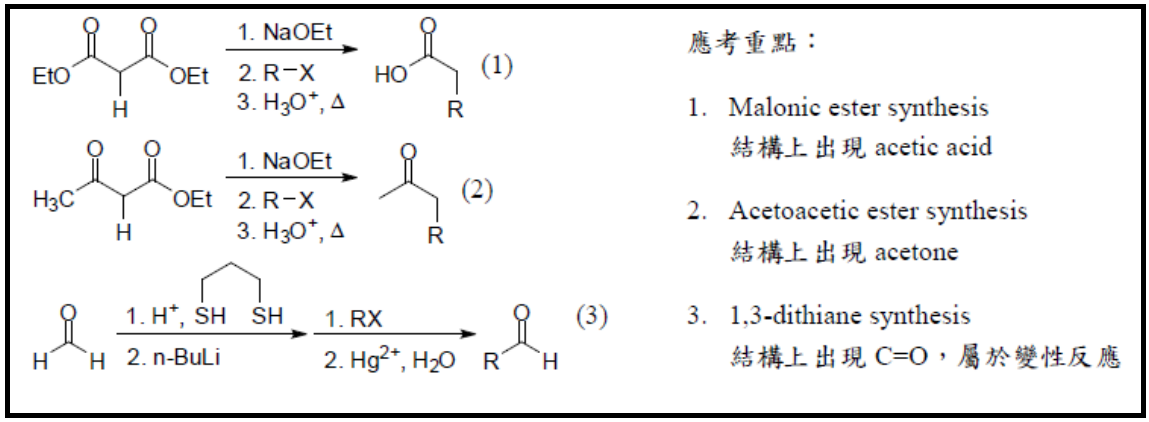


應考重點：

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 Hα，則可能會進行 Retro Claisen Rxn
5. Dieckmann Condensation
   分子內的 Claisen condensation
6. Stork Rxn
   $E^+ = CH_3X$, 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 NH_3(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

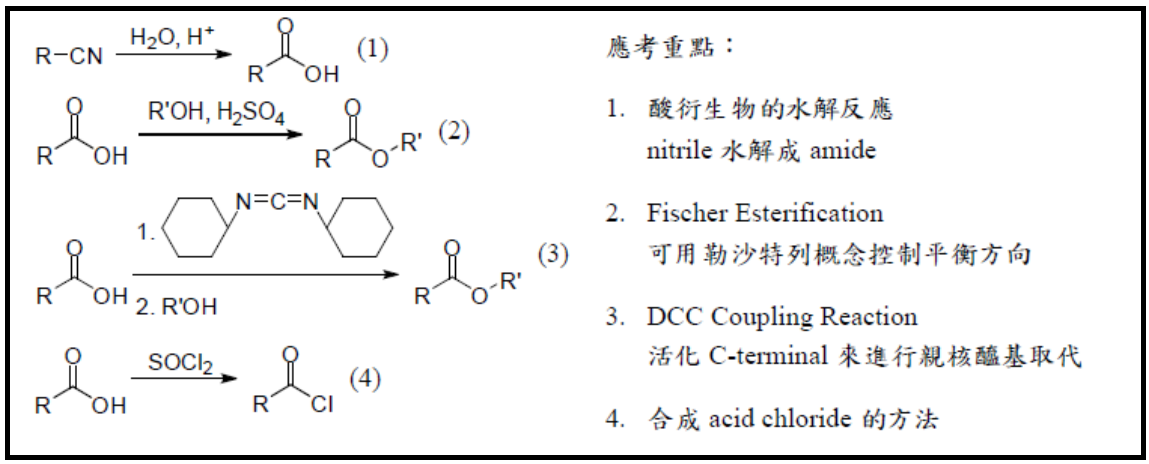
注意：生物合成fatty acid 是利用malonyl thioester 和acetyl thioester 進行Claisen Condensation

重點 **10.3**：醛、酮的合成

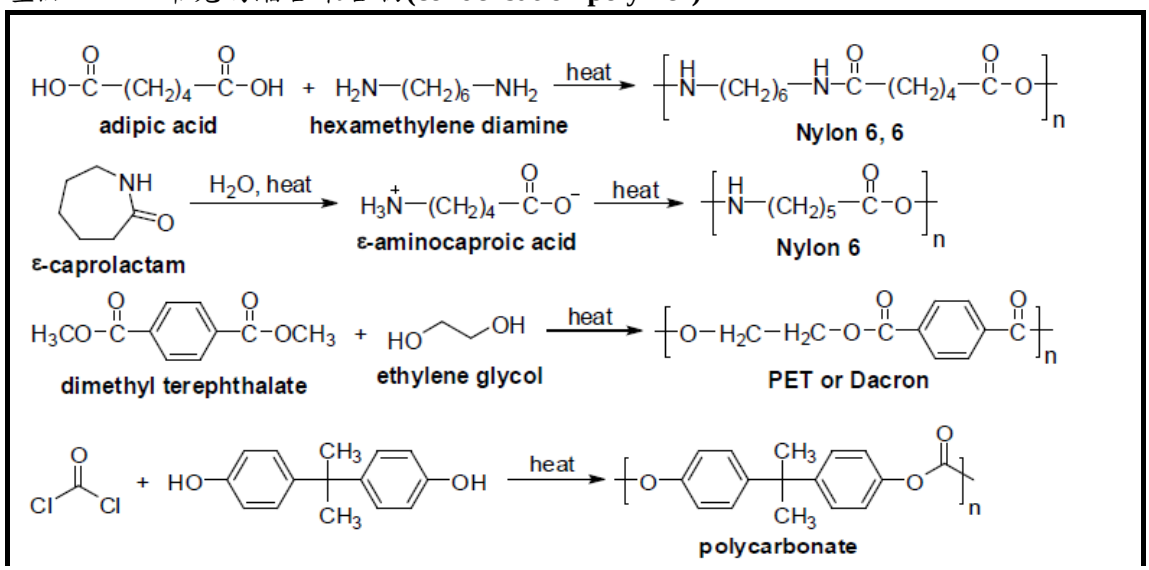


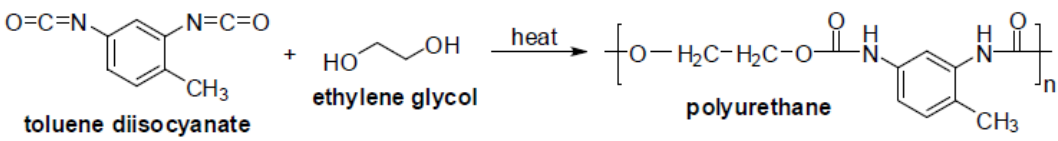
Chapter 11 酸和酸的衍生物 Acid, Acid Derivatives

重點 **11.1**：酸和酸的衍生物的反應



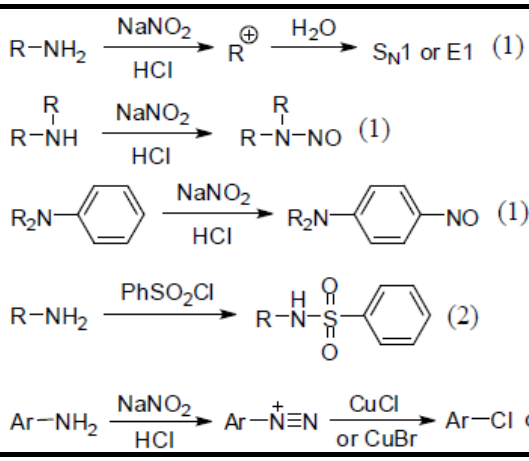
重點 **11.2**：常見的縮合聚合物**(condensation polymer)**





Chapter 12 胺 Amines

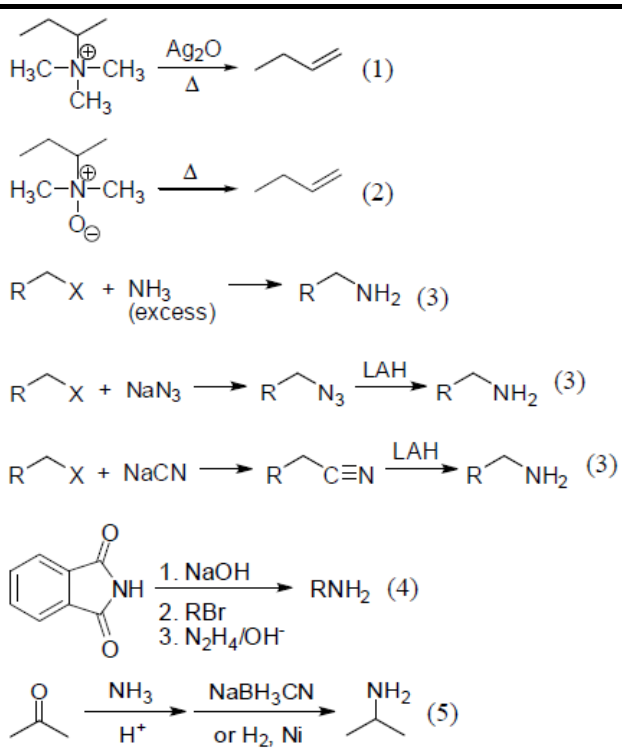
重點 12.1：胺類化合物的反應



應考重點：

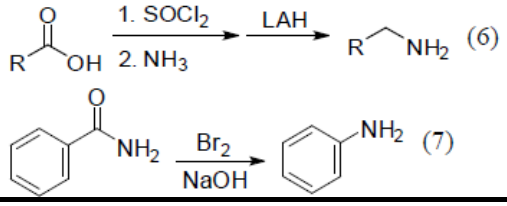
1. 不同 amine 與 HNO_2 反應的產物結果不同
   1°胺得到 S_N1 和 E1 混合產物
   2°胺得到 N-nitroso amine
   $Ph-NR_2$ 得到親電取代反應產物
2. 反應的應用：Hinsberg Test (胺類分級)
3. Sandmeyer Reaction

重點 12.2：胺類化合物的合成



應考重點：

1. Hofmann Elimination
2. Cope Elimination
3. S_N2 mechanism
4. Gabriel Reaction
   經過 S_N2，RX 選立障小的
5. Reductive Amination
6. Acylation Reduction
7. Hofmann Rearrangement



[試題練習]

(D) 1. 分子式，$C_4H_{10}O$，結構異構物數自有

(A) 4 (B) 5 (C) 6 (D) 7

(B) 2. 尿素($CO(NH_2)_2$）碳原子混成軌域爲

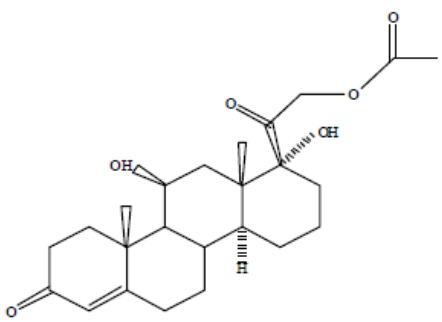
(A) sp3 (B) sp2 (C) sp (D)不混成

(C) 3. F_3B-NH_3，氮原子形式電荷（Formal charge）爲

(A) 0 (B)-1 (C)+1 (D)-2

(A) 4.Cortisone acetate（active ingredient in steroid skin creams）含有幾種官能基（functional groups）？

Cortisone acetate



Cortisone acetate

(A) 4 (B) 5 (C) 6 (D) 7

(B) 5. 鐵覆蓋那一種金屬稱之Galvanic iron，可防止鐵生銹？

(A) Cr (B) Zn (C) Mn (D) Al (E) Sn

(D) 6. 在鹼性電池何種物質被還原？

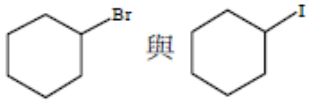
(A) $Zn_{(s)}$ (B) $Zn^{2+}{}_{(aq)}$ (C) $NH4^{+}{}_{(aq)}$ (D) $MnO2_{(s)}$ (E) $KOH_{(aq)}$

(D) 7. 某核種有70 個中子，且中子與質子比值小於1，試問此核種如何穩定？

(A) beta decay (B) alpha decay (C) gamma emission (D) electron capture (E) neutron emission

(C) 8.下列何者鹼性最強？

(A) NaOH (B) HC≡CNa (C) CH_3MgBr (D) $NaNH_2$

(C) 9.  可使用下列何種圖譜區別？

(A) NMR (B) IR (C) MS (D) UV

(E) 10. 依Cahn-Ingold -Prelog rule，取代基大小順序爲

1 —CHO 2 —CH = $CHCH_3$ 3 —CH = NCH_3 4 —C≡CCH_3

(A) 1＞2＞3＞4 (B) 3＞4＞2＞1 (C) 1＞4＞3＞2 (D) 4＞3＞2＞1 (E) 1＞3＞4＞2

(C) 11. C_4H_8 四種烯類異構物莫耳氫化熱各爲 —30.1, —28.6, —27.6 及—27.3 kcal／mol，試問下列何者表示 trans-2-butene 的莫耳氫化熱？

(A)—30.1 kcal/mol (B)—28.6 kcal/mol (C)—27.6 kcal/mol (D)—27.3 kcal/mol (E) 無法決定

(A) 12. 下列那一種輻射穿透人體皮膚最小？

(A) alpha rays (B) gamma rays (C) X-rays (D) neutron beam (E) beta rays

(A) 13. 定溫定壓下，下列那一個熱力函數表示自然發生過程？

(A) VG < 0 (B) VG = 0 (C) VH = 0 (D) VS > 0 (E) VH < 0

(B) 14. 將NH_4Cl 固體加入到0.10M $NH_{3(aq)}$ 1L 溶液中：

(A) 溶液PH 值增加 (B) 溶液PH 值降低 (C) 溶液PH 值不變 (D) NH_3 解離度增大 (E) NH_3 平衡常數增大

(C) 15. 下列何者可增加AgCl 溶解度？

(A) $HC_2H_3O_2$ (B) NaOH (C) NH_3 (D) HF (E) NaCl

(D) 16. 有關隔離系統自發吸熱過程，下列那些正確？

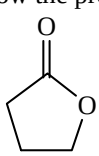
(1) $VG_{sys} < 0$ (2) $VG_{sys} > 0$ (3) $VS_{sys} < 0$ (4) $VS_{sys} > 0$ (5) $VS_{surr} < 0$ (6) $VS_{univ} > 0$

(A) (1),(3),(4) (B) (2),(4),(6) (C) (1),(4),(5) (D) (1),(4),(6) (E) (2),(4),(5)

(B) 17. 0.250M NH_3 ($K_b=1.8\times10^{-5}$)，50.00 mL，用0.500M HCl 滴定試問當量點時PH 值若干？

(A) 2.52 (B) 5.02 (C) 6.49 (D) 10.03 (E) 以上皆非

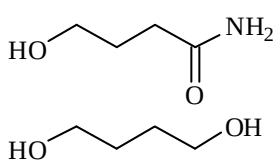
18. Show the product of treating r-butyrolactone with



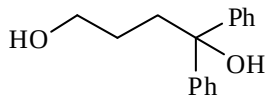
(a) NH_3

(b)1. $LiAlH_4$ 2. H_2O

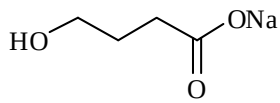
解：



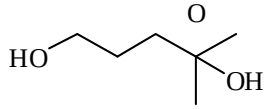
(c) 1. 2 phMgBr, ether 2. H_2O , HCl



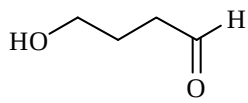
(d) NaOH, H_2O , heat



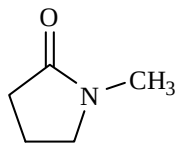
(e) 1. 2 CH_3Li , ether 2. H_2O , HCl



(f) 1. DIBAL–H, ether, –78°C 2. H_2O , HCl

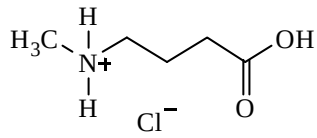


19. Show the product of treating the following r-lactam with

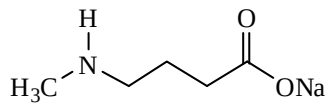


解：

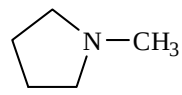
(a) H_2O , HCl, heat



(b) H_2O , NaOH, heat

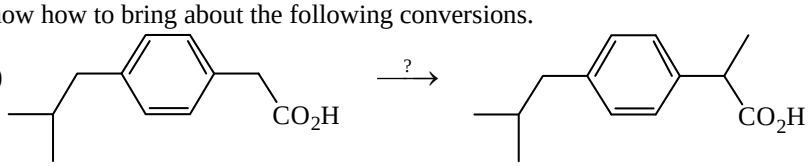


(c) 1. $LiAlH_4$ 2. H_2O



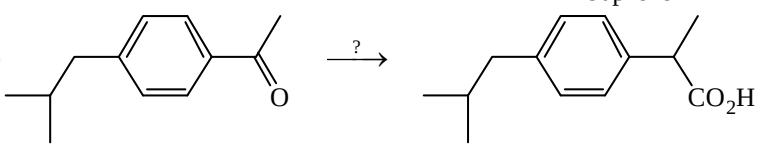
20. Show how to bring about the following conversions.

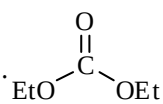
(a)



Ibuprofen

(b)



解：(a) 1. C_2H_5OH , H_2SO_4 2.  , EtONA 3. CH_3I 4. KOH, H_2O 5. HCl, H_2O

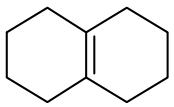
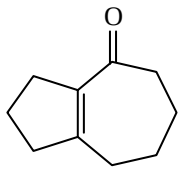
6. heat

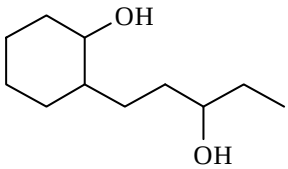
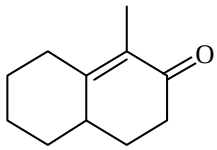
(b)Systhesis I: 1. $ClCH_2CN$, EtONa 2. $LiClO_4$ 3. H_2O , HCl

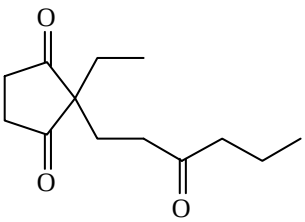
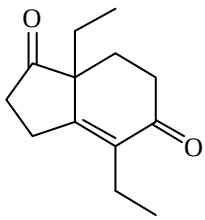
Systhesis II: 1. H_2 , catalyst 2. CO, H_2O , Pd catalyst

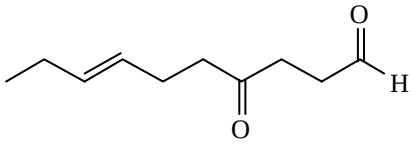
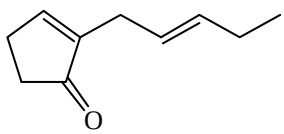
21. Give the major product of the following reactions.

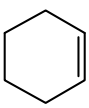
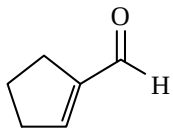
解：

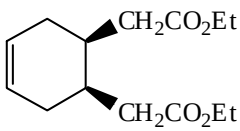
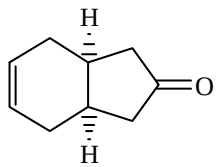
(a)  $\xrightarrow[2.\ OH^-,\ H_2O]{1.\ CrO_3,\ H_2SO_4}$ 

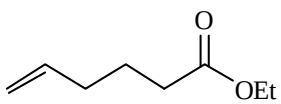
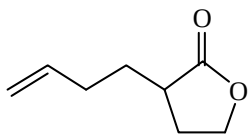
(b)  $\xrightarrow[2.\ EtONa,\ EtOH]{1.\ CrO_3,\ Pyridine}$ 

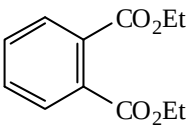
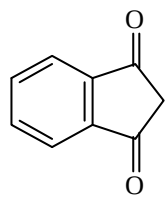
(c)  $\xrightarrow{ArSO_3H}$ 

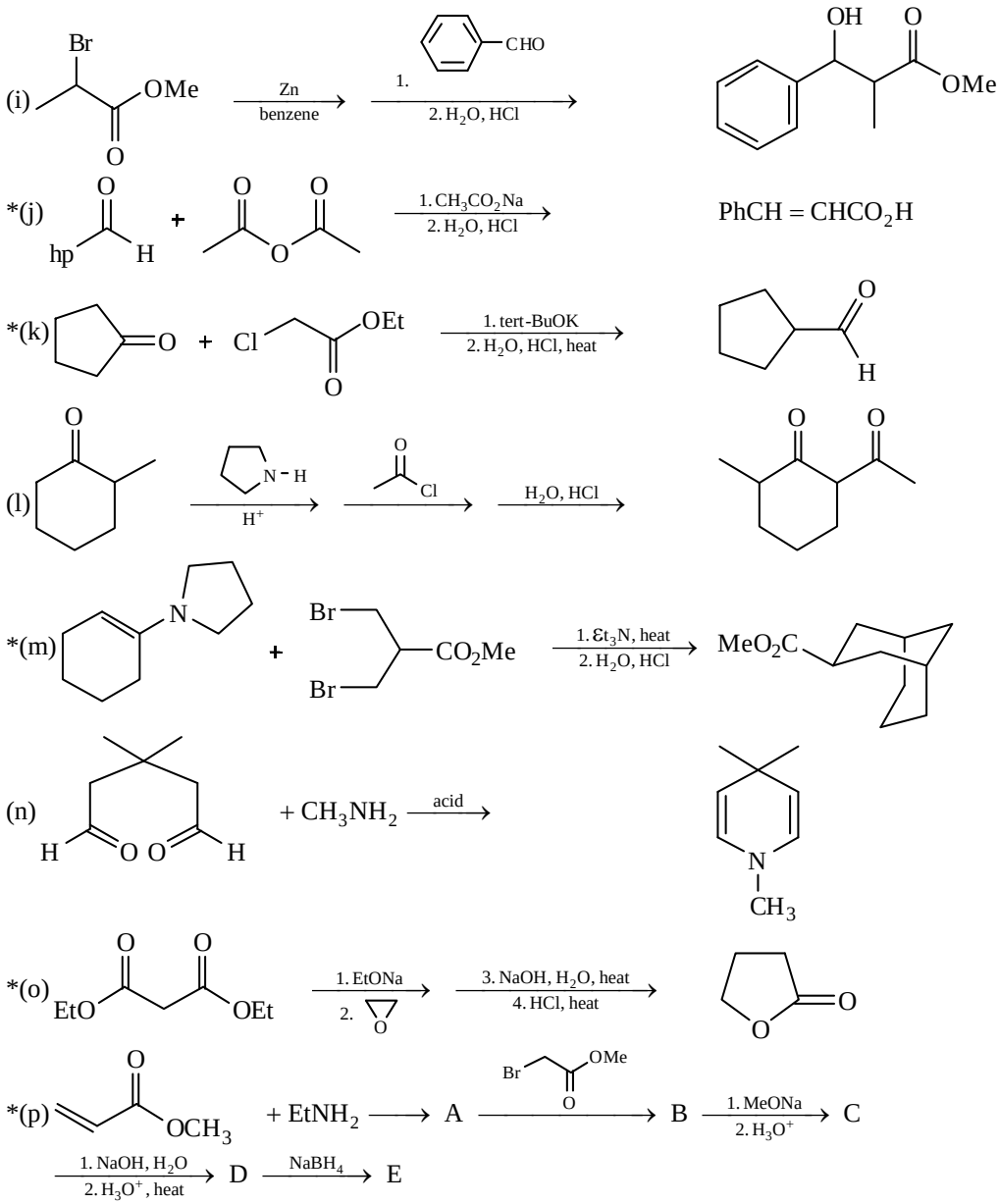
(d)  $\xrightarrow{base}$ 

(e)  $\xrightarrow[3.\ OH^-,\ H_2O_2]{1.\ OsO_4,\ H_2O_2\ \ 2.\ HIO_4}$ 

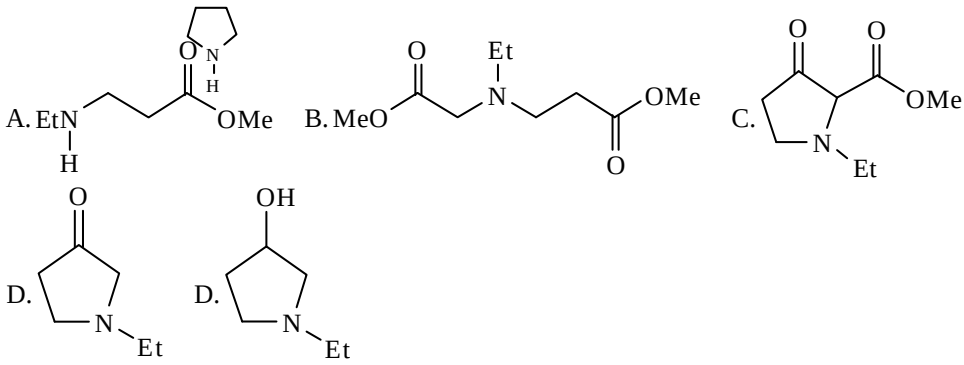
(f)  $\xrightarrow[2.\ HCl,\ H_2O]{1.\ EtONa}$ $\xrightarrow[heat]{NaOH,\ H_2O}$ $\xrightarrow[heat]{HCl,\ H_2O}$ 

(g)  $\xrightarrow[2.\ \ O]{1.\ NaH}$ 

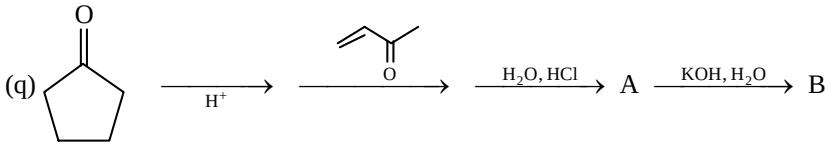
*(h)  + CH_3CO_2Et $\xrightarrow[2.\ HCl,\ H_2O]{1.\ EtONa}$ $\xrightarrow[heat]{NaOH,\ H_2O}$ $\xrightarrow[heat]{HCl,\ H_2O}$ 

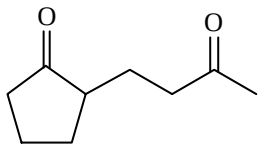

(i)
Br
OMe
O
Zn
benzene
1.
CHO
2. H2O, HCl
OH
O
OMe
*(j)
hp
H
O
O
O
1. CH3CO2Na
2. H2O, HCl
PhCH = CHCO2H
*(k)
O
Cl
OEt
O
1. tert-BuOK
2. H2O, HCl, heat
O
H
(l)
O
N - H
H+
O
Cl
H2O, HCl
O
O
*(m)
N
Br
Br
CO2Me
1. Et3N, heat
2. H2O, HCl
MeO2C
(n)
H
O
O
H
+ CH3NH2
acid
N
CH3
*(o)
EtO
OEt
O
O
1. EtONa
2.
O
3. NaOH, H2O, heat
4. HCl, heat
O
O
*(p)
OCH3
O
+ EtNH2
A
Br
OMe
O
B
1. MeONa
2. H3O+
C
1. NaOH, H2O
2. H3O+, heat
D
NaBH4
E

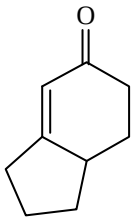
解：

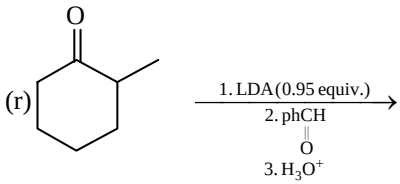

A. EtN
H
O
N
H
OMe
B. MeO
O
Et
N
OMe
O
C.
O
O
OMe
N
Et

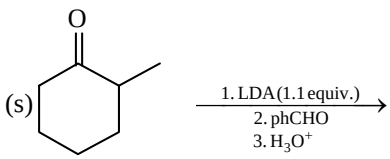
D.
O
N
Et
D.
OH
N
Et

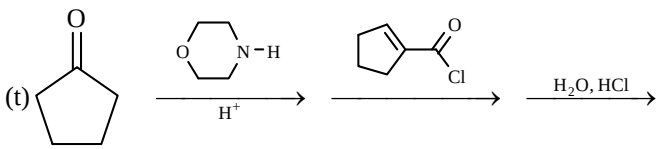
(q) 

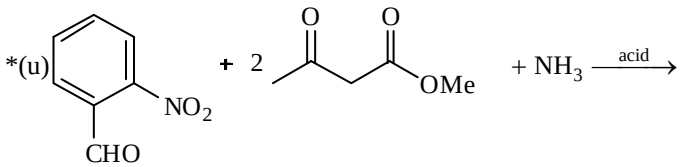
解：A. 

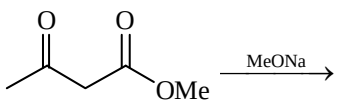
B. 

(r) 

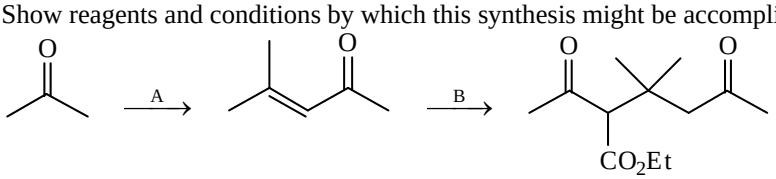
(s) 

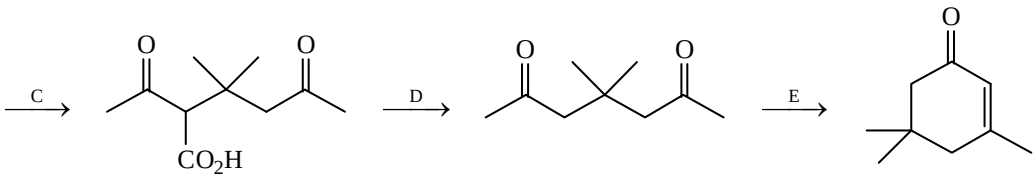
(t) 

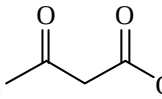
*(u) 

*(v) PhCHO + 2 

22. Show reagents and conditions by which this synthesis might be accomplished.

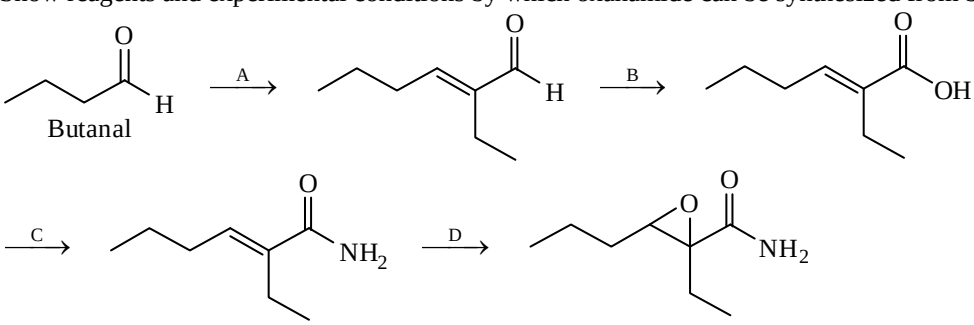






解：A. OH^-, H_2O, Δ　B.　, EtONa　C. 1. NaOH, H_2O　2. H_2O, HCl　D. heat　E. OH^-

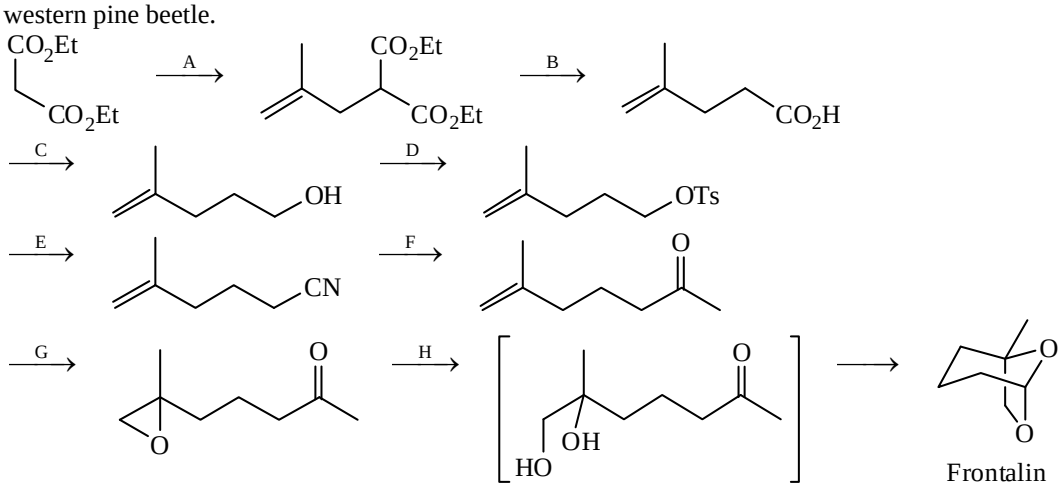
23. Show reagents and experimental conditions by which oxanamide can be synthesized from butanal.



Oxanamide

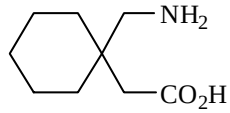
解：A. OH^-, H_2O　B. Ag_2O, H_2O, THF　C. 1. $SOCl_2$　2. NH_3　D. RCO_2OH

24. Following are the steps in one of the several published synthesis of frontalin, a pheromone of the western pine beetle.

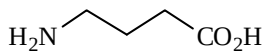


解：A. 1. EtONa　2.　Br　B. 1. NaOH, H_2O　2. H_2O, HCl　3. heat　C. 1. $LiAlH_4$　2. H_2O　D. TsCl, Pyridine　E. NaCN, DMSO　F. 1. CH_3MgBr　2. H_2O　G. H_2O, H^+

25. Gabapentin, an anticonvulsant used in the treatment of epilepsy, is structurally related to the neurotransmitter 4-aminobutanoic acid (GABA)

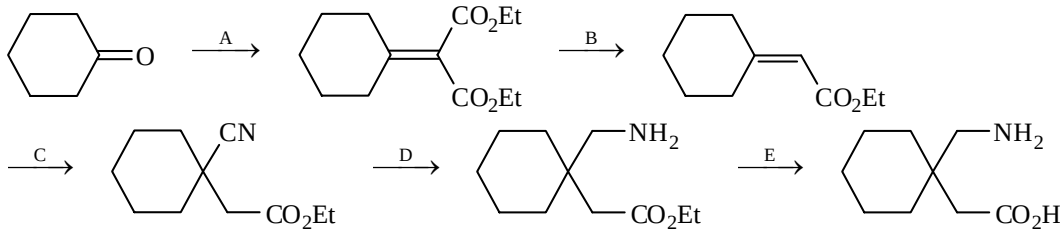


Gabapentin



GABA

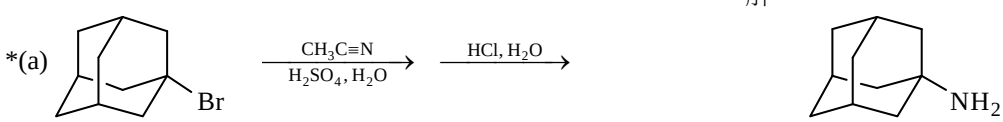
Show experimental conditions by which to carry out the following synthesis.

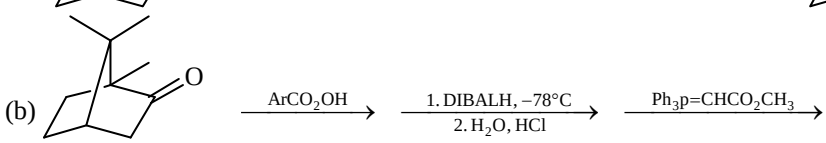


解：A. $CH_2(CO_2Et)_2$, EtONa　B. 1. NaOH, H_2O　2. HCl, H_2O　3. heat　4. EtOH, H^+　C. HCN　D. H_2, Pd　E. H_2O, H^+

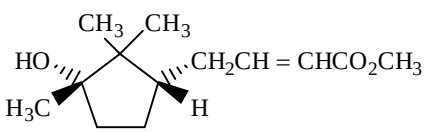
26. Give the major product of the following reactions.

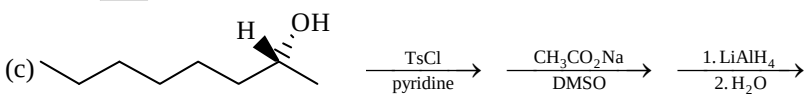
解：



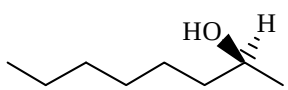


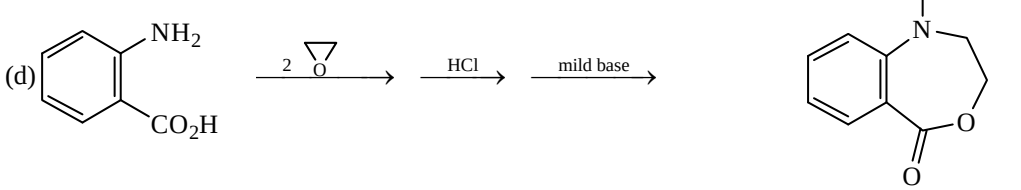
解：

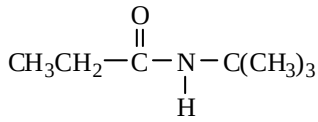


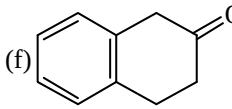
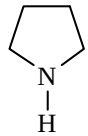
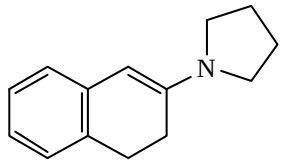


解：

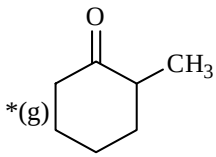
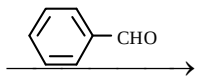
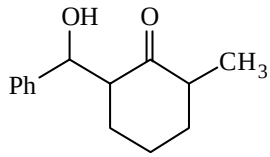


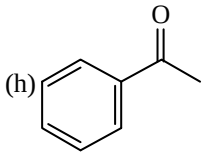
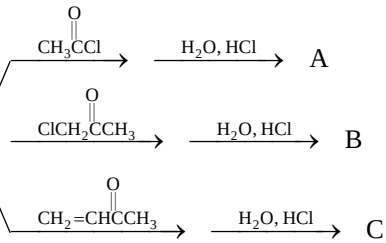


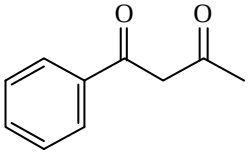
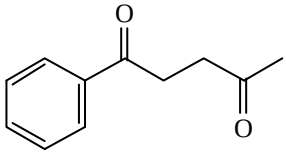
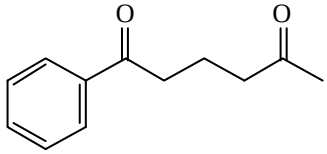
*(e) $CH_3CH_2C\equiv N + (CH_3)_3COH \xrightarrow{H_2SO_4}$ 

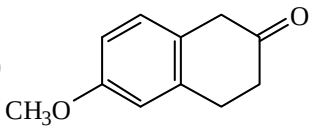
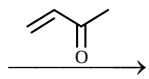
(f)  +  $\xrightarrow{H^+}$ 

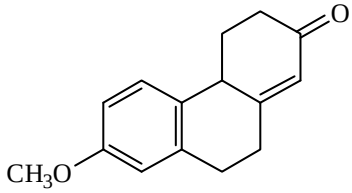
Conjugated with the aromatic ring

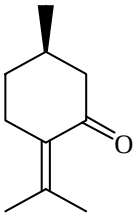
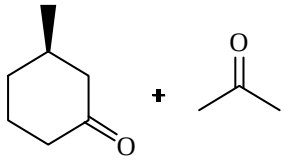
*(g)  $\xrightarrow[THF,\ 0°C]{LDA\ (1.1\ equiv.)}$  

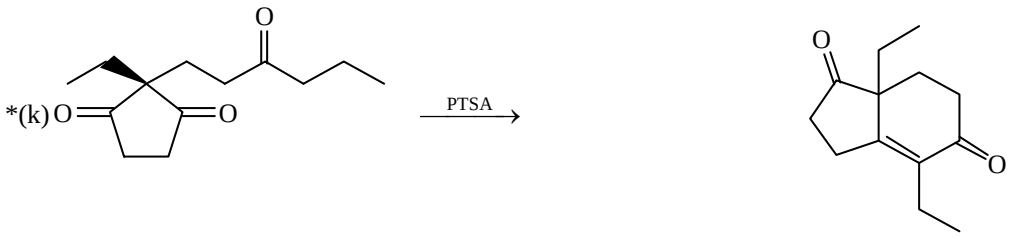
(h)  $\xrightarrow[H^+]{N-H}$ 

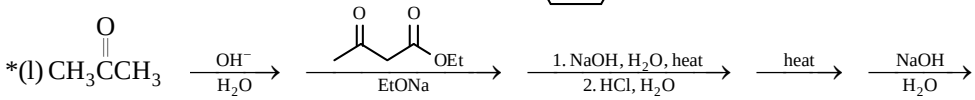
解：A.  B.  C. 

(i)  $\xrightarrow{LDA}$  $\xrightarrow[H_2O,\ \Delta]{OH^-}$

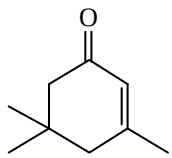
解： 

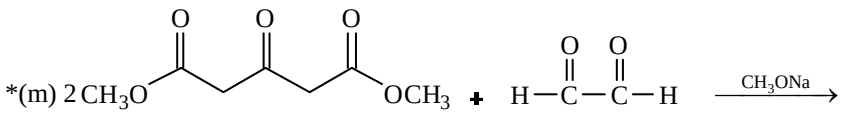
(j)  $+ H_2O \xrightarrow{steam}$ (Retro aldol reaction) 



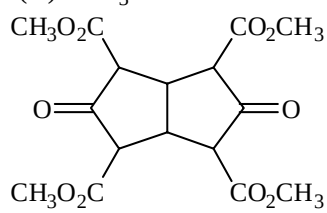


解：

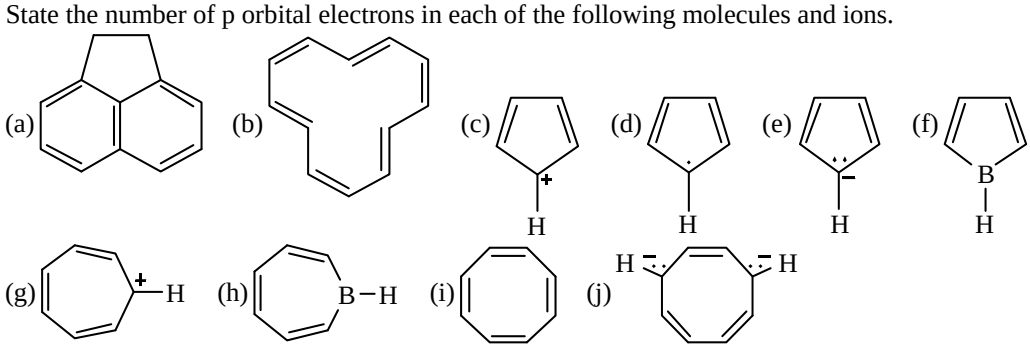




解：



27. State the number of p orbital electrons in each of the following molecules and ions.

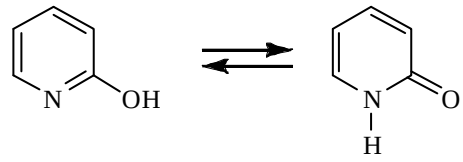


解：(a) 10 (b) 12 (c) 4 (d) 5 (e) 6 (f) 4 (g) 6 (h) 6 (i) 8 (j) 10

28. Which of the molecules and ions given in the previous problem are aromatic according to the Hückel criteria? Which, if planar, would be antiaromatic?

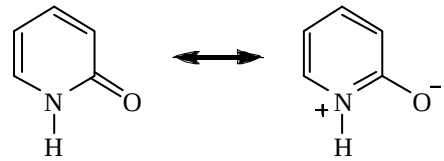
解：Aromatic: a, e, g, h, and j；Antiaromatic: b, c, f, and i

29. The compound 2-hydroxypyridine, a derivative of pyridine, is in equilibrium with 2-pyridone. 2-Hydroxypyridine is aromatic. Does 2-pyridone have comparable aromatic character?

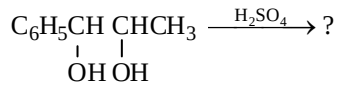


2-Hydroxypyridine　　2-Pyridone

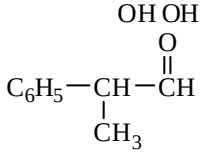
解：2-Pyridone have aromatic character because of the contributing structure shown on the right.



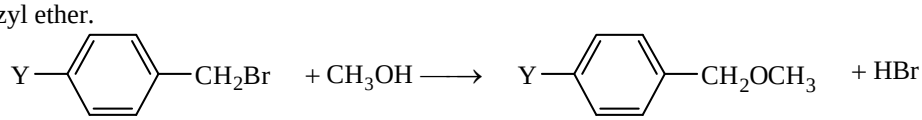
30. When warmed in dilute sulfuric acid, 1-phenyl-1,2-propanediol undergoes dehydration to give .



解：

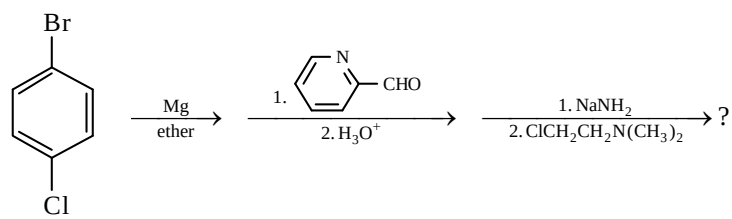


31. Para-substituted benzyl bromide undergo reaction with methanol by an _____ mechanism to give a benzyl ether.

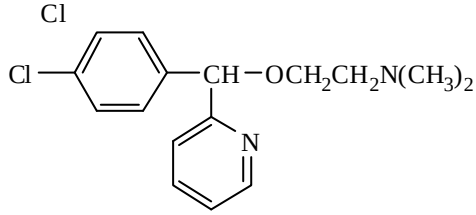


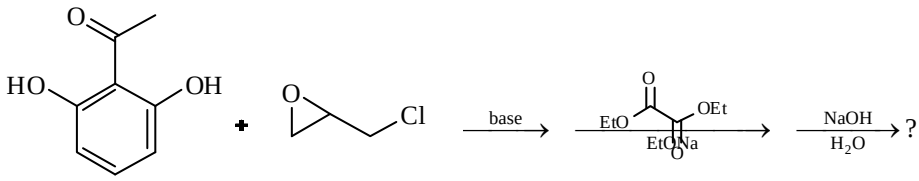
解：Rate of SN1 reaction: $Y = CH_3O^- > CH_3^- > H^- > NO_2^-$

32.

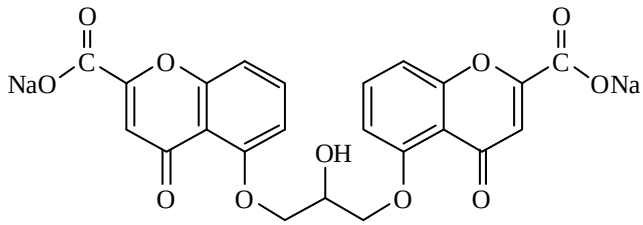


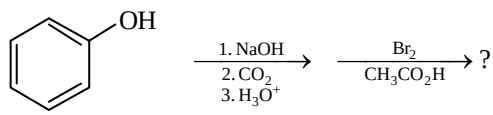
解：

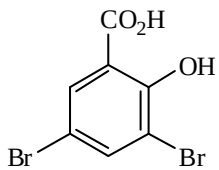


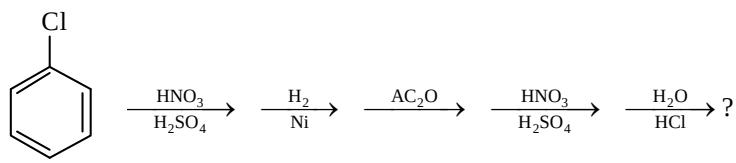
33. 

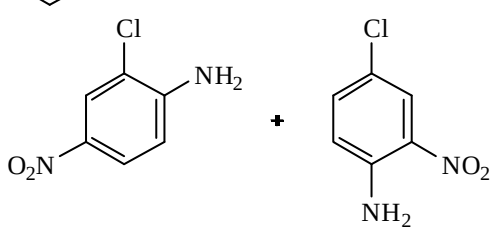
(2 equiv.)

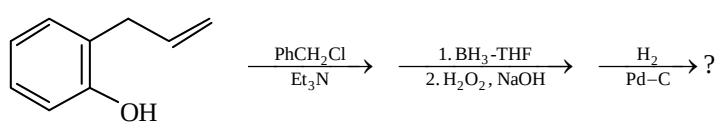
解： 

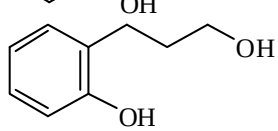
34. 

解： 

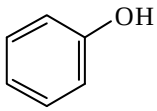
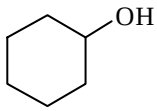
35. 

解： 

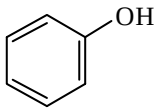
36. 

解： 

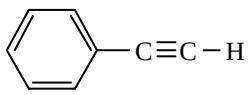
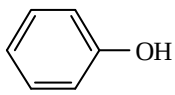
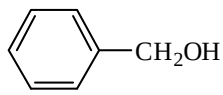
37. Arrange the molecules and ions in each set in order of increasing acidity.

(a)   CH_3CO_2H

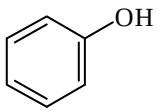
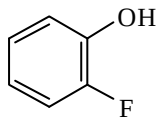
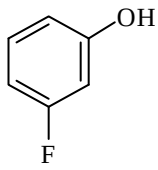
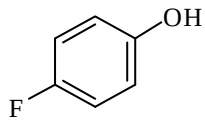
1 2 3

(b)  HCO_3^- H_2O

4 5 6

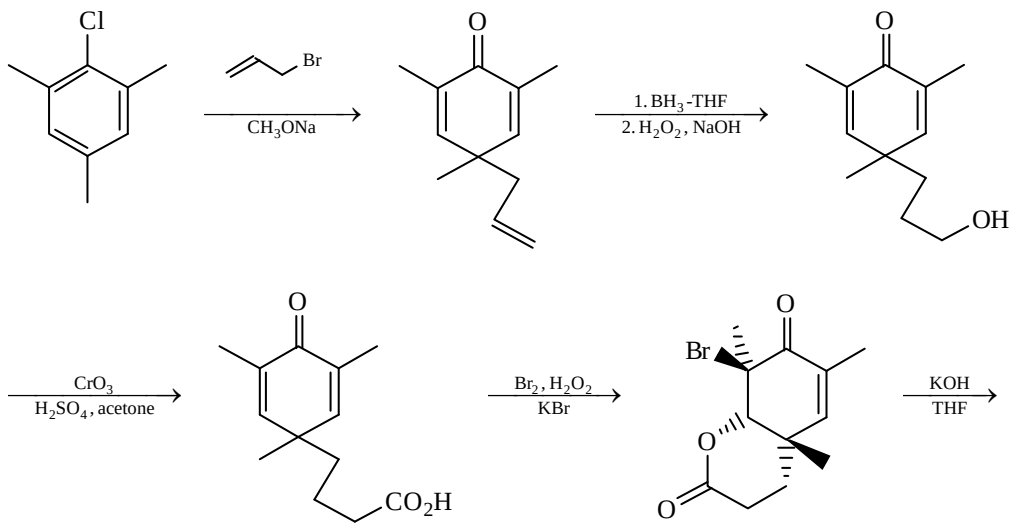
(c)   

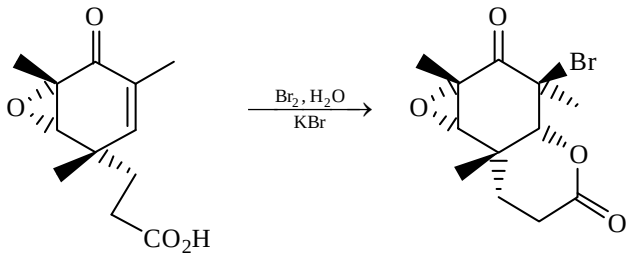
7 8 9

(d)    

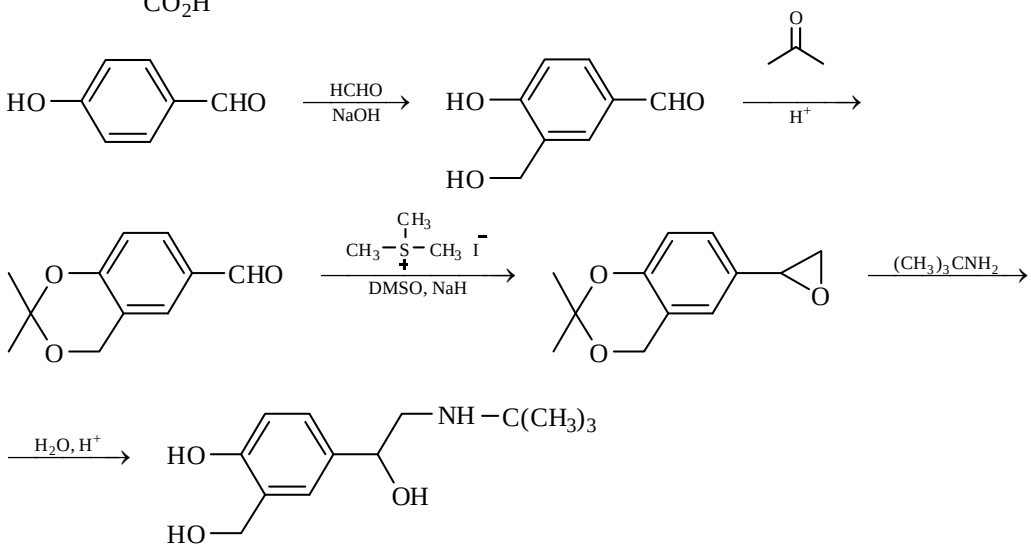
10 11 12 13

解：(a) 2 < 1 < 3 (b) 6 < 5 < 4 (c) 7 < 9 < 8 (d) 10 < 13 < 12 < 11

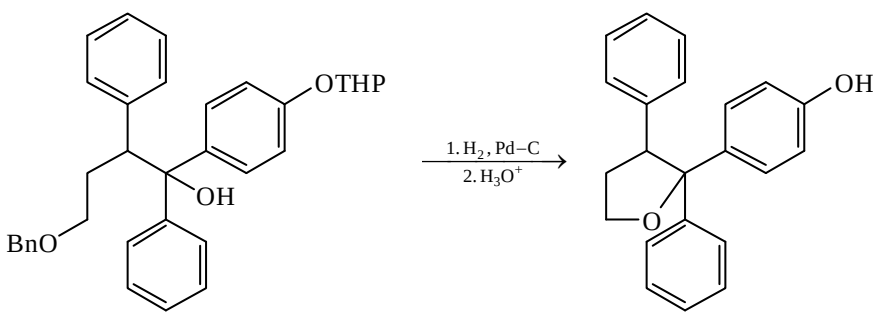
38. 


O
O
CO2H
Br2, H2O
KBr
O
Br
O
O
O

39.


HO
CHO
HCHO
NaOH
HO
CHO
HO
O
H+
CHO
O
O
CH3
CH3 S CH3 I
DMSO, NaH
O
O
(CH3)3CNH2
H2O, H+
HO
NH C(CH3)3
OH
HO

40.


OTHP
OH
BnO
1. H2, Pd–C
2. H3O+
OH
O