

第六章 有机化合物常见增长和缩短碳链的方法

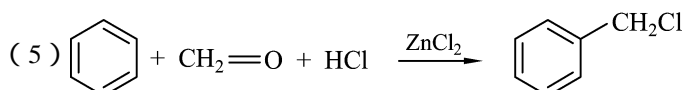
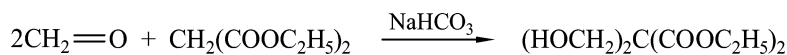
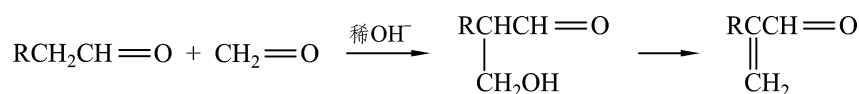
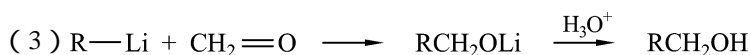
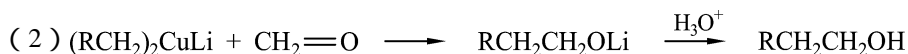
第一节 增长碳链的方法

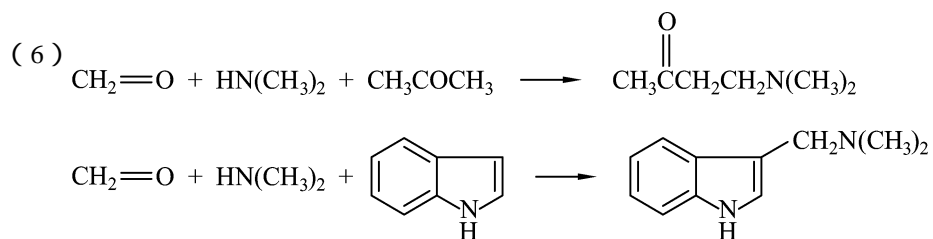
一、增加一个碳原子的常见方法

含有一个碳的化合物都可以作为增加一个碳的反应试剂。如 $\text{HCH}=\text{O}$, HCOOC_2H_5 , $\text{HC}(\text{OC}_2\text{H}_5)_3$, CO , CO_2 , COCl_2 , CHX_3 , CH_2X_2 , HCN , CH_2N_2 , DMF , $\text{CO}(\text{NH}_2)_2$, CH_3Li , $(\text{CH}_3)_2\text{CuLi}$, CH_3MgX , $\text{Ph}_3\text{P}=\text{CH}_2$ 等, 与这些试剂的相关反应如下:

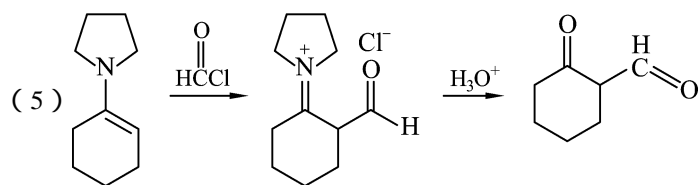
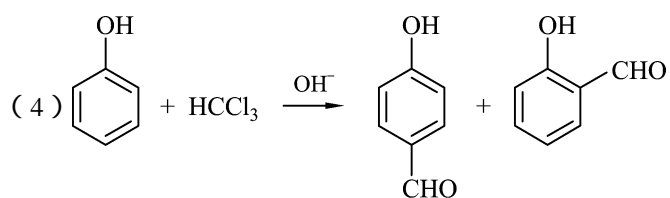
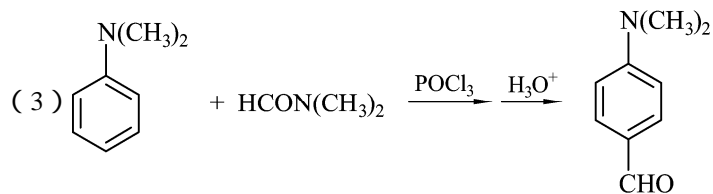
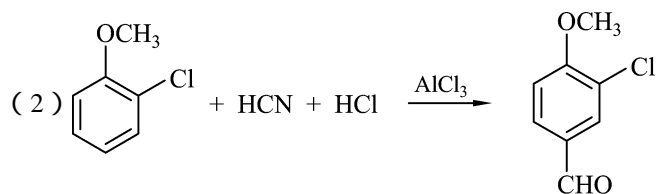
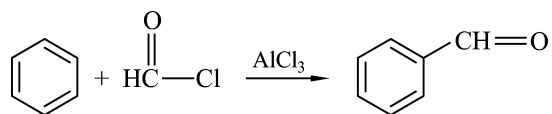
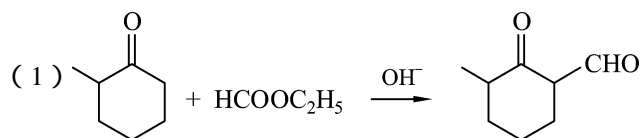
1. 亲核试剂与甲醛反应

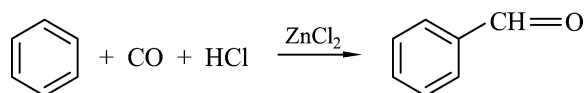
转变成羟甲基, 或氯甲基, 或氨甲基。





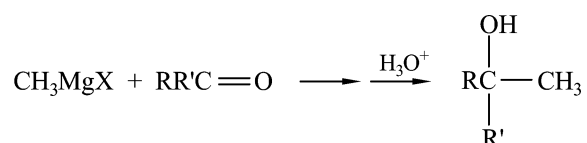
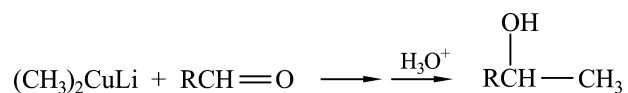
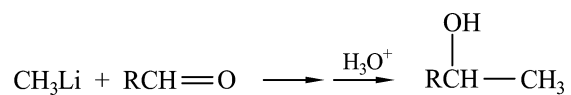
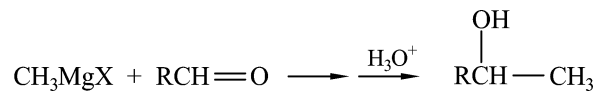
2. 甲酰化反应, 引入甲酰基



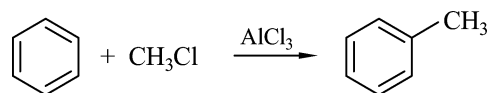


3. 通过反应, 引入甲基

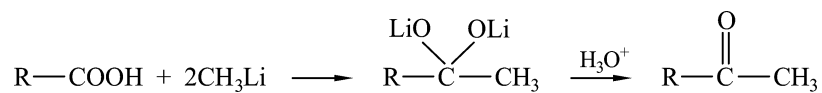
(1) 亲核加成



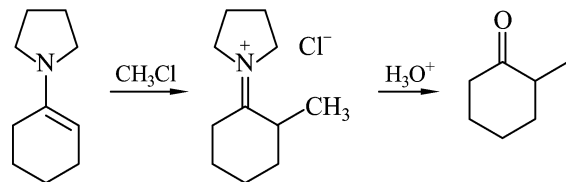
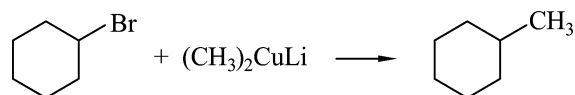
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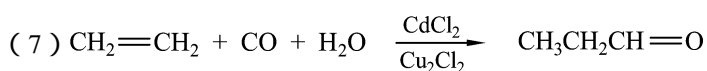
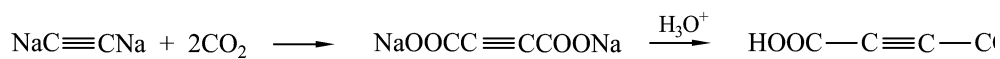
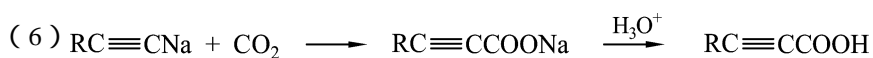
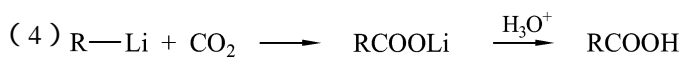
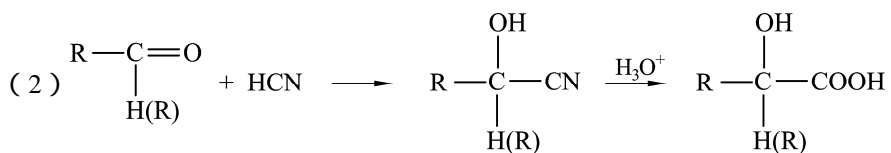
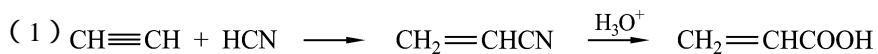
(3) 亲核加成和消去



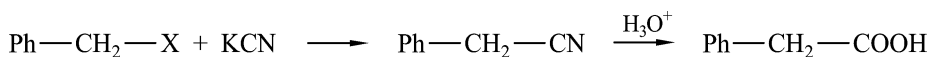
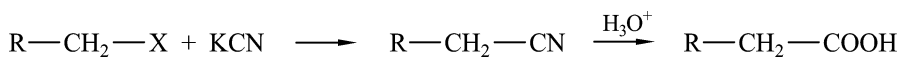
(4) 亲核取代



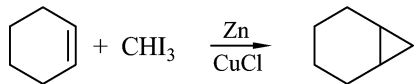
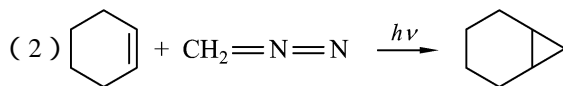
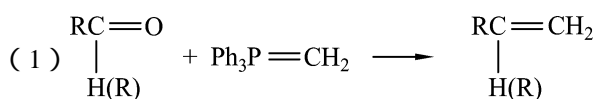
4. 通过亲核加成, 增加一个碳

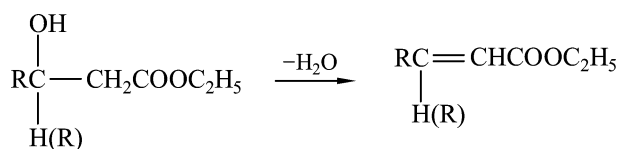
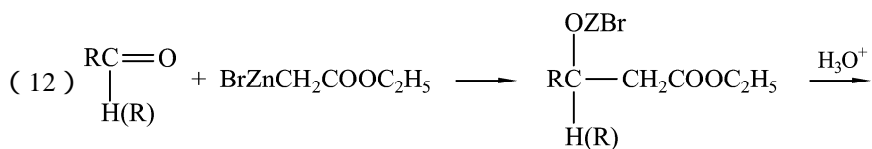
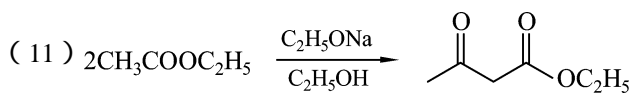
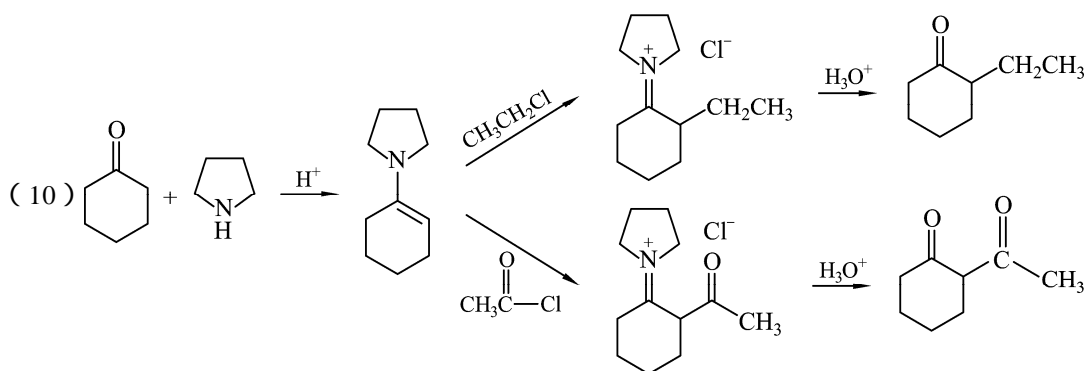
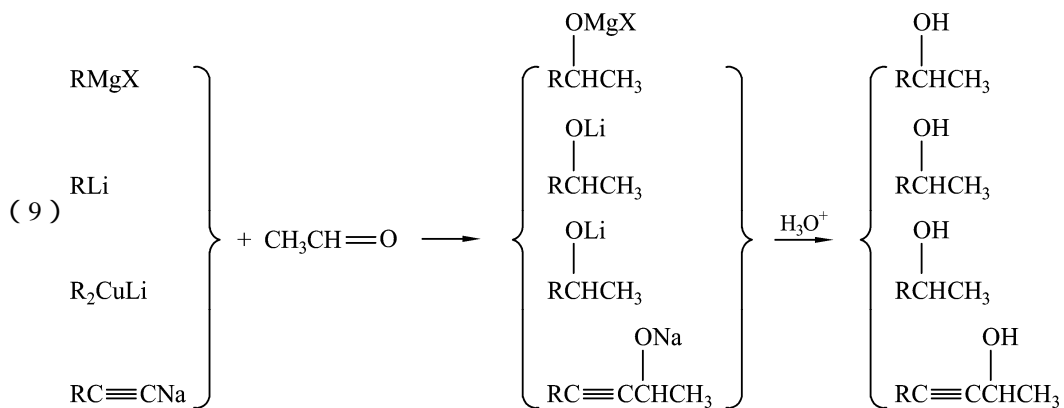
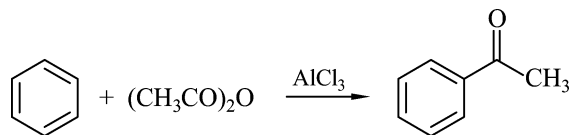
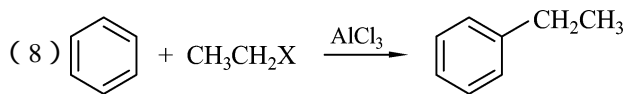
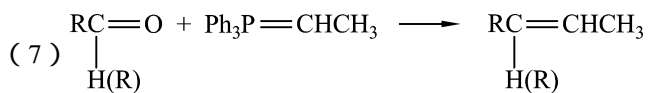
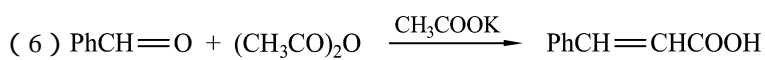


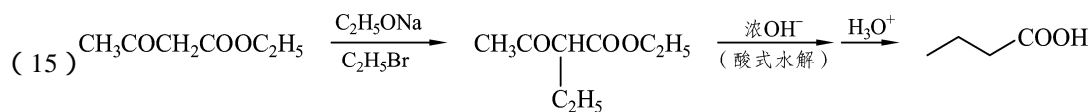
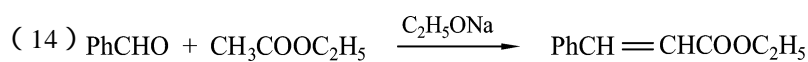
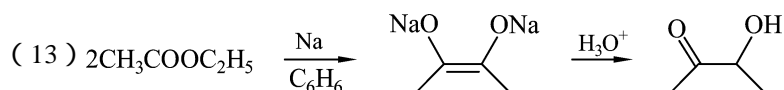
5. 通过亲核取代, 增加一个碳



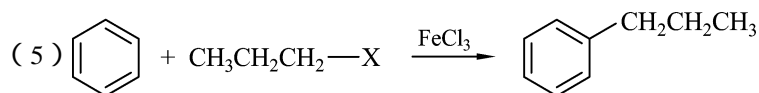
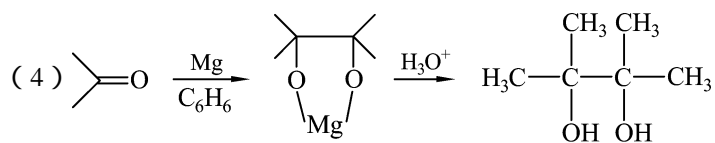
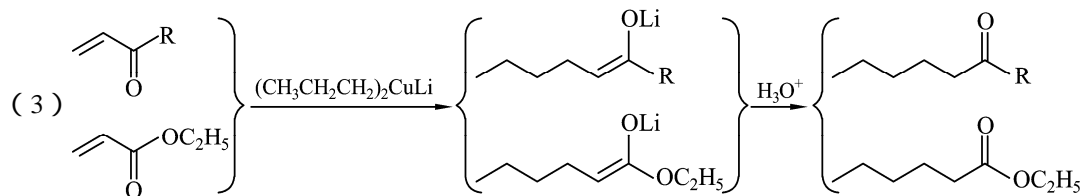
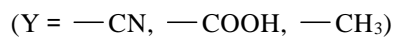
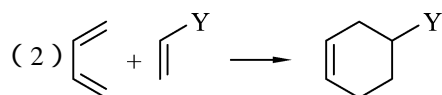
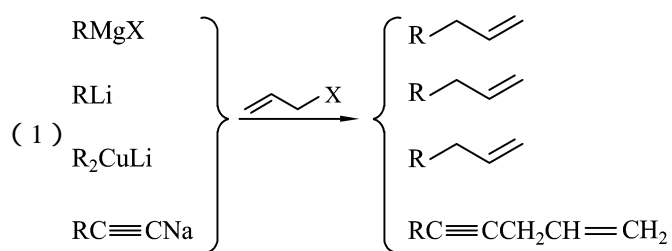
6. 通过其他方法

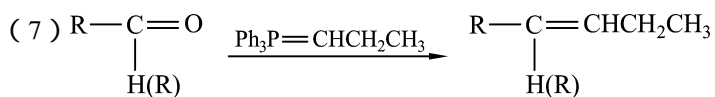
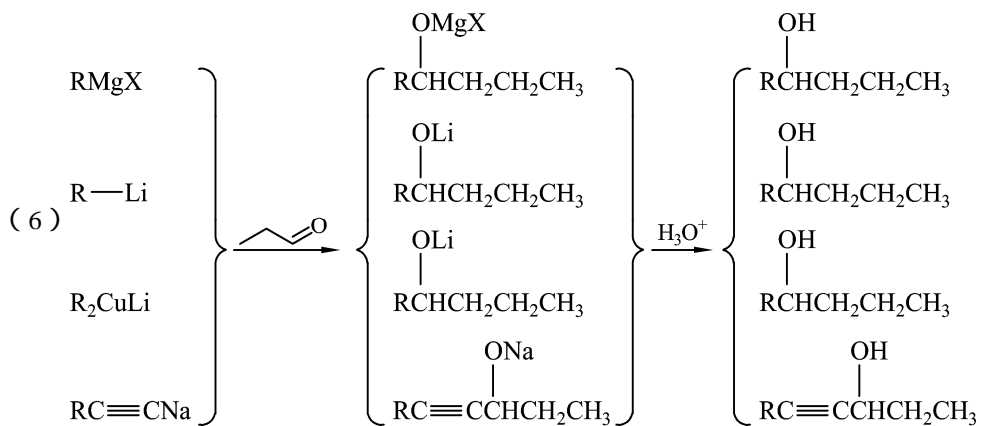
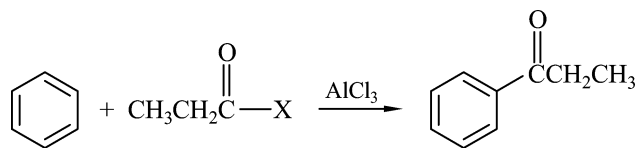




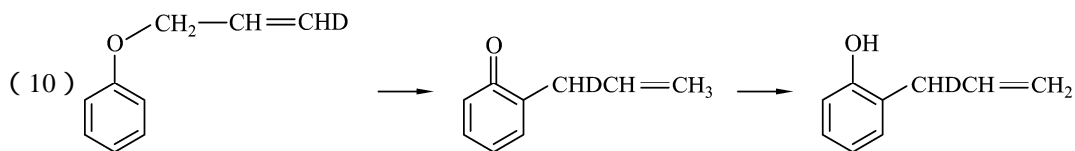
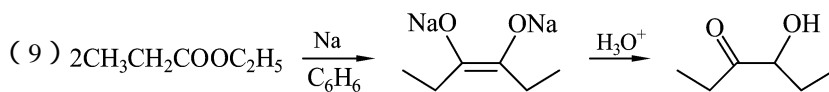
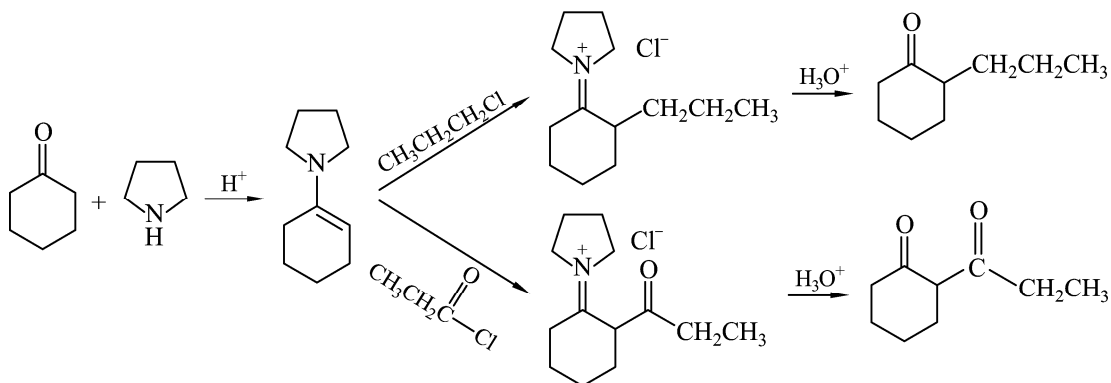


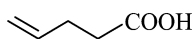
三、增加三个碳原子的常见方法



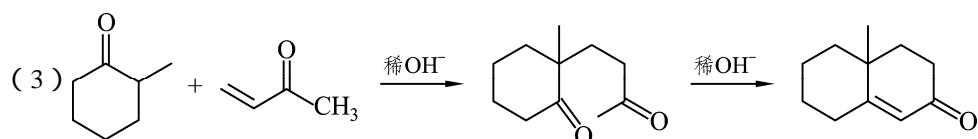
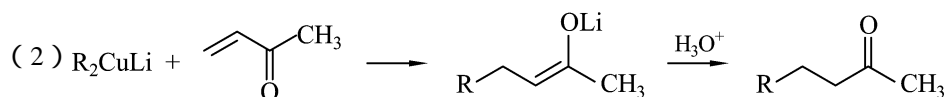
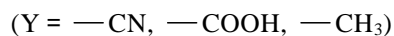
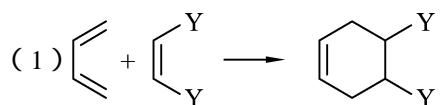


(8)





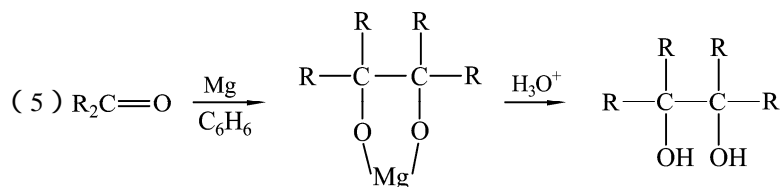
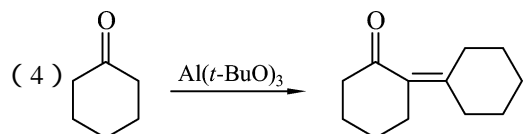
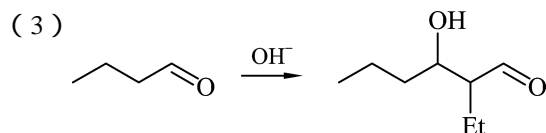
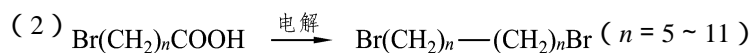
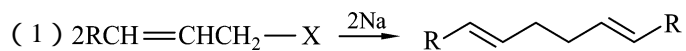
四、增加四个碳原子的常见方法

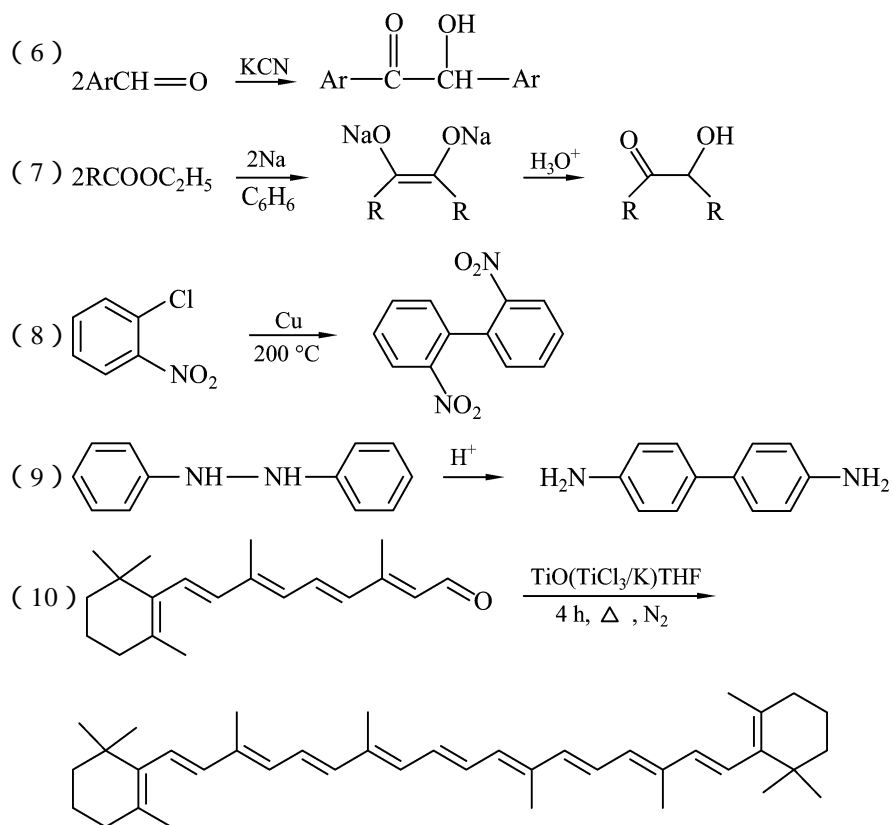


增加更多碳原子的方法与增加三个碳原子的方法相似，这里不再一一列举。

五、碳链倍增法

成倍增长碳链的反应有 Kolbe、Wurtz、羟醛缩合、安息香缩合、羰基化合物的双分子还原、醛酮的偶联反应、羰基化合物与等碳原子数的试剂反应、Ullmann 偶合、联苯胺的重排等。

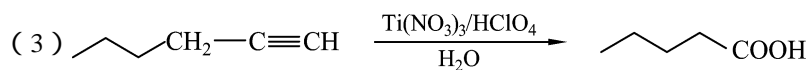
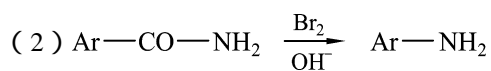
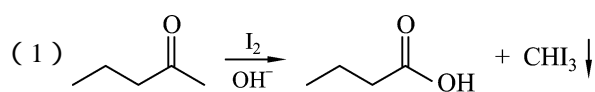


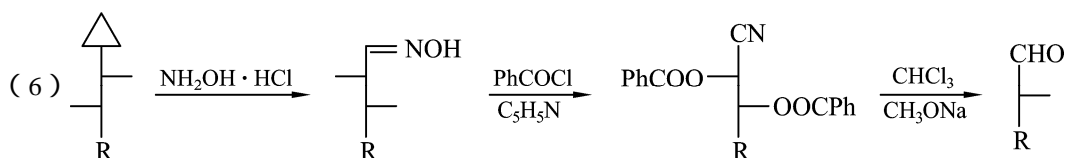
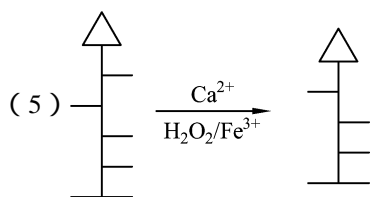
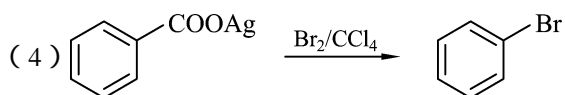


第二节 缩短碳链的方法

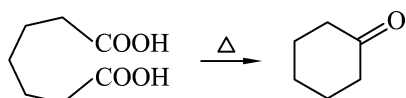
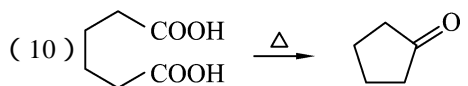
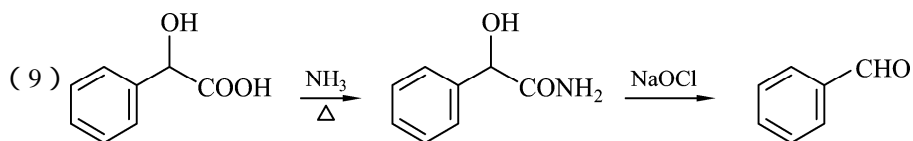
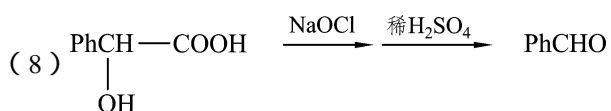
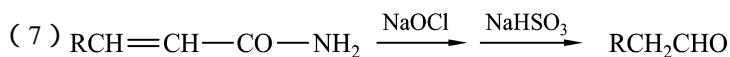
根据有机合成的需要，有时需要减少一个碳的反应，即碳链的降级反应。常用的这类反应有：卤仿反应、Hofmann 重排、链端不饱和烃的氧化、Hunsdiecker 反应、Ruff 降级反应、Wohl 降级反应等。

一、减少一个碳原子的常见方法



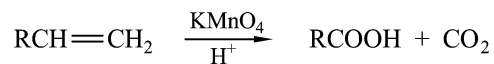


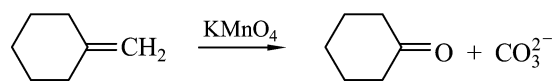
α, β -不饱和酰胺、 α -羟基酰胺、 α -甲氧基酰胺在碱性条件下，用次卤酸钠处理，可得到少一个碳的醛，称为 Weerman 降级。



二、烯烃通过氧化断键减去一个及多个碳的方法

1. 氧化断键减少一个碳的方法





2. 氧化断键减少多个碳的方法

