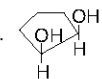
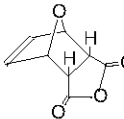
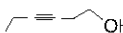
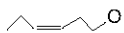
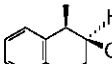
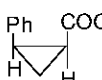
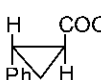
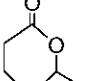
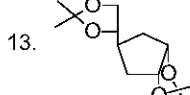


中国科学院

1999 年硕士学位研究生入学考试试题

有机化学参考答案

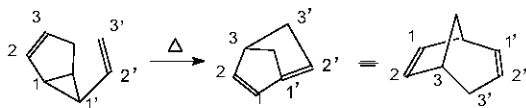
一, 完成反应:

- $\text{CH}_2\text{CHCH}_2\text{C}\equiv\text{CH}$
Br Br
- 
-  (endo为主)
-  
- $\text{CH}_3\text{-C}_6\text{H}_4\text{-C(CH}_3)_3$
- 
- $\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{HCOOH}$
- $\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}=\text{CHC}(\text{CH}_3)=\text{CHCHO}$
-   (主)
-   (顺反各一对对映体)
- $\text{CH}_3\text{C(=O)CH}_2\text{Ph}$
- 
- 
- $\text{CH}_3\text{-C}_5\text{H}_4\text{-N=N-C}_6\text{H}_5$
- 

二, 机理题:

1. 苯位上的氯极易离去, 水又是弱亲核试剂, 故水解反应属于 $\text{S}_{\text{N}}1$ 历程的亲核取代。3-位上的 $\text{CH}_3\text{-O-}$ 对 1-位主要起 -I 效应, 使苯位氯难离去, 而 4-位上的 $\text{CH}_3\text{-O-}$ 对 1-位则 +C>-I, 苯位氯电离大大加快。

2. 这是一个 3, 3'-迁移的周环反应,



3. 片呐醇重排的立体化学要求迁移基团必须处于离去基团的反式交叉位置上, 故只有如下:

