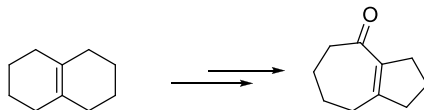


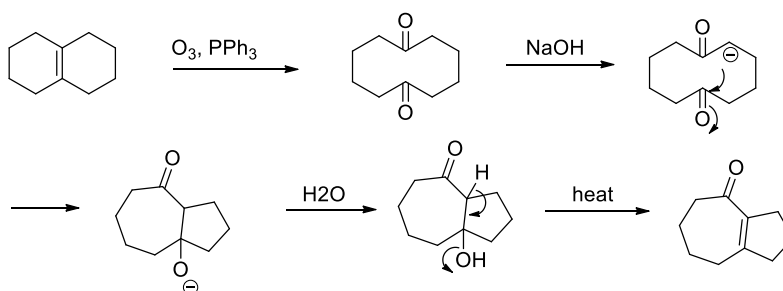
## Solutions to problems - Set 9: Carbonyl compounds (Parts III-IV)

### Problem 1

Propose a pathway leading to the product, more than one step is necessary (hint: the double bond must be broken by ozonolysis first).

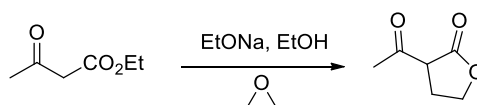


### Solution

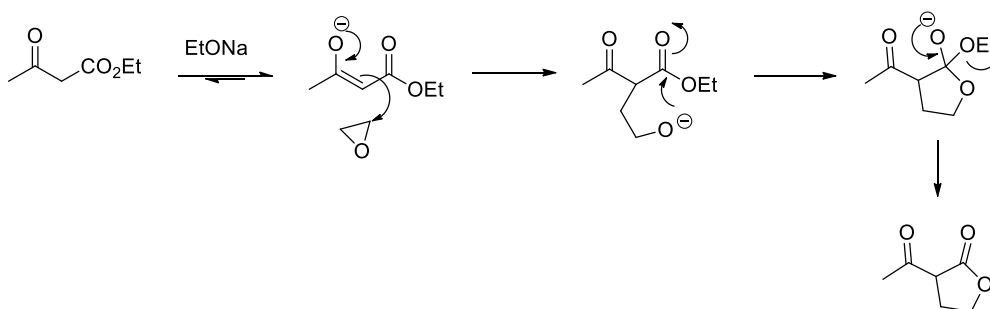


### Problem 2

Give the mechanism.



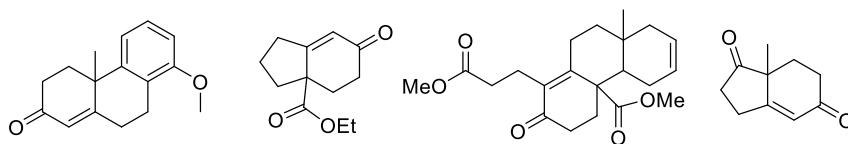
### Solution



Alkylation of the enolate with the epoxide gives an alkoxide anion that cyclizes to the lactone.

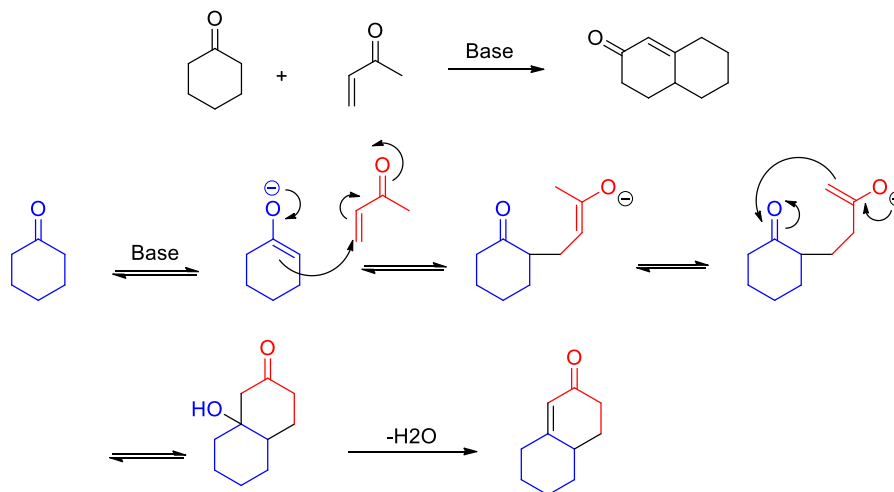
### Problem 3

Propose a synthetic pathway to form these compounds using Robinson annulation (Michael addition followed by aldol condensation).



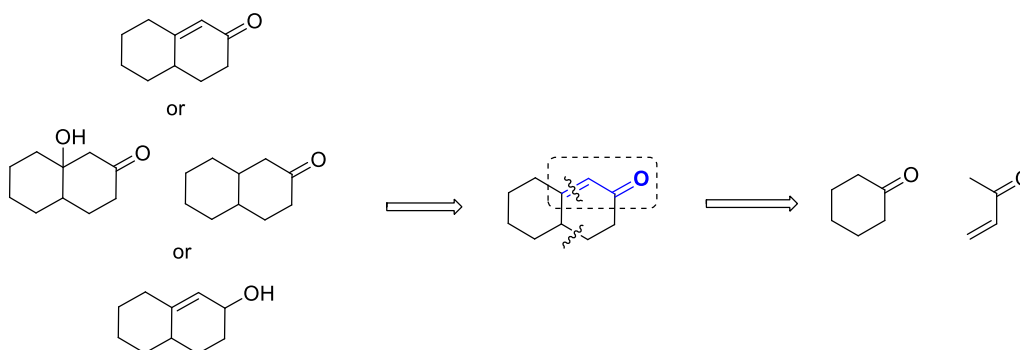
### Solution

The Robinson annulation is a useful reaction to form fused ring systems with  $\alpha,\beta$ -unsaturated ketone moiety from cyclic ketone and methyl vinyl ketone.

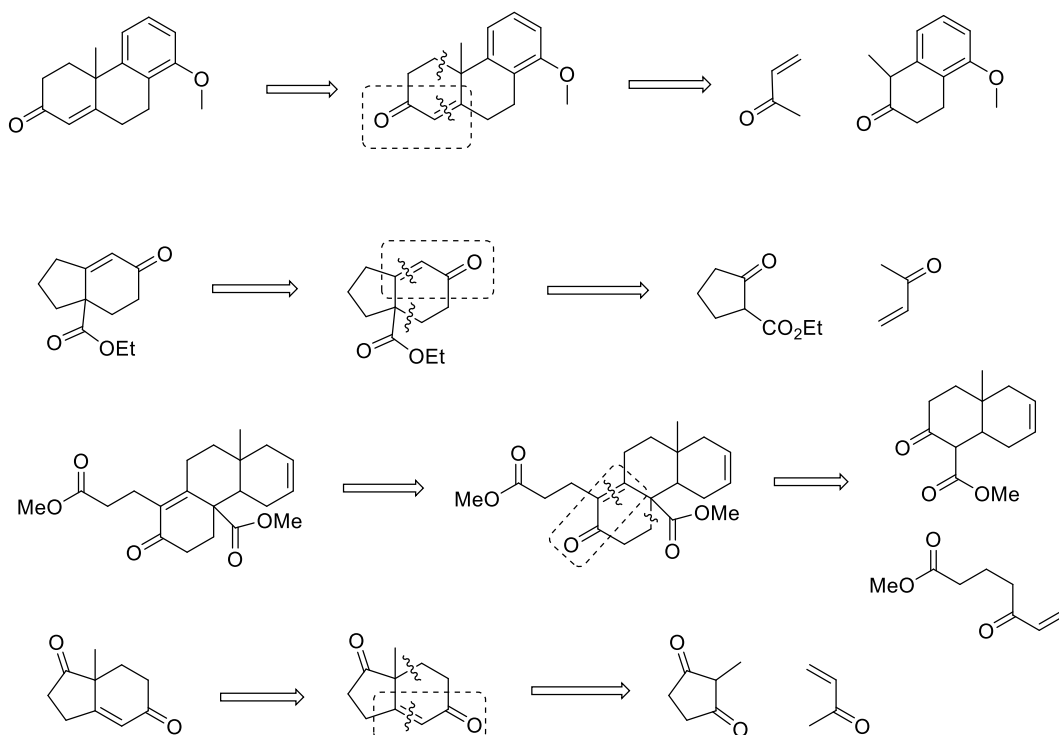


To find precursors for Robinson annulation product:

1. Identify  $\alpha,\beta$ -unsaturated ketone moiety
2. Make one bonding association between  $\alpha,\beta$ -double bond and another in order to appear methyl vinyl ketone.

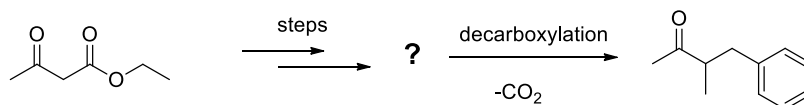


Apply to above examples:

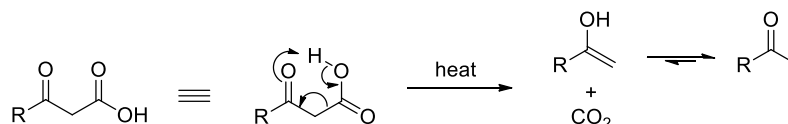


#### Problem 4

Propose a pathway leading to the product, more than one step is necessary.



Notes:  $\beta$ -ketocarboxylic acid can be easily decarboxylated by heating to generate ketone



#### Solution

From the suggestion, the last step is decarboxylation, rationally; the key intermediate should be dialkylated ethyl acetoacetate ( $\beta$ -ketoesters are easily decarboxylated). This intermediate can be obtained by alkylating twice, in which Methyl – less steric hindered group is preferred to introduce first, then Benzyl.

