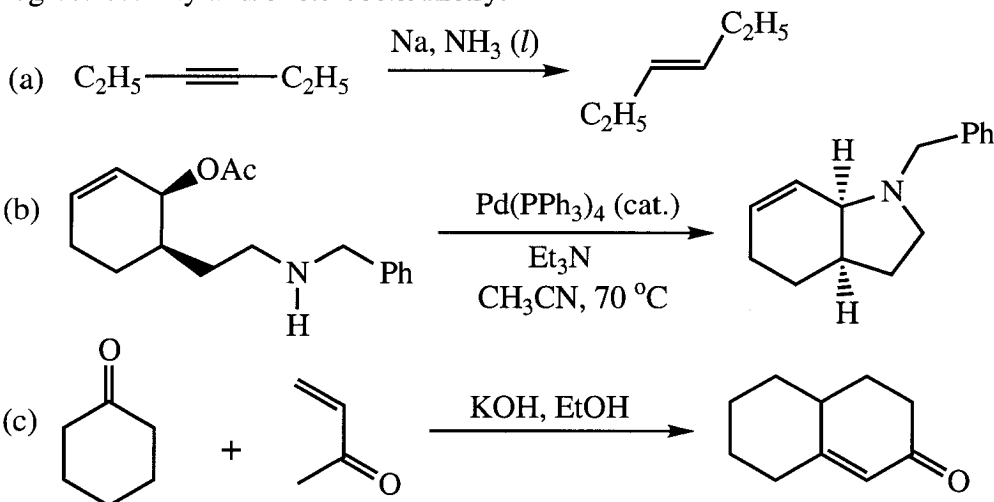
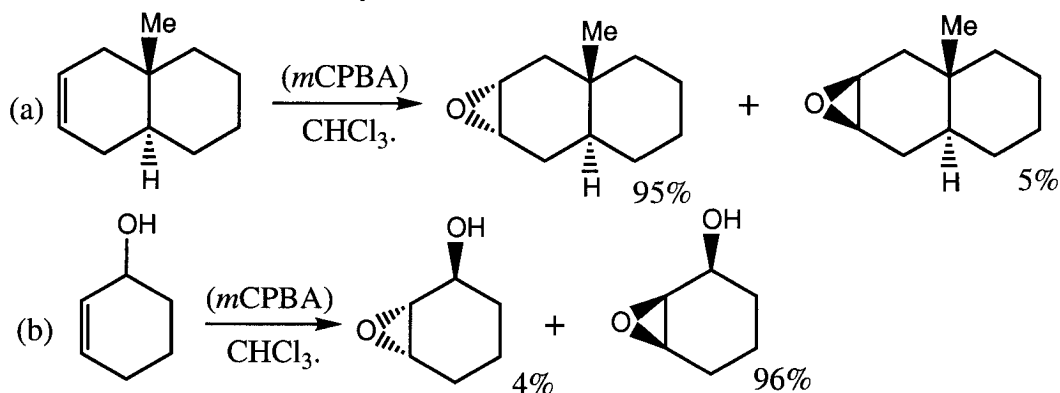


15% (1) Propose a mechanism for each of the following transformations that explains the observed regioselectivity and/or stereochemistry.



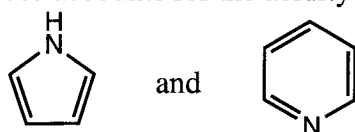
10% (2) Given below are the observed epoxide ratios from epoxidations of the compounds A and B, respectively, with *m*-chloroperbenzoic acid (*m*CPBA) in CHCl_3 . How do you explain the differences in stereoselectivity?



10% (3) Take an example to explain the following questions:

- Grignard reagents and in reactions with α,β -unsaturated carbonyl compounds
- Gilman reagents and in reactions with α,β -unsaturated carbonyl compounds

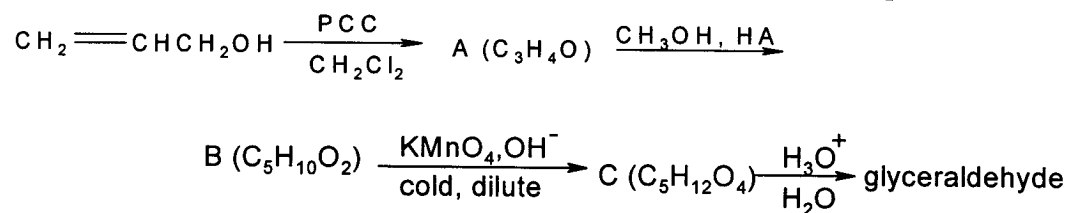
5% (4) How do you suppose accounts for the acidity or basicity for the following pair.



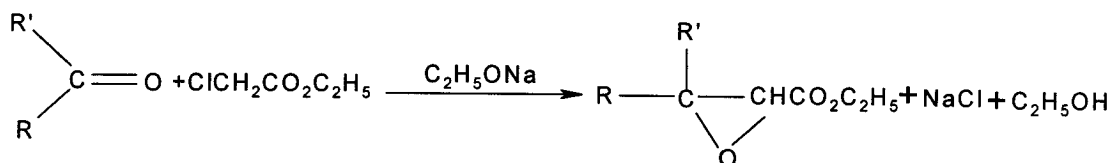
10% (5) *Trans*-1-chloro-2-methylcyclohexane, and *cis*-1-chloro-2-methylcyclohexane can undergo E_2 eliminations. Explain the following observations:

- Is the more substituted alkene always necessarily the major product.
- Does *trans* isomer react faster than *cis* isomer?

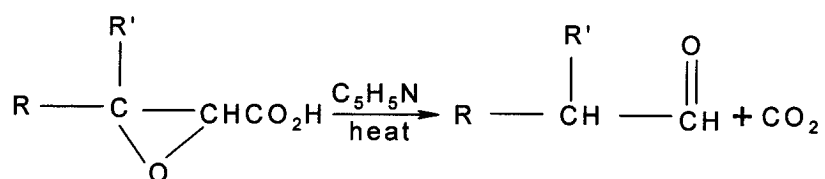
(10%)(6). Outlined here is a synthesis of glyceraldehyde. What are the in-intermediates A-C, and what stereoisomeric form of glyceraldehyde would you expect to obtain?



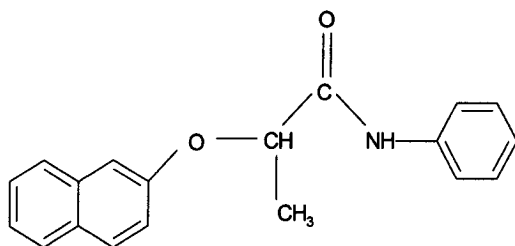
(10%)(7). When an aldehyde or a ketone is condensed with ethyl α -chloroacetate in the presence of sodium ethoxide, the product is an α, β -epoxy ester called a glycidic ester. The synthesis is called the Darzens condensation .



(a) Outline a reasonable mechanism for the Darzens condensation. (b) Hydrolysis of the epoxy ester leads to an epoxy acid that, on heating with pyridine, furnishes an aldehyde. What is happening here?



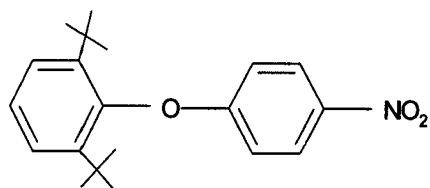
(10%)(8). Using as starting materials propanoic acid, aniline, and 2-naphthol, propose a synthesis of naproanilide, a herbicide used in rice paddies in the Orient.



Naproanilide

(10%)(9). The widely used antioxidant and food preservative called BHA (butylated hydroxyanisole) is actually a mixture of 2-tert-butyl-4-methoxyphenol and 3-tert-butyl-4-methoxyphenol. BHA is synthesized from p-methoxyphenol and 2-methylpropene. (a) Suggest how this is done. (b) Another widely used antioxidant is BHT (butylated hydroxytoluene). BHT is actually 2,6-di-tert-butyl-4-methylphenol, and the raw materials used in its production are p-cresol and 2-methylpropene. What reaction is used here?

(10%)(10). p-Chloronitrobenzene was allowed to react with sodium 2,6-di-tert-butylphenoxide with the intention of preparing the diphenyl ether **1**. The product was not **1**, but rather was an isomer of **1** that still possessed a phenolic hydroxyl group.



1

What was this product, and how can one account for its formation?