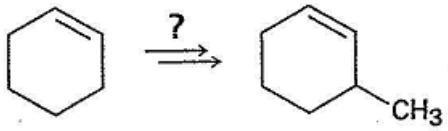
Problem 10.11

How would you carry out the following transformations using an organocopper coupling reaction? More than one step is required in each case.

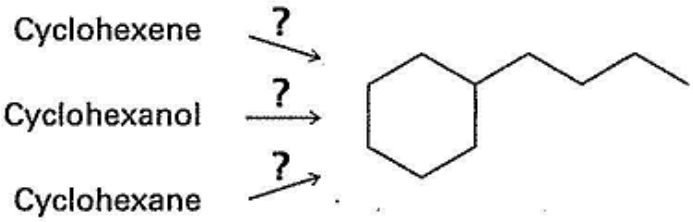
(a) 

(b) $CH_3CH_2CH_2CH_2Br \xrightarrow{?} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

(c) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{?} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

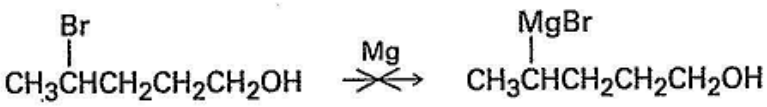
Problem 10.34

How would you carry out the following syntheses?



Problem 10.36

Why do you suppose it's not possible to prepare a Grignard reagent from a bromo alcohol such as 4-bromo-1-pentanol? Give another example of a molecule that is unlikely to form a Grignard reagent.



Problem 22.1

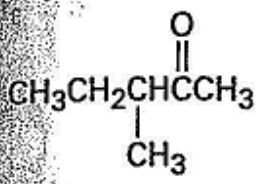
Draw structures for the enol tautomers of the following compounds:

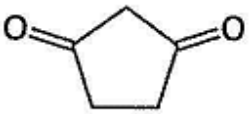
(a) Cyclopentanone **(b)** Methyl thioacetate **(c)** Ethyl acetate

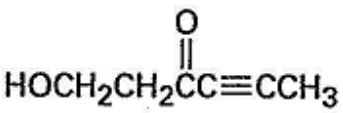
(d) Propanal **(e)** Acetic acid **(f)** Phenylacetone

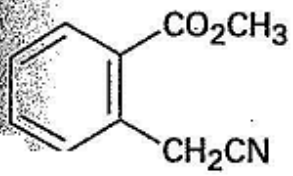
Problem 22.20

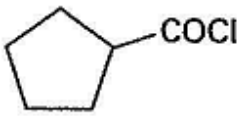
Identify all the acidic hydrogens ($pK_a < 25$) in the following molecules:

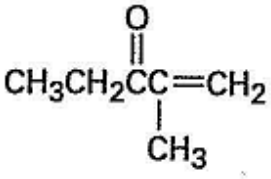
(a) 

(b) 

(c) 

(d) 

(e) 

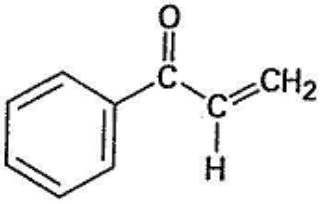
(f) 

Problem 22.2

How many acidic hydrogens does each of the molecules listed in Problem 22.1 have? Identify them.

Problem 22.24

Treatment of 1-phenyl-2-propenone with a strong base such as LDA does not yield an anion, even though it contains a hydrogen on the carbon atom next to the carbonyl group. Explain.



1-Phenyl-2-propenone

Problem 22.34

When optically active (*R*)-2-methylcyclohexanone is treated with either aqueous base or acid, racemization occurs. Explain.

Problem 22.35

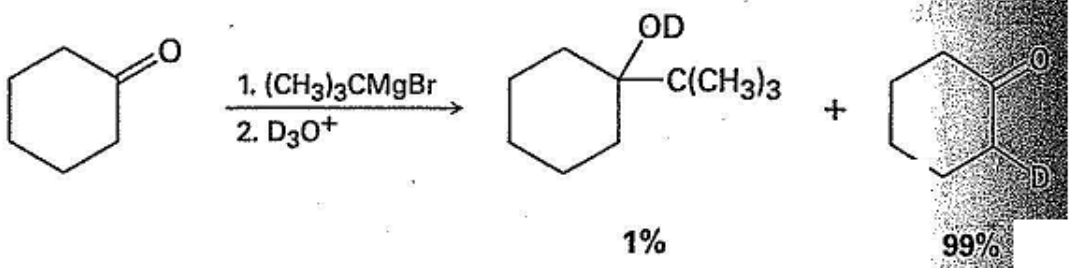
Would you expect optically active (*S*)-3-methylcyclohexanone to be racemized on acid or base treatment in the same way as 2-methylcyclohexanone (Problem 22.34)? Explain.

Problem 22.46

The two isomers *cis*- and *trans*-4-*tert*-butyl-2-methylcyclohexanone are each converted by base treatment. Which isomer do you think is more stable and why?

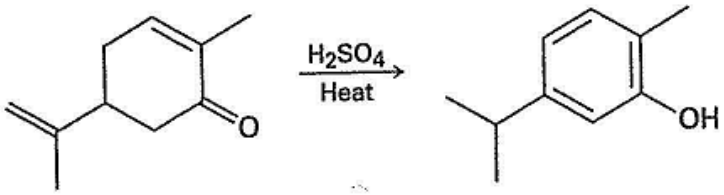
Problem 22.48

Attempted Grignard reaction of cyclohexanone with *tert*-butylmagnesium bromide gives only about 1% yield of the expected addition product along with 99% unreacted cyclohexanone. If D_3O^+ is added to the reaction mixture after a suitable period, however, the "unreacted" cyclohexanone is found to have one deuterium atom incorporated into it. Explain.



Problem 22.58

Heating carvone with aqueous sulfuric acid converts it into carvacrol. Propose a mechanism for the isomerization.



Carvone **Carvacrol**