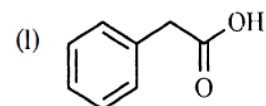
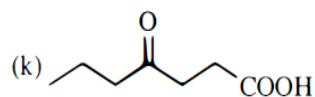
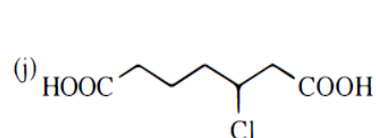
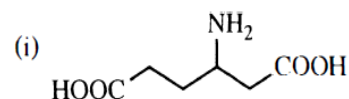
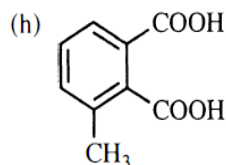
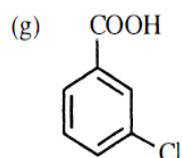
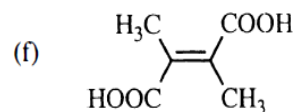
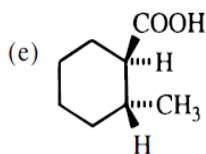
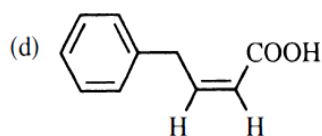
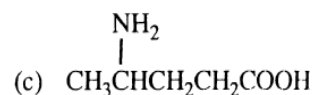
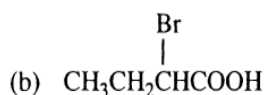
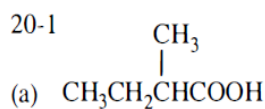


PROBLEM 20-1

Draw the structures of the following carboxylic acids.

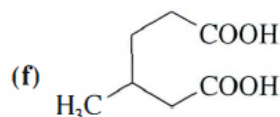
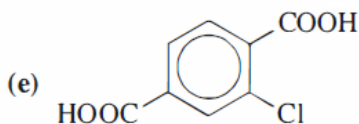
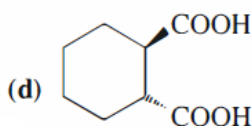
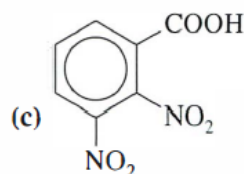
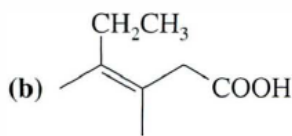
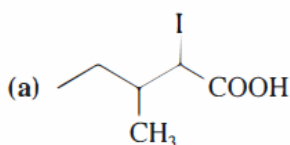
- | | |
|--|--|
| (a) α -methylbutyric acid | (b) 2-bromobutanoic acid |
| (c) 4-aminopentanoic acid | (d) <i>cis</i> -4-phenyl-2-butenoic acid |
| (e) <i>trans</i> -2-methylcyclohexanecarboxylic acid | (f) 2,3-dimethylfumaric acid |
| (g) <i>m</i> -chlorobenzoic acid | (h) 3-methylphthalic acid |
| (i) β -amino adipic acid | (j) 3-chloroheptanedioic acid |
| (k) 4-oxoheptanoic acid | (l) phenylacetic acid |

ANSWER



PROBLEM 20-2

Name the following carboxylic acids (when possible, give both a common name and a systematic name).



ANSWER

20-2 IUPAC name first; then common name.

- (a) 2-iodo-3-methylpentanoic acid; α -iodo- β -methylvaleric acid
(b) (Z)-3,4-dimethylhex-3-enoic acid
(c) 2,3-dinitrobenzoic acid; no common name
(d) *trans*-cyclohexane-1,2-dicarboxylic acid; (*trans*-hexahydrophthalic acid)
(e) 2-chlorobenzene-1,4-dicarboxylic acid; 2-chloroterephthalic acid
(f) 3-methylhexanedioic acid; β -methyladipic acid

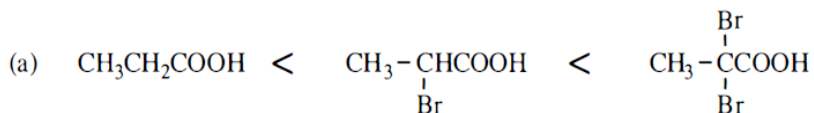
PROBLEM 20-3

Rank the compounds in each set in order of increasing acid strength.

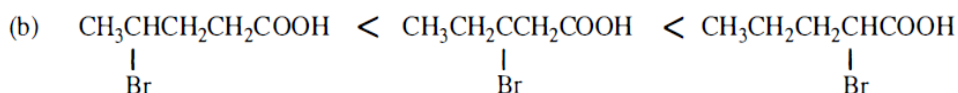
- (a) $\text{CH}_3\text{CH}_2\text{COOH}$ $\text{CH}_3\text{CHBrCOOH}$ $\text{CH}_3\text{CBr}_2\text{COOH}$
(b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCOOH}$ $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{COOH}$ $\text{CH}_3\text{CHBrCH}_2\text{CH}_2\text{COOH}$
(c) $\text{CH}_3\text{CH}(\text{NO}_2)\text{COOH}$ $\text{CH}_3\text{CH}(\text{Cl})\text{COOH}$ $\text{CH}_3\text{CH}_2\text{COOH}$ $\text{CH}_3\text{CH}(\text{C}\equiv\text{N})\text{COOH}$

ANSWER

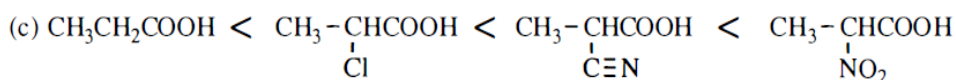
20-3 Listed in order of increasing acid strength (weakest acid first). (See Appendix 2 for a review of acidity.)



The greater the number of electron-withdrawing substituents, the greater the stabilization of the carboxylate ion.



The closer the electron-withdrawing group, the greater the stabilization of the carboxylate ion.



The stronger the electron-withdrawing effect of the substituent, the greater the stabilization of the carboxylate ion.

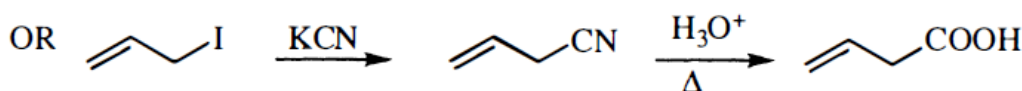
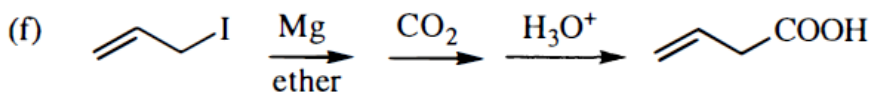
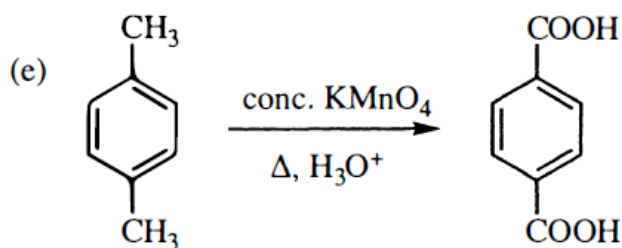
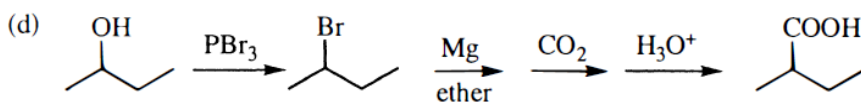
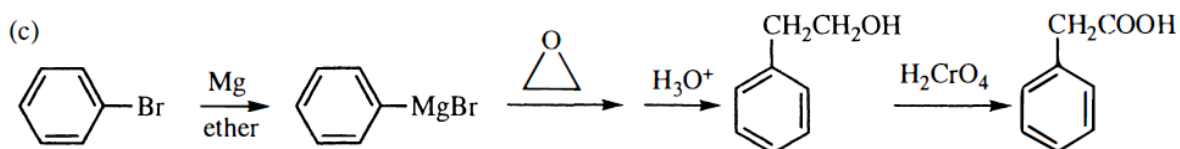
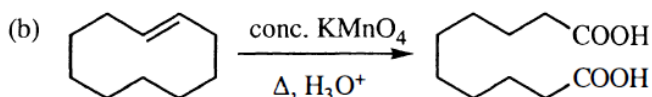
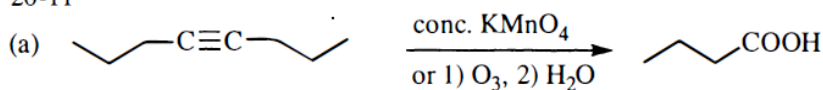
PROBLEM 20-11

Show how you would synthesize the following carboxylic acids, using the indicated starting materials.

- (a) 4-octyne \rightarrow butanoic acid
(b) *trans*-cyclodecene \rightarrow decanedioic acid
(c) bromobenzene \rightarrow phenylacetic acid
(d) 2-butanol \rightarrow 2-methylbutanoic acid
(e) *p*-xylene \rightarrow terephthalic acid
(f) allyl iodide \rightarrow 3-butenic acid

ANSWER

20-11



PROBLEM 20-12

(b) Propose a mechanism for the acid-catalyzed reaction of acetic acid with ethanol to give ethyl acetate.

ANSWER

(b) The mechanism of acid-catalyzed nucleophilic acyl substitution may seem daunting, but it is simply a succession of steps that are already very familiar to you.

Typically, these mechanisms have six steps: four proton transfers (two on, two off), a nucleophilic attack, and a leaving group leaving, with a little resonance stabilization thrown in that makes the whole thing work. The six steps are labeled in the mechanism below:

Step A proton on (resonance stabilization)

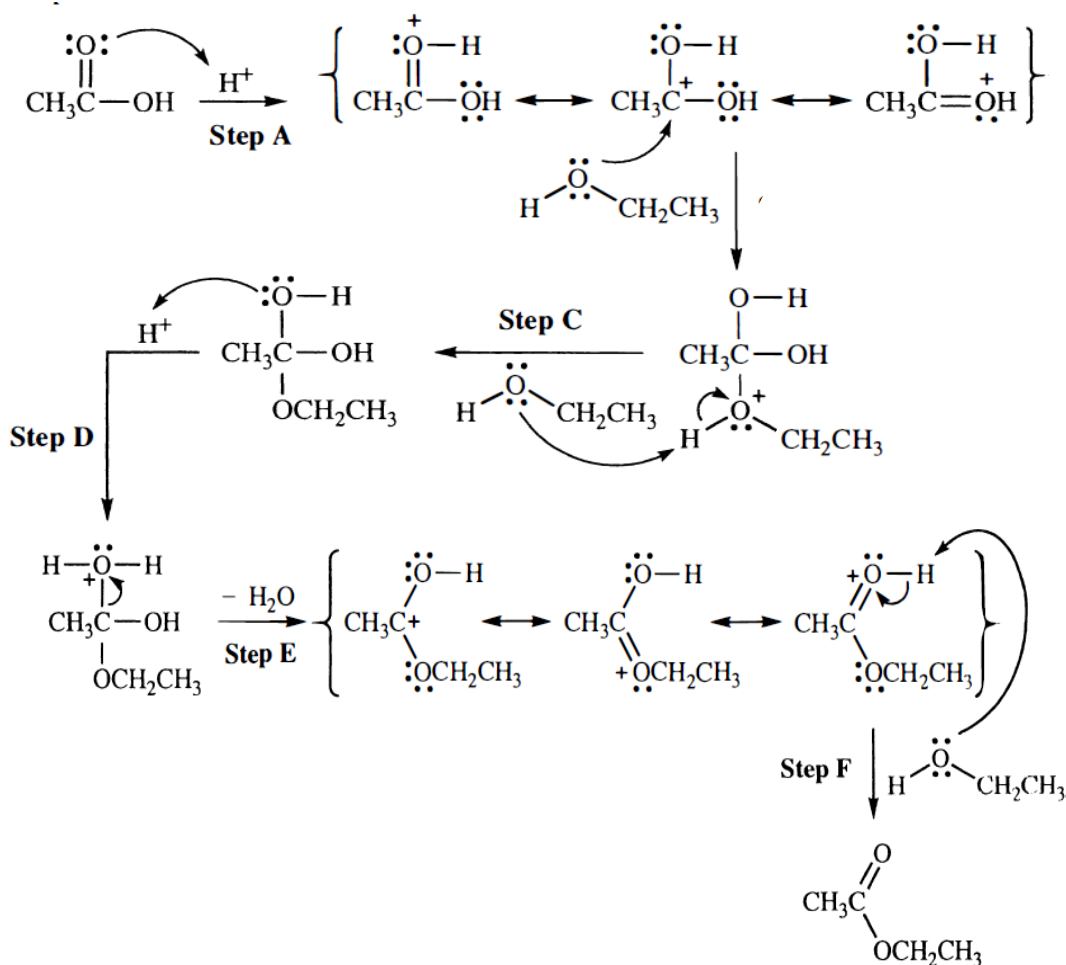
Step B nucleophile attacks

Step C proton off

Step D proton on

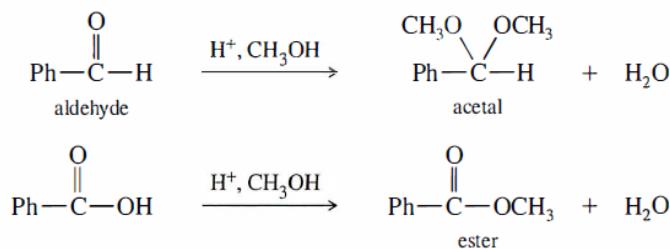
Step E leaving group leaves (resonance stabilization)

Step F proton off



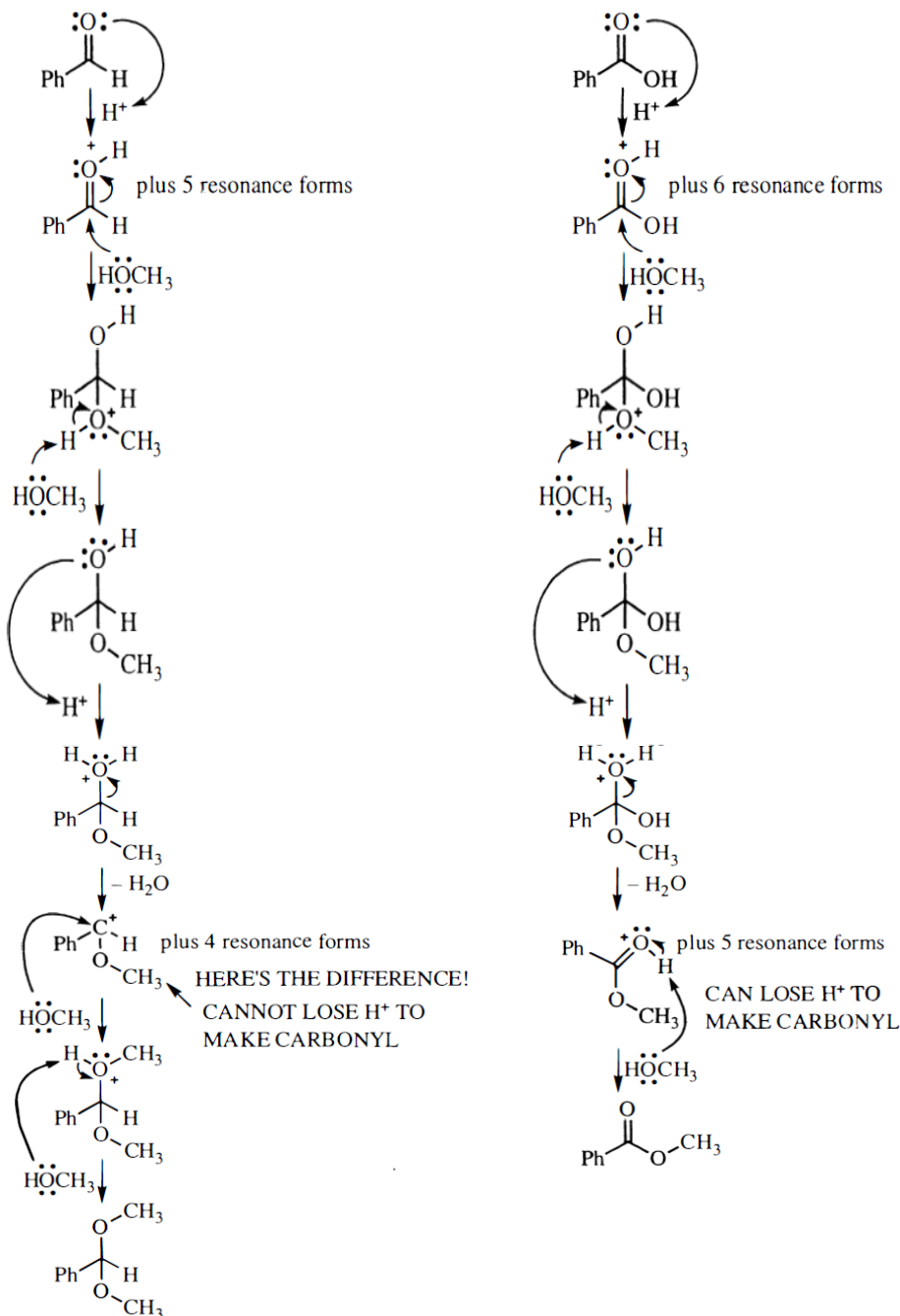
PROBLEM 20-13

Most of the Fischer esterification mechanism is identical with the mechanism of acetal formation. The difference is in the final step, where a carbocation loses a proton to give the ester. Write mechanisms for the following reactions, with the comparable steps directly above and below each other. Explain why the final step of the esterification (proton loss) cannot occur in acetal formation, and show what happens instead.



ANSWER

20-13 For the sake of space in this problem, resonance forms will not be drawn, but remember that they are critical!



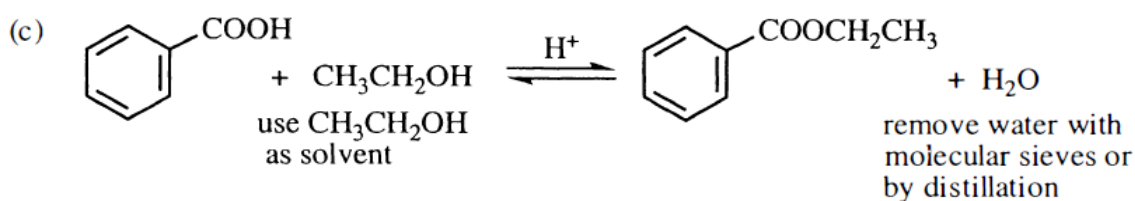
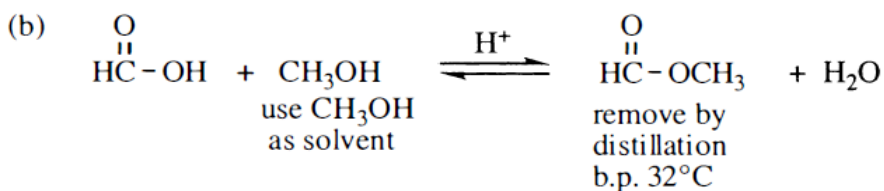
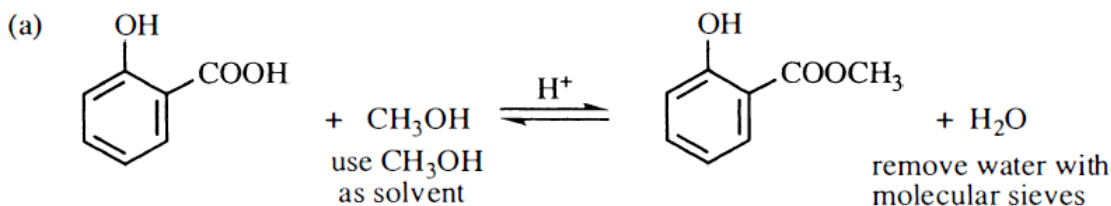
PROBLEM 20-15

Show how Fischer esterification might be used to form the following esters. In each case, suggest a method for driving the reaction to completion.

- (a) methyl salicylate (b) methyl formate (bp 32°C) (c) ethyl benzoate

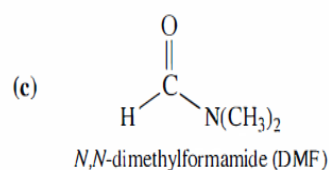
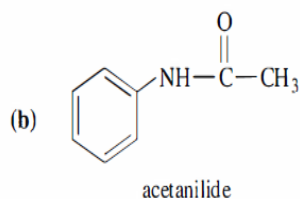
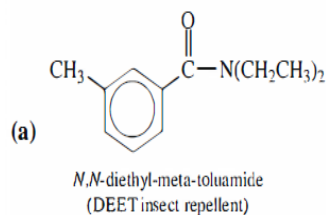
ANSWER

20-15

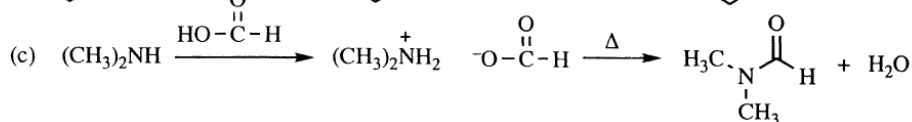
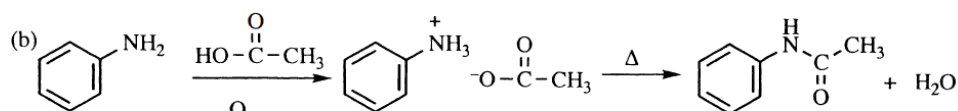
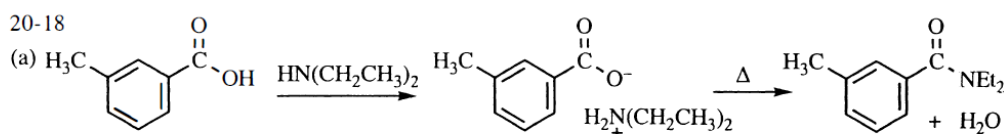


PROBLEM 20-18

Show how to synthesize the following compounds, using appropriate carboxylic acids and amines.

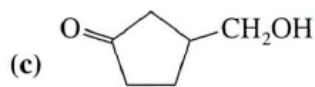
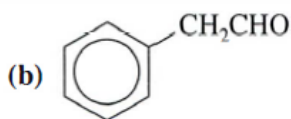
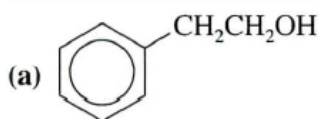


ANSWER



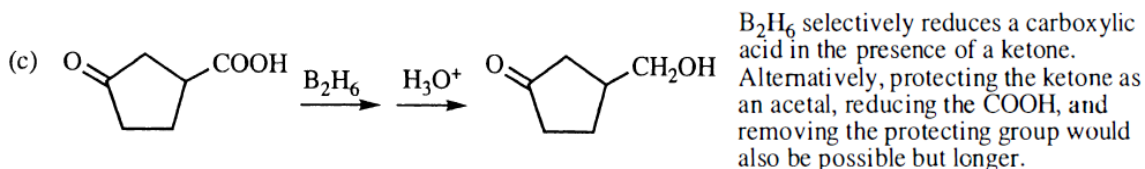
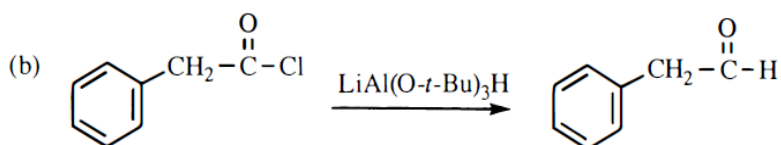
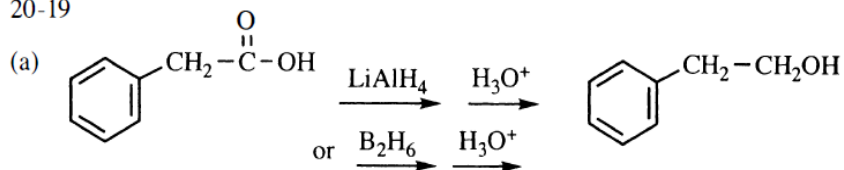
PROBLEM 20-19

Show how you would synthesize the following compounds from the appropriate carboxylic acids or acid derivatives.



ANSWER

20-19

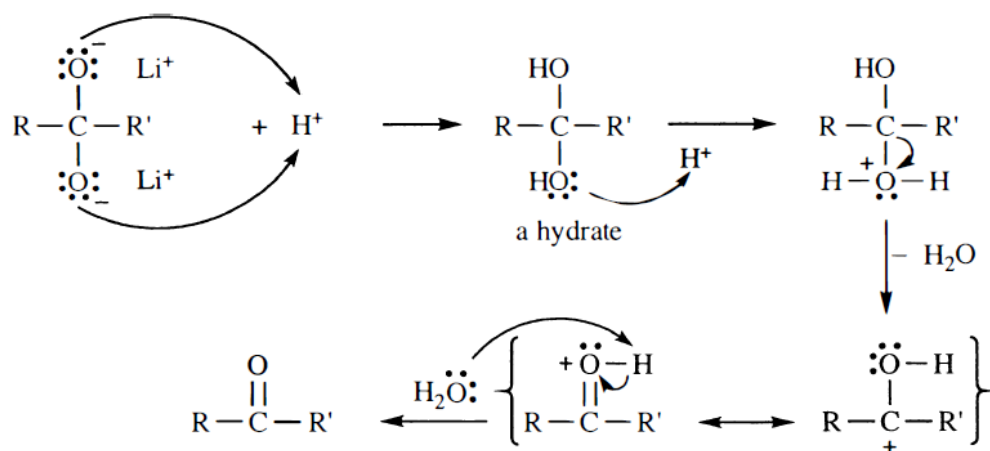


PROBLEM 20-20

Propose a mechanism for conversion of the dianion to the ketone under mildly acidic conditions.

ANSWER

20-20



PROBLEM 20-21

Show how the following ketones might be synthesized from the indicated acids, using any necessary reagents.

- (a) propiophenone from propionic acid (two ways, using alkylation of the acid and using Friedel–Crafts acylation)
(b) methyl cyclohexyl ketone from cyclohexanecarboxylic acid

ANSWER

20-21

