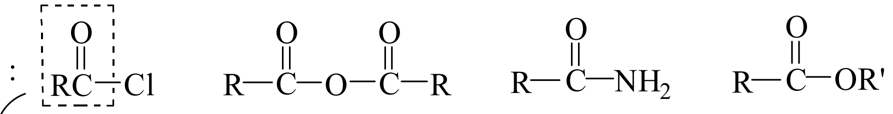
Chapter 20

functional derivatives of carboxylic acids :



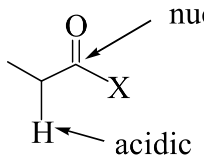
acid chloride	anhydride	amide	ester
acyl group			
− ic acid → − yl chloride	acid → anhydride	−oic acid → amide	−ic acid → ate

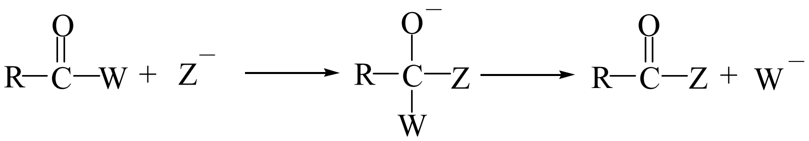
nomenclature

⇓

p 754

amide : highest b.p due to hydrogen bonding





(W : −OH, −Cl, −OCR (with C=O), −NH$_2$, −OR')

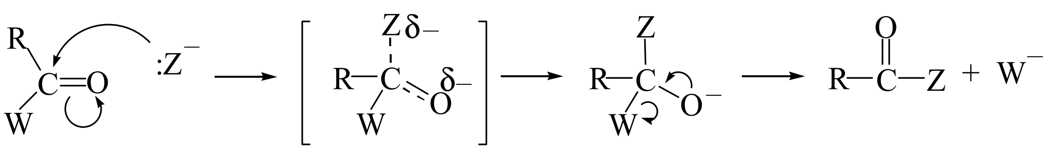
⇓

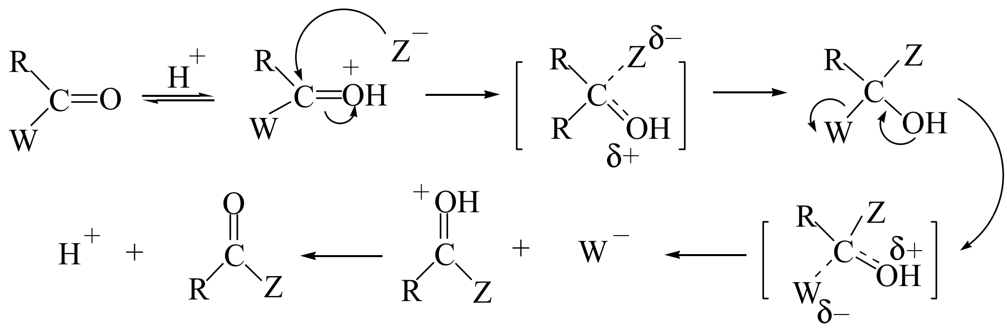
nucleophilic substitution cf) aldehyde & ketone : nucleophilic addition

⇓

depending on the basicity of W : the weaker the base, the better the leaving group

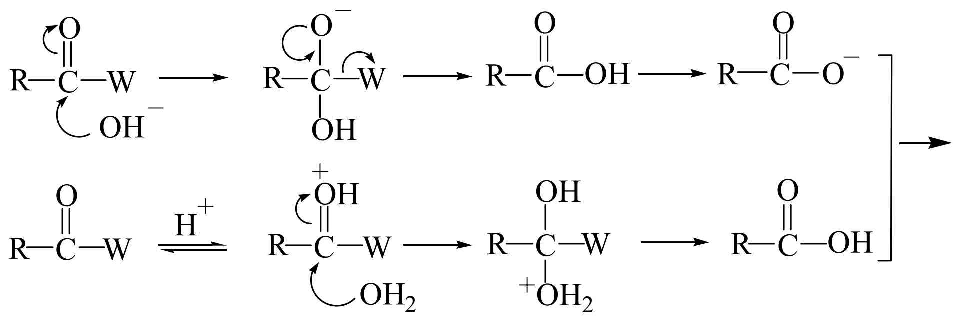
$Cl^- > RCOO^- > R'O^- > NH_2^-$ ($:H^-$ & R^- are the strongest bases)





⇓

acid - catalyzed nucleophilic acyl substitution



hydrolyzed more readily in acidic or basic sol'n than neutral sol'n

nucleophilic substitution

RCOCl	RCl
$RCONH_2$	RNH_2
RCOOR'	ROR'

⟵ more reactive ⟹ due to electronic effect & steric effect from carbonyl group.

$$RCOCl \xrightarrow[\text{or } PCl_3]{PCl_5,\ SOCl_2} RCOOH$$

⇓

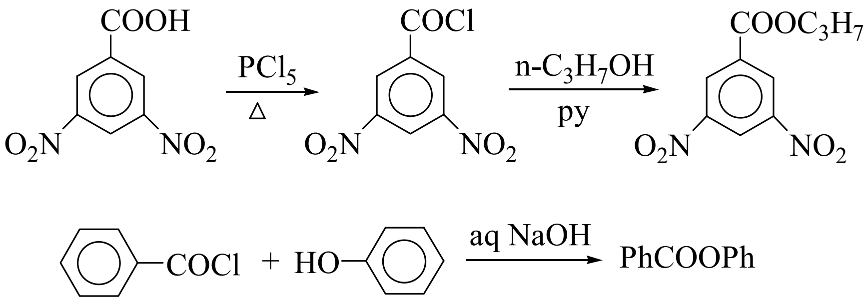
the most reactive of carboxylic acid derivatives due to the lowest basicity of Cl^-

$$RCOCl + ArH \xrightarrow{L.A.} RC(=O)-Ar$$

$$+ R'_2CuLi \longrightarrow RC(=O)-R'$$

$$+ LiAlH(OBu^t)_3 \longrightarrow RC(=O)-H$$

$$n\text{-}C_{17}H_{35}COOH \xrightarrow[\Delta]{SOCl_2} n\text{-}C_{17}H_{35}COCl \xrightarrow{NH_3} n\text{-}C_{17}H_{35}CONH_2$$

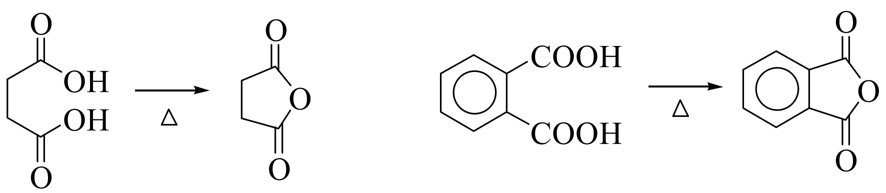


aromatic acid chlorides are considerably less reactive than aliphatic acid chlorides.

$$CH_3COOH \xrightarrow[700℃]{AlPO_4} CH_2{=}C{=}O \xrightarrow{CH_3COOH} (H_3C{-}\overset{O}{\overset{\|}{C}}{-})_2O$$

ketene

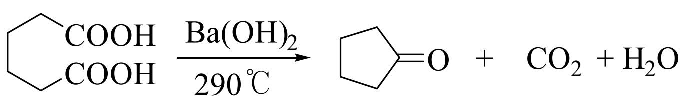
$$CH_3COCH_3 \xrightarrow[700\sim750℃]{-CH_4} CH_2{=}C{=}O$$



succinic anhydride

phthalic anhydride

(simple heating is applicable to making 5- or 6-membered cyclic anhydride)



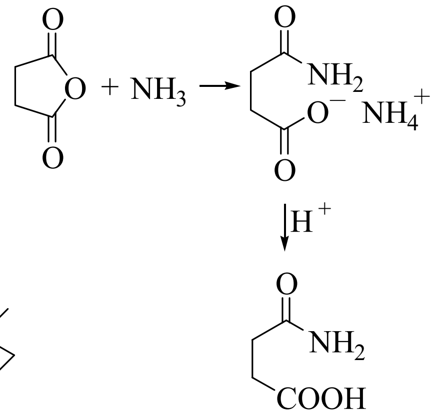
adipic acid

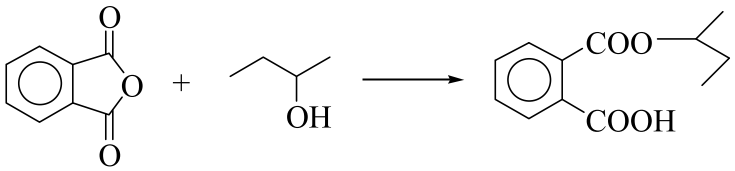
acid anhydrides undergo the same rxns as acid chlorides with a little slower rate.

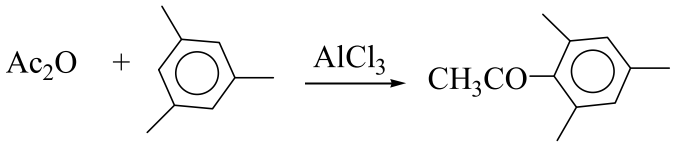
$$Ac_2O + H_2O \longrightarrow AcOH$$

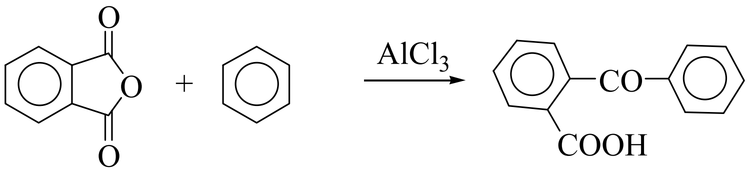
$$+ NH_3 \longrightarrow AcNH_2 + AcONH_4$$

$$+ CH_3OH \longrightarrow AcOCH_3 + AcOH$$

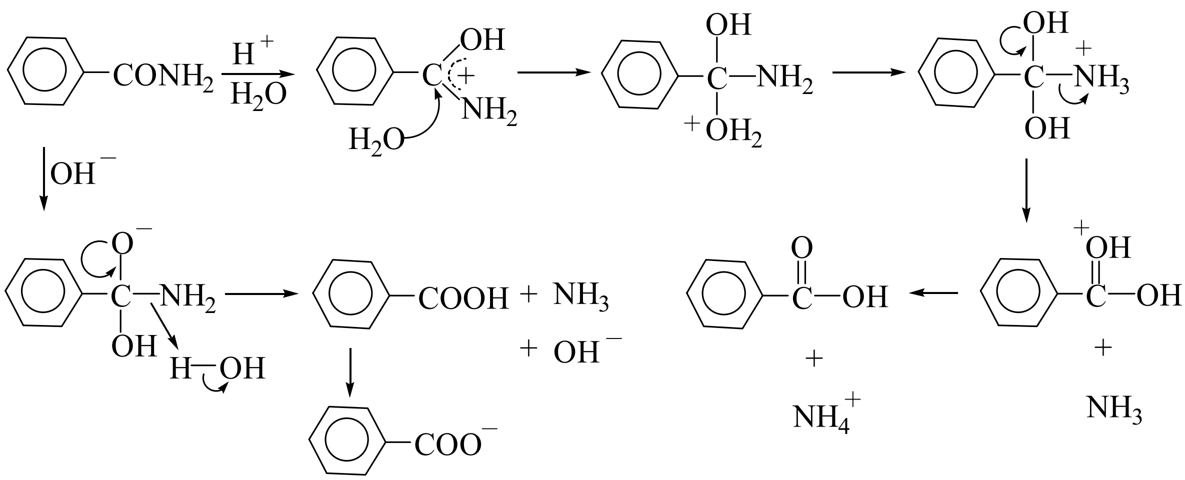


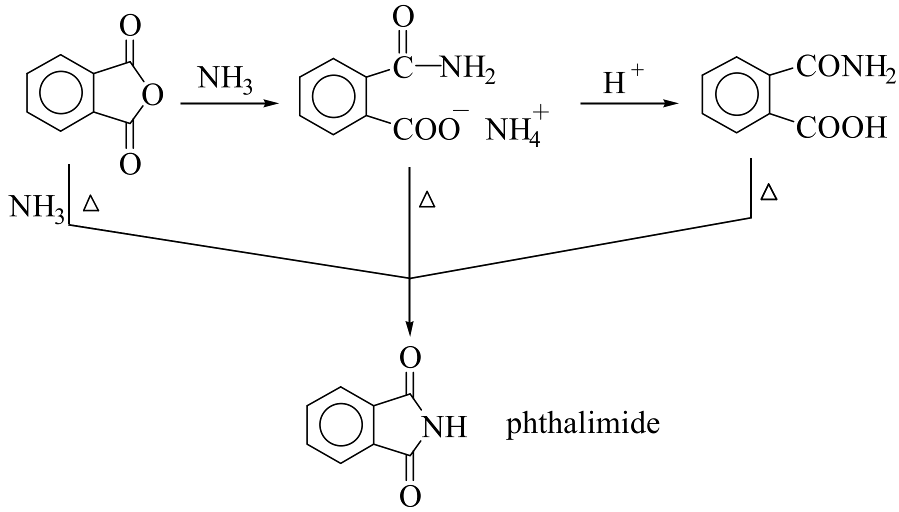






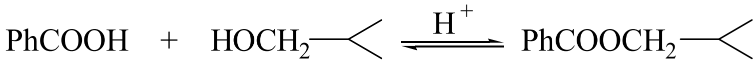
$$\left.\begin{matrix} RCOCl \\ (RCO)_2O \end{matrix}\right. + NH_3 \longrightarrow RCONH_2 \xleftarrow[\Delta]{} RCOO^- NH_4^+$$

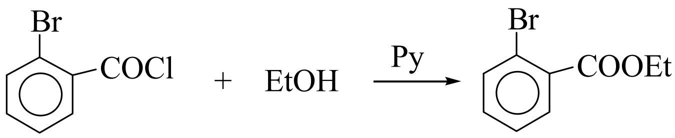


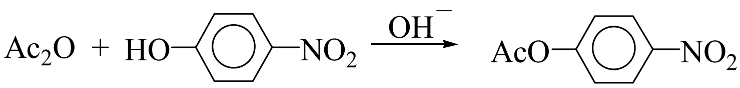


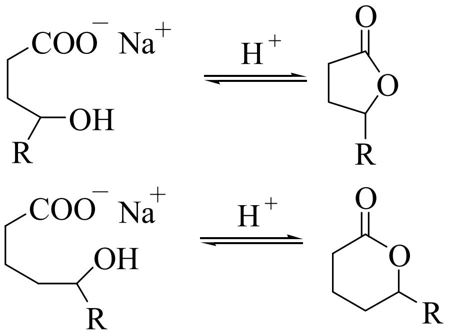
phthalimide

$$CH_3COOH + HOCH_2Ph \xrightleftharpoons{H^+} CH_3COOCH_2Ph$$





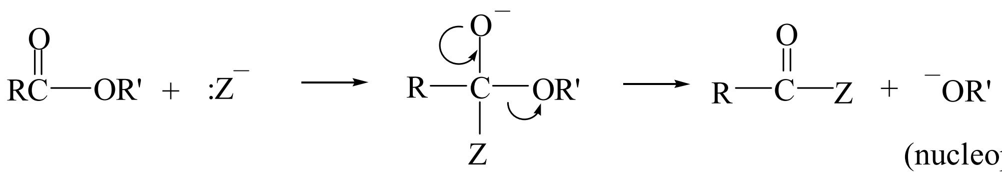




γ-lactone

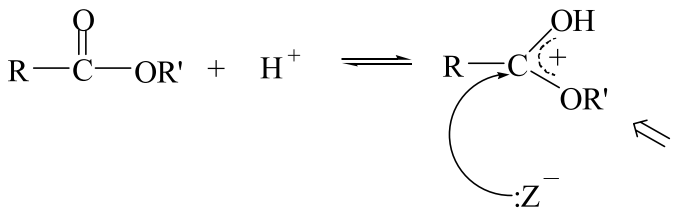
δ-lactone

spontaneously occur in acidic media
intramolecular esterification

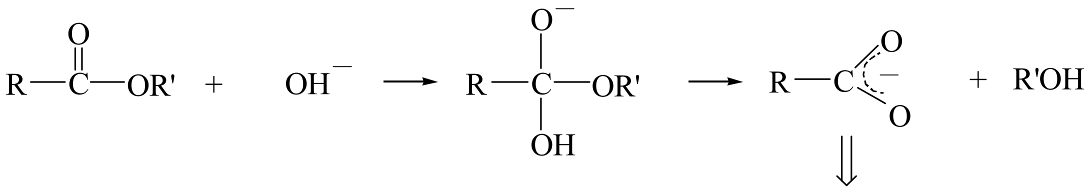


(nucleophilic substitution)

acid-catalyzed

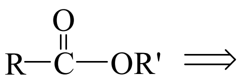


more susceptible to nucleophile



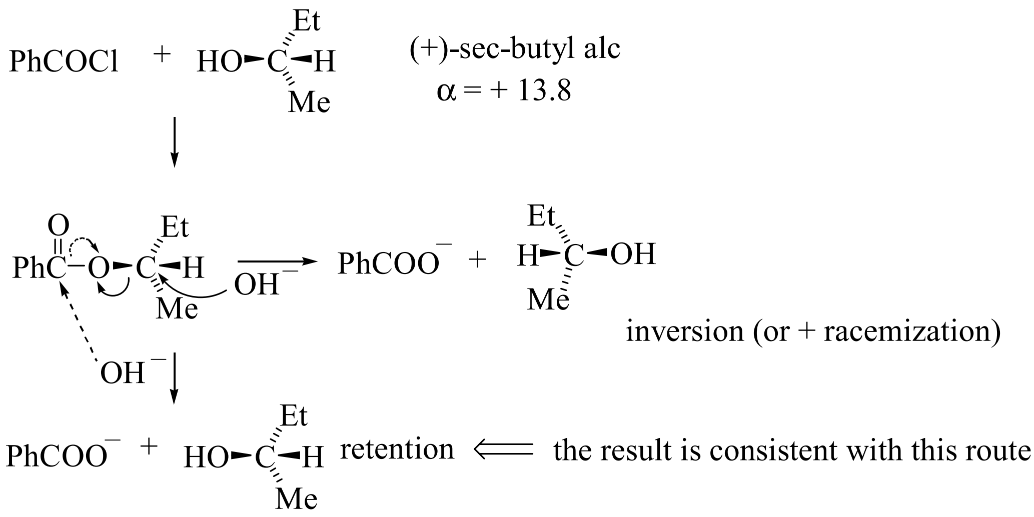
irreversible due to the inertness of carboxylate anion to R'OH

rate = k_2 [ester] [OH^-] $\Longrightarrow$ consistent with the attack on the ester by OH^-

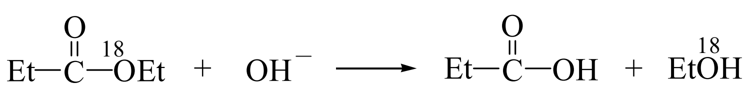


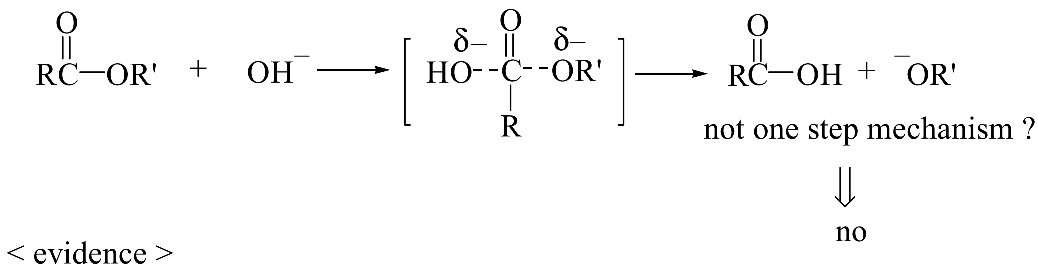
C—OR' bond is cleaved

< stereochemistry evidence >

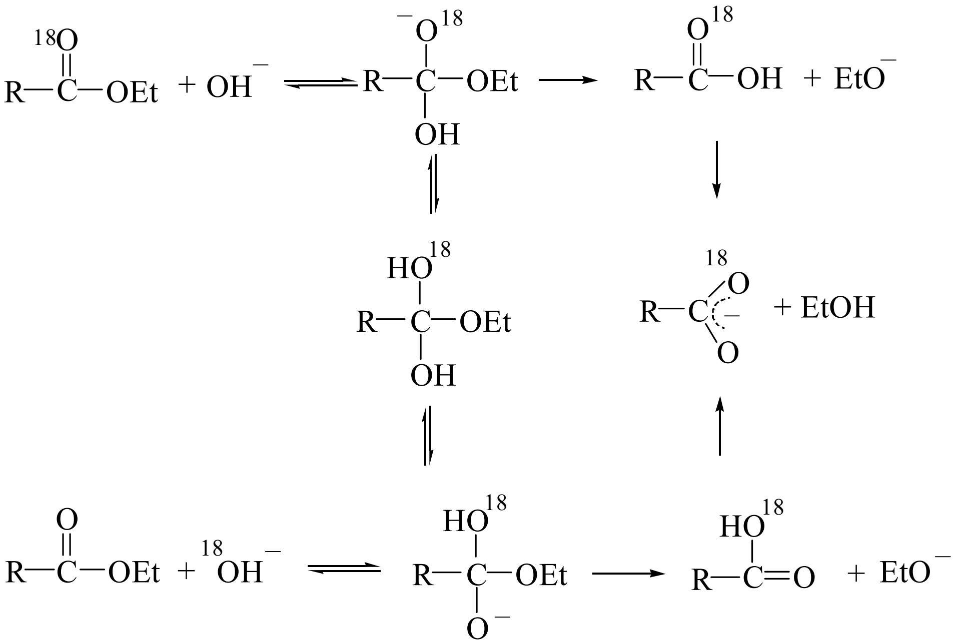


< tracer studies >

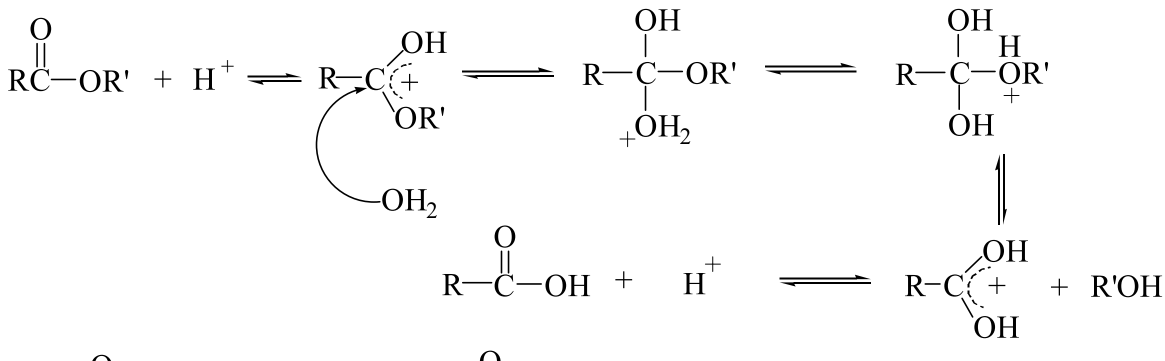




< evidence >

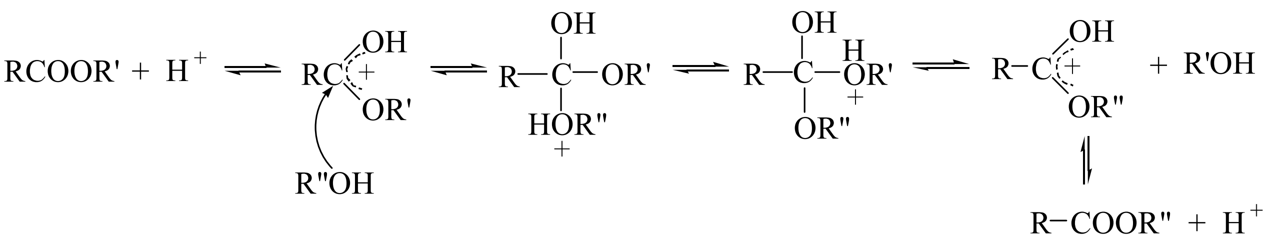


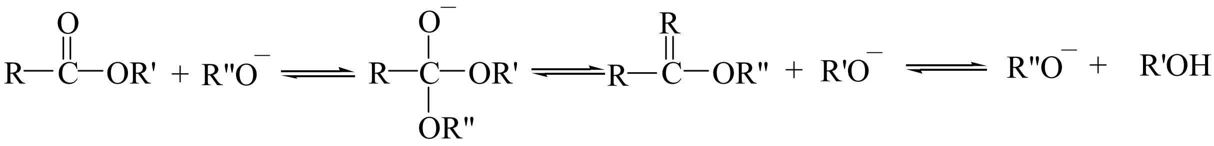
also true for amides, anhydrides and acid chlorides.

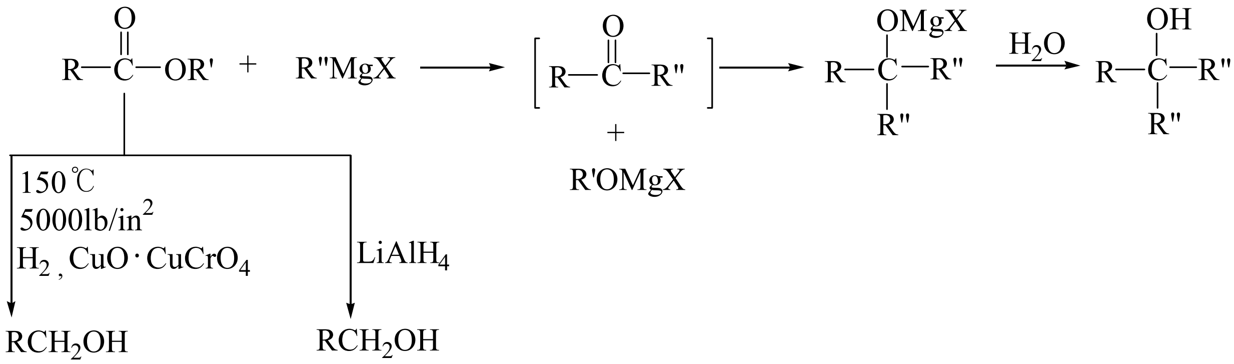


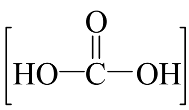
$$H_3C{-}C({=}O){-}OEt + NH_3 \longrightarrow CH_3{-}C({=}O){-}NH_2 + EtOH$$ (ammonolysis)

$$R{-}COOR' + R''OH \xrightleftharpoons{H^+ \text{ or } R''O^-} RCOOR'' + R'OH$$ (alcoholysis, transesterification)

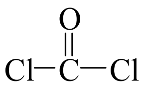




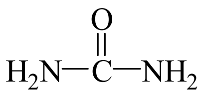




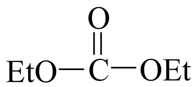
carbonic acid



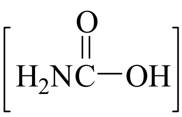
phosgen
(carbonyl chloride)



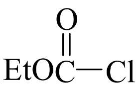
urea
(carbamide)



ethyl carbonate



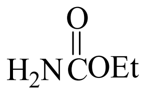
carbamic acid



ethyl chlorocarbonate
(formate)

$H_2N-C\equiv N$

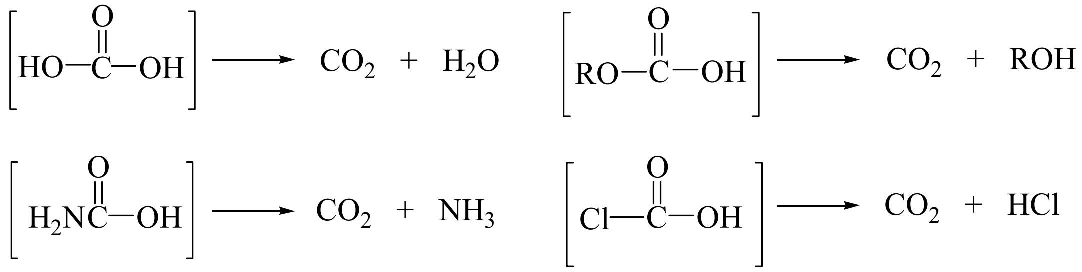
cyanamide

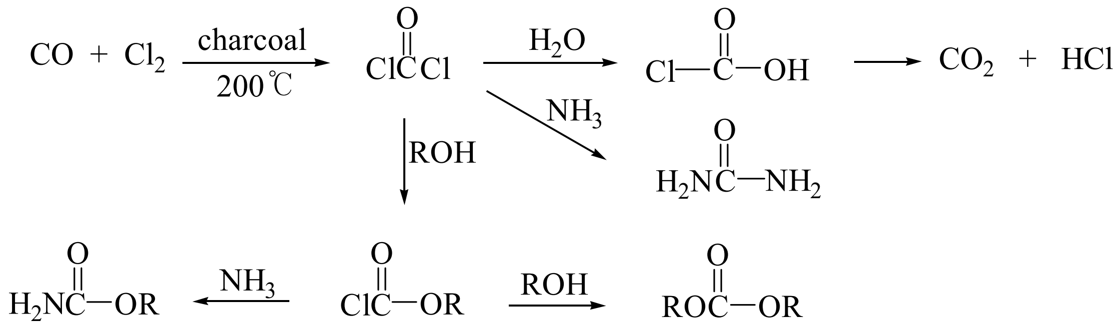


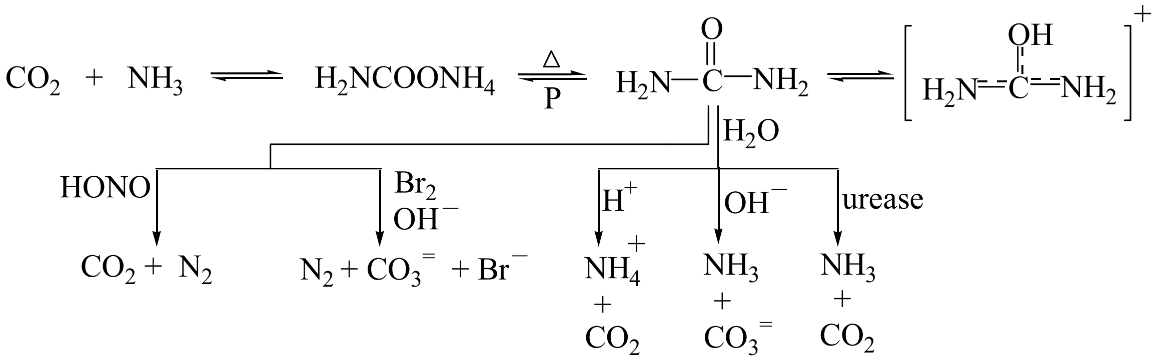
ethyl carbamate
(urethane)

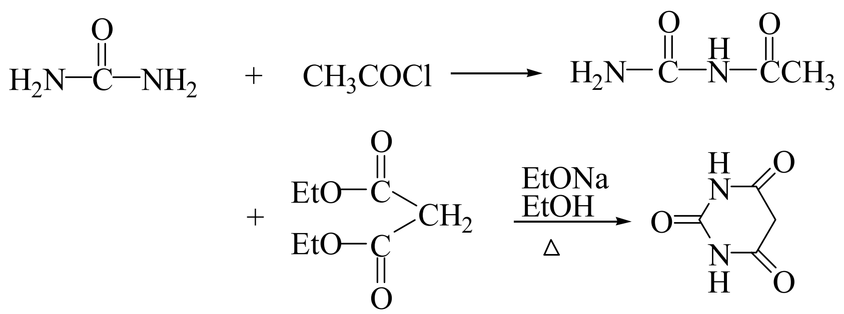
$HO-C\equiv N$

cyanic acid



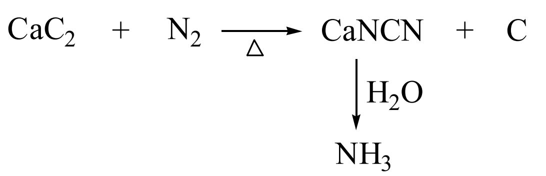




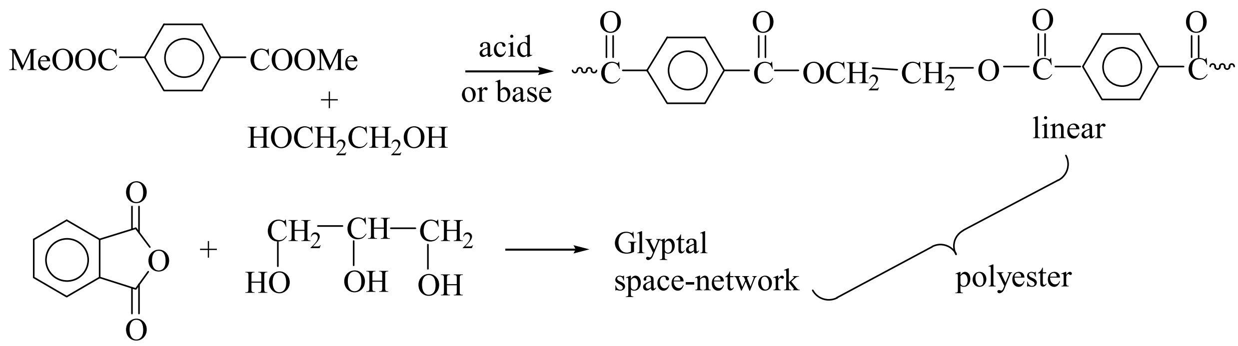


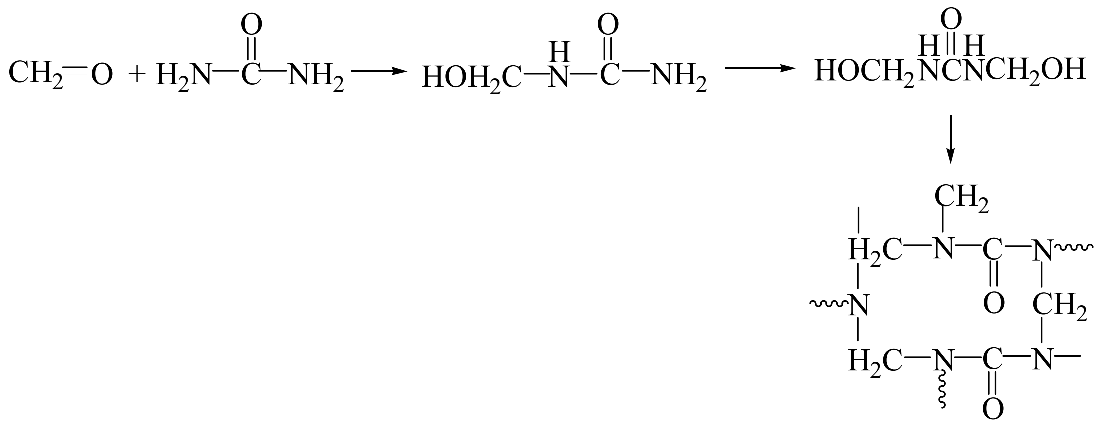
acetylurea (ureide)

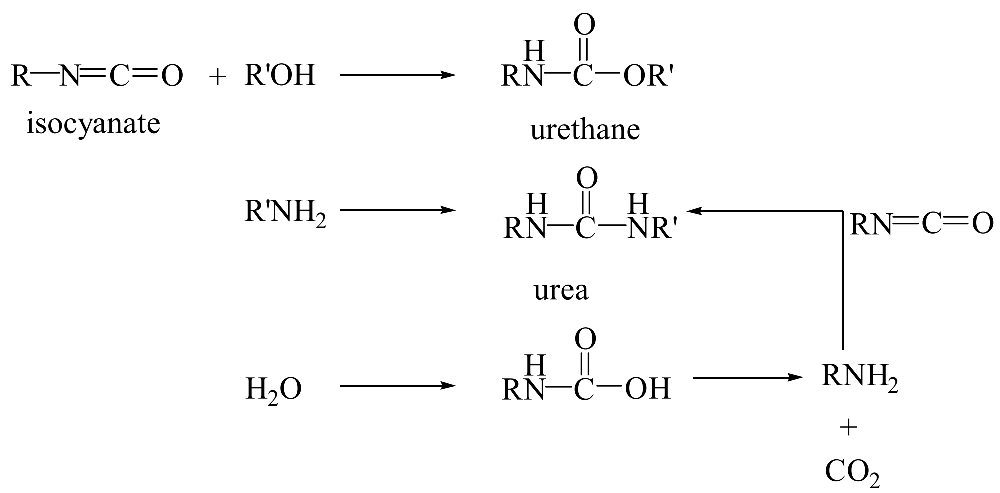
malonylurea
babituric acid

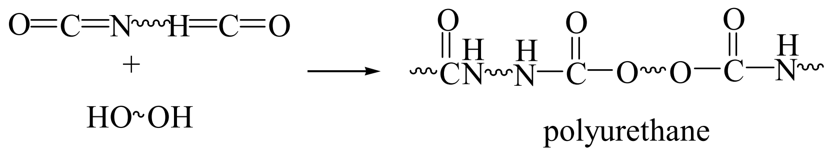


(nitrogen fixation)


MeOOC
COOMe
HOCH2CH2OH
acid
or base
linear
Glyptal
space-network
polyester


space-network


isocyanate
urethane
urea


polyurethane