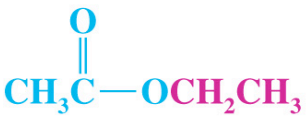
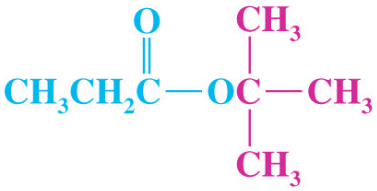
Azido Karboxilikoen Deribatuak (I)

- **Esterrak**
  - ➡ **Dagozkion azido karboxiliko eta alkoholaren izenetik eraikitzen da esterraren izena**
    - ★ Lehenik alkohola izendatzen da –IL atzizkiaz
    - ★ Gero azido karboxilikoaren izena –ATE edo -OATE atzizkiez



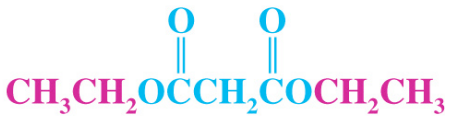
Ethyl acetate or
ethyl ethanoate



tert-Butyl propanoate

Vinyl acetate or
ethenyl ethanoate

Methyl *p*-chlorobenzoate

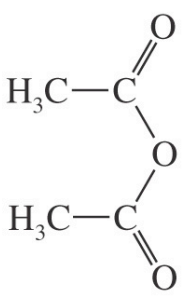


Diethyl malonate

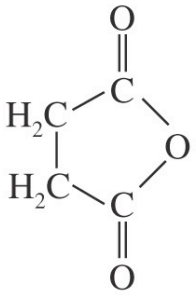
  - ➡ **Esterrek ezin dituzte hidrogeno zubiak eman beraien artean eta ondorioz azidoek baino irakite-tenperatura bajuagoak dauzkate**
    - ★ Urarekin eman ditzakete, eta beraz nahiko nahaskorrak dira uretan

Name	Structure	mp (°C)	bp (°C)	Solubility in Water (g 100 mL^{-1} at 20°C)
Methyl formate	HCO_2CH_3	−99	31.5	Very soluble
Ethyl formate	$HCO_2CH_2CH_3$	−79	54	Soluble
Methyl acetate	$CH_3CO_2CH_3$	−99	57	24.4
Ethyl acetate	$CH_3CO_2CH_2CH_3$	−82	77	7.39 (25°C)
Propyl acetate	$CH_3CO_2CH_2CH_2CH_3$	−93	102	1.89
Butyl acetate	$CH_3CO_2CH_2(CH_2)_2CH_3$	−74	125	1.0 (22°C)
Ethyl propanoate	$CH_3CH_2CO_2CH_2CH_3$	−73	99	1.75
Ethyl butanoate	$CH_3(CH_2)_2CO_2CH_2CH_3$	−93	120	0.51
Ethyl pentanoate	$CH_3(CH_2)_3CO_2CH_2CH_3$	−91	145	0.22
Ethyl hexanoate	$CH_3(CH_2)_4CO_2CH_2CH_3$	−68	168	0.063
Methyl benzoate	$C_6H_5CO_2CH_3$	−12	199	0.15
Ethyl benzoate	$C_6H_5CO_2CH_2CH_3$	−35	213	0.08
Phenyl acetate	$CH_3CO_2C_6H_5$		196	Slightly soluble
Methyl salicylate	*o*-$HOC_6H_4CO_2CH_3$	−9	223	0.74 (30°C)

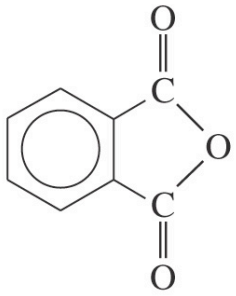
- **Azido Anhidridoak**
  - ➡ **Gehienetan azido hitza kendu eta anhidrido hitza gehitzearekin egina dago**



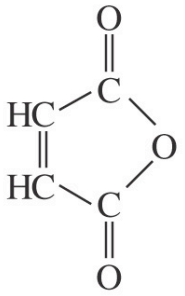
Acetic anhydride (ethanoic anhydride) mp −73°C



Succinic anhydride mp 121°C

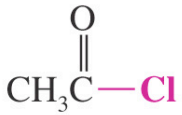


Phthalic anhydride mp 131°C

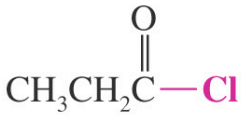


Maleic anhydride mp 53°C

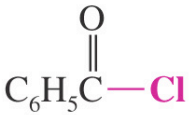
- **Azido Kloruroak**
  - ➡ **Azidoen izenetik *azido –iko* izena kendu eta *–il kloruro* gehituz izendatzen dira**



Acetyl chloride (ethanoyl chloride) mp −112°C; bp 51°C

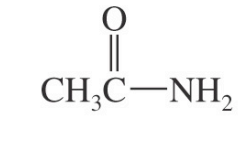


Propanoyl chloride mp −94°C; bp 80°C

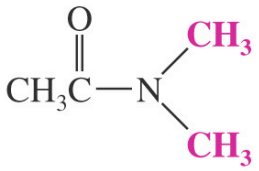


Benzoyl chloride mp −1°C; bp 197°C

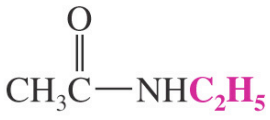
- **Amidak**
  - ➡ **Nitrogenoan ordezkatzailerik ez badute *azido –iko* atzizkia kenduz eta -*amida* gehituz osatzen da izena**
    - ★ **Ordezkatuak direnean *N*-an, ordezkatzaileen izenak gehitzen dira**



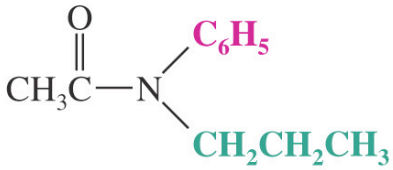
Acetamide
(ethanamide)
mp 82°C; bp 221°C



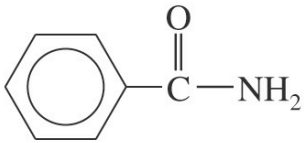
***N*,*N*-Dimethylacetamide**
mp −20°C; bp 166°C



***N*-Ethylacetamide**
bp 205°C



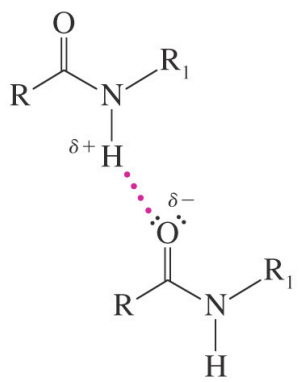
***N*-Phenyl-*N*-propylacetamide**
mp 49°C; bp 266°C at 712 torr



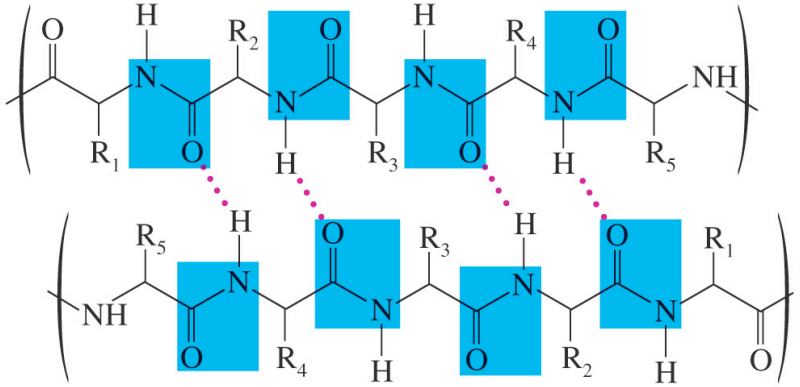
Benzamide
mp 130°C; bp 290°C

  - ➡ **Nitrogenoan 1 edo 2 H dituzten amidek hidrogeno-lotura oso sendoak ematen dituzte (urtze- eta irakite-tenperatura altuak)**

➡ **Proteinetan eta peptidoetan amiden arteko hidrogeno-loturak dira egitura hirudimentsionala egonkortzen dutenak**



Hydrogen bonding (red dots) between amide molecules



Hydrogen bonding between amide groups of peptide chains. This interaction between chains (called a β sheet) is important to the structure of many proteins.

- **Nitriloak**
  - ➡ **Atzizki moduan *–nitrilo* hitza erabiltzen da**
    - ★ **Nitriloaren karbonoa izaten da 1-a**
    - ★ **Etanonitriloak azetonitriloa izena hartzen du**

Ethanenitrile (acetonitrile)

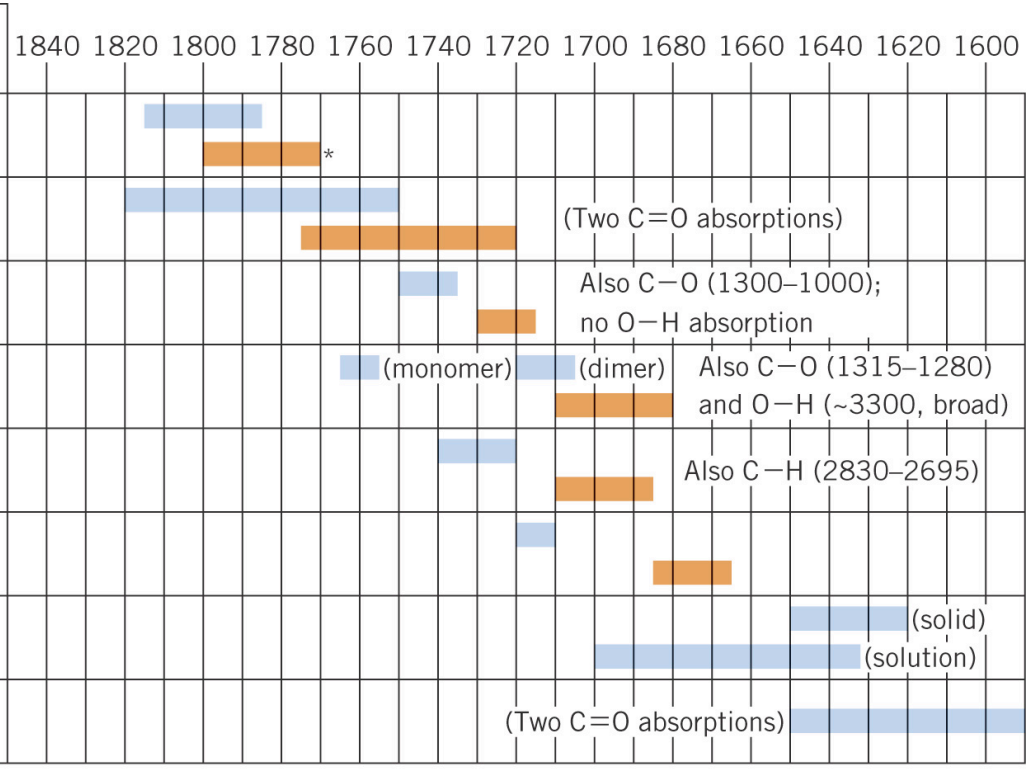
Propenenitrile (acrylonitrile)

● Azil Konposatuen Propietate Espektroskopikoak

➡ IG

- ★ **Karboniloaren dardarketa-maiztasuna deribatuaren arabera aldatzen da**
- ★ **O-H taldearen dardarketak banda zabal bat ematen du 2500-3100 cm^{-1} tartean**
- ★ **Amiden N-H dardarketa 3140-3500 cm^{-1} bitartean azaltzen da**

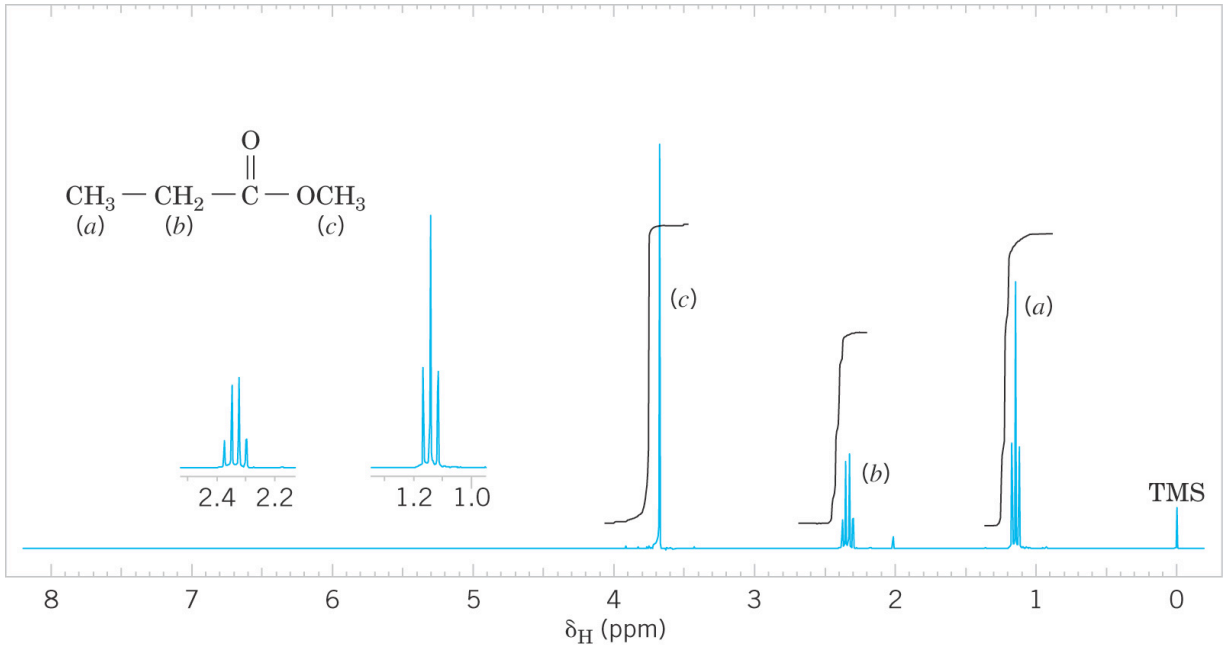
Functional Group	Approximate Frequency Range (cm^{-1})
Acid chloride	1815–1785 1800–1770 (conj.)
Acid anhydride	1820–1750 1775–1720 (conj.)
Ester/Lactone	1750–1735 1730–1715 (conj.)
Carboxylic acid	~1760 or 1720–1705 1710–1680 (conj.)
Aldehyde	1740–1720 1710–1685 (conj.)
Ketone	1720–1710 1685–1665 (conj.)
Amide/lactam	1650–1640
Carboxylate salt	1650–1550



*Orange bars represent absorption ranges for conjugated species.

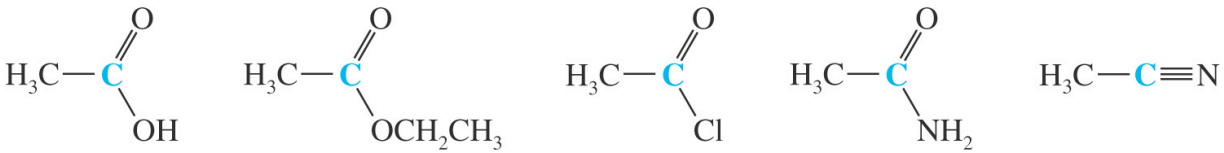
➡ ^{1}H EMN

- ★ **Azido karboxiliko eta deribatuen α hidrogenoak δ 2.0-2.5 tartean azaltzen dira**
- ★ **Hidrogeno azidoa δ 10-12 tartean**



➡ ^{13}C EMN

- ★ **Karboniloaren karbonoa δ 160 to 180 bitartean**

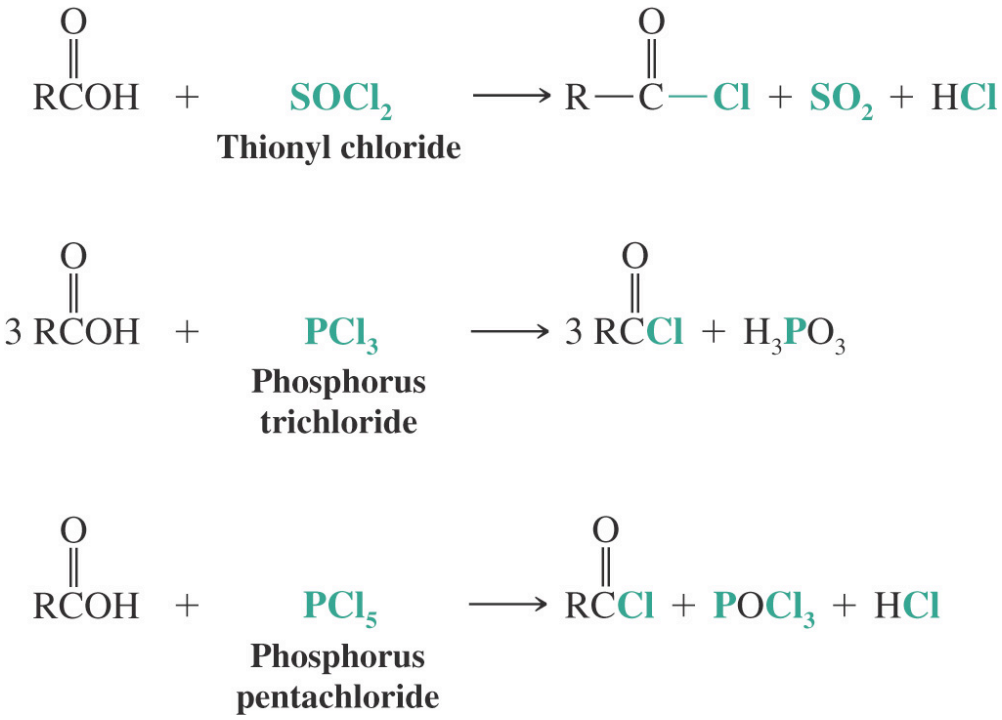


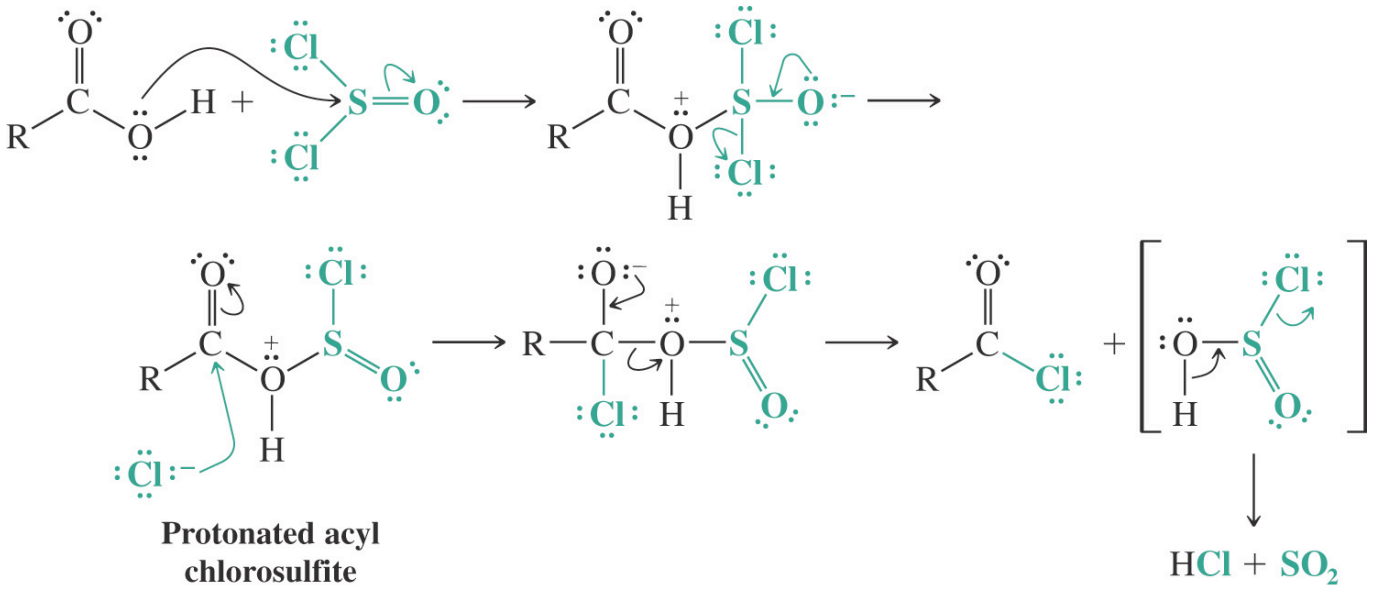
^{13}C NMR chemical shifts for the carbonyl or nitrile carbon atom

♦ Azido Kloruroak

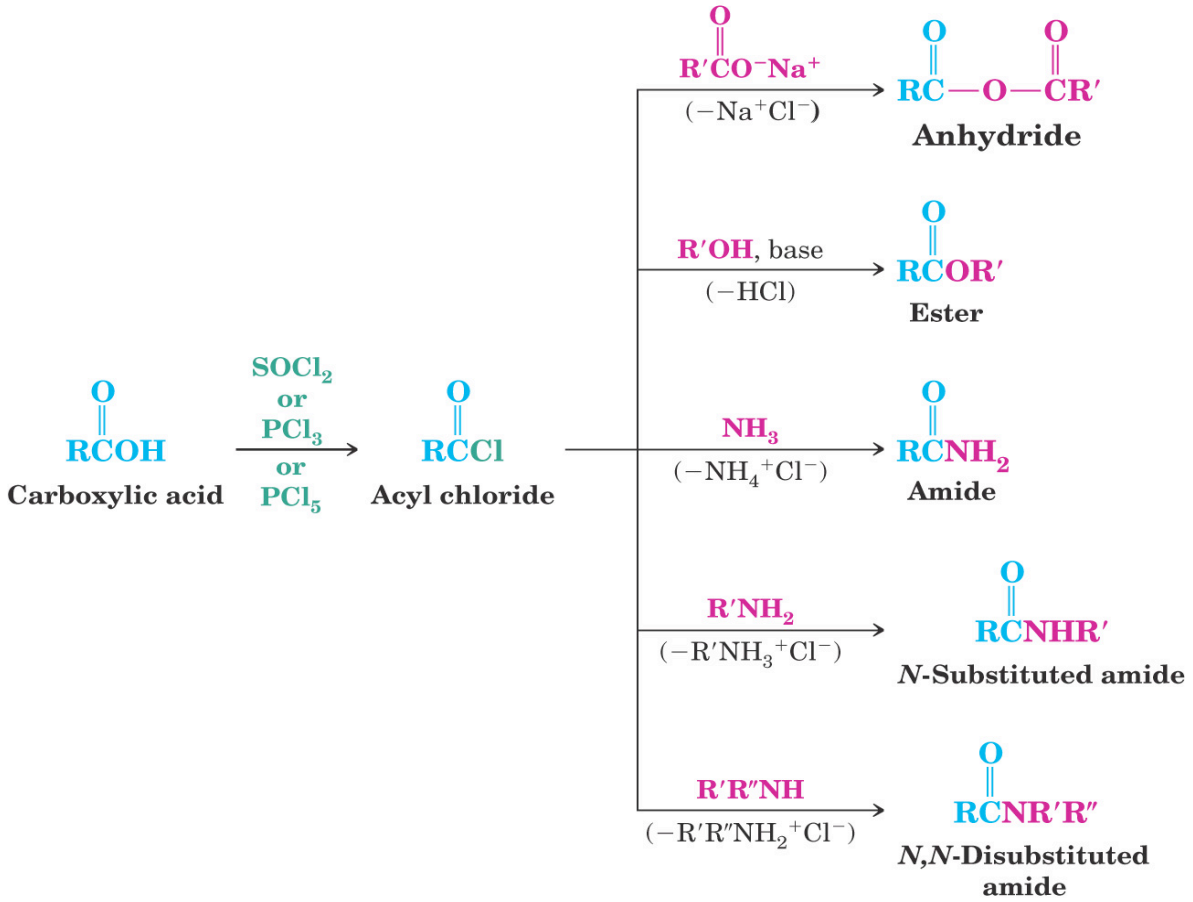
● Azido Kloruroen Sintesibideak

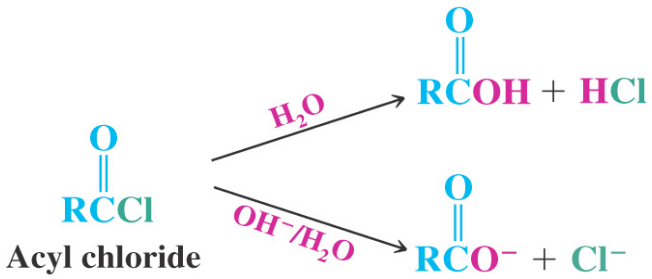
➡ **Azido karboxilikoetatik abiatuz tionilo kloruroarekin, fosforo trikloruroarekin edo fosforo pentakloruroarekin erreakzionatuz**





- **Azido Kloruroen Erreakzioak**
  - ➡ **Azido karboxilikoen deribaturik erreaktiboenak dira**
  - ➡ **Beste azido karboxilikoen deribatuak prestatzeko balio dute**
  - ➡ **Urarekin erreakzionatzean azido karboxilikoak ematen dituzte**


RCOH
Carboxylic acid
SOCl2
or
PCl3
or
PCl5
RCCl
Acyl chloride
R′CO⁻Na⁺
(−Na⁺Cl⁻)
RC—O—CR′
Anhydride
R′OH, base
(−HCl)
RCOR′
Ester
NH3
(−NH4⁺Cl⁻)
RCNH2
Amide
R′NH2
(−R′NH3⁺Cl⁻)
RCNHR′
N-Substituted amide
R′R″NH
(−R′R″NH2⁺Cl⁻)
RCNR′R″
N,N-Disubstituted amide

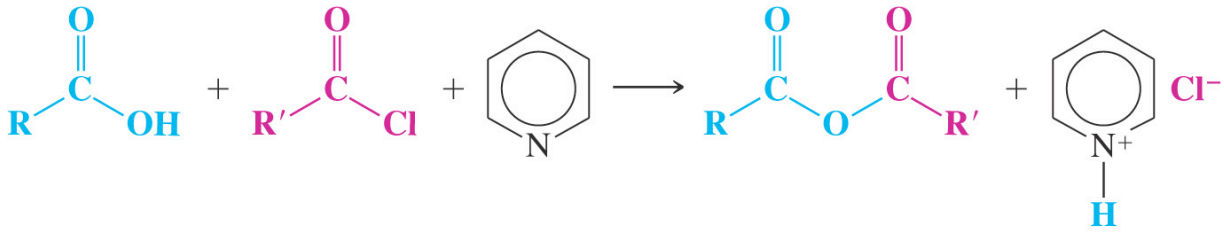

RCCl
Acyl chloride
H2O
RCOH + HCl
OH⁻/H2O
RCO⁻ + Cl⁻

♦ Azido Anhidridoak

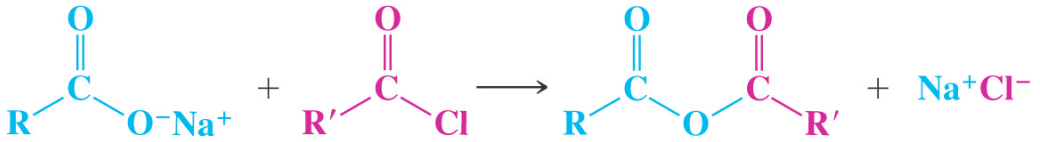
● Sintesia

➡ Azido kloruroek erreakzionatzean azido karboxilikoekin

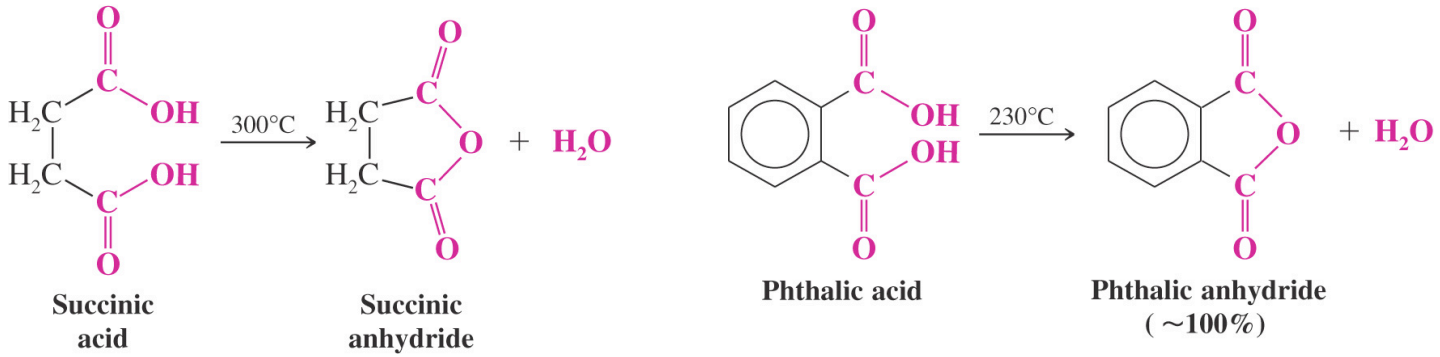
★ Piridina edo antzeko base baten beharra dago erreakzioan



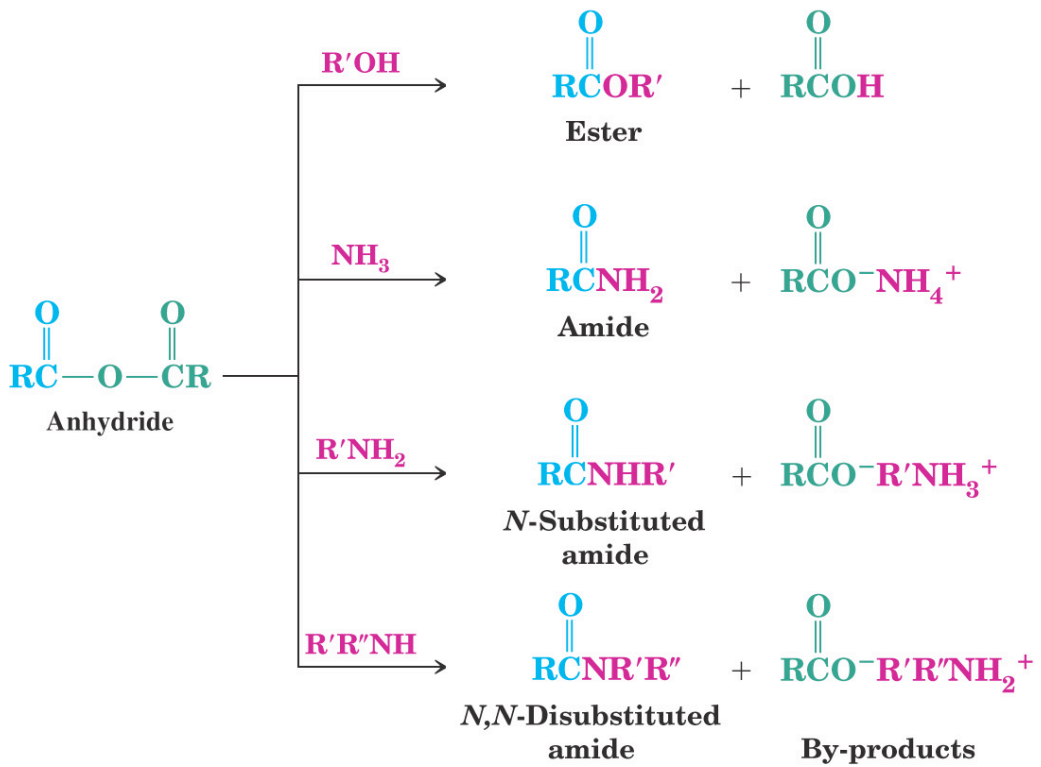
➡ Sodio karboxilatoek ere azido kloruroekin erreakzionatzean anhidridoak ematen dituzte

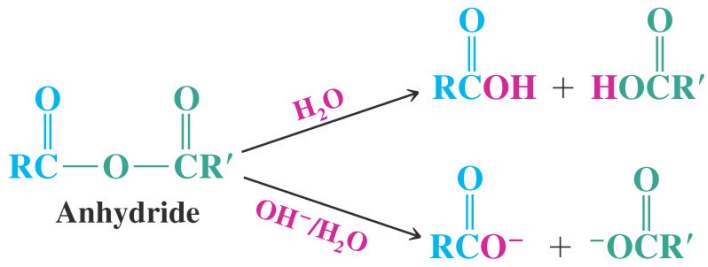


➡ **Anhidrido ziklikoak (5 edo 6 atomokoak) prestatzeko azido dikarboxilikoak berotuz egin daiteke, ura galduz**



- **Azido Anhidridoen Erreakzioak**
  - ➡ **Oso erreaktiboak dira eta esterrak zein amidak prestatzeko baliagarriak**
    - ★ **Anhidridoren hidrolisiak azido karboxilikoa ematen du**


R′OH
NH3
R′NH2
R′R″NH
RC—O—CR
Anhydride
RCOR′
Ester
RCOH
RCNH2
Amide
RCO⁻NH4⁺
RCNHR′
N-Substituted amide
RCO⁻R′NH3⁺
RCNR′R″
N,N-Disubstituted amide
RCO⁻R′R″NH2⁺
By-products


RC—O—CR′
Anhydride
H2O
OH⁻/H2O
RCOH + HOCR′
RCO⁻ + ⁻OCR′

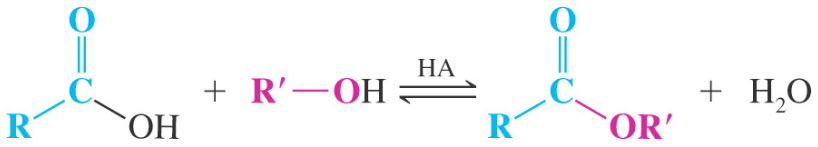
♦ Esterrak

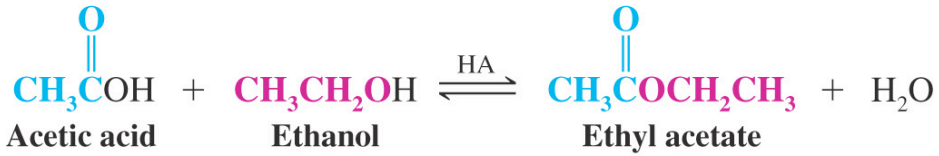
● Sintesia: Esterifikazioa

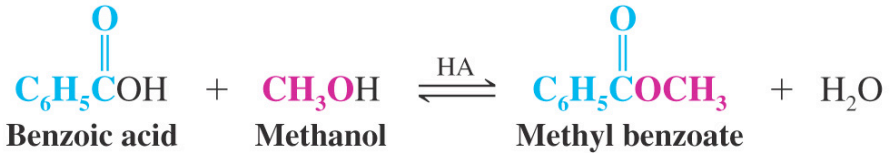
➡ Fischer-en esterifikazioa: azidoz katalizaturiko alkohol baten eta azido karboxilikoren arteko erreakzioa

➡ Fischer-en esterifikazioa itzulkorra da

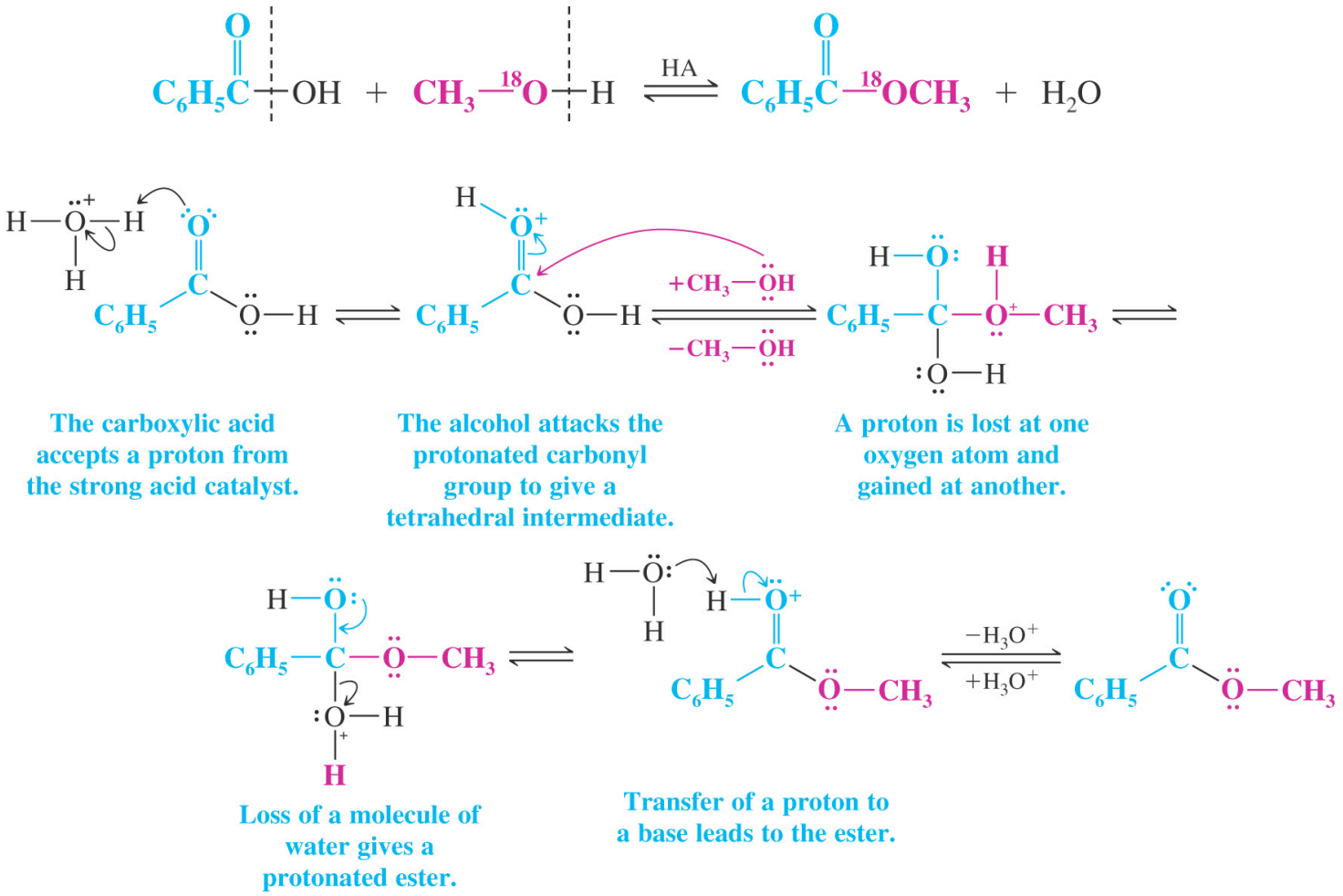
- ★ Esterreruntz lerrotzeko alkohola edo azido karboxilikoa soberan erabiltzen da
- ★ Sortzen den ura nahastetik kentzeak laguntzen du





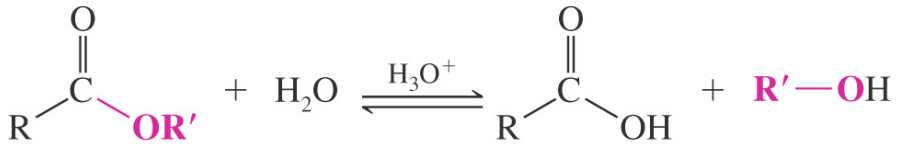


➡ Erreakziobidea: metanol markaturekin erreakzioa



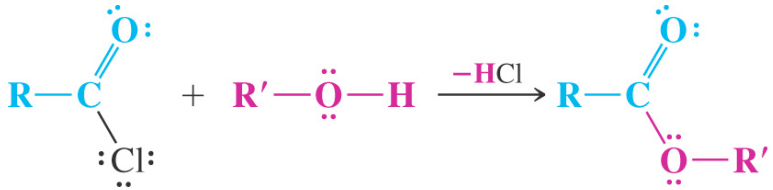
➡ Atzerabideko erreakzioa esterren hidrolisi azidoa litzateke

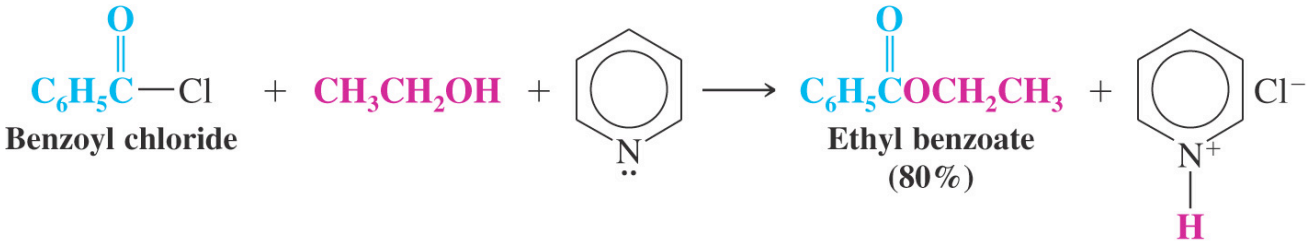
★ **Azidoen ur disoluzio diluituek errazten dutena**



➡ Esterrak Azido Kloruroetatik Abiatuz

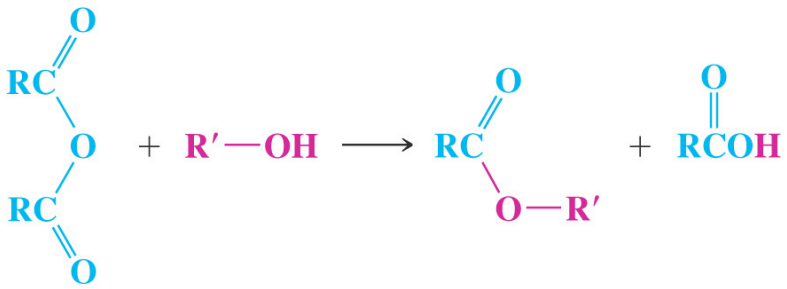
★ **Azido kloruroek alkoholekin erreakzionatzen dute base baten laguntzaz**

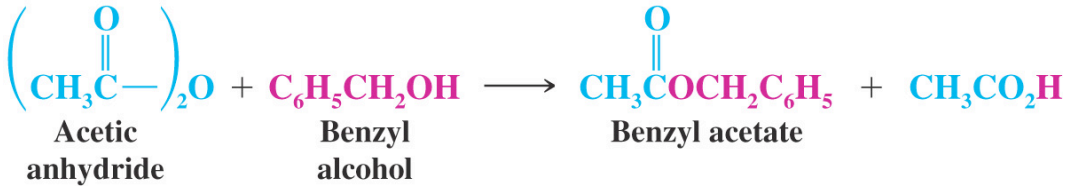


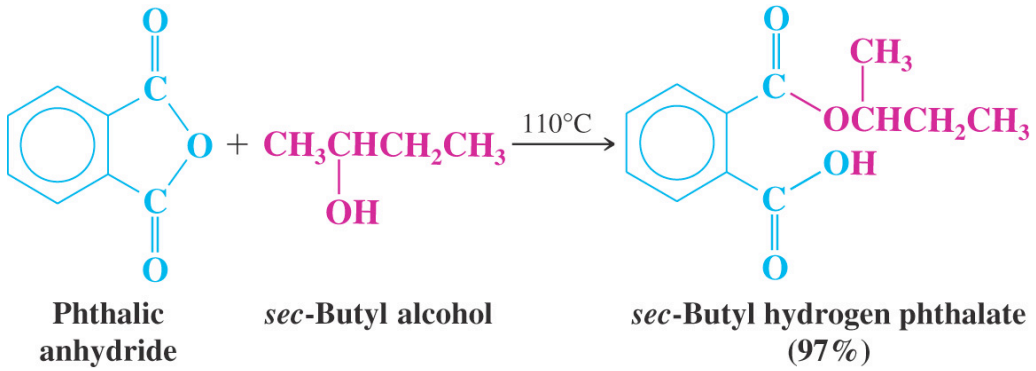


➡ Esterrak Azido Anhidridoetatik Abiatuz

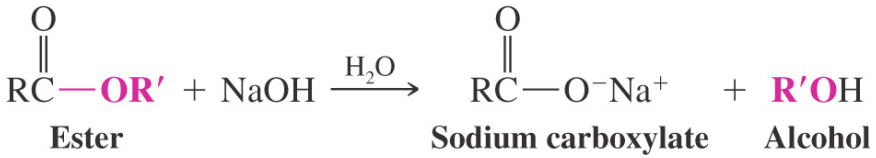
★ **Base baten laguntza ez da beharrezkoa**



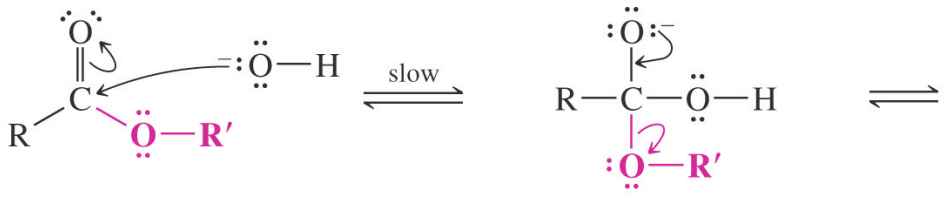


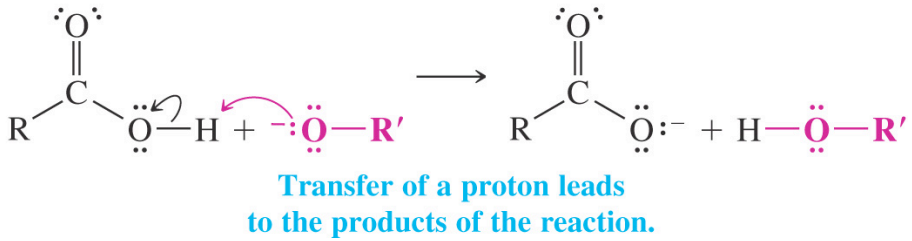


- **Basez-Lagunduriko Hidrolisia: Esterren Saponifikazioa**
  - ➡ **Sodio hidroxidoz erreakzionatzean alkohola eta sodio karboxilatoa (xaboia) lortzen dira**

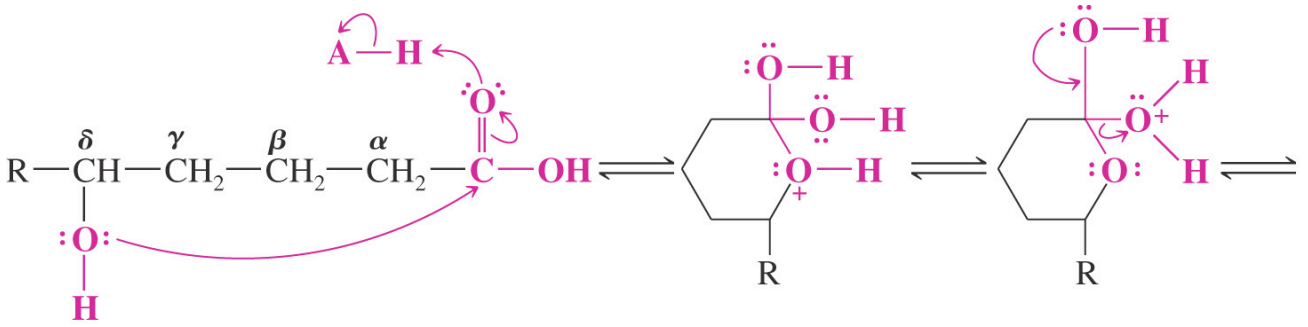


  - ➡ **Sortzen den alkoxidoaren protonazioa ez-itzulkorra da, prozesu osoa eskuineruntz lerrotuz**

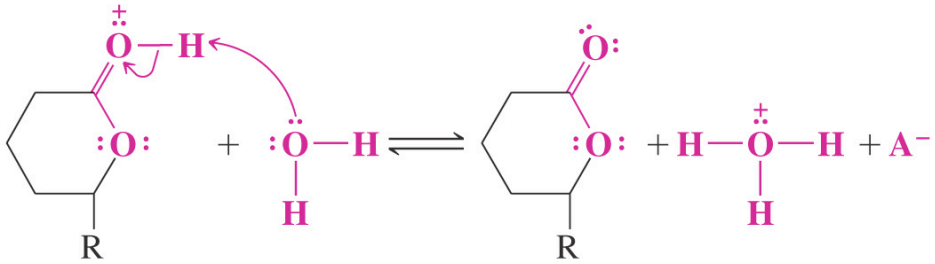




- **Laktonak**
  - ➡ **γ- edo δ-Hidroxiazidoek azidoz lagunduriko esterifikazioa ematen dute ester ziklikoa (laktona) osatuz**



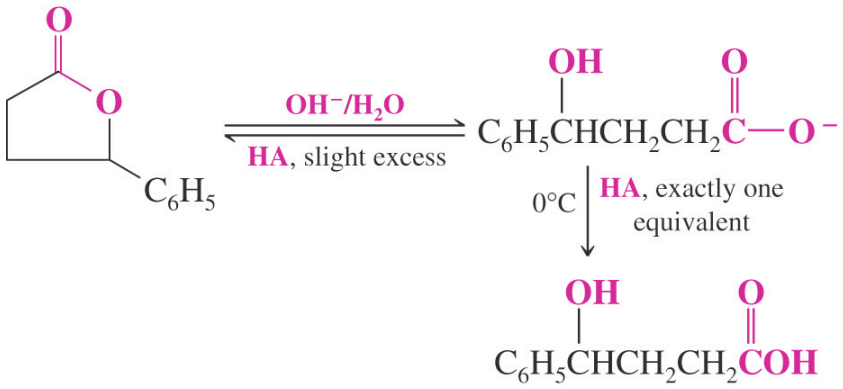
A δ-hydroxy acid



A δ-lactone

➡ Laktonak ere hidroliza daitezke ur-disoluzio basikopean

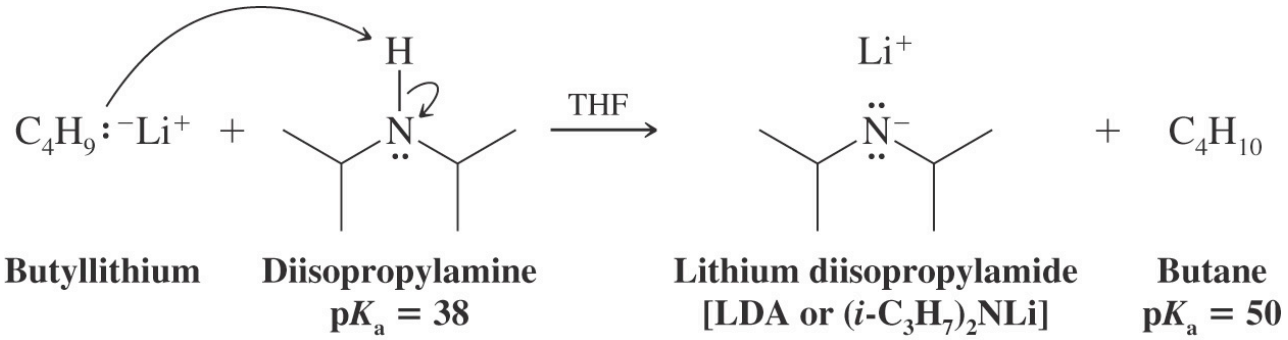
★ **Erreakzioaren produktua azidotzean, hasierako laktona berriz osa daiteke azido sendoegia erabiliz gero**

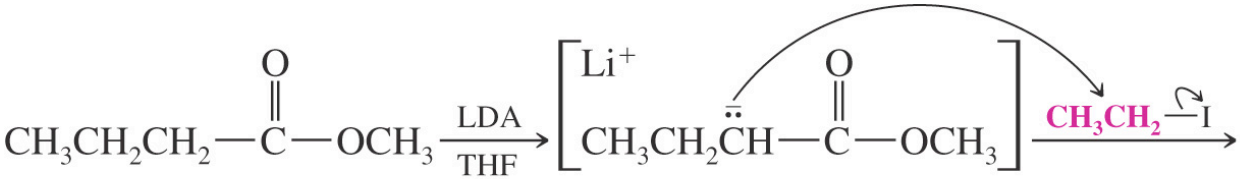


♦ Ester eta Nitriloen Alkilazioa

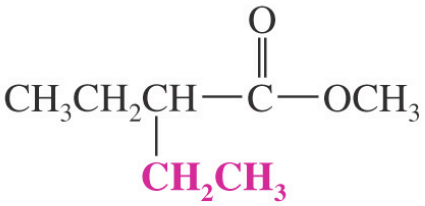
➡ **Base sendo bat erabiliz (adibidez LDA), esterrak zein nitriloak erabat enolizatu daitezke Claisen-en kondentsazioa ekiditUz**

★ **Alkilatzaile bat gehituz gero, alkilazioa emango da**

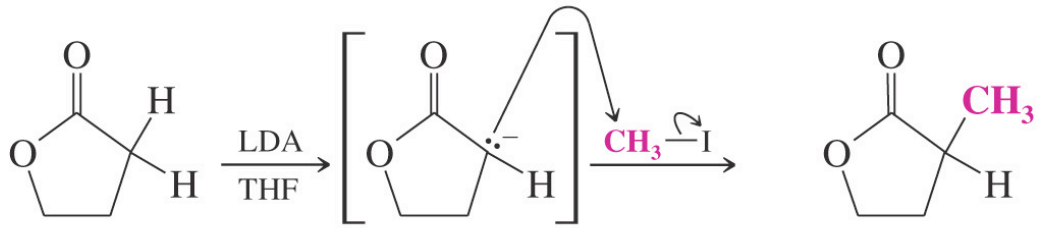




Methyl butanoate



Methyl 2-ethylbutanoate
(96%)



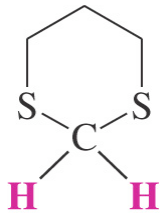
Butyrolactone

2-Methylbutyrolactone
(88%)

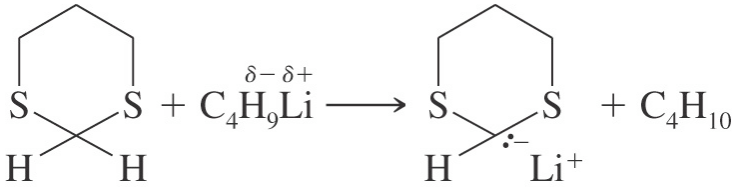
♦ 1,3-Ditianoen Alkilazioa

➡ 1,3-ditiano baten tarteko karbonoko protoiak azidoak dira

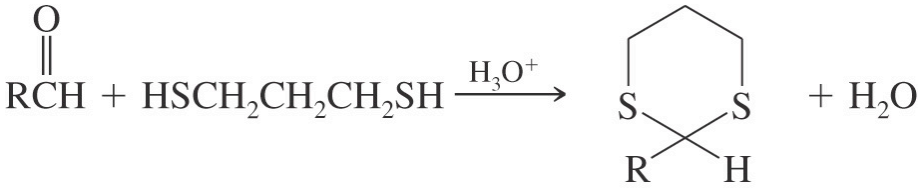
★ **Base sendoek anioia sor dezaketelarik**



1,3-Dithiane
pK_a = 32

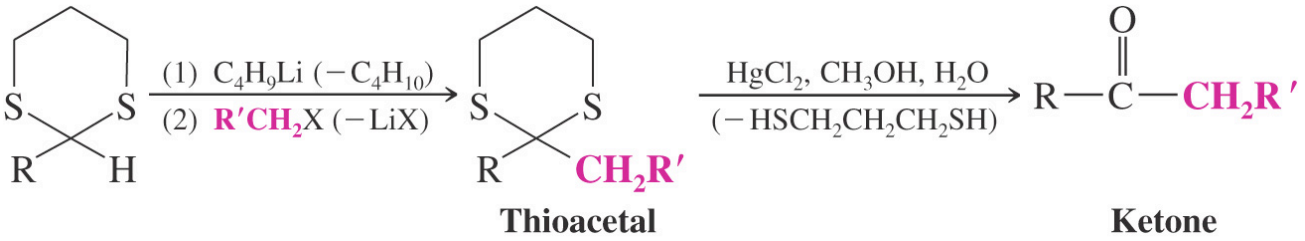


➡ Ditianoak 6-atomodun tioazetal ziklikoak dira

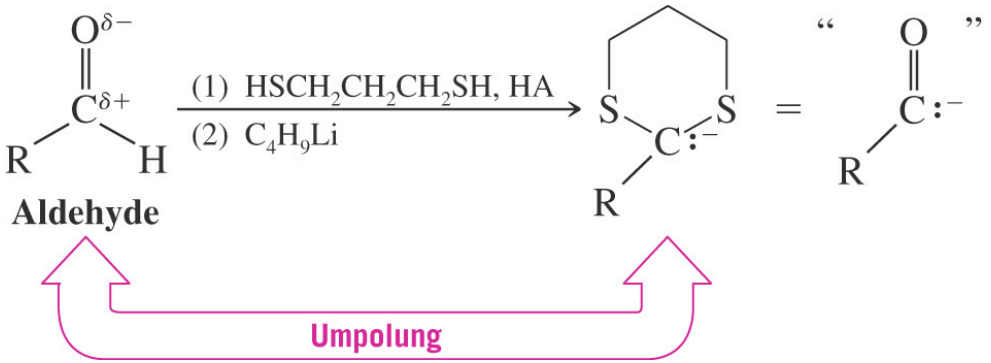


A 1,3-dithiane

➡ **Aldehido bat nola zetona batean bihurtu:**



➡ **Prozesu honetan karboniloaren karbonoa positiboki polarizatua egotetik (elektrozale) negatibora pasatzen da (nukleozale). Polaritate aldaketa honi *umpulong* deitzen zaio**

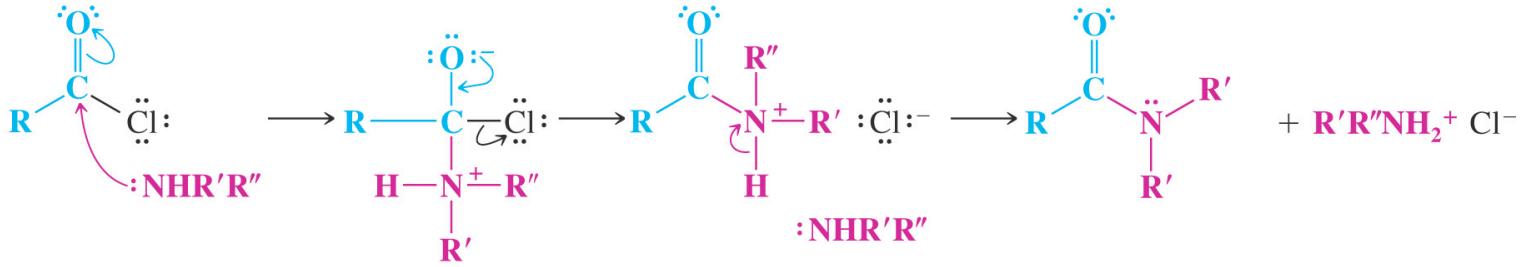


♦ Amidak

● Sintesia

➡ Azido Kloruroetatik abiatuz

- ★ **Amoniakoak, amina primario zein sekundarioek azido kloruroekin erreakzionatzean amidak sortzen dira**
- ★ **Askatzen dan HCl neutralizatu asmoz, aminaren soberakin bat gehitzen da**

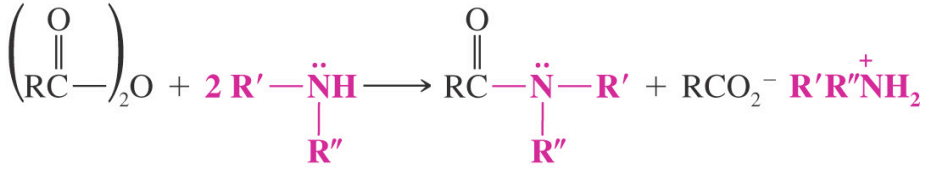


Reactant
Ammonia; R′, R″ = H
1° Amine; R′ = H, R″ = alkyl, aryl
2° Amine; R′, R″ = alkyl, aryl

Product
Unsubstituted amide; R′, R″ = H
N-Substituted amide; R′ = H, R″ = alkyl, aryl
N,*N*-Disubstituted amide; R′,R″ = alkyl, aryl

➡ Amidak Azido Anhidridoetatik Abiatuz

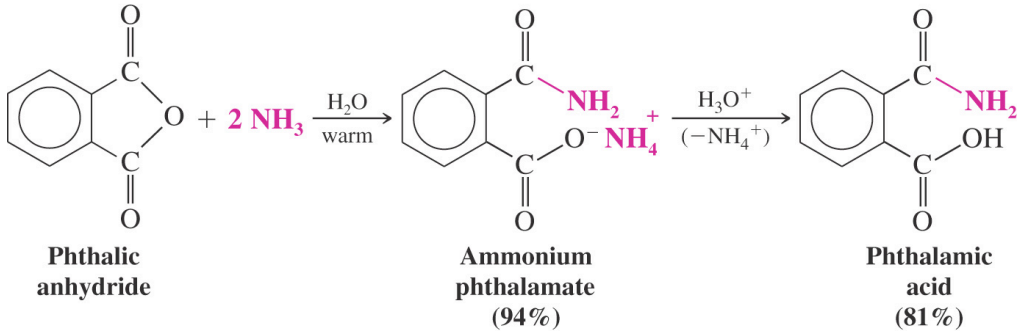
★ **Anhidridoek aminaren 2 baliokiderekin amida bat gehi amonio karboxilatoa ematen dute**



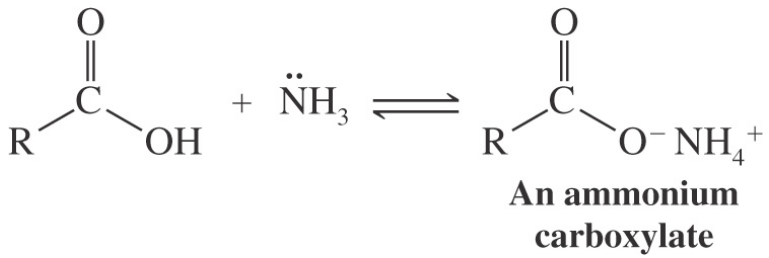
R′, R″ can be H, alkyl or aryl

★ **Anhidridoa ziklikoa bada, amida eta azido karboxilikoa batera den produktua lortzen da**

★ **Produktu hau berotzean imida ziklikoa lor daiteke**

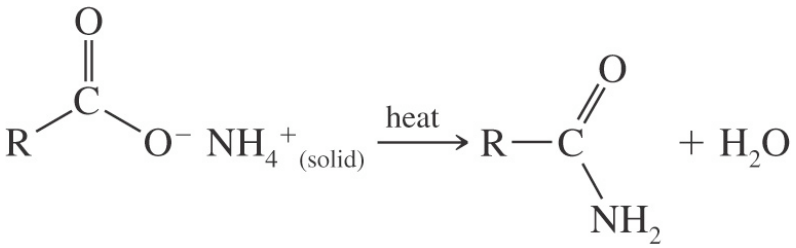


➡ Amidak, Azido Karboxiliko eta Amonio Karboxilatoetatik Abiatuz

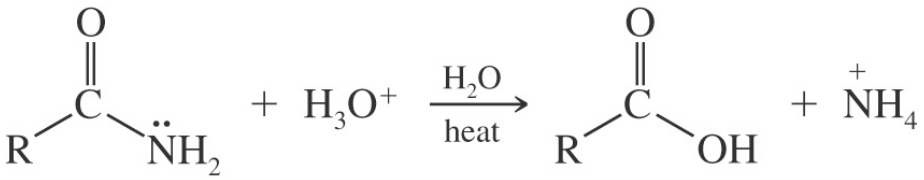


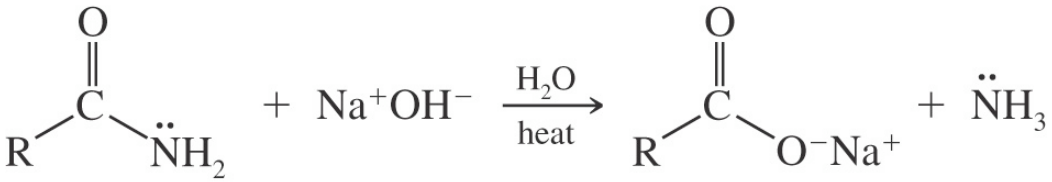
An ammonium carboxylate

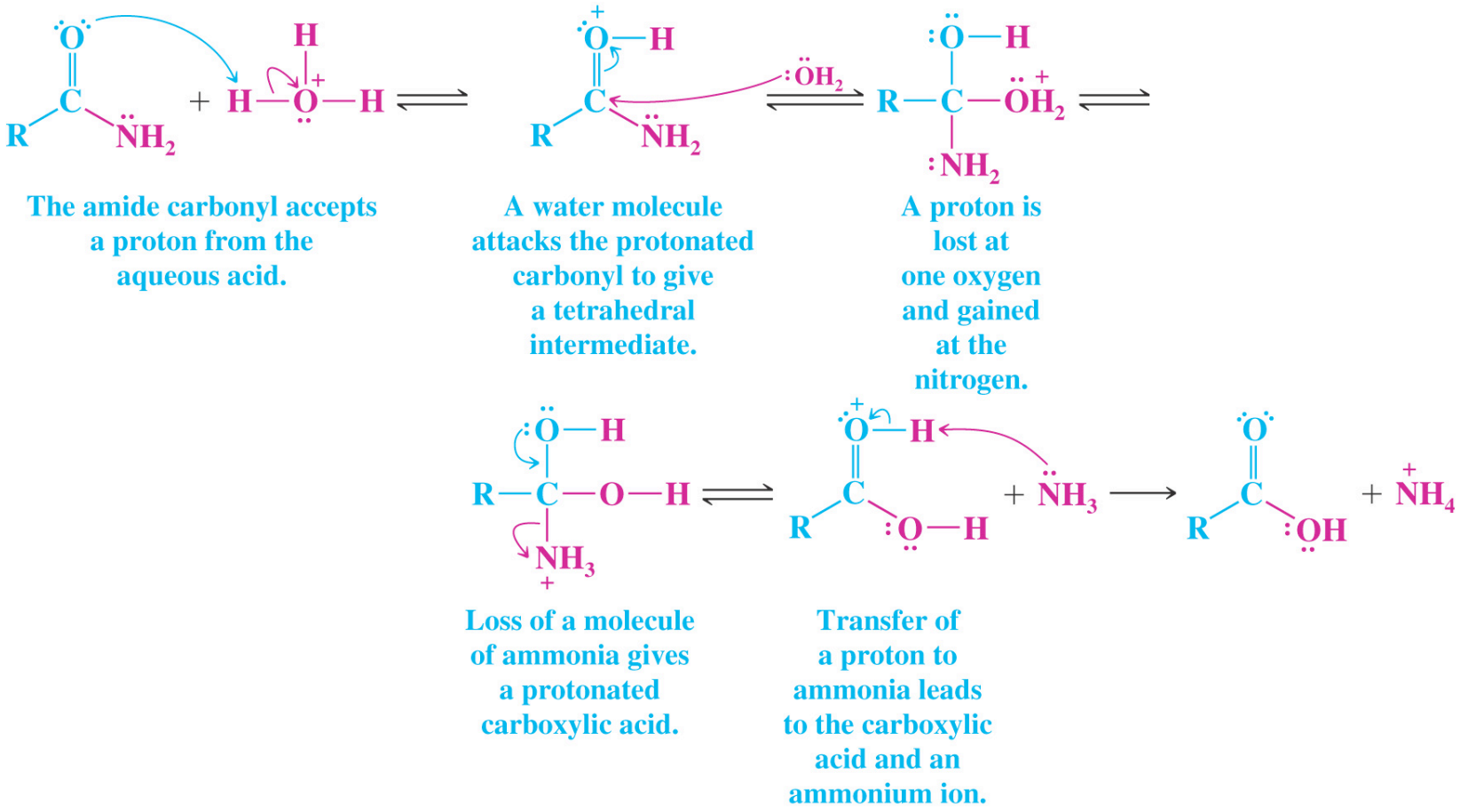
★ **Amonio gatz zenbait eta azido karboxiliko bat berotuz amida bat lor daiteke (Sarritan etekin bajuan) gehi ura**

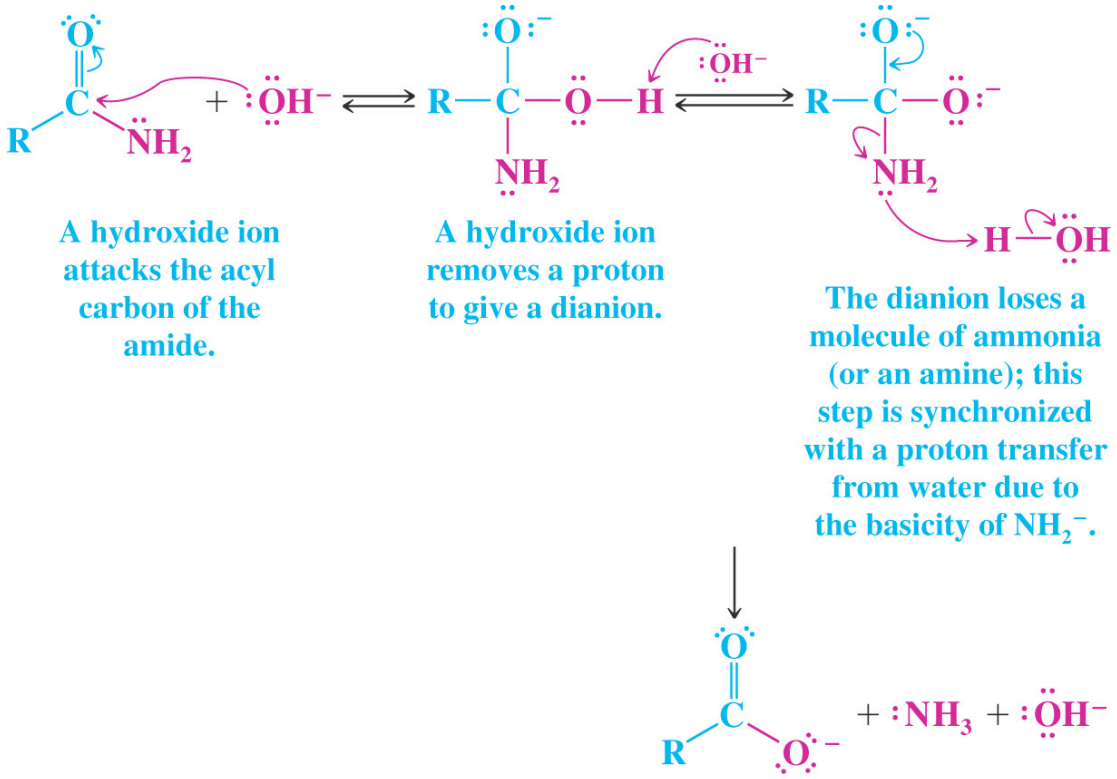


- **Amiden Hidrolisia**
  - ➡ **Amida bat berotuz gero ur-disoluzio azido edo basiko batekin hidrolisia ematen da**
    - ★ **Amidak hidrolizatzea esterrak hidrolizatzea baino zailagoa da**

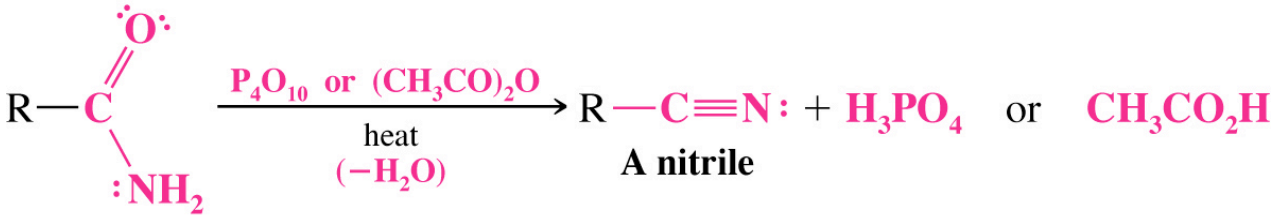




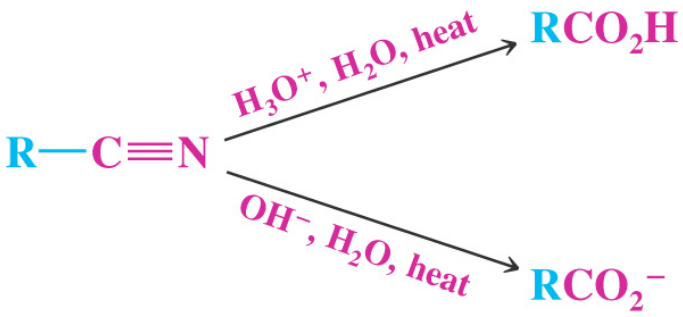

The amide carbonyl accepts a proton from the aqueous acid.
A water molecule attacks the protonated carbonyl to give a tetrahedral intermediate.
A proton is lost at one oxygen and gained at the nitrogen.
Loss of a molecule of ammonia gives a protonated carboxylic acid.
Transfer of a proton to ammonia leads to the carboxylic acid and an ammonium ion.

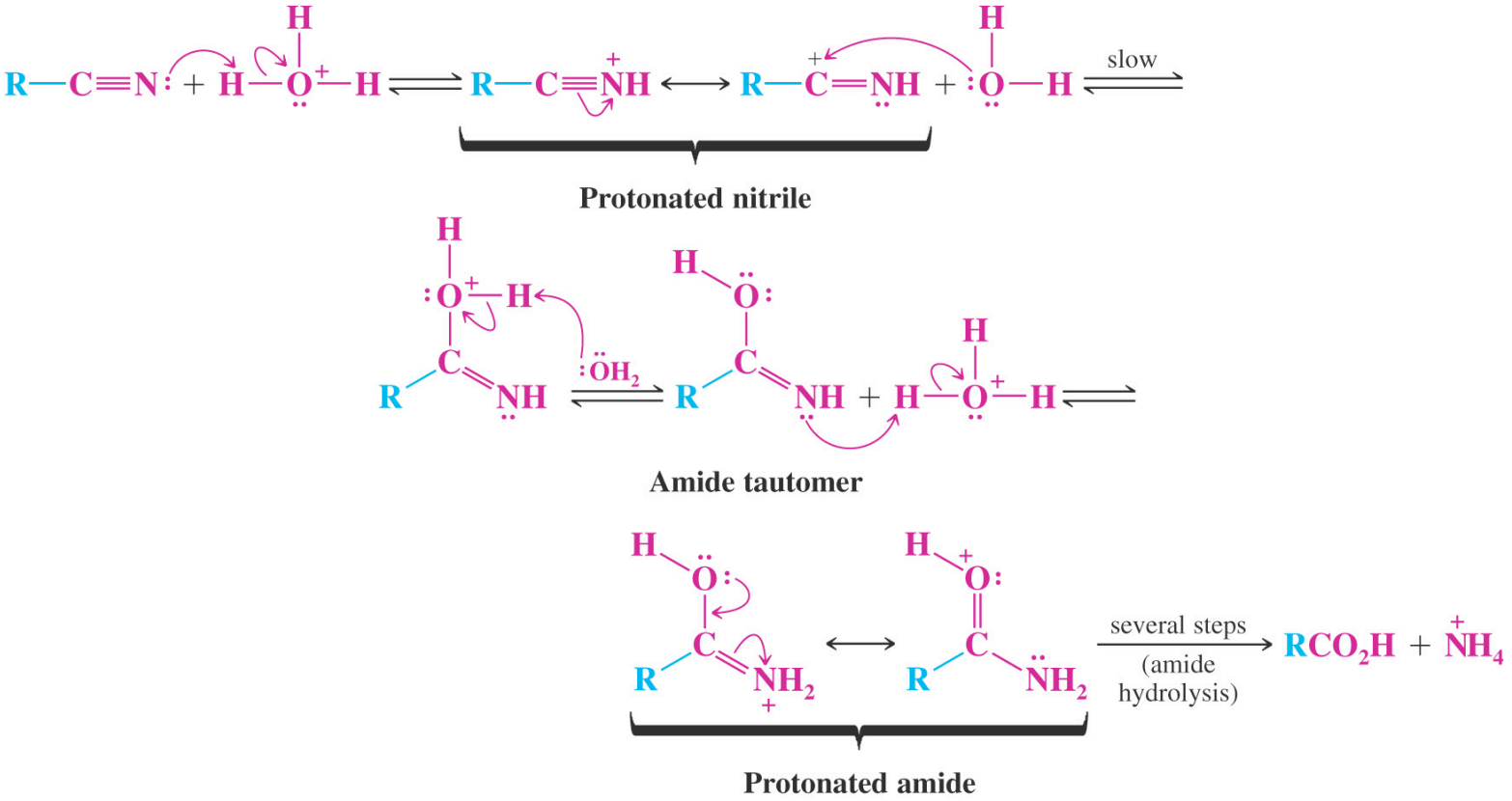

A hydroxide ion attacks the acyl carbon of the amide.
A hydroxide ion removes a proton to give a dianion.
The dianion loses a molecule of ammonia (or an amine); this step is synchronized with a proton transfer from water due to the basicity of NH_2^-.

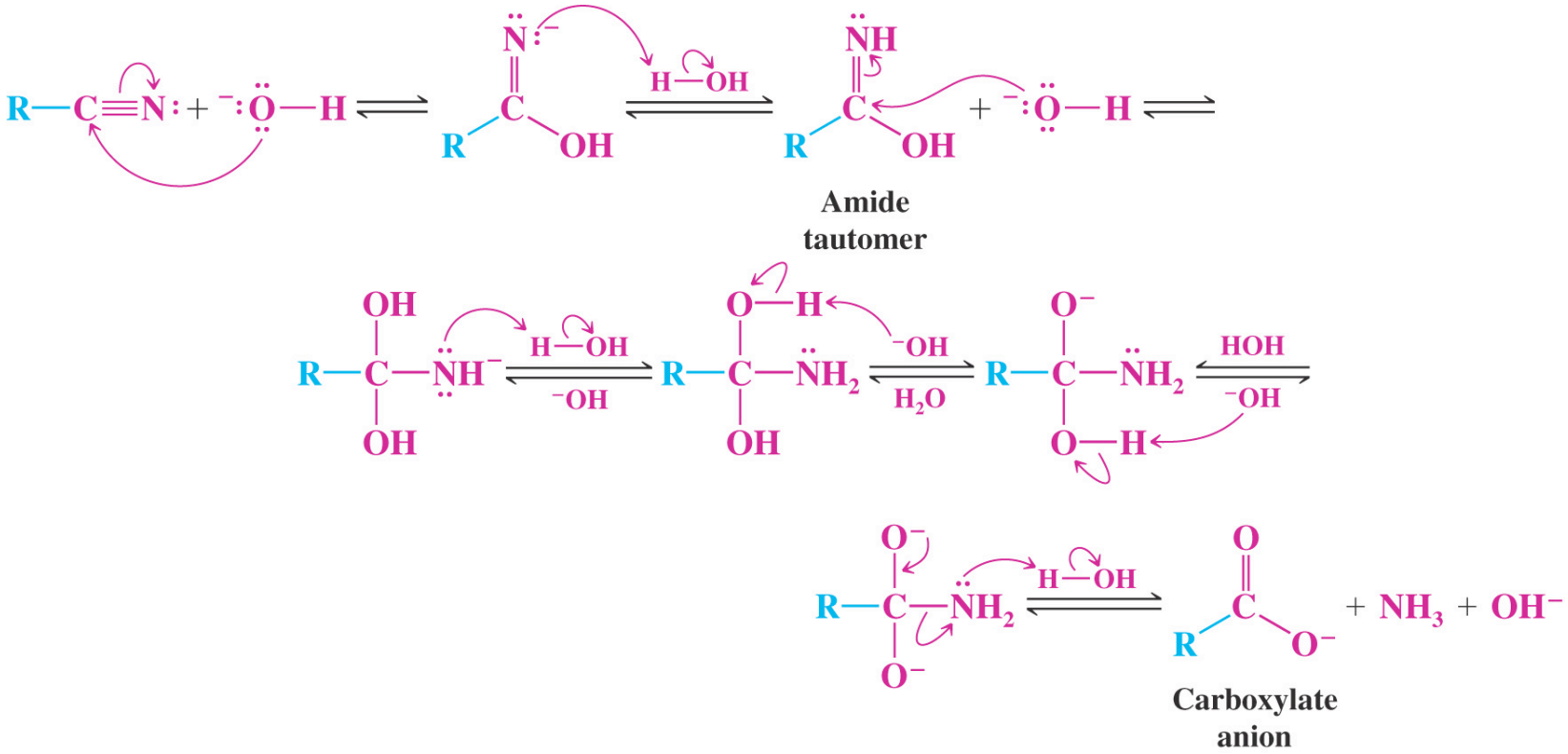
- **Nitriloak Amiden Dehidratazioz**
  - ➡ **Nitriloa sor daiteke amida primarioa fosforo pentoxidoz edo anhidrido azetiko beroan tratatzean**



- **Nitriloen Hidrolisia**




slow
Protonated nitrile
Amide tautomer
several steps
(amide
hydrolysis)
Protonated amide


Amide
tautomer
Carboxylate
anion
+ NH3 + OH−