

Acid Derivatives I

General/ Naming

Reactivity

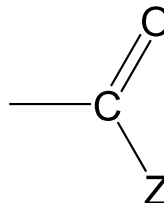
Ref 18: 2E - 2I, 4

Prob 18: 5, 20

Adv Rdg 18: 5 – 8

General

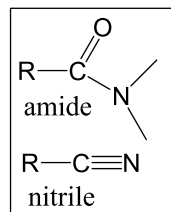
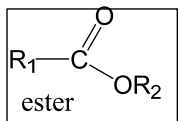
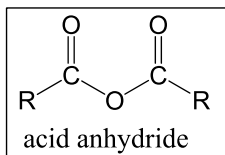
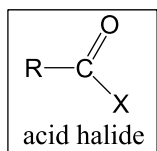
- have modified $\text{-CO}_2\text{H}$ group
- retain “acyl” group



where Z is e/n group
halides, esp., chloride
OR, esters
 NR_1R_2 , amides (R's can be H)

General ...

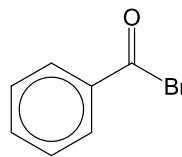
All produce RCO_2H when treated w/ H_2O ;
but different conditions are required



Naming

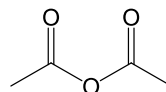
Halides

-ic acid \longrightarrow -yl halide

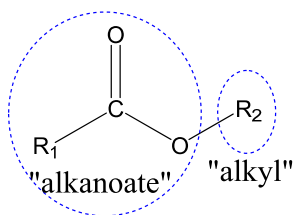


Anhydrides

-ic acid \longrightarrow -ic anhydride

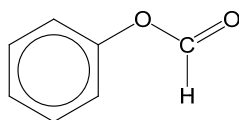
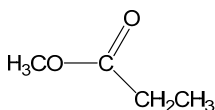
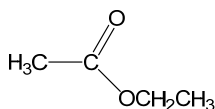


Naming ...

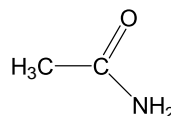
Esters

“as if it were a salt”

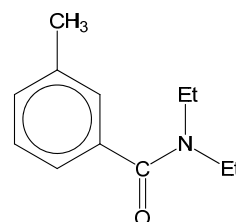
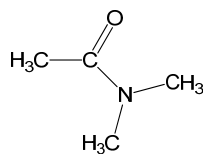
Examples



Naming ...

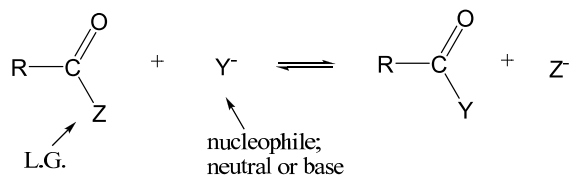
Amides-(o)ic acid \longrightarrow -amide

“substitution at N indicated by prefix N”

**Nitriles**
 -(o)ic acid \longrightarrow -onitrile
 $\text{CH}_3\text{C}\equiv\text{N}$ acetonitrile
General Reactivity

most characteristic rxn:

“nucleophilic acyl substitution”



subject to acid/base catalysis (similar to A/K rxns)

rxn is favored if

Z is better L.G. than Y, i.e.,

- Z^- is weaker base than Y^-
- HZ is stronger acid than HY

e.g., Cl^- is good L.G. (weak base; HCl strong acid),
and, therefore, acyl chlorides react easily

Mechanism

Superficially

looks like direct substitution

Actually

2 steps involved:

- nucleophilic attack/ addⁿ
- expulsion/ elimination

Generally, reversible equilib. rxn;

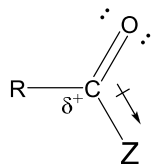
reverse (green) direction favored, if Z^- strong nucleophile

Ranking of Reactivity

General Principle:

1st step is nucleophilic addⁿ,
slow, rate limiting step

∴ if δ^+ on carbonyl C \uparrow
nucleophile will be attracted more
= reactivity \uparrow



if Z = (strong) EWG,
C becomes more pos. and reactivity \uparrow ;

and v.v.:

if Z has e⁻ donating feature (is EDG),
carbonyl C becomes less pos. & reactivity \downarrow

3.) Esters

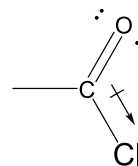
tetrahedral O withdraws by induction
donates by conjugation

∴ **less reactive than halides**

(less reactive than anhydrides, see next page)

Ranking Specifics

1.) Acyl Halides (esp., chlorides)



- Cl withdraws e⁻ density by induction
- little e⁻ donation by conjugation

∴ **highly reactive !**

3.) Anhydrides

A) e⁻ withdrawal by induction
same as in ester

B.) e⁻ donation effect reduced b/c 2 carbonyl C's;
“split in ½”

∴ δ^+ on C=O is larger than in esters

∴ **anhydrides more reactive than esters**

4.) Amides

in comparison with esters

less e^- withdrawal by induction
since N is less e/n than O

e^- donation by conjugation similar

\therefore reduced reactivity,

least reactive of all acid derivatives we studied

Summary

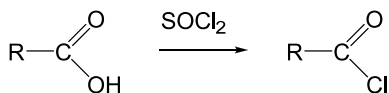
halides
anhydrides
esters
amides, nitriles

reactivity \uparrow

Illustration: Rxn w/ H_2O

halides	react at r.t., no cat. needed
anhydrides:	react at r.t., if cat. present
esters:	need cat. & $T \uparrow$
amides, nitriles	need cat., $T \uparrow$, $t \uparrow$

General Prep. Methods



“make acyl chloride,
then all other acid deriv^s can be made from there.”

