Course Chem 345 Lecturer Gellman

Day Wednesday Date 4/8/2015

Notes Taken By Leslie Total # of Pages 4

Submit a *Single-sided Copy* to the Undergraduate Office

NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

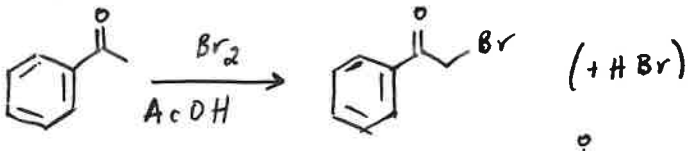
Recall: Rxns involving acidity of H's α to a C=O.

1) H/D exchange

2) stereocenter isomerization.

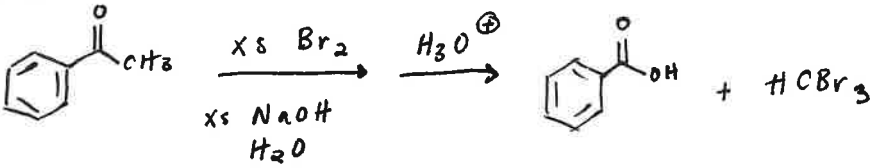
3) α-halogenation

Ex:

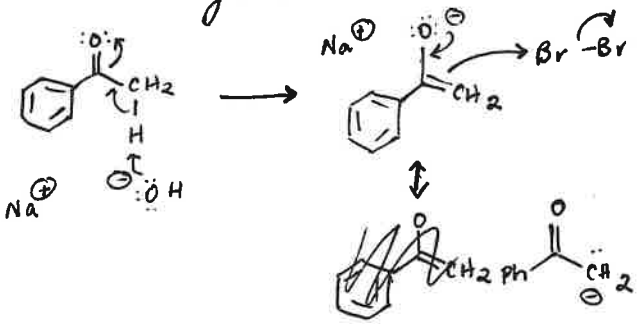


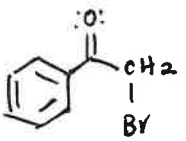
[Note: acidic conditions, AcOH = ]

Different outcome under alkaline conditions:



Mech: Begin w/ enolate formation.





[Note: more acidic than starting ketone]

+ NaBr

continued on next page

Course Chem 345 Lecturer Gellman

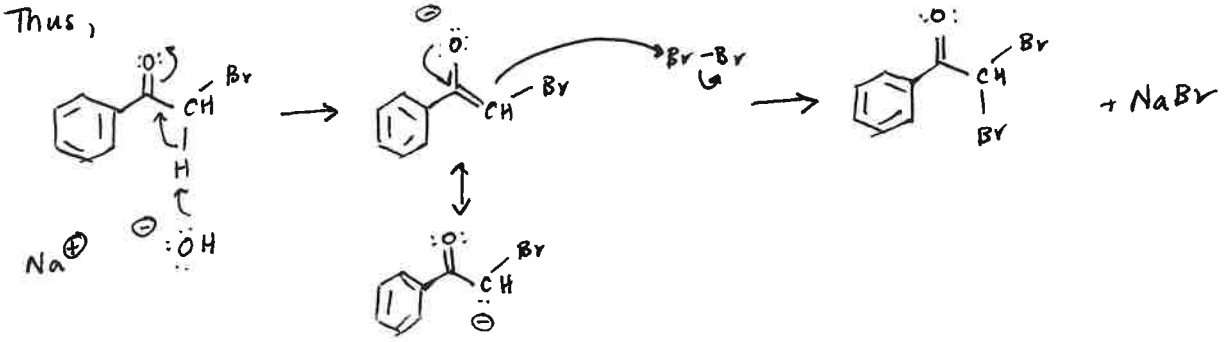
Day Wednesday Date 4/8/2015

Notes Taken By Leslie Total # of Pages 4

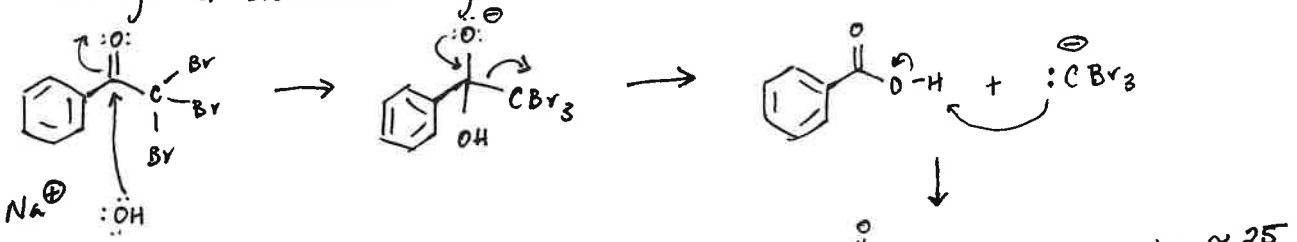
Submit a *Single-sided Copy* to the Undergraduate Office

NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

Thus,

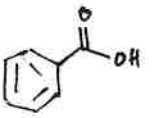


Third cycle of bromination – you fill in mechanism

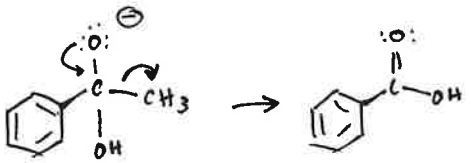


etc. ↔ + $HCBr_3$ pka ~ 25

↓ Acid



Note:



"Haloform rxn"

$\ominus : CH_3$

$H-CH_3$ pka ≥ 50

Course Chem 345 Lecturer Bellman

Day Wednesday Date 4/8/2015

Notes Taken By Leslie Total # of Pages 4

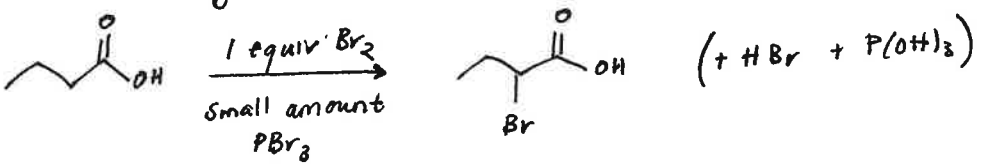
Submit a *Single-sided Copy* to the Undergraduate Office

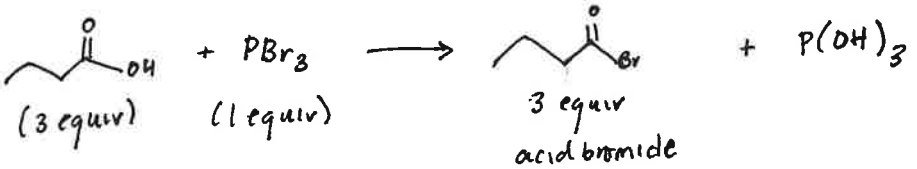
NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

Rxns involving acidity of H's α to a C=O continued...

④ α-halogenation (bromination) of carboxylic acids

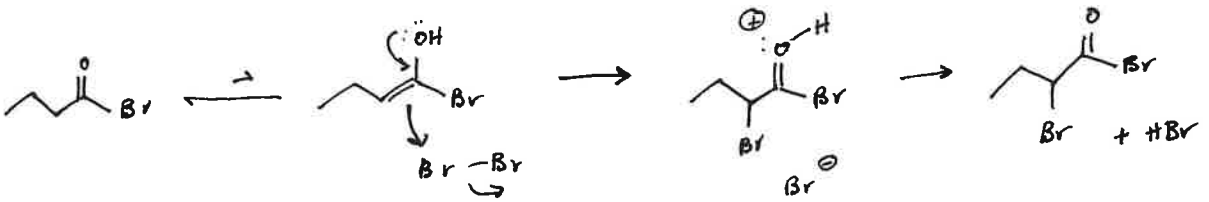
→ Bromine only

Ex: 

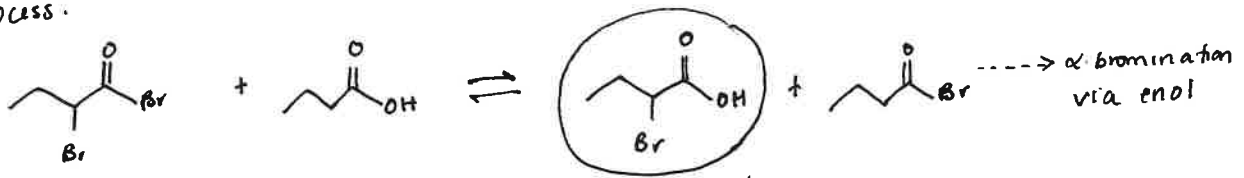


Enol forms of carboxylic acids no not occur.

HOWEVER, enol can form for acid bromide

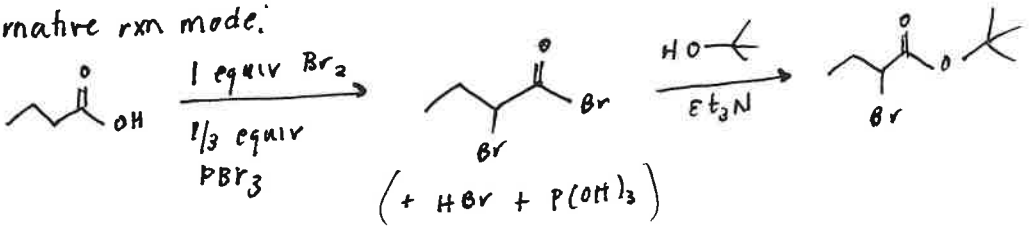


Key Process:



Fill in mechanism! final product

Alternative rxn mode:



Course Chem 345 Lecturer Gellman

Day Wednesday Date 4/8/2015

Notes Taken By Leslie Total # of Pages 4

Submit a *Single-sided Copy* to the Undergraduate Office

NO NOT STAPLE - ONLY WRITE NOTES INSIDE THE SQUARE BELOW

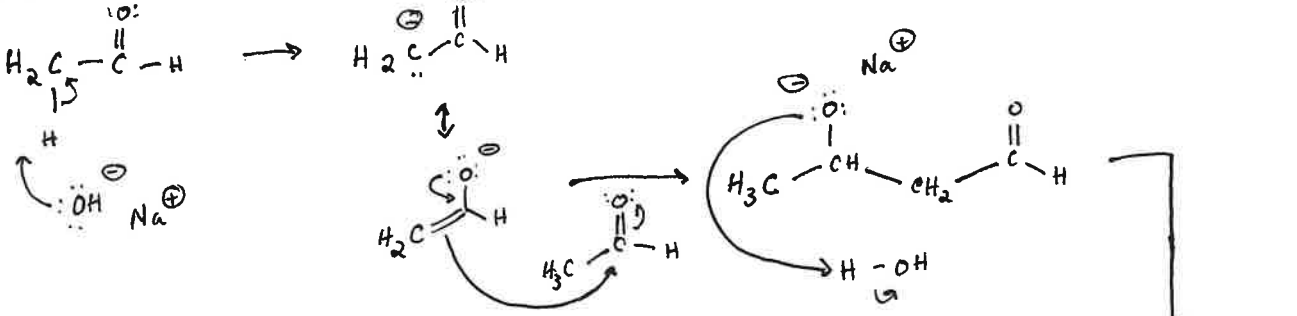
Aldol Rxn

"Aldol"

Ex: (2) $\xrightarrow[H_2O]{NaOH}$ $H_3C-CH(OH)-CH_2-C(=O)-H$

new C–C bond

Mechanism:



Sometimes, an additional rxn occurs – "dehydration"

2 (2) $\xrightarrow[H_2O]{NaOH}$ $\xrightarrow{\Delta}$ [not isolated] $\xrightarrow{\text{further rxn}}$ α,β-unsaturated aldehyde + H_2O

"α-β-unsaturated aldehyde"

Mechanism: