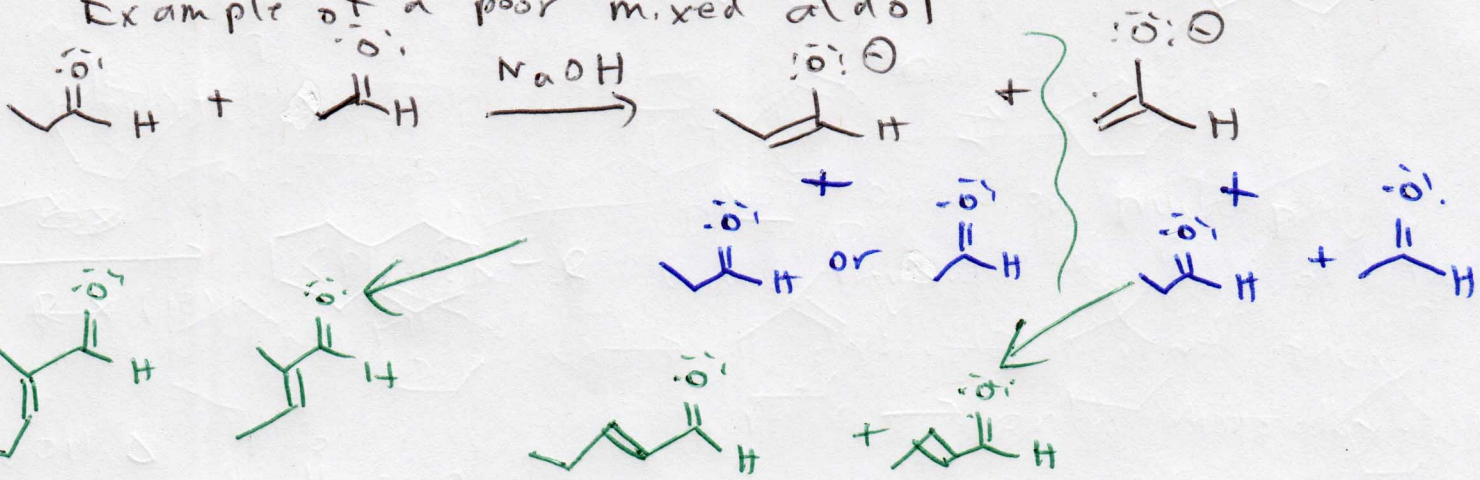
5/9/12

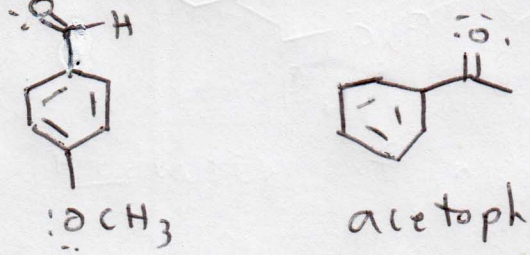
1) Aldol condensation

Mixed aldol

Example of a poor mixed aldol



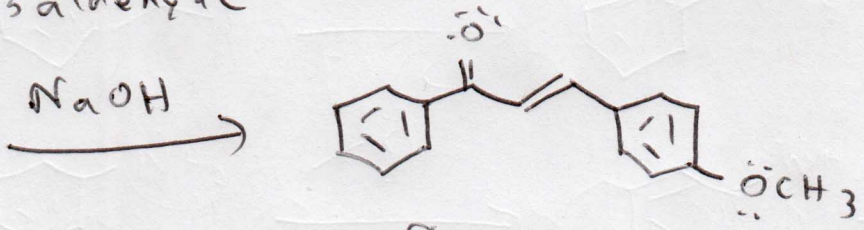
Example of an ideal crossed-aldol condensation



p-anisaldehyde

acetophenone

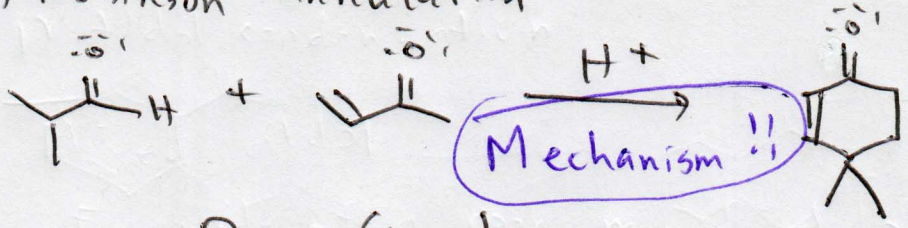
- Only one reagent is able to form an enolate
- Aldehyde much more reactive than ketone



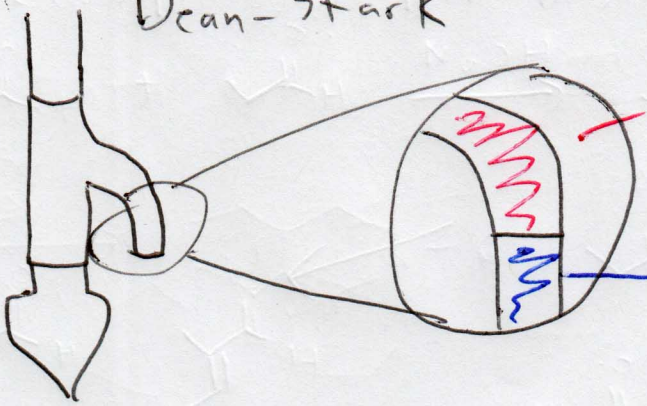
Spectroscopic confirmation

- The product contains a conjugate C=O that would have a noticeably different foequency than either starting material,
- The product contains an conjugate alkene not present in either regotant,

2) Robinson annulation

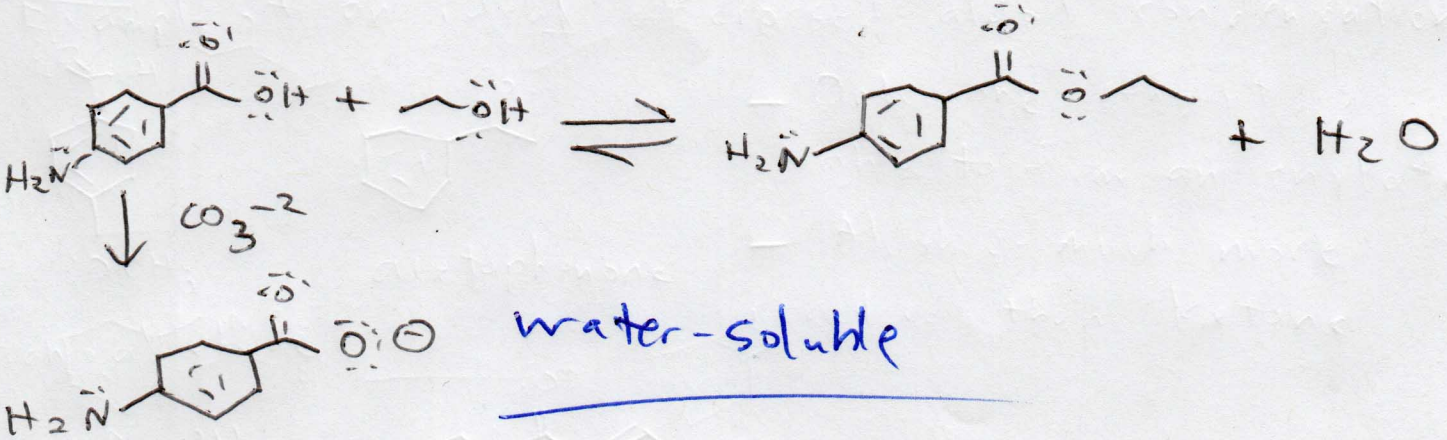


Dean-Stark



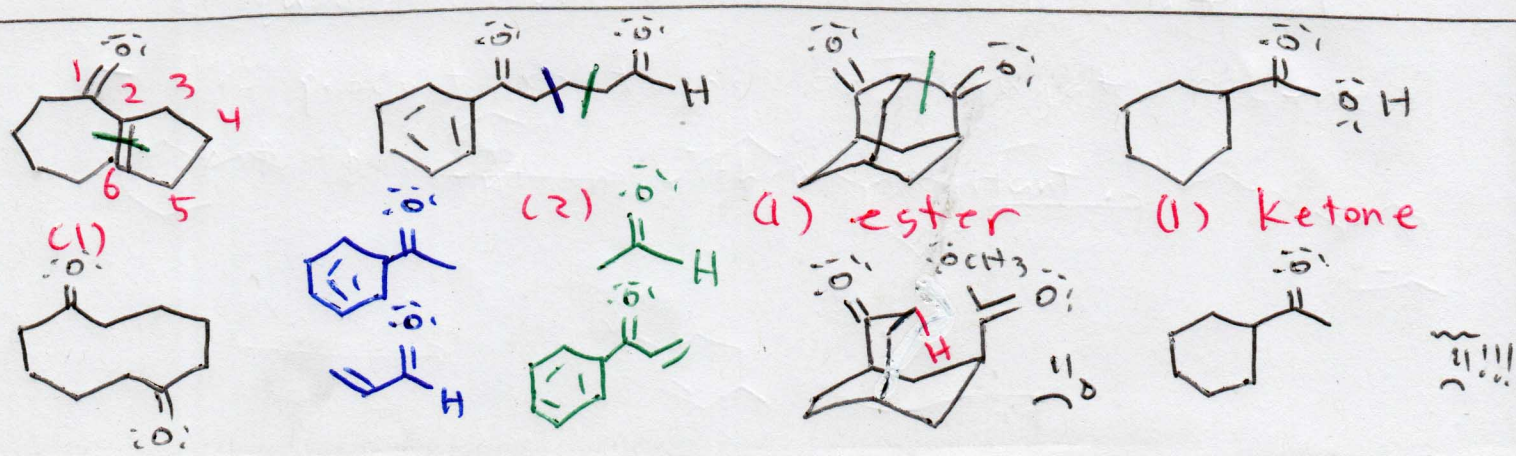
azeotrope – a gasseous mixture that phase separates upon condensation

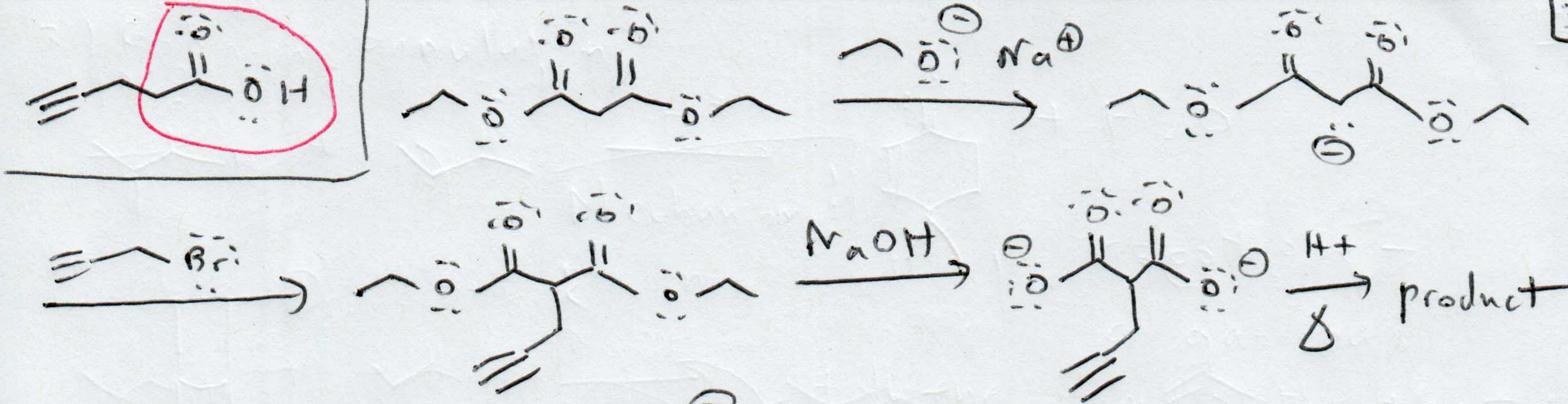
3) Benzocaine

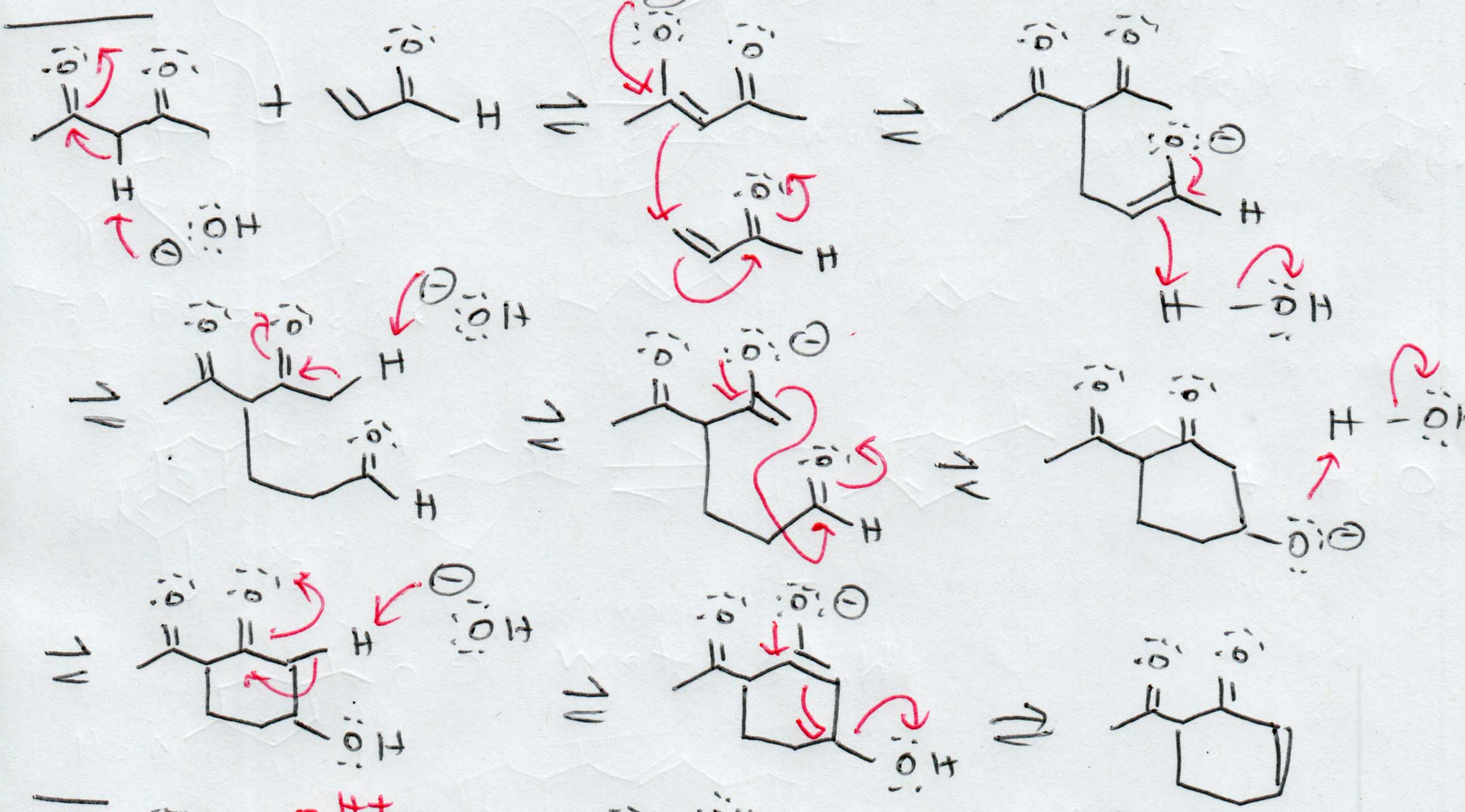


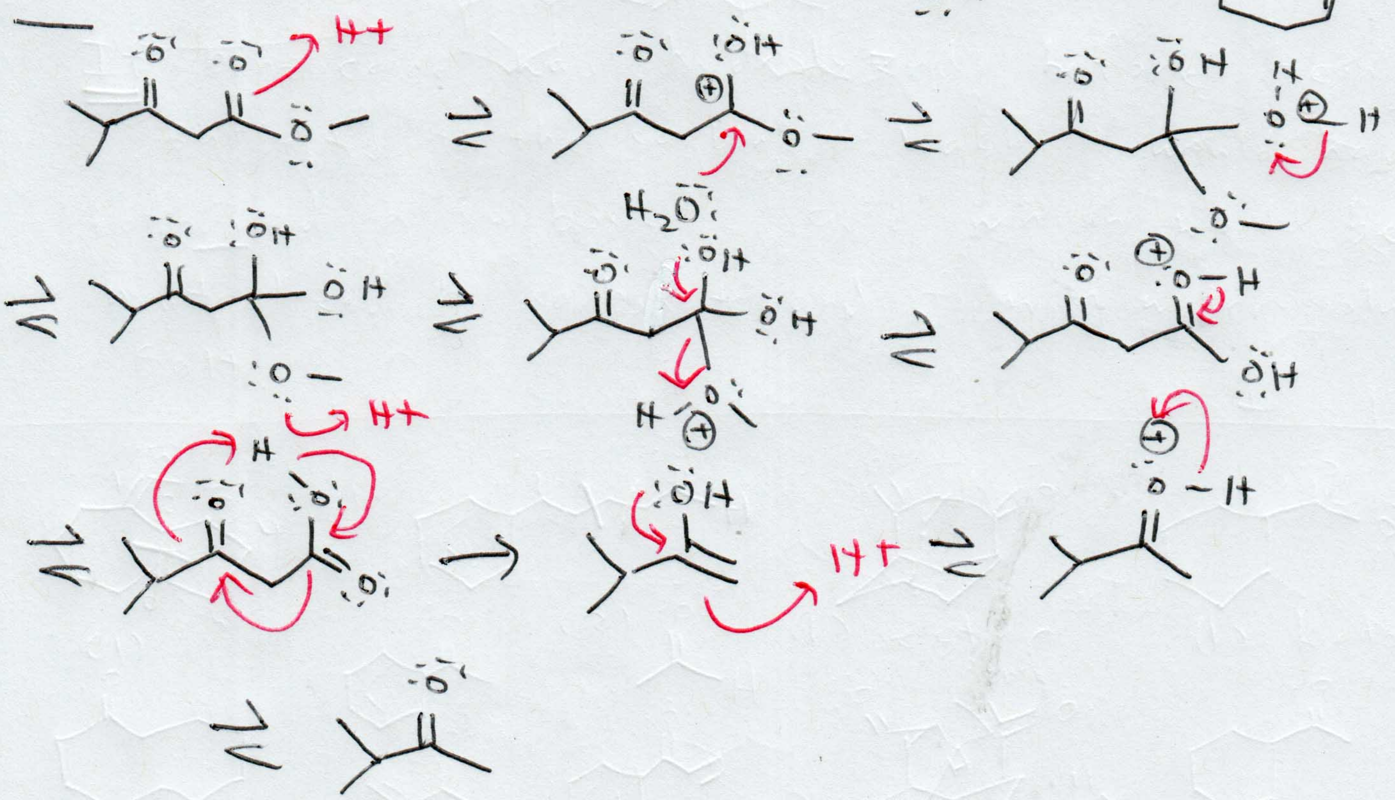
water-soluble

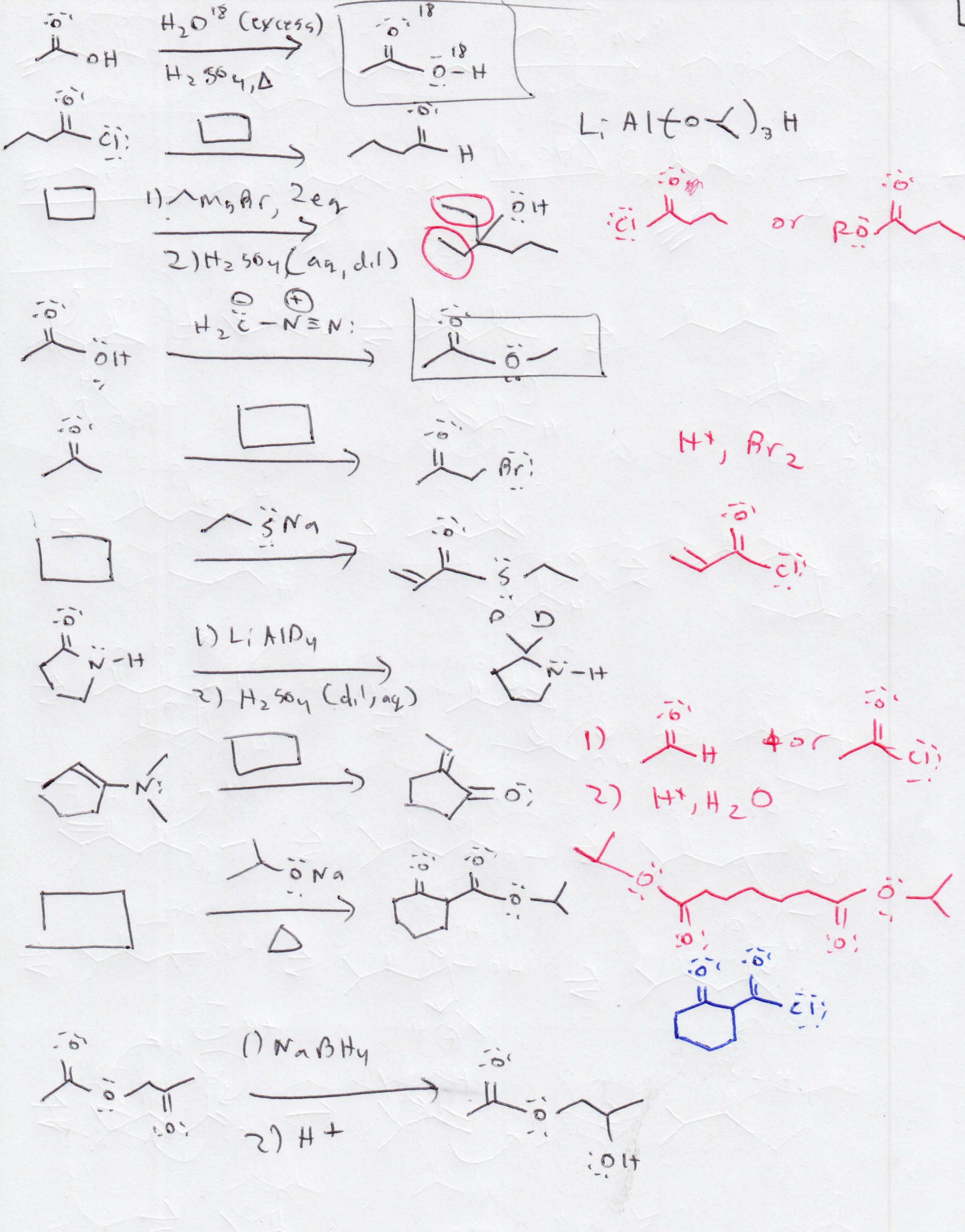
If benzocaine was hydrolyzed before being subjected to the carbonate wash, it would have reformed a carboxylic acid, which would be neutralized by carbonate and form a water-soluble salt.

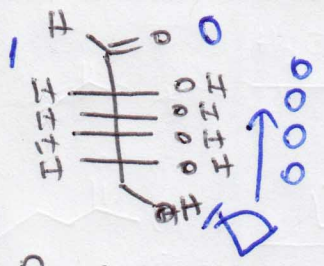



NaOH
H+
product



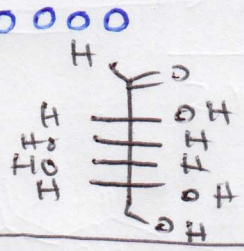

H+

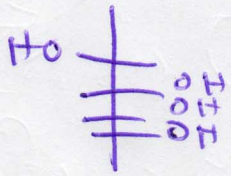

H_2O^{18} (excess)
H_2SO_4, Δ
$LiAl(O-tBu)_3H$
1) MgBr, 2eq
2) H_2SO_4 (aq, dil)
or
$H_2\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N$
H^+, Br_2
SNa
1) $LiAlD_4$
2) H_2SO_4 (dil, aq)
1)
or
2) H^+, H_2O
ONa
Δ
1) $NaBH_4$
2) H^+



D- sugar

0	1	2	3	4	5	6	7
0000	0001	0010	0011	0100	0101	0110	0111
1st	2nd	3rd	4th	5th	6th	7th	8th
RRRR	RRRL						





- # of carbons (hexose)
- functional group (aldose)
- enantiomer (D)
- anomer (α, β)
- ring size (5 vs 6)

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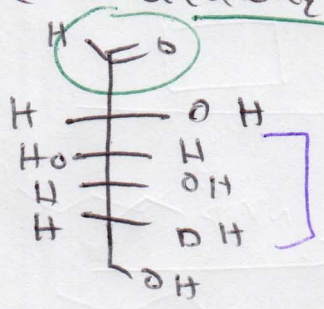
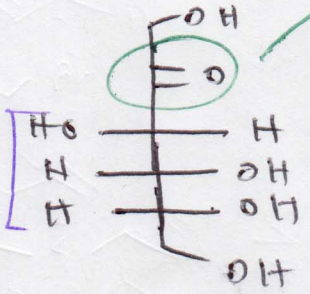
aldose – aldehyde



D- glucose

ketose – ketone



D- fructose

hexose – 6 carbons

pentose – 5 carbons

aldose + hexose → aldohexose

tetraose – 4 carbons

triose – 3 carbons

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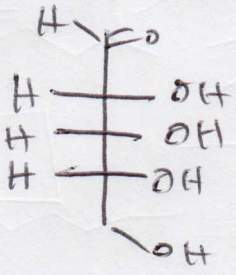
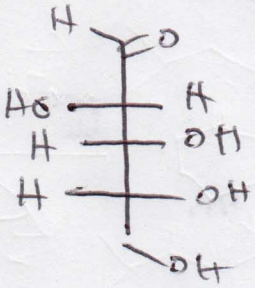
aldopentoses



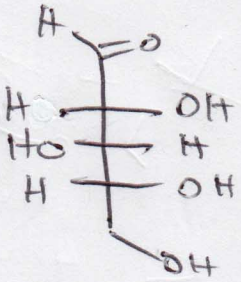
0000

D-ribose



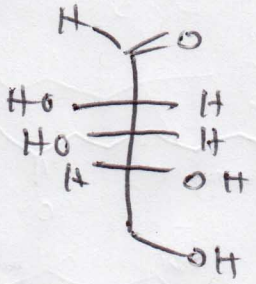
0001

D-arabinose



0010

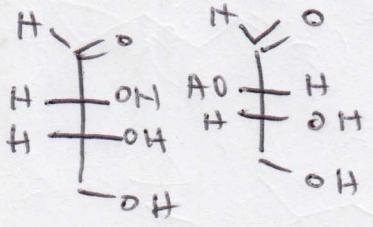
D-xylose



0011

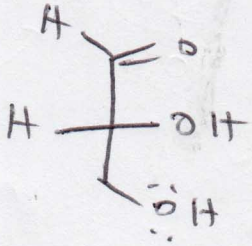
D-lyxose

aldotetrose



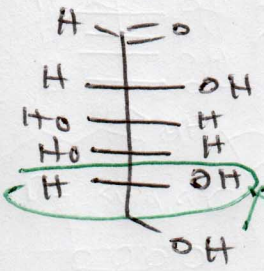
D-erythrose D-threose

aldotriose



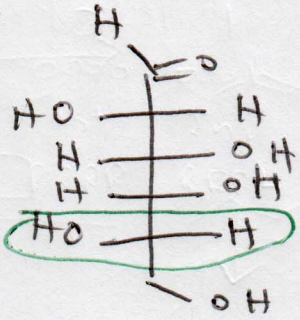
D-glyceraldehyde

D/L



D-galactose

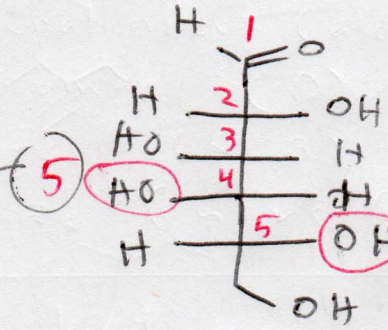
right



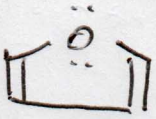
L-galactose

D/L determined by last stereocenter

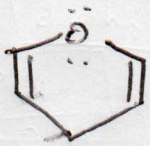
left



pyranose

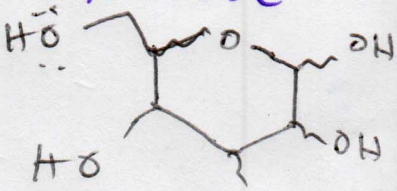


furan

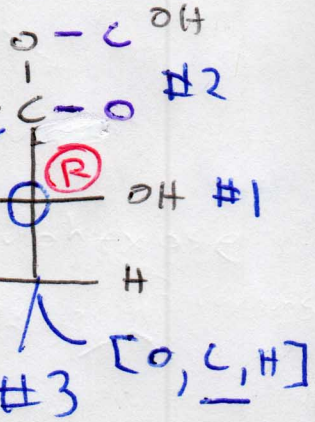


pyran

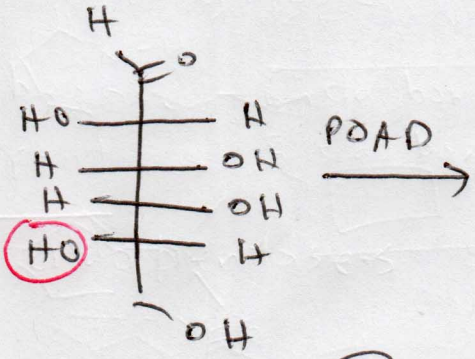
furanose



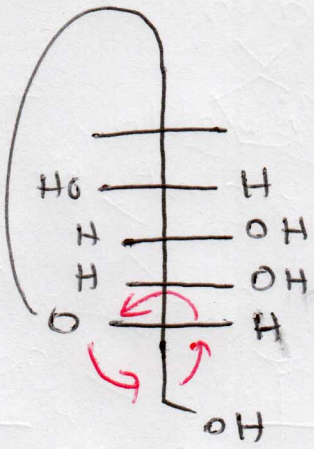
[O,O,H]

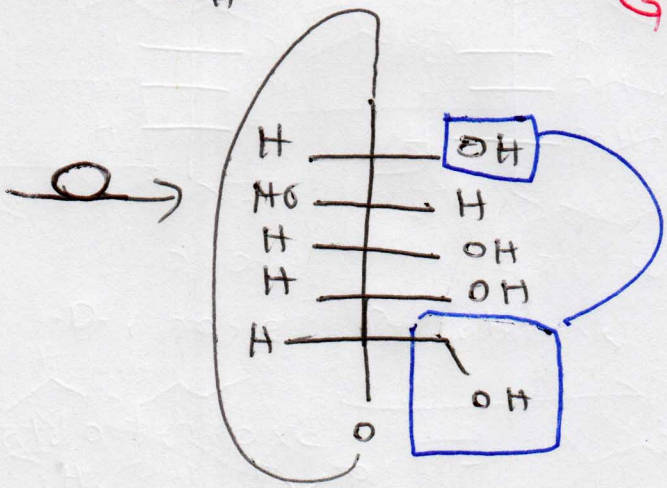


β-L-galactopyranose



POAD





β=

cis

Haworth