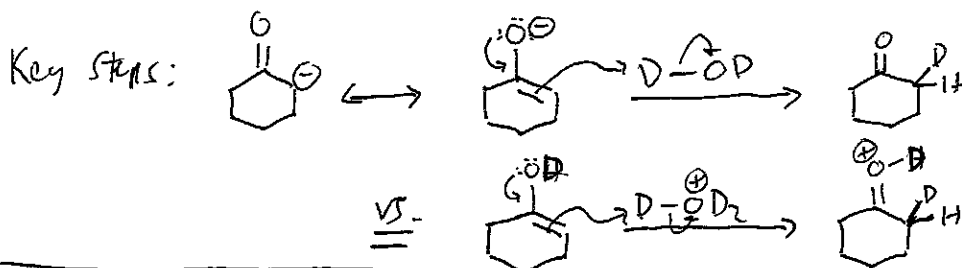


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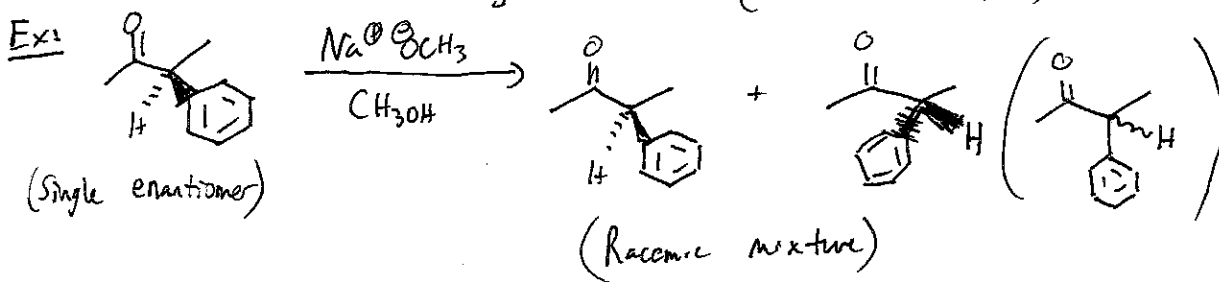
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Recall: office hour today after lecture (instead of wednesday)

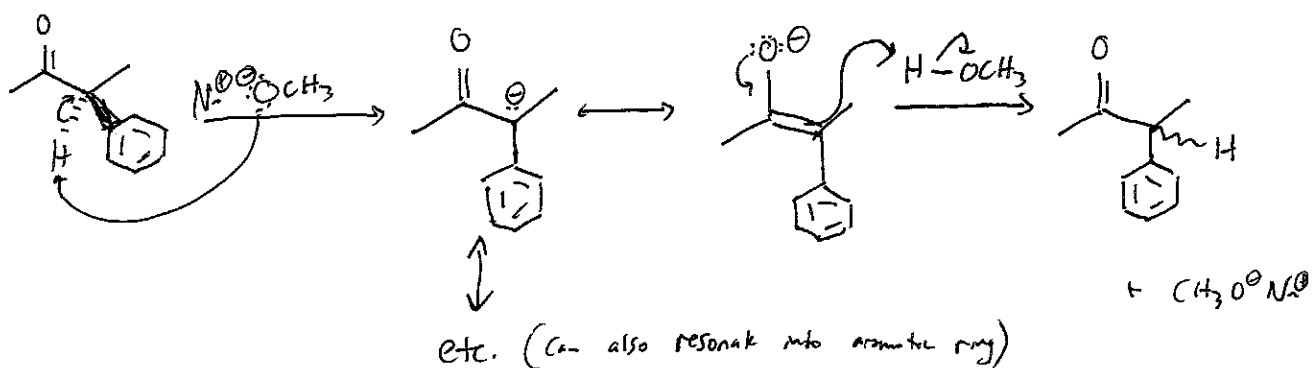
Reactions of enolates & enols - H/D exchange @ α -positions.



2) Isomerization of α -stereogenic center (ketones & aldehydes)



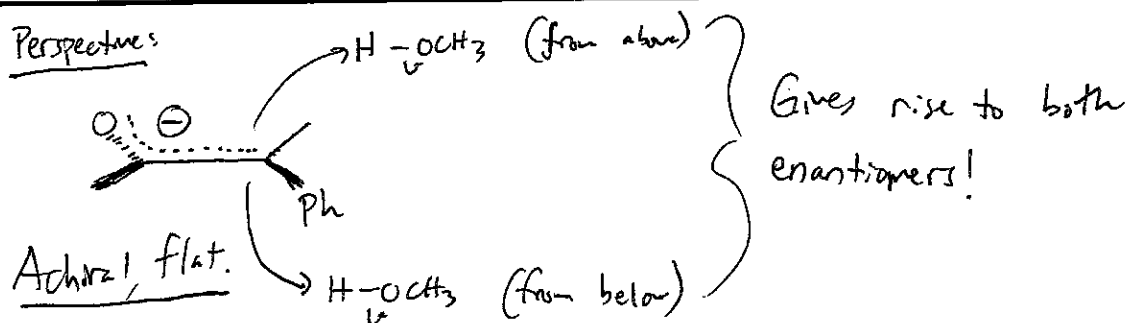
Mechanistic Insight:



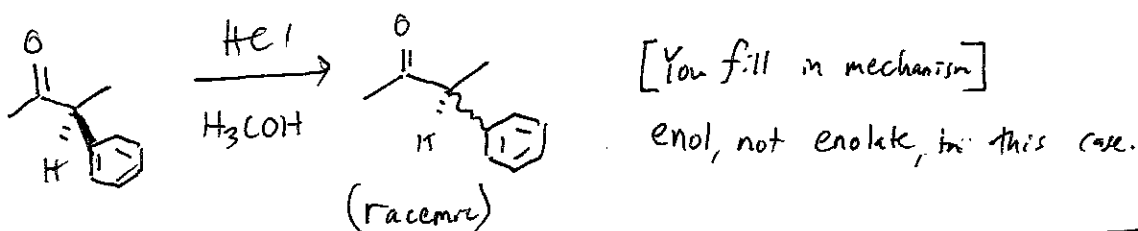
The enolate is no longer a chiral entity. So the stereogenic center is lost in the intermediate.

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Perspectives

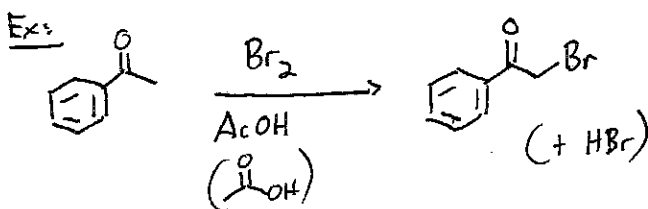


Similar isomerization can also occur under acid-catalyzed conditions!

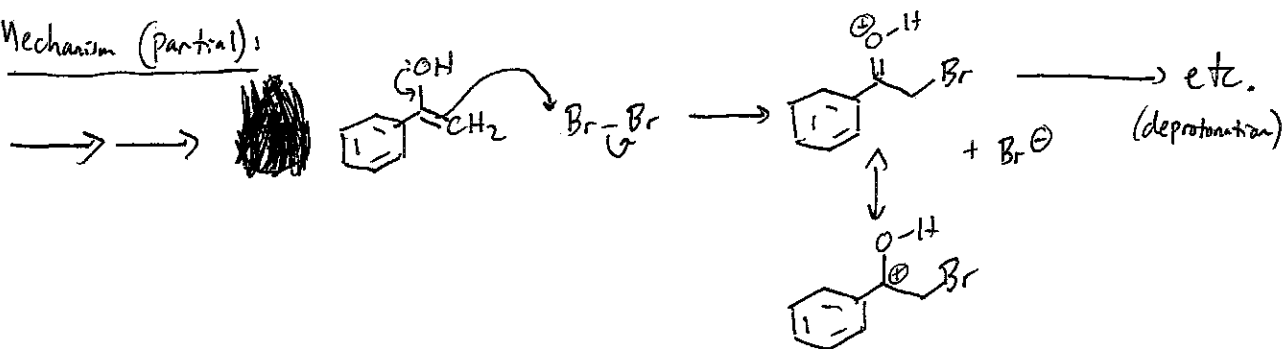


3) α -Halogenation of aldehydes/ketones (Cl, Br, I)

(a) Acid-catalyzed \rightarrow easy to stop after 1 addition

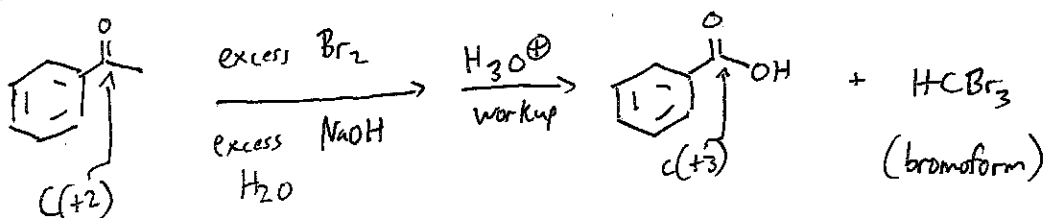


Mechanism (partial):

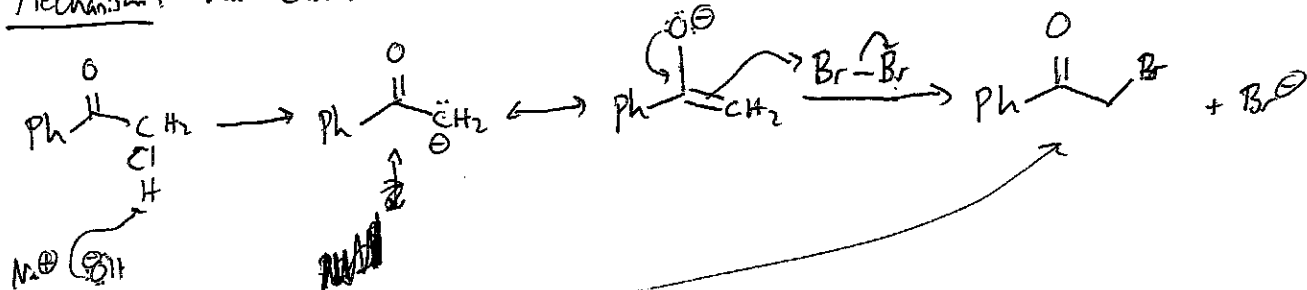


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(b) Alkaline Conditions \rightarrow multiple reactions \rightarrow "Haloforn reactions"

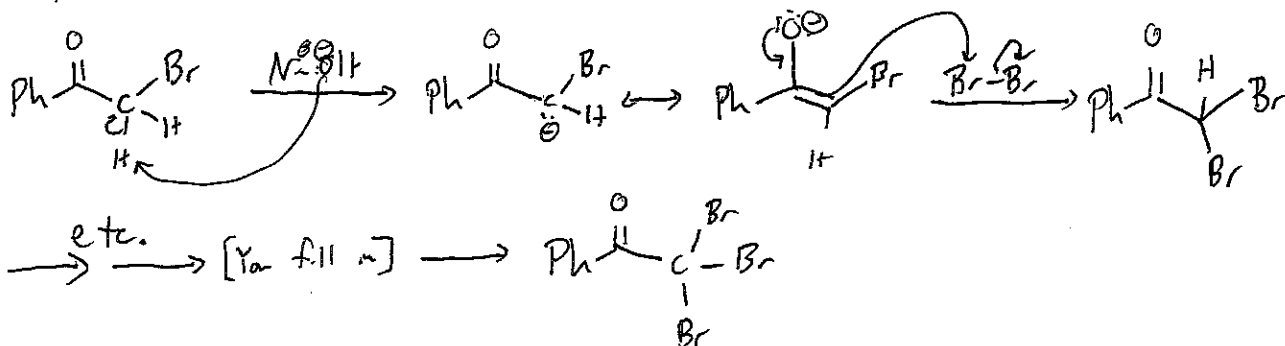


Mechanism: via enolate

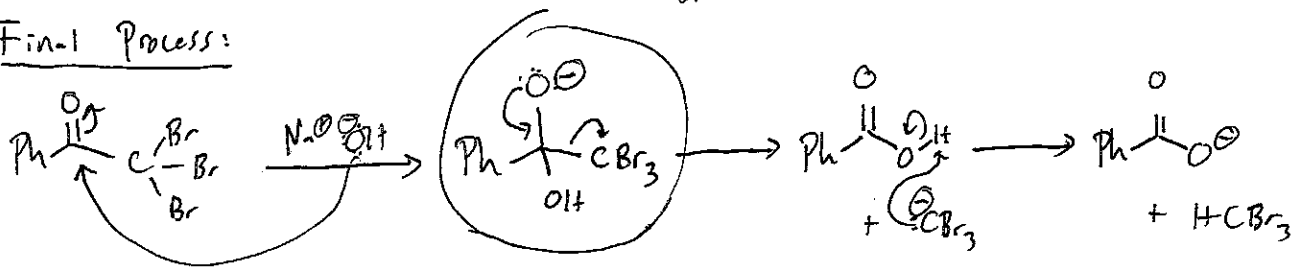


Note that α -Br ketone is more acidic than starting material!

So, we can't stop at just one bromination. Thus,

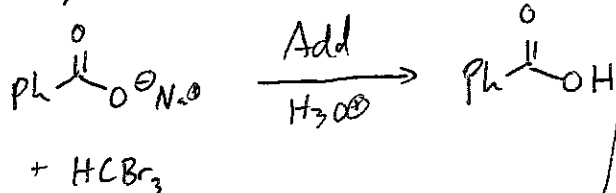


Final Process:



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Then, final H_3O^+ workup step



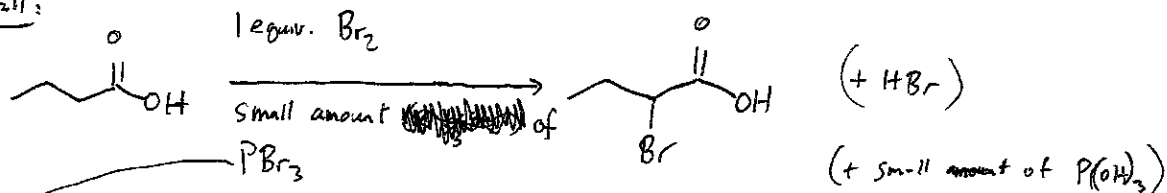
This is an unusual case ...
 Why can a carbanion serve as a leaving group?!

$\text{p}K_a$ of $\text{HClBr}_3 \approx 25$, so the

anion CBr_3^- is actually an OK leaving group, in contrast to a "normal" alkane (e.g. $\text{C}(\text{H}_3)_3^-$)

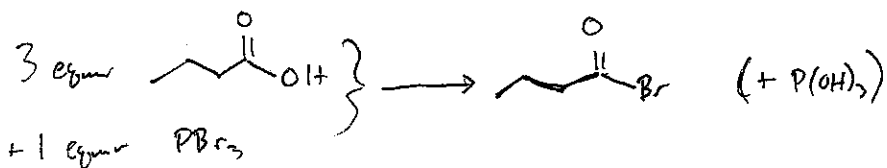
4) ~~Halogenation~~ of Carboxylic acids. Bromination

Overall:



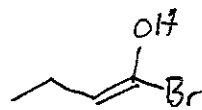
technically not a catalyst because it is not regenerated at the end.

Role of PBr_3 - generate transient acid bromide



To introduce α -Br, we need an enol species to act as nucleophile. However, the expected enol $\left(\text{CH}_3\text{CH}=\text{C}(\text{OH})\text{CH}_2\text{OH} \right)$ does not form.

BUT the acid bromide's enol is accessible



Course Chem 345

Instructor Gellman

Day Monday

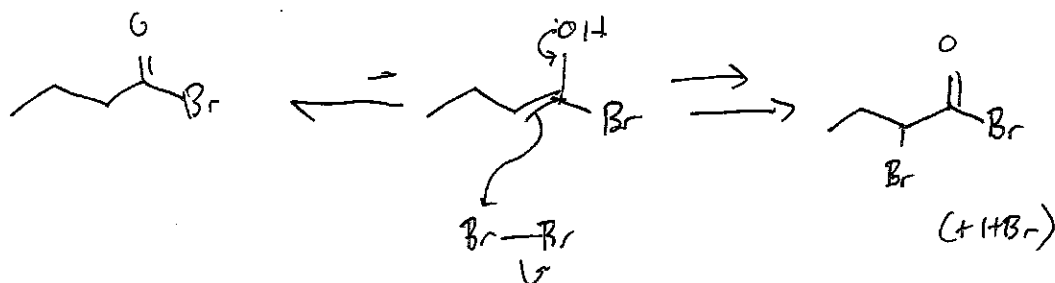
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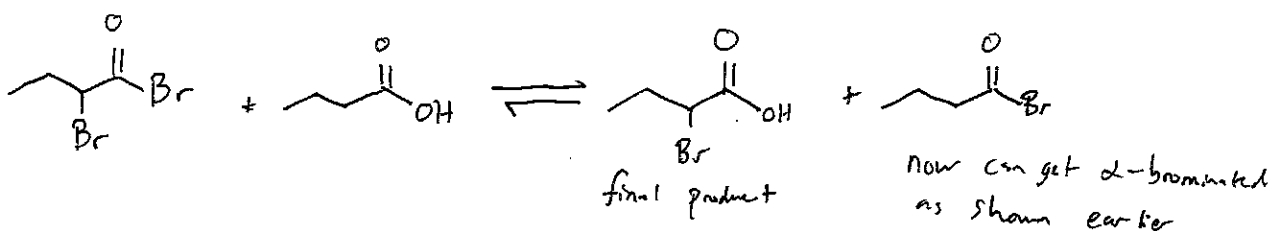
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The difference is that the acid CCCC(=O)O has resonance stabilization (disfavors enol) whereas the acid bromide CCCC(=O)Br essentially only has C-O resonance. Br does not contribute to any appreciable degree.

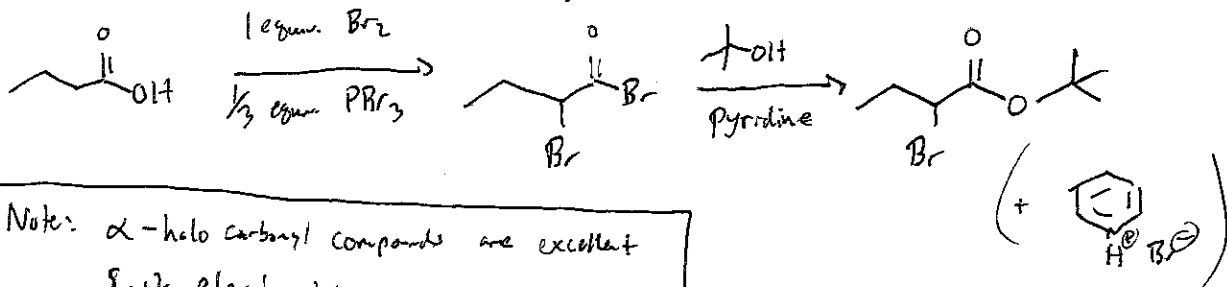


Then, each kind of Br must be transferred to a carboxylic acid molecule to enable the α -Bromination.



[You figure out the exchange mechanism]

Variation: use stoichiometric PBr_3 and form ester



Note: α -halo carbonyl compounds are excellent S_N2 electrophiles