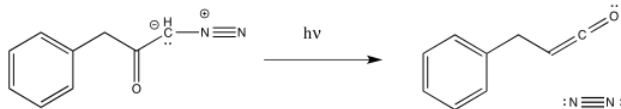
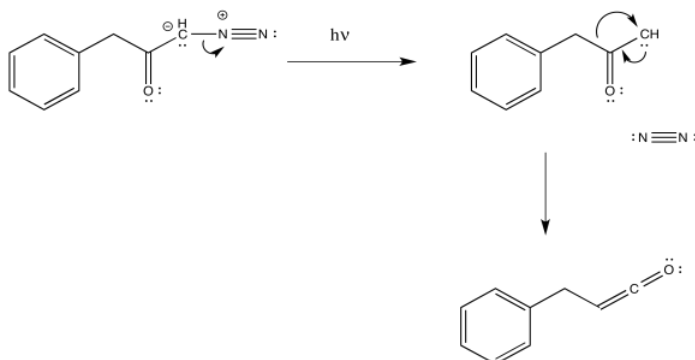


11.5: Wolff Rearrangement

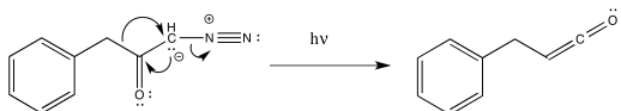
The Wolff rearrangement is the conversion of a diazoketone to a ketene, usually under photolytic conditions.



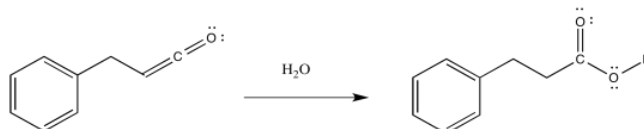
The loss of dinitrogen from the diazonium compound would result in an electron-deficient carbene. Like a carbocation, the carbene would be susceptible to a 1,2-shift. If accompanied by π -donation from the carbene to the carbonyl, a ketene would result.



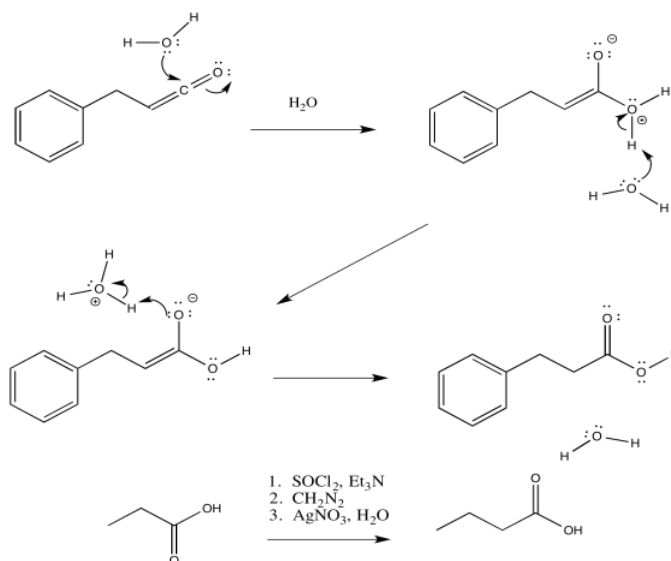
As with other rearrangements, the 1,2-shift could occur at the same time as the loss of the dinitrogen.

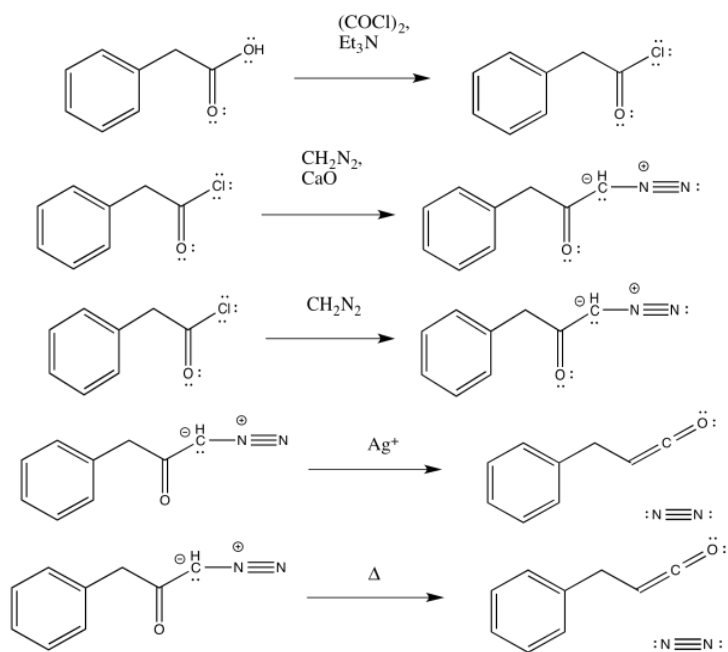


Ketenes are not terribly stable. In the presence of nucleophilic solvents such as water or alcohol, the ketene easily undergoes nucleophilic addition. Addition of water would result in a carboxylic acid.



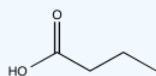
The mechanism of that addition involves keto-enol tautomerism.



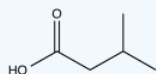
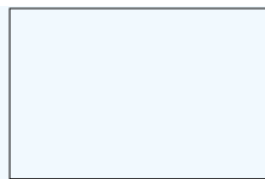


Exercise 11.5.1

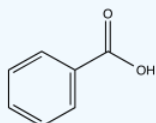
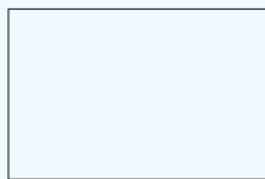
Predict the products of the following Wolff rearrangements.



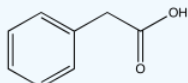
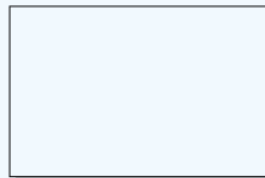
1. $(\text{COCl})_2$, Et_3N
2. CH_2N_2
3. $h\nu$, EtNH_2



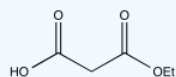
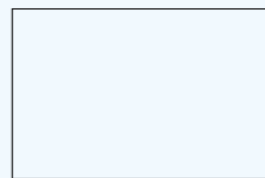
1. SOCl_2 , Et_3N
2. CH_2N_2
3. Δ , $\text{CH}_3\text{CH}_2\text{OH}$



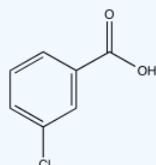
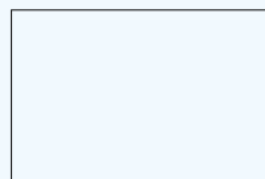
1. SOCl_2 , Et_3N
2. CH_2N_2
3. AgNO_3 , H_2O



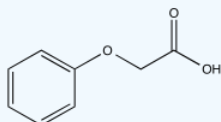
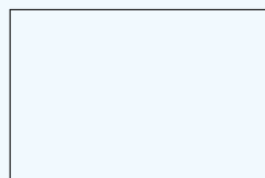
1. $(\text{COCl})_2$, Et_3N
2. CH_2N_2
3. $h\nu$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$



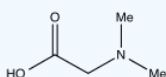
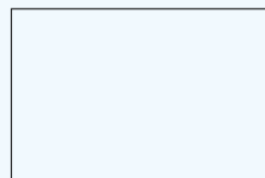
1. $(\text{COCl})_2$, Et_3N
2. CH_2N_2
3. $h\nu$, H_2O



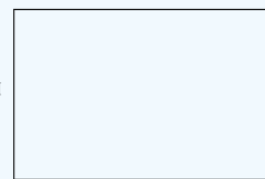
1. SOCl_2 , Et_3N
2. CH_2N_2
3. Δ , CH_3OH



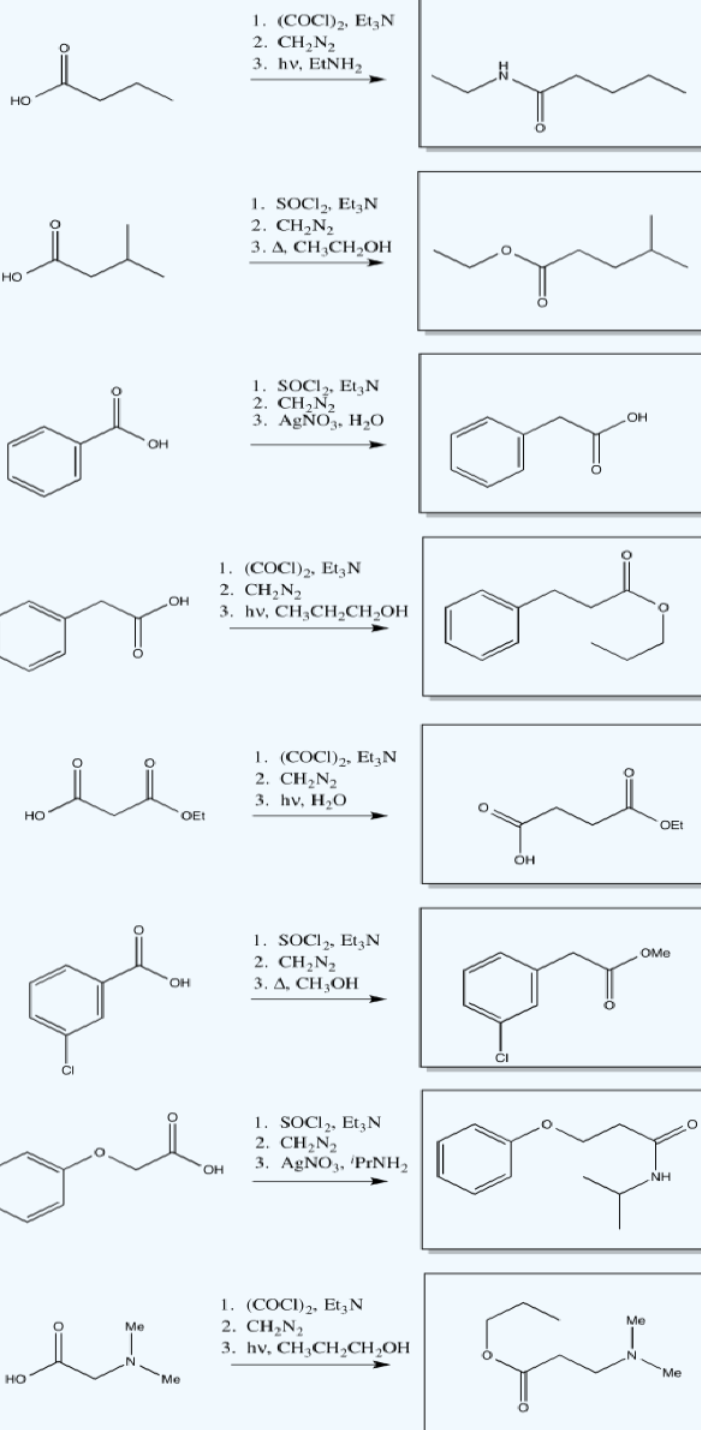
1. SOCl_2 , Et_3N
2. CH_2N_2
3. AgNO_3 , $i\text{PrNH}_2$



1. $(\text{COCl})_2$, Et_3N
2. CH_2N_2
3. $h\nu$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$



Answer



This page titled [11.5: Wolff Rearrangement](#) is shared under a [CC BY-NC 3.0](#) license and was authored, remixed, and/or curated by [Chris Schaller](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.