19.9: NUCLEOPHILIC ADDITION OF HYDRAZINE - THE WOLFF-KISHNER REACTION

OBJECTIVES

After completing this section, you should be able to

- write an equation to illustrate the Wolff-Kishner reduction of an aldehyde or ketone.
- identify the product formed from the Wolff-Kishner reduction of a given aldehyde or ketone.

KEY TERMS

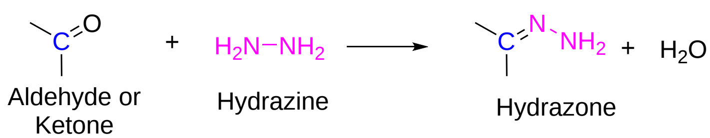
Make certain that you can define, and use in context, the key term below.

- Wolff-Kishner reduction

STUDY NOTES

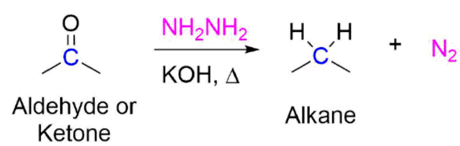
After studying this section, you can add yet another method of reducing organic compounds to your growing list of reduction reactions.

Aldehydes and ketones can be converted to a hydrazone derivative by reaction with hydrazine (H_2NNH_2). Hydrazone formation is a variation of the imine forming reaction discussed in the previous section.



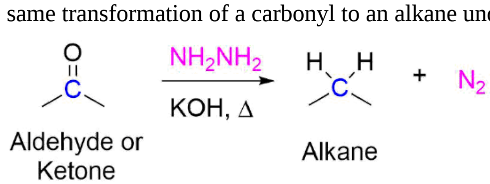
REACTION WITH A BASE AND HEAT CONVERTS A HYDRAZONE TO AN ALKANE

Hydrazones can be further converted to the corresponding alkane by reaction with a base, usually KOH, and heat. Typically a high boiling point solvent, such as ethylene glycol, is used to provide the high temperatures needed for this reaction to occur. In the examples below the symbol "Δ" represents the addition of heat to a reaction. During this reaction nitrogen gas, which contains a very stable N-N triple bond, is produced.

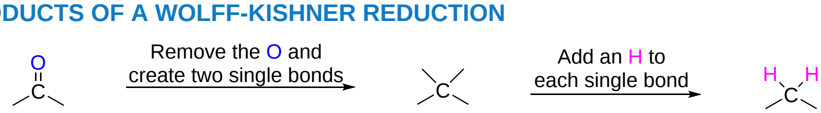


BOTH REACTIONS TOGETHER PRODUCE THE WOLFF-KISHNER REDUCTION

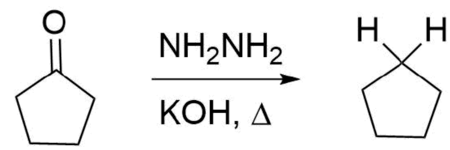
These two steps previously discussed can be combined to provide a general reaction for the conversion of aldehydes and ketones to alkanes called the Wolff-Kishner Reduction. Overall, the Wolff-Kishner reduction removes the carbonyl oxygen in the form of water by forming an intermediate hydrazone. The hydrazone then undergoes loss of N_2 gas along with protonation to give the alkane reaction product. Note that the Clemmensen reduction accomplishes the same transformation of a carbonyl to an alkane under acidic conditions.



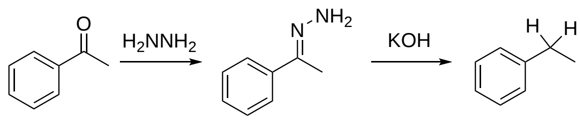
PREDICTING THE PRODUCTS OF A WOLFF-KISHNER REDUCTION



EXAMPLES



Conversion of Cyclopentanone to cyclopentane

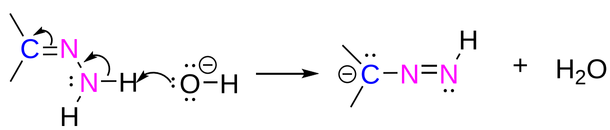


Conversation of Acetophenone to Ethylbenzne

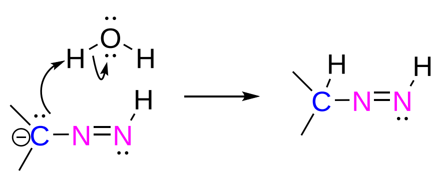
MECHANISM OF THE WOLFF-KISHNER REDUCTION

Hydrazine reacts with a carbonyl to form a hydrazone using a mechanism similar to that of an imine formation discussed in the previous section. The weakly acidic N-H bond is deprotonated to form the hydrazone anion. The hydrazone anion has a resonance structure that places a double bond between the nitrogens and a negative charge on carbon. The hydrazone anion is then protonated to form a neutral intermediate. A second weakly acidic N-H bond is deprotonated which causes the formation of N_2 gas and a carbanion. In the final step the carbanion is protonated to form an alkane product.

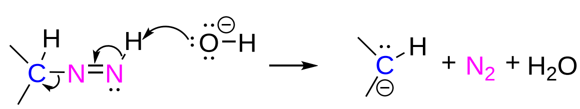
STEP 1: DEPROTONATION



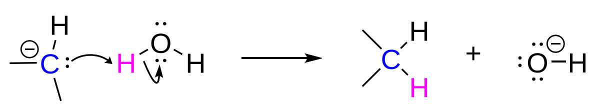
STEP 2: PROTONATION



STEP 3: SECOND DEPROTONATION

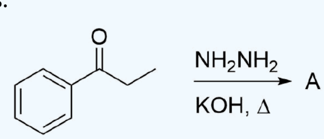


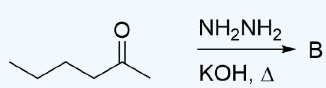
STEP 4: THE CARBANION IS PROTONATED TO FORM THE ALKANE PRODUCT.



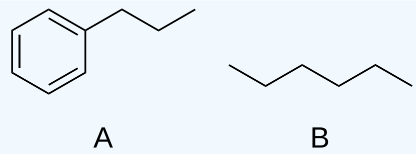
? EXERCISE 19.9.1

Please draw the products of the following reactions.





Answer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