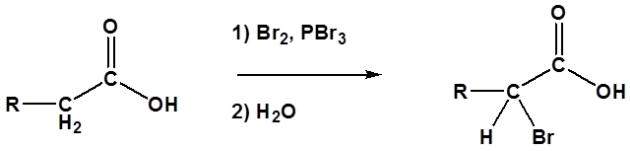
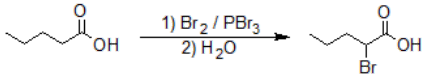
23.5: BROMINATION OF ACIDS- THE HVZ REACTION

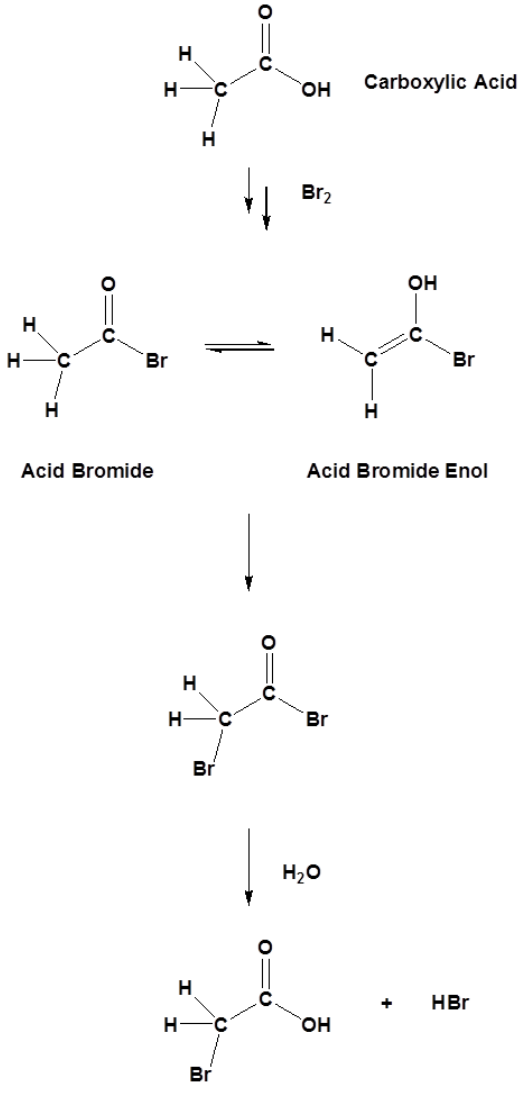
Although the alpha bromination of some carbonyl compounds, such as aldehydes and ketones, can be accomplished with Br_2 under acidic conditions, the reaction will generally not occur with acids, esters, and amides. This is because only aldehydes and ketones enolize to a sufficient extent to allow the reaction to occur. However, carboxylic acids, can be brominated in the alpha position with a mixture of Br_2 and PBr_3 in a reaction called the Hell-Volhard-Zelinskii (HVZ) reaction.



For example, pentanoic acid can be converted to 2-bromopentanoic acid as shown in the example below.

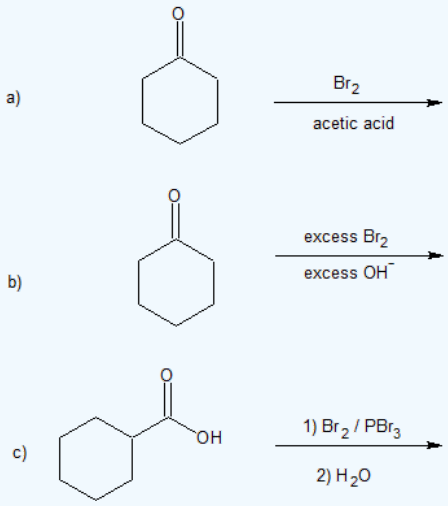


The mechanism of this reaction involves an acid bromide enol instead of the expected carboxylic acid enol. The reaction starts with the reaction of the carboxylic acid with PBr_3 to form the acid bromide and HBr. The HBr then catalyzes the formation of the acid bromide enol which subsequently reacts with Br_2 to give alpha bromination. Lastly, the acid bromide reacts with water to reform the carboxylic acid.



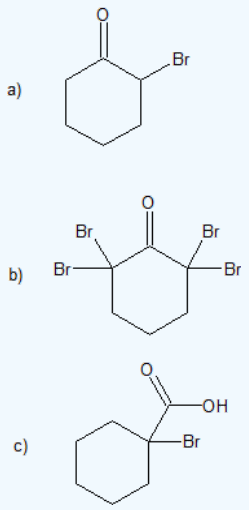
Exercise

8. Draw the bond-line structure for the product of each reaction below.



Answer

8.



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