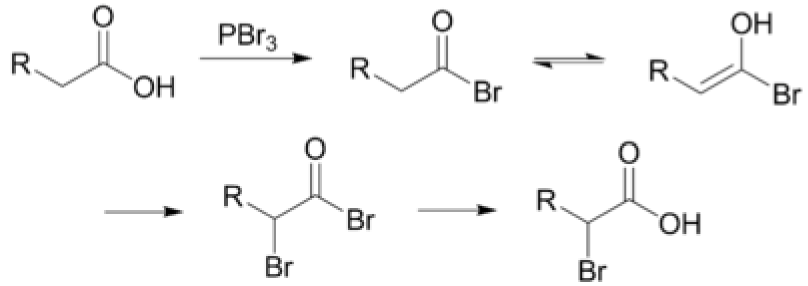
Hell–Volhard–Zelinsky halogenation

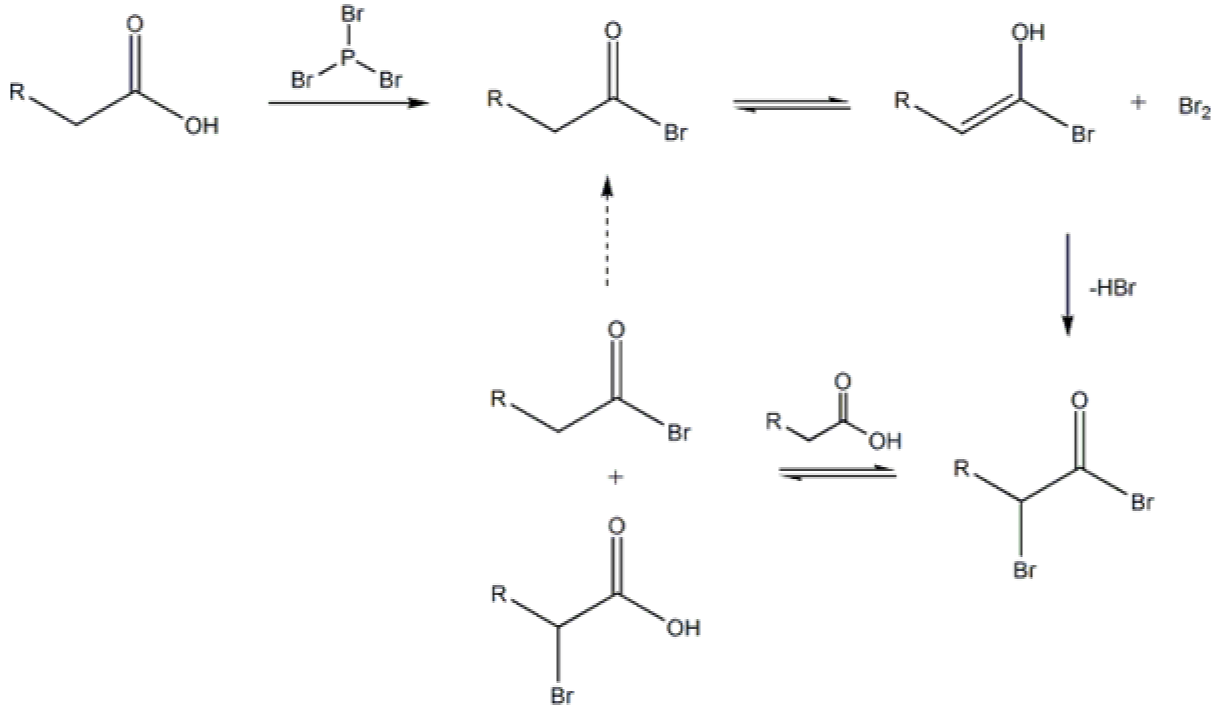
The **Hell–Volhard–Zelinsky halogenation** reaction halogenates carboxylic acids at the α carbon. The reaction is named after three chemists, the German chemists Carl Magnus von Hell (1849–1926) and Jacob Volhard (1834–1910) and the Russian chemist Nikolay Zelinsky (1861–1953).[1][2][3][4]

Hell–Volhard–Zelinsky halogenation	
Named after	Carl Magnus von Hell Jacob Volhard Nikolay Zelinsky
Reaction type	Substitution reaction
Identifiers	
Organic Chemistry Portal	hell-volhard-zelinsky-reaction



Scheme

Unlike other halogenation reactions, this reaction takes place in the absence of a halogen carrier. The reaction is initiated by addition of a catalytic amount of PBr_3, after which one molar equivalent of Br_2 is added.

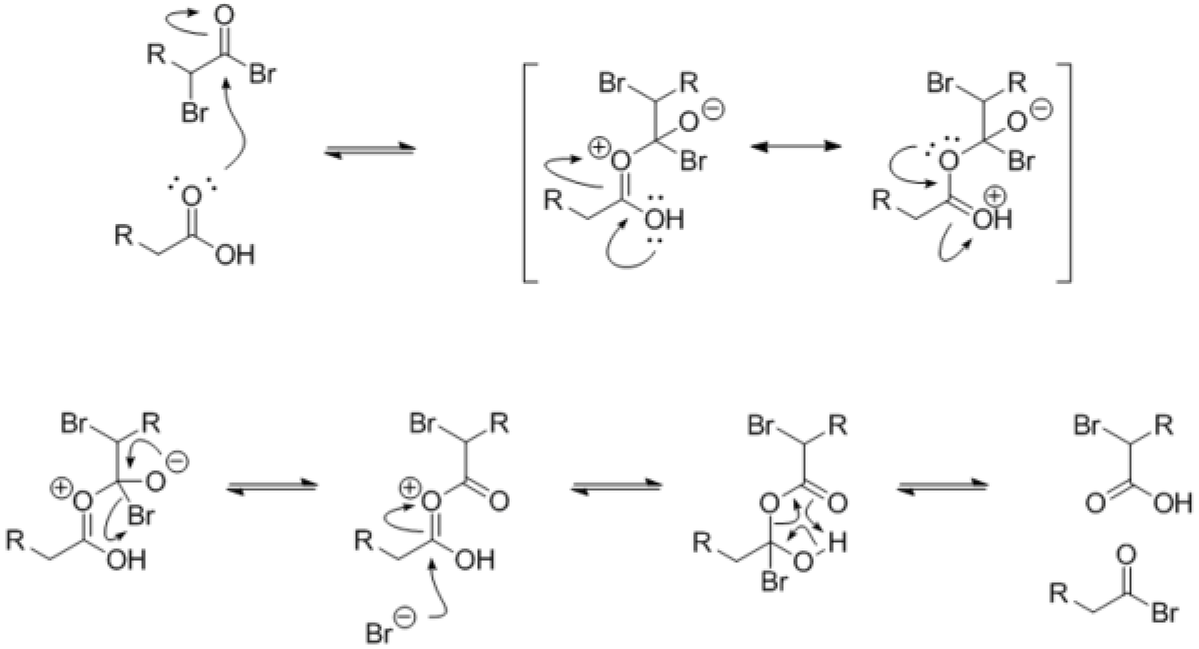


PBr_3 replaces the carboxylic OH with a bromide, resulting in a carboxylic acid bromide. The acyl bromide can then tautomerize to an enol, which will readily react with the Br_2 to brominate a second time at the α position.

In neutral to slightly acidic aqueous solution, hydrolysis of the α-bromo acyl bromide occurs spontaneously, yielding the α-bromo carboxylic acid in an example of a nucleophilic acyl substitution. If an aqueous solution is desirable, a full molar equivalent of PBr_3 must be used as the catalytic chain is disrupted.

If little nucleophilic solvent is present, reaction of the α-bromo acyl bromide with the carboxylic acid yields the α-bromo carboxylic acid product and regenerates the acyl bromide intermediate. In practice a molar equivalent of PBr_3 is often used anyway to overcome the slow reaction kinetics.

The mechanism for the exchange between an alkanoyl bromide and a carboxylic acid is below. The α-bromoalkanoyl bromide has a strongly electrophilic carbonyl carbon because of the electron-withdrawing effects of the two bromides.



See also

- Reformatsky reaction

References

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2. *Volhard J. (1887). "Ueber Darstellung α-bromirter Säuren". Annalen der Chemie. **242**: 141–163. doi:10.1002/jlac.18872420107 .*

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4. *Allen C. F., Kalm M. J. (1963). "2-Methylenedodecanoic Acid" . Organic Syntheses.; Collective Volume, **4**, p. 616*

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