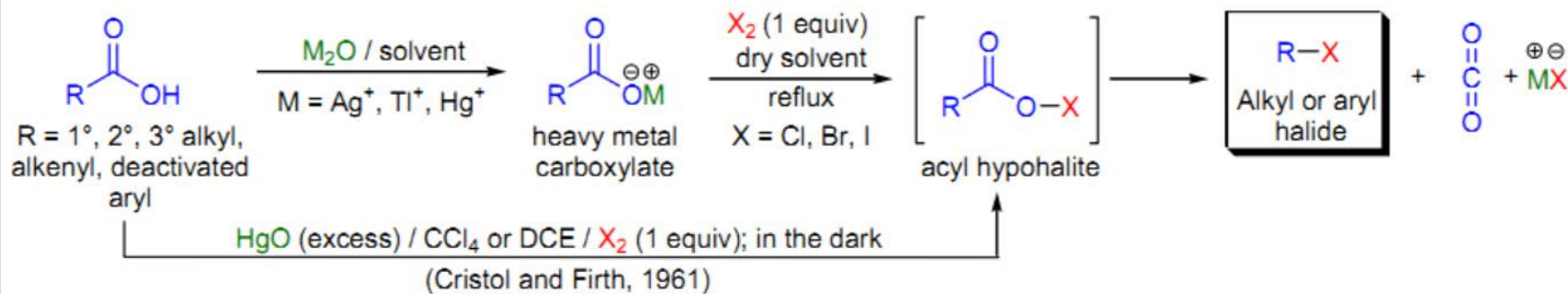
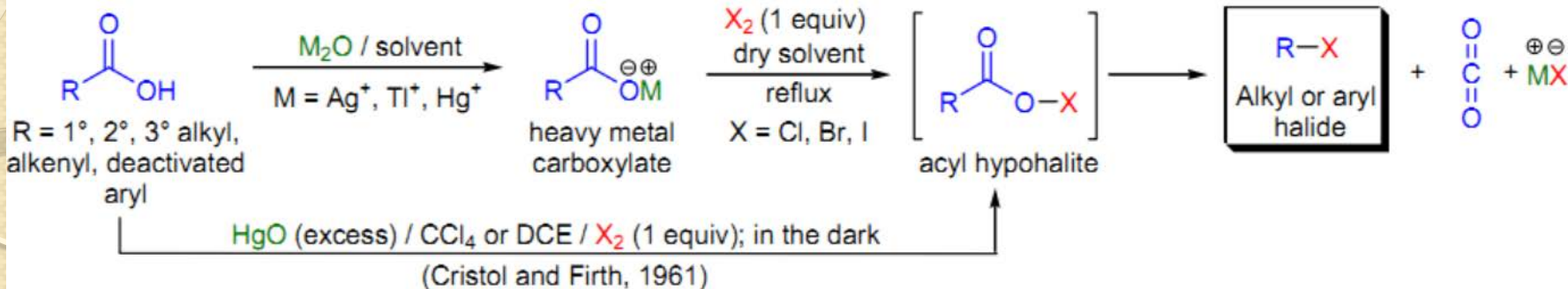


HUNSDIECKER REACTION

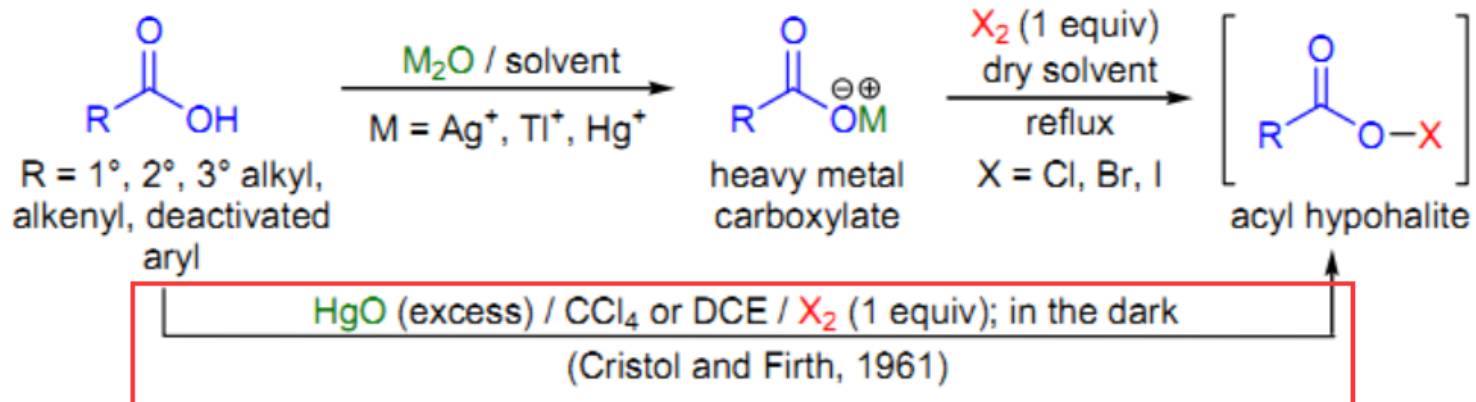




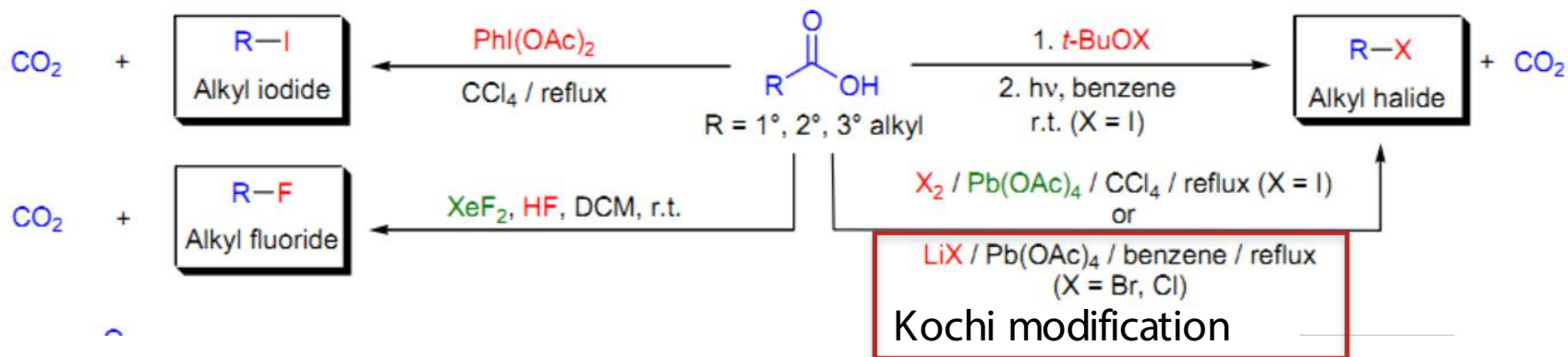
- In 1939, H. Hunsdiecker reported that when the dry silver salts of aliphatic carboxylic acids were treated with bromine, the corresponding one-carbon shorter alkyl bromides were obtained.
- In order to obtain high yields, the silver salts must be pure and scrupulously dry, which is not easy to achieve, since the silver salt is often heat sensitive
- Aliphatic carboxylic acids are the best substrates, but aromatic carboxylic acids with electron-withdrawing substituents are also suitable
- If optically active silver carboxylates are used, there is a significant loss of optical activity in the product alkyl halides

Some modifications

1. Cristol-Firth modification



2. Suárez modification and Kochi modification

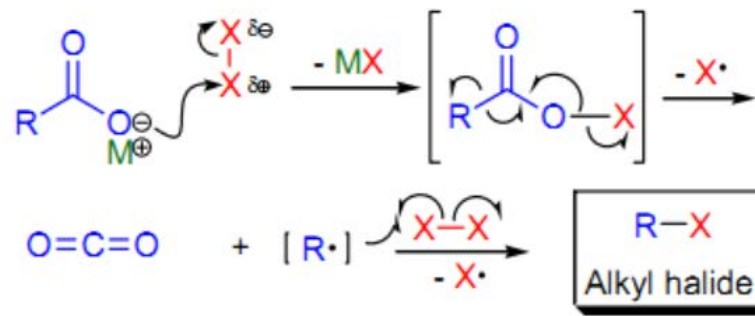


3. Barton modification

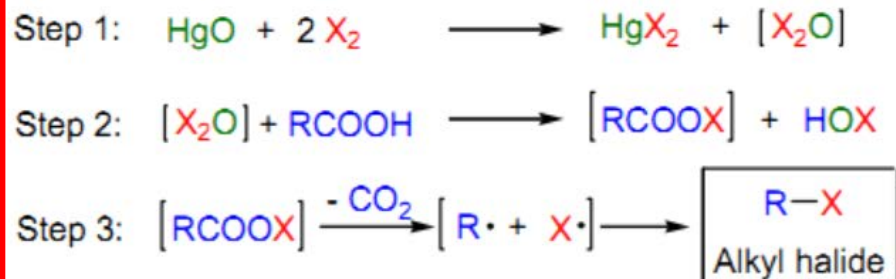


Mechanism

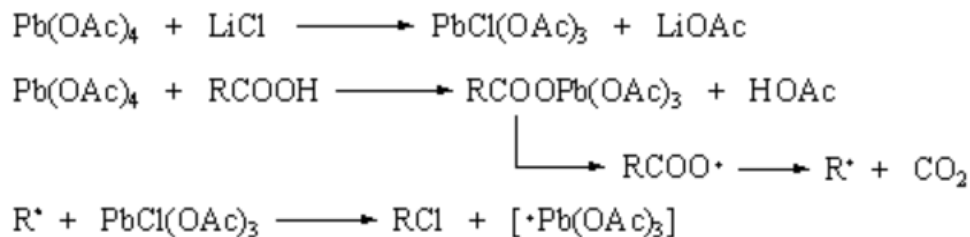
Classical Hunsdiecker reaction:



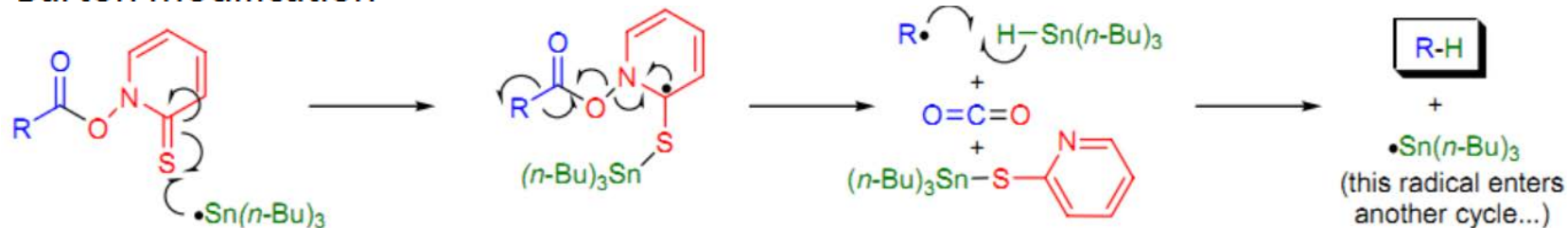
Cristol-Firth modified Hunsdiecker reaction:



Kochi modification

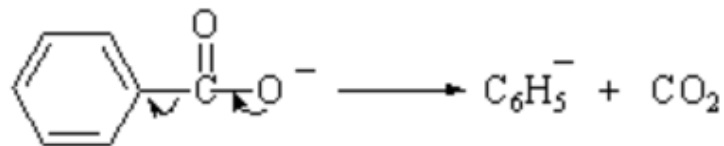


Barton modification

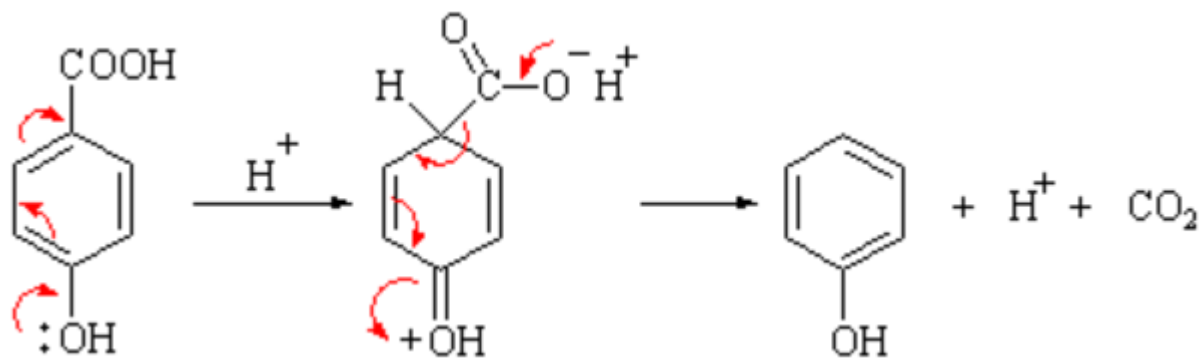


2. 芳香族脱羧反应

一般芳香族羧酸比脂肪酸容易脱羧，因为苯基可以作为一个吸电子基团，有利于碳碳键的断裂。若是邻、对位有吸电子基团的化合物易脱羧。



邻、对位有给电子基团的羧酸脱羧较难，但在强酸（如 H_2SO_4 ）作用下邻对位苯酚也能脱羧。

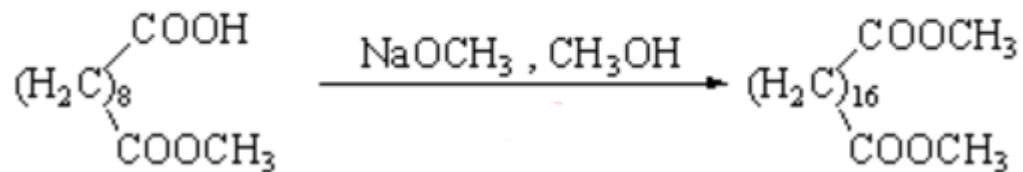


3. 电化学脱羧反应 (Kolbe合成法)

电解羧酸盐溶液，在阳极发生烷基偶联生成烃。此法称为Kolbe合成法。此法也成功地用于二元羧单酯盐电解长链的二元酸酯。机理应该是自由基反应。



例：



There are a few efficient methods for the stereoselective synthesis of vinyl halides, and this transformation remains a synthetic challenge. Research by S. Roy showed that the *Hunsdiecker reaction* can be made metal free and catalytic (*catalytic Hunsdiecker reaction*) and can be used to prepare (*E*)-vinyl halides from aromatic α,β -unsaturated carboxylic acids.²⁷ The unsaturated aromatic acids were mixed with catalytic amounts of TBATFA and the *N*-halo-succinimide was added in portions over time at ambient temperature. The yields are good to excellent even for activated aromatic rings which do not undergo the *classical Hunsdiecker reaction*. The fastest *halodecarboxylation* occurs with NBS, but NCS and NIS are considerably slower. The nature of the applied solvents is absolutely critical, and DCE proved to be the best. This strategy was extended and applied in the form of a *one-pot tandem Hunsdiecker reaction-Heck coupling* to prepare aryl substituted (*2E,4E*)-dienoic acids, esters, and amides.

