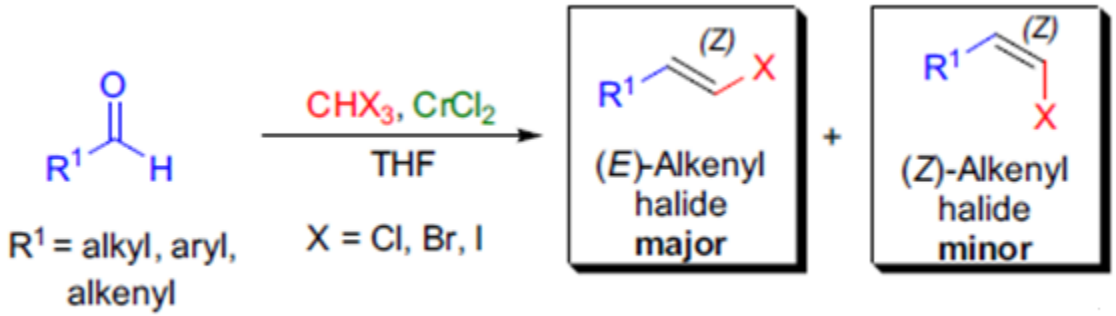
# TAKAI-UTIMOTO OLEFINATION (TAKAI REACTION)

Until the second half of the 1980s there was no general method available for the stereoselective preparation of alkenyl halides from carbonyl compounds. In 1987, K. Takai and K. Utimoto introduced a simple and stereoselective method for the conversion of aldehydes to the corresponding (*E*)-alkenyl halides by treating the aldehydes with a haloform-chromium(II)-chloride (CHX3-CrCl2) system.1 The chromium(II)-mediated one-carbon homologation of aldehydes with haloform to give the corresponding (*E*)-alkenyl halides is known as the *Takai-Utimoto olefination* (*Takai reaction*).



**General features of the reaction are:**

**1)** The anhydrous $CrCl_2$ can be dissolved in the solvent just prior to the reaction or can be generated by reacting $CrCl_3$ with $LiAlH_4$.

**2)** Aldehydes react much faster than ketones,so the chemoselective transformation of aldehydes in the presence of ketones is possible.

**3)** For aliphatic and aromatic aldehydes the major product is the (E)-alkenyl halide but for α,β-unsaturated aldehydes the stereoselectivity is usually poor.

**4)** The rate of the reaction is a function of the haloform used: I>Br>Cl.

**5)** Iodoform reacts rapidly at low temperatures (~0 ° C), while other haloforms require higher temperatures to react.

**6)** The (E/Z) ratio is also dependent on the haloform used (Cl>Br>I) and the best (E)-selectivity is observed when X=Cl.

**7)** When $CHBr_3/CrCl_2$ is used, a mixture of alkenyl chlorides and bromides is obtained due to a Finkelstein reaction of $CrCl_2$ with bromide ($Br^-$). However, by preparing $CrBr_2$ from $CrBr_3/LiAlH_4$ this problem is eliminated.

**8)** Reducing agents other than Cr(II) give unsatisfactory or no yield of the desired alkenyl halides.

**9)** In certain cases the applied solvent is critical to achieve good yield and stereoselectivity.

**10)** The reaction conditions tolerate almost any functional group.

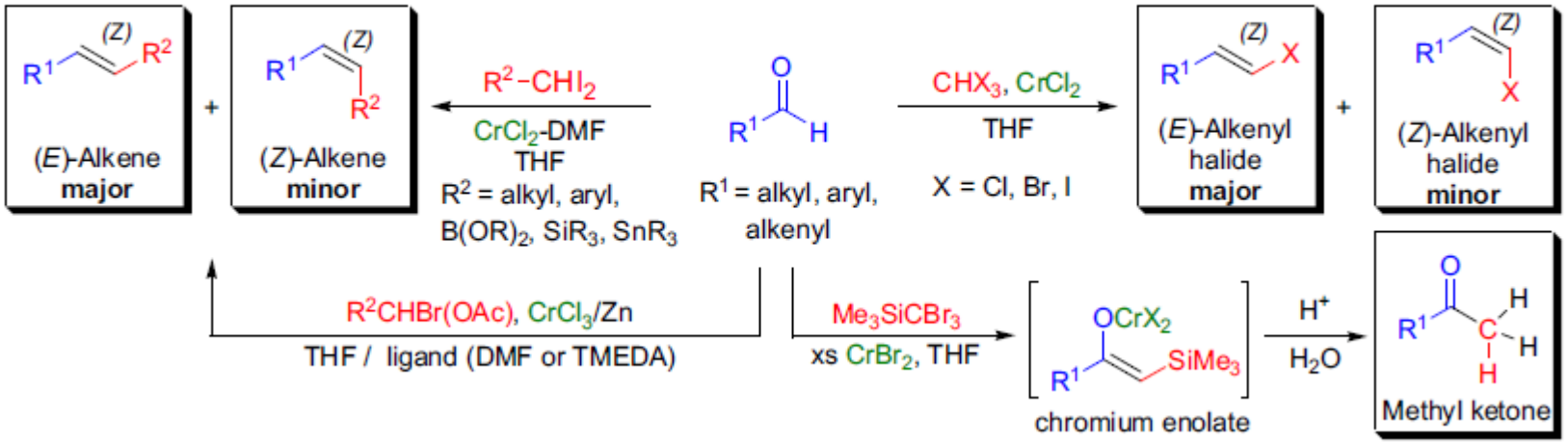
**11)** The reaction conditions are mild enough (the reagent is practically nonbasic) that even highly enolizable substrates do not racemize at their α-position.

**There are several important modification of the T-U olefination:**

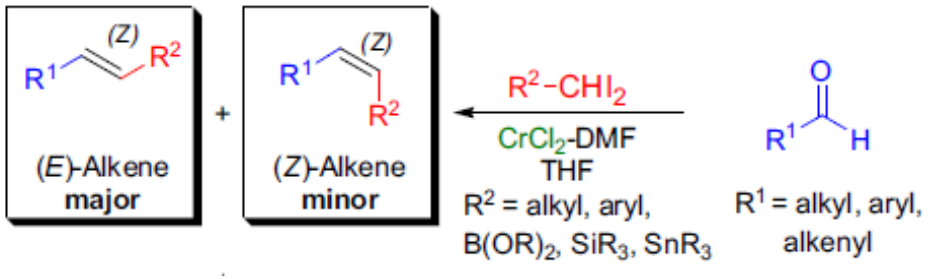
**1)** Instead of haloforms,1,1-geminal dihalides are used to afford predominantly (E)-olefins.

**2)** Instead of 1,1-geminal dihalides, α-acetoxy bromides can be used, which are more stable and easier to prepare and handle than 1,1-geminal dihalides.

**3)**One-carbon homologation of aldehydes via chromium enolates to the corresponding methyl ketones using TMSCBr3/CrBr2.



## When 1,1-geminal dihalides are used, the following can be expected:




**1)** The (E)-selectivity is especially high for aliphatic substrates, and it increases with the size of R1.

**2)** Only 1,1-geminal diiodoalkanes are suitable; the dichlorides and dibromides undergo reduction under the reaction conditions.

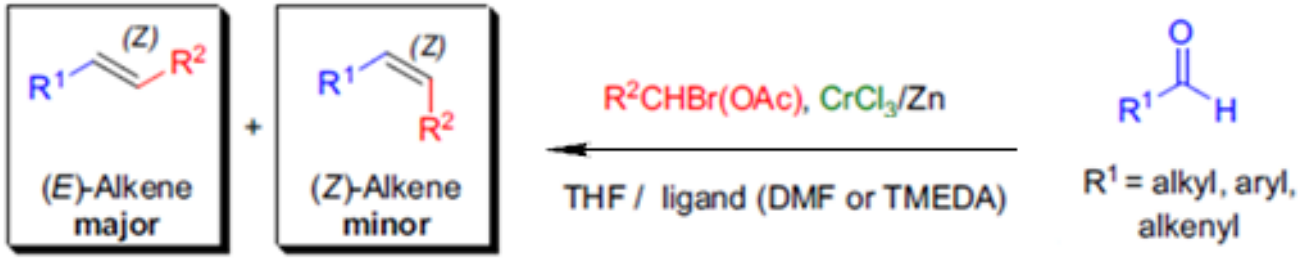
**3)** CH2I2 is the most reactive. The higher homologs react slower and give lower yields.

**4)** The R2 substituent can contain heteroatoms so the preparation of alkenyl silanes, -boronates, –stannanes, and sulfides is possible.

**5)** The reaction can be carried out with catalytic amounts of CrCl3 in the presence of samarium metal or samarium diiodide.

**6)** Aldehydes react faster than ketones.

**The use of α-acetoxy bromides has the following features:**



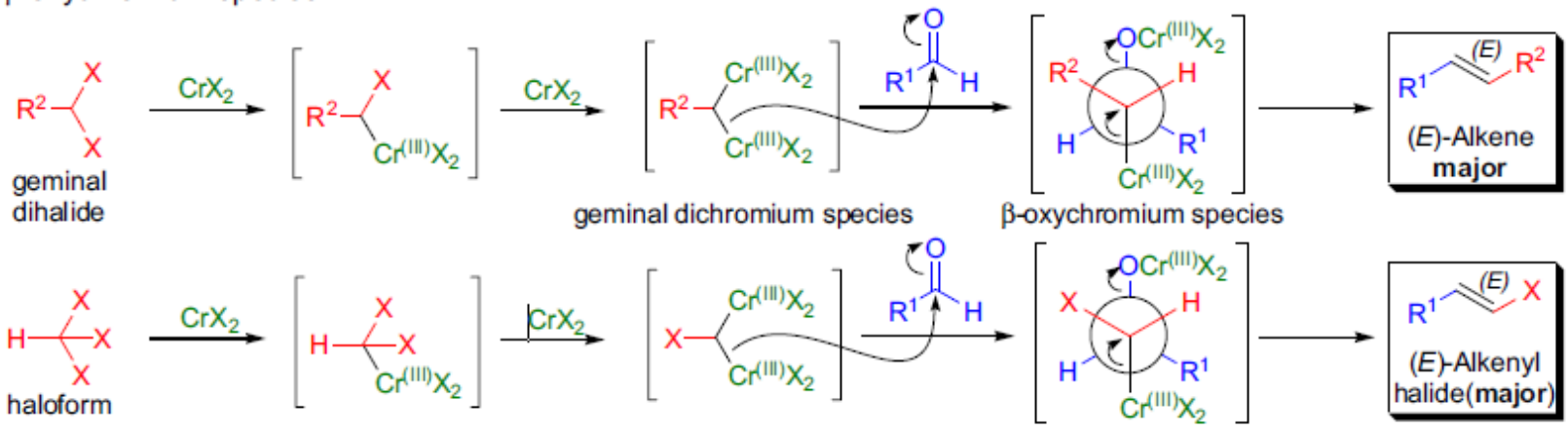

**1)** The in situpreparation of the chromium(II) reagent and donor ligand such as DMF or TMEDA should be present.

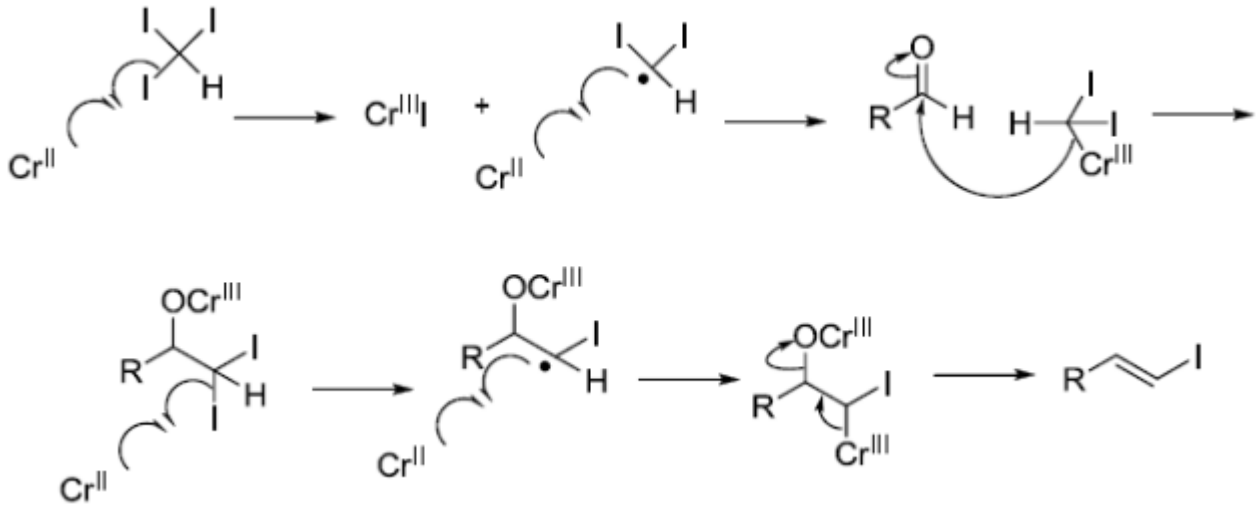
**2)** High (E)-selectivity.

**3)** Exclusive reaction with aldehydes

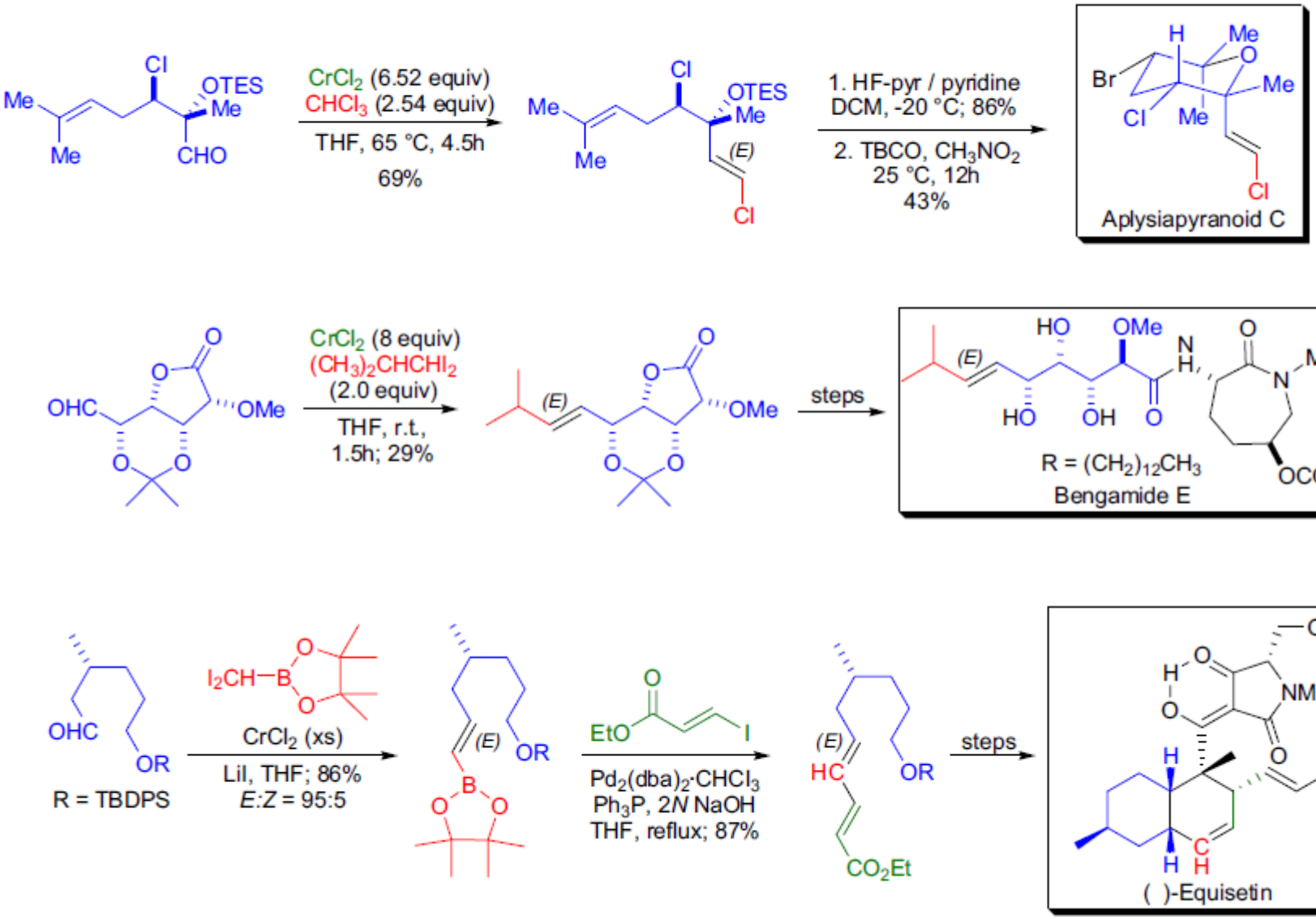
**Mechanism:** [20,21,2,3,15,7]

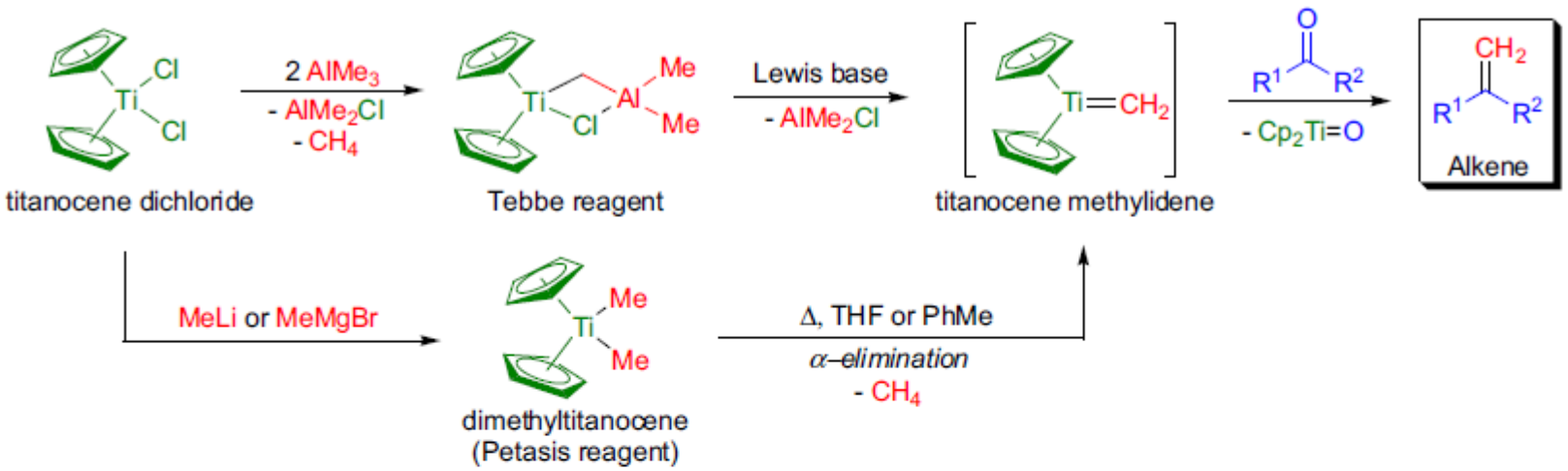
The exact mechanistic pathway is not known. However, it is believed that the *T-U olefination* proceeds *via* geminal-dichromium intermediates that are nucleophilic and attack the carbonyl compound. The (*E*)-alkene is formed from the β-oxychromium species.

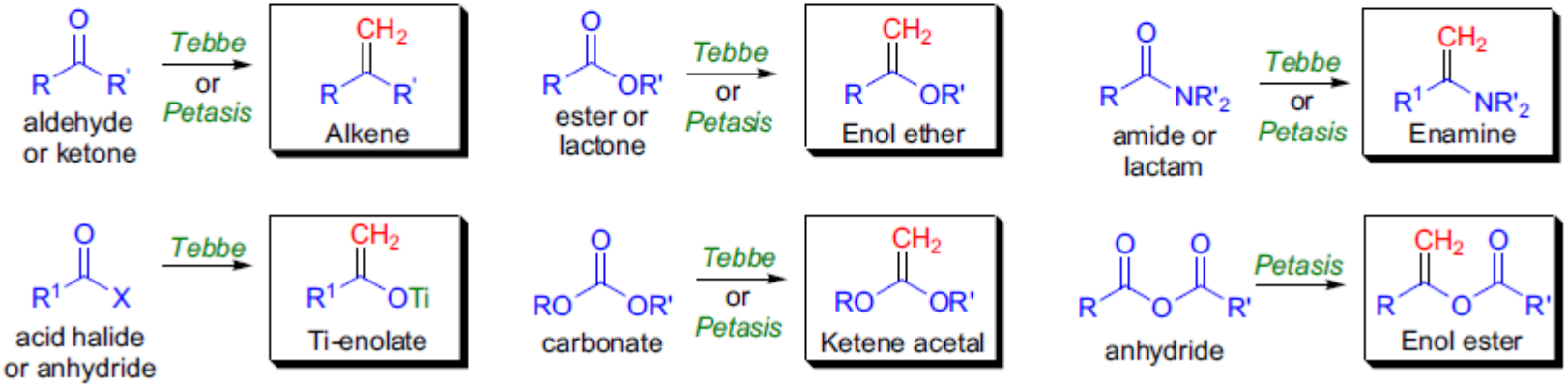


## Synthetic Applications:




titanocene dichloride
2 AlMe3
- AlMe2Cl
- CH4
Tebbe reagent
Lewis base
- AlMe2Cl
titanocene methylidene
- Cp2Ti=O
Alkene
MeLi or MeMgBr
dimethyltitanocene
(Petasis reagent)
Δ, THF or PhMe
α–elimination
- CH4


aldehyde
or ketone
Tebbe
or
Petasis
Alkene
ester or
lactone
Enol ether
amide or
lactam
Enamine
acid halide
or anhydride
Ti-enolate
carbonate
Ketene acetal
anhydride
Enol ester