Prins Reaction

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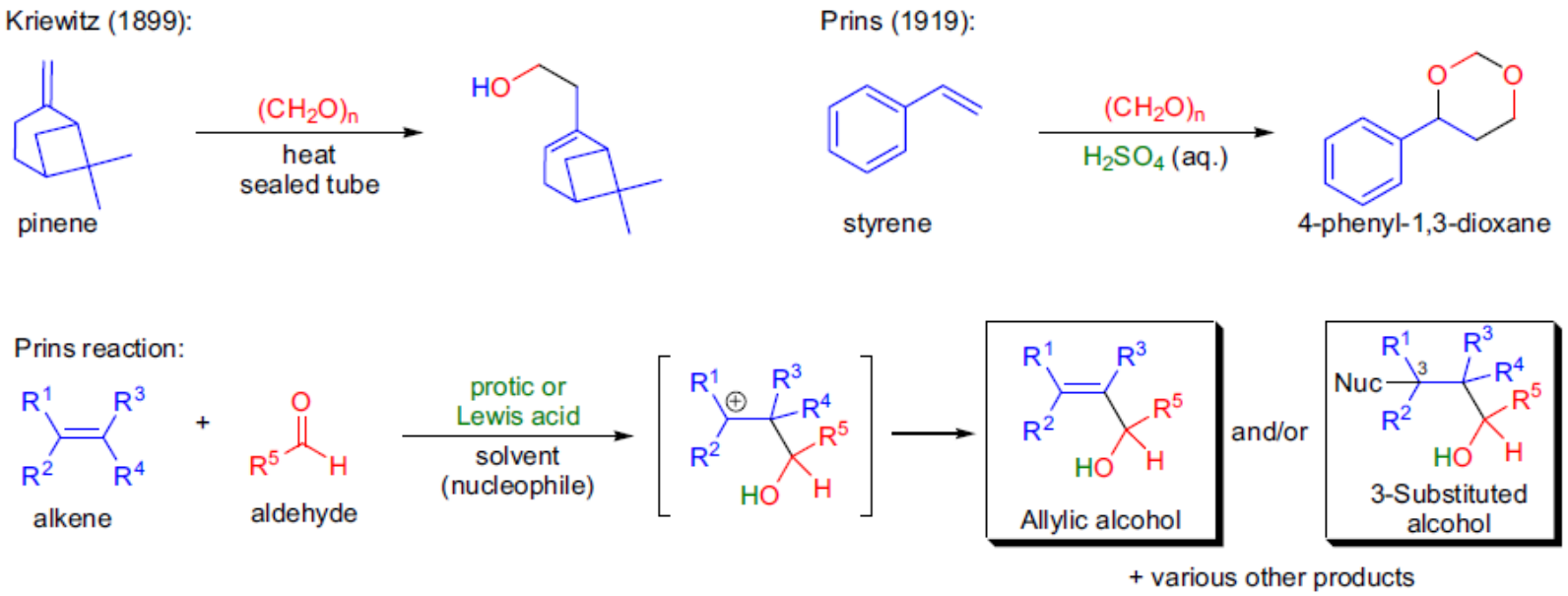
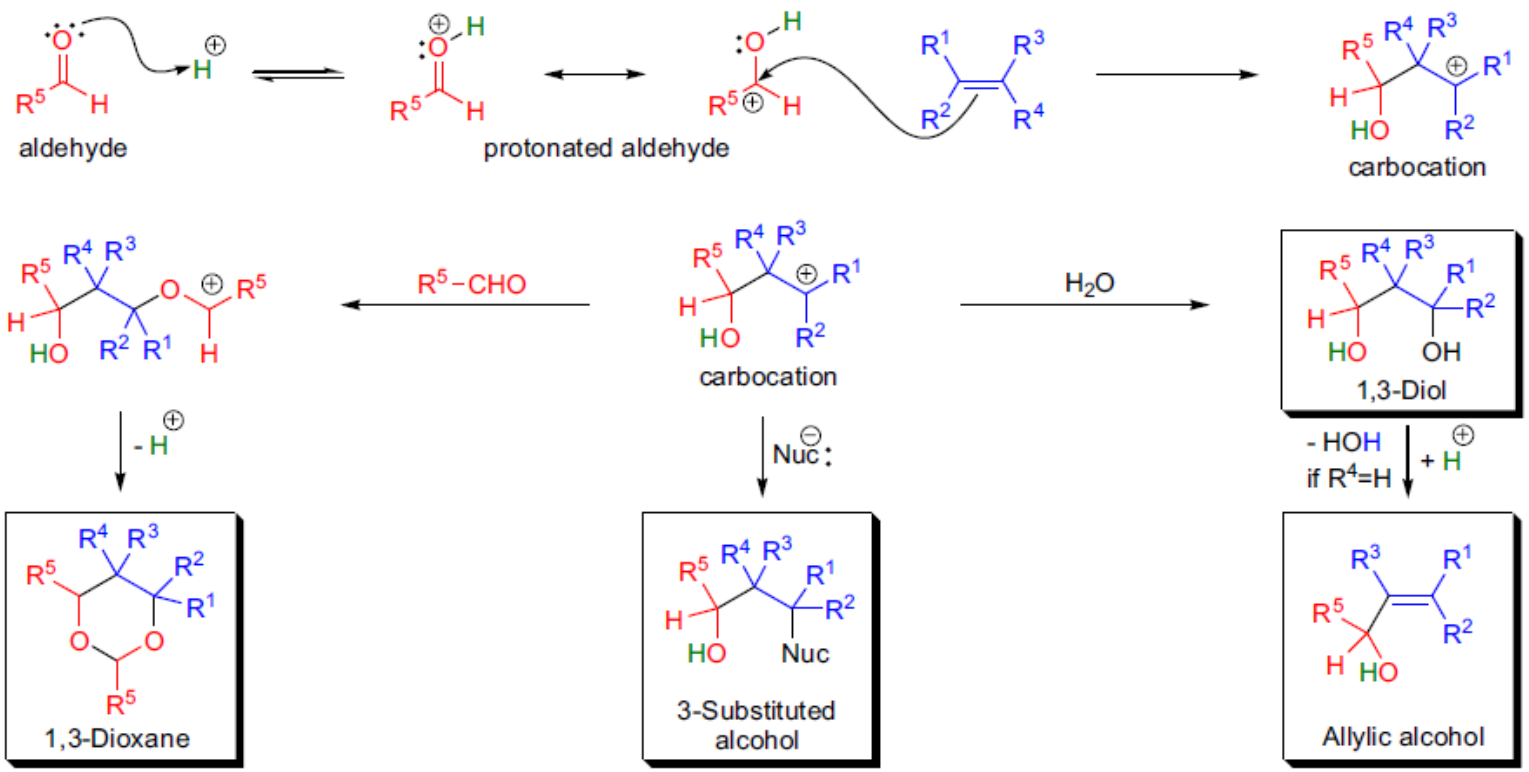
Discovery



R^{1-4} = H, alkyl, aryl, heteroaryl; R^5 = H, alkyl, aryl; protic acid: dilute aqueous H_2SO_4, HCl, H_3PO_4, HOCl, *p*-TsOH, HNO_3; Lewis acid: BF_3, $AlCl_3$, $ZnCl_2$, $TiCl_4$, cation-exhange resin; solvent: H_2O, ROH, benzene; nucleophile: could be the solvent or the conjugate base derived from the protic acid; other products: dienes, 1,3-dioxanes, 1,3-diols, etc.

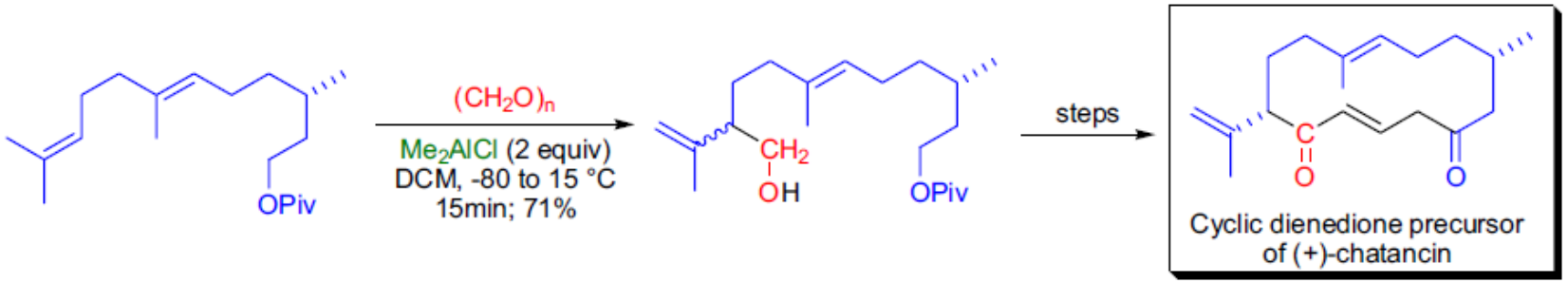
Mechanism

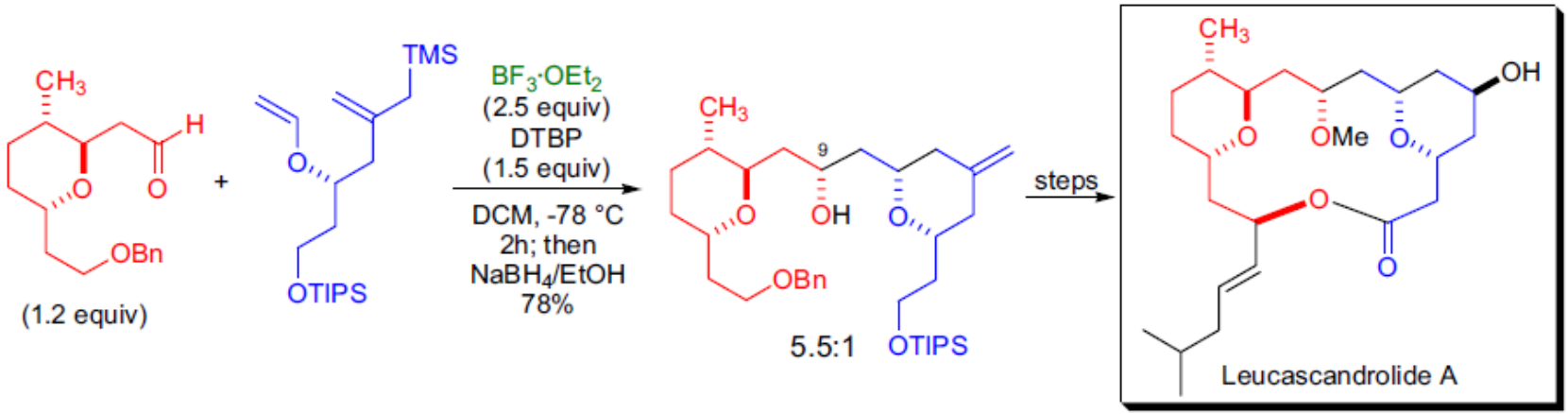

aldehyde
protonated aldehyde
carbocation
R5–CHO
H2O
carbocation
- H
Nuc:
- HOH
if R4=H
+ H
1,3-Diol
1,3-Dioxane
3-Substituted
alcohol
Allylic alcohol

General features

- Potentially a large number of different products can be formed;
- A variety of protic and Lewis acids may be used as catalyst;
- The reaction is fastest with formaldehyde and with highly substituted alkenes;
- *Marknovnikoff's rule*;
- Cyclic alkenes have *anti* stereochemistry due to neighboring group participation;
- *Carbonyl ene reaction* takes place when conducted under anhydrous conditions.

Synthetic applications





Synthetic applications