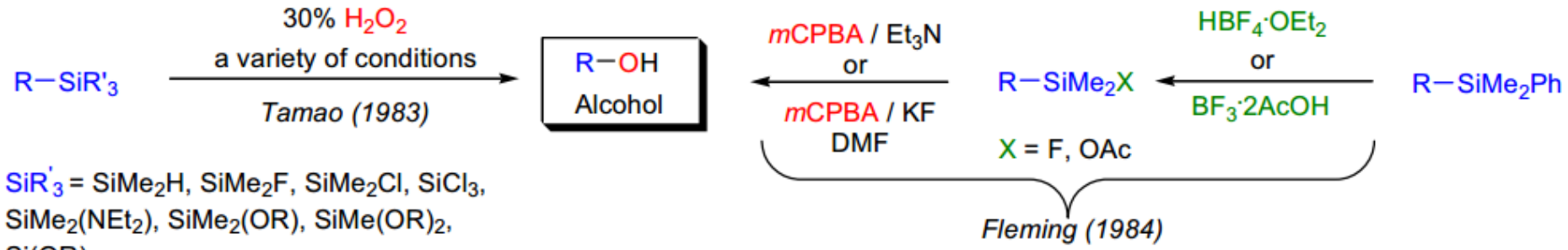
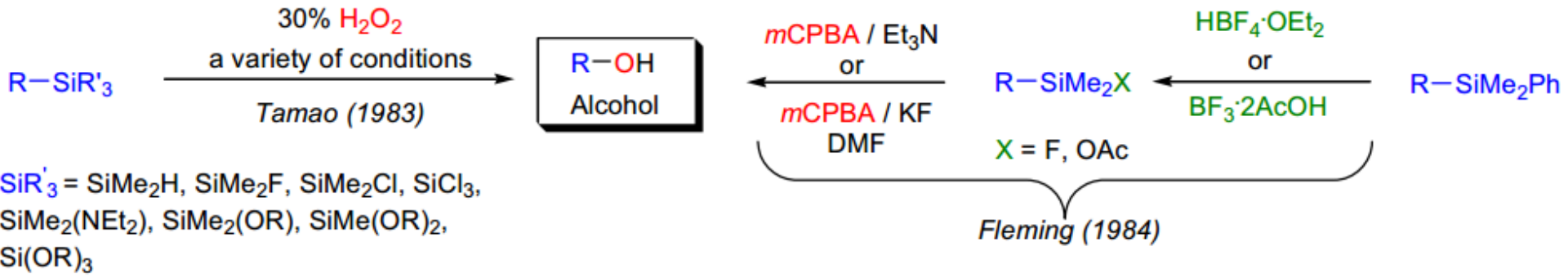
FLEMING-TAMAO OXIDATION



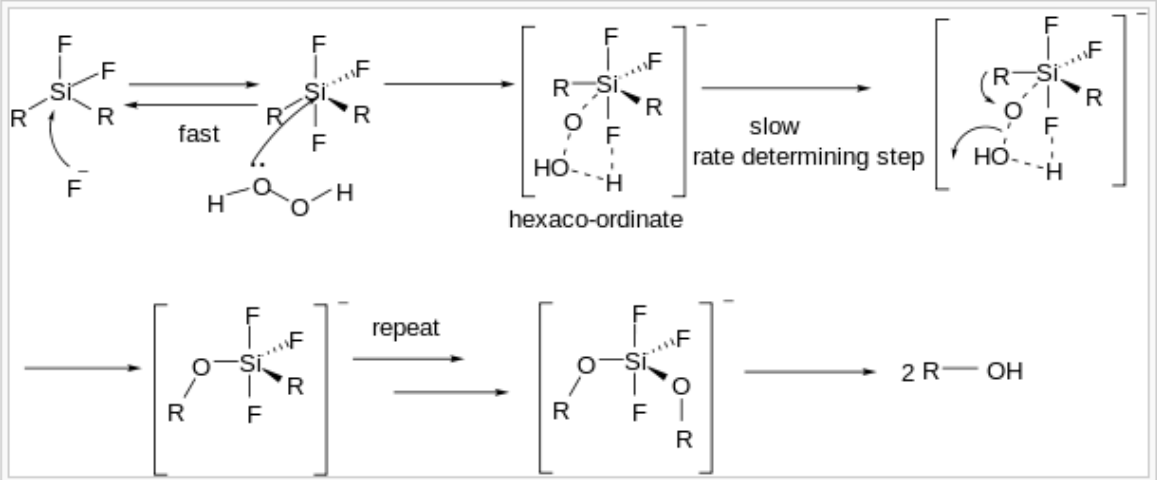
SiR'_3 = $SiMe_2H$, $SiMe_2F$, $SiMe_2Cl$, $SiCl_3$, $SiMe_2(NEt_2)$, $SiMe_2(OR)$, $SiMe(OR)_2$, $Si(OR)_3$



Advantages:

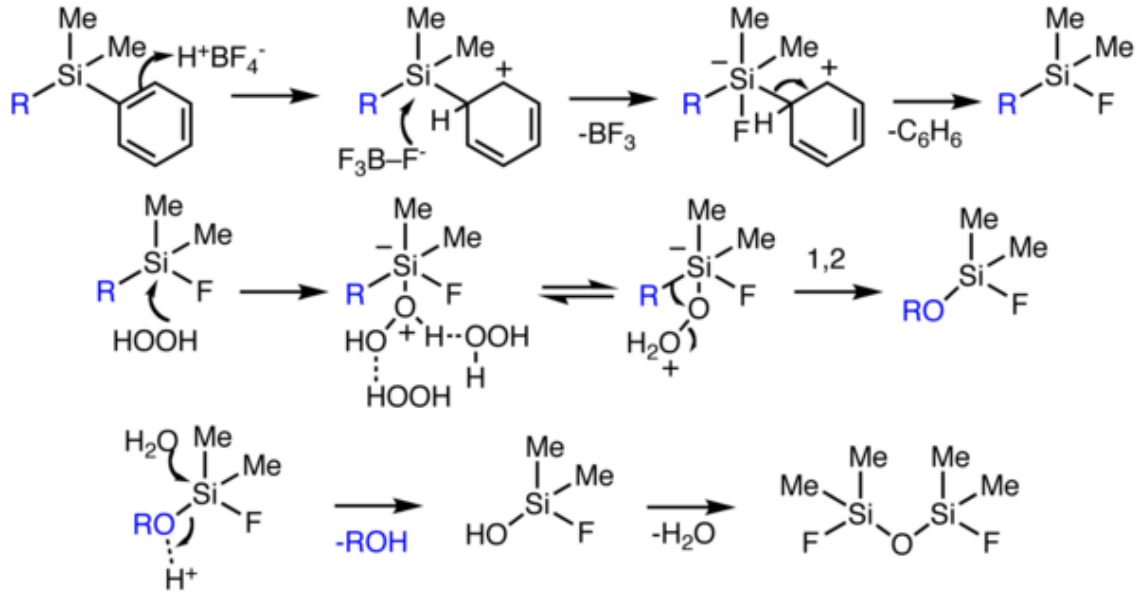
1) Phenylsilanes are more robust than alkoxysilanes.
2) Carbon-silicon bonds can be introduced stereospecifically.
3) The oxidation conditions are mild enough to tolerate a wide range of functional groups even in complex substrates.
4) The two-step reaction can also be conducted in one-pot by using Hg^{2+} or Br^{+} as electrophiles.

Mechanism of Tamao oxidation

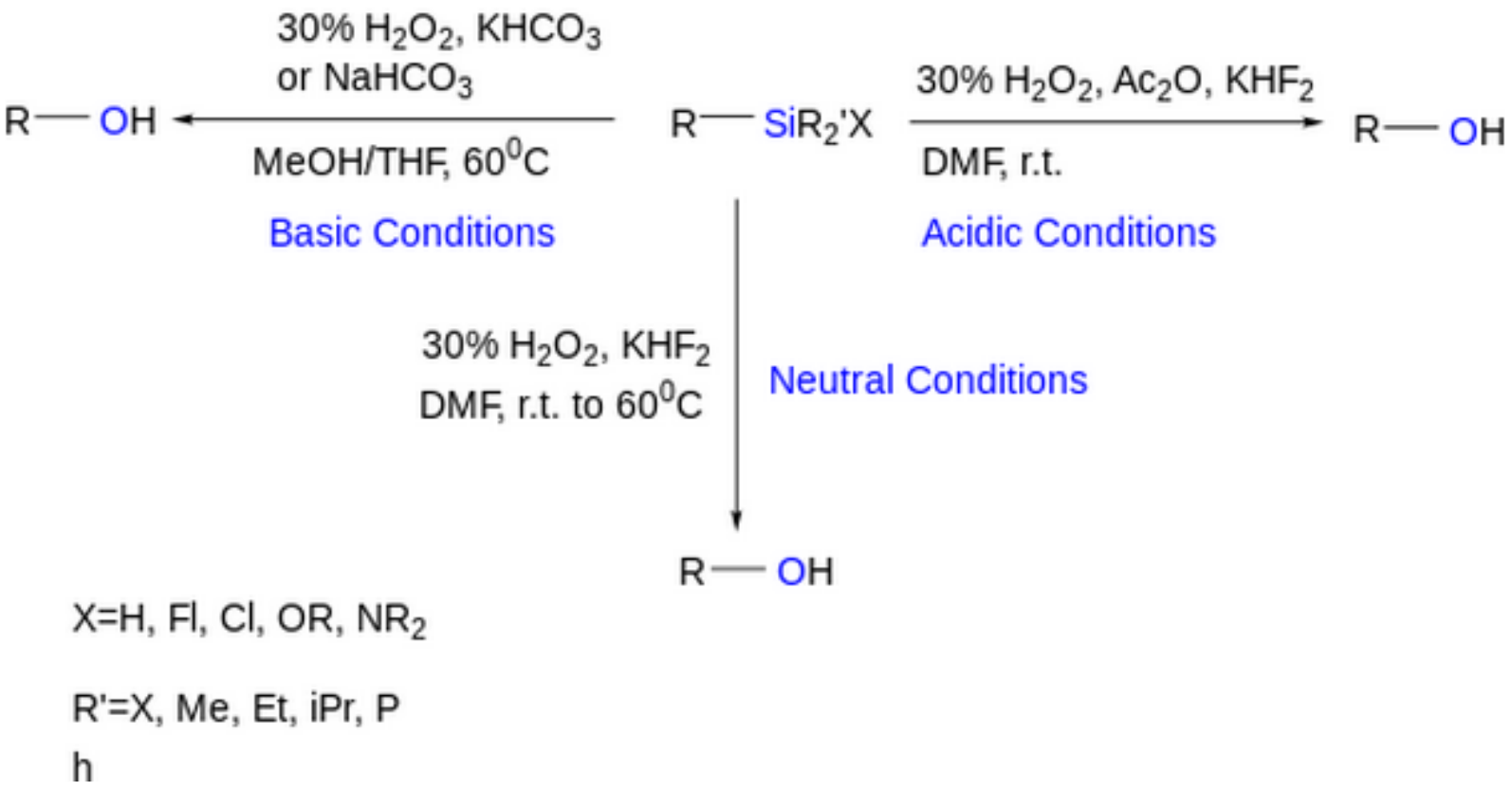


Mechanism of Tamao oxidation

Mechanism of Fleming oxidation



Tamao oxidation



X=H, Fl, Cl, OR, NR_2

R'=X, Me, Et, iPr, P

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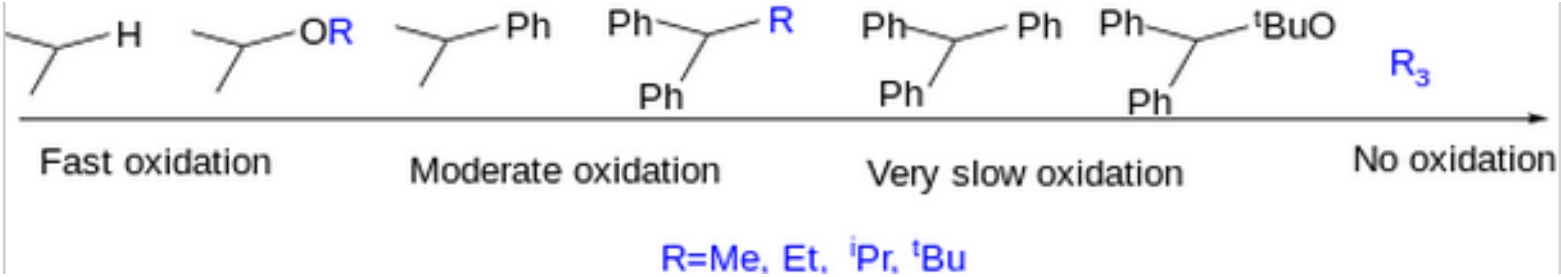
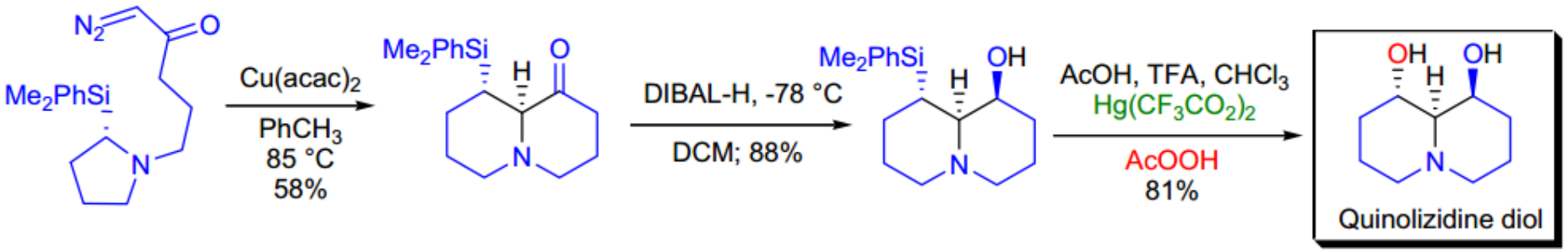
Disadvantages

1) The oxidation of silyl groups attached to tertiary carbons of cyclic systems do not always proceed with ease;

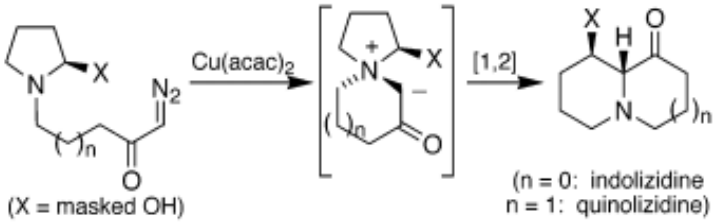


2) In the presence of tertiary amines, special conditions are required to avoid N-oxide formation.

In the laboratory of F.G. West, the stereoselective *silyl-directed [1,2]-Stevens rearrangement* of ammonium ylides was investigated as a potential key step toward the enantioselective synthesis of various hydroxylated quinolizidines.[19] The dimethylphenylsilyl group served as a surrogate for one of the hydroxyl groups in the product. The *Fleming-Tamao oxidation* was performed under Denmark's conditions to avoid oxidation of the tertiary amine to the corresponding *N*-oxide, and the desired quinolizidine diol was obtained in 81% yield.[17]



Scheme 1



It was discovered that *N*-oxide production could be controlled by conducting the oxidation at room temperature rather than the standard 50 °C protocol.

Synthetic Applications

The synthesis of the C1-C21 subunit of the protein phosphatase inhibitor tautomycin was accomplished by J.A. Marshall et al.[22] During the last steps of the synthetic sequence, the *hydrosilylation* of a terminal alkyne afforded a five-membered siloxane that was oxidized by the *Fleming-Tamao oxidation*. The initially formed enol tautomerized to the corresponding methyl ketone.