Reaction Mechanism

(CHEM-563)

Online Lecture-10 (Week-4)

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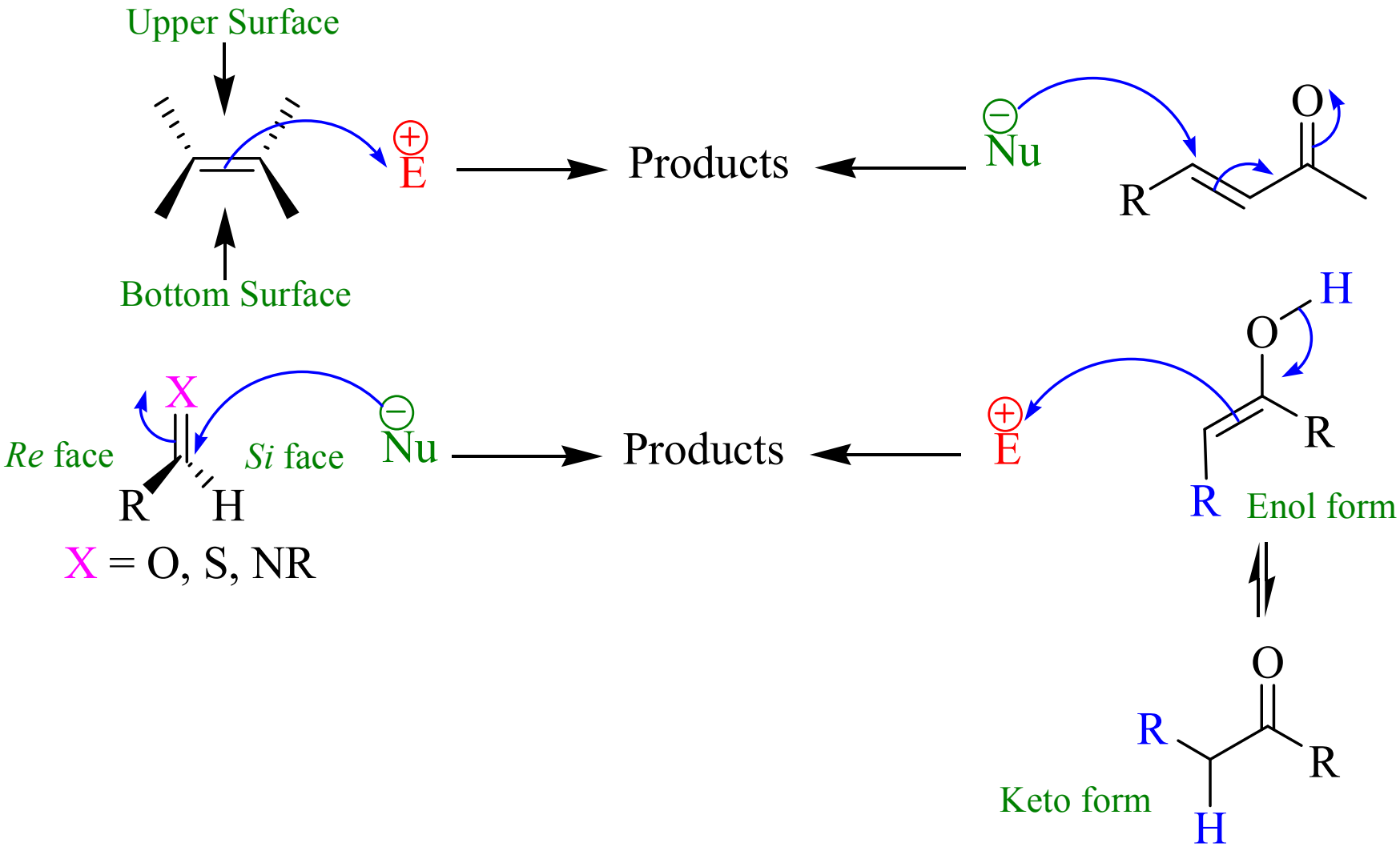
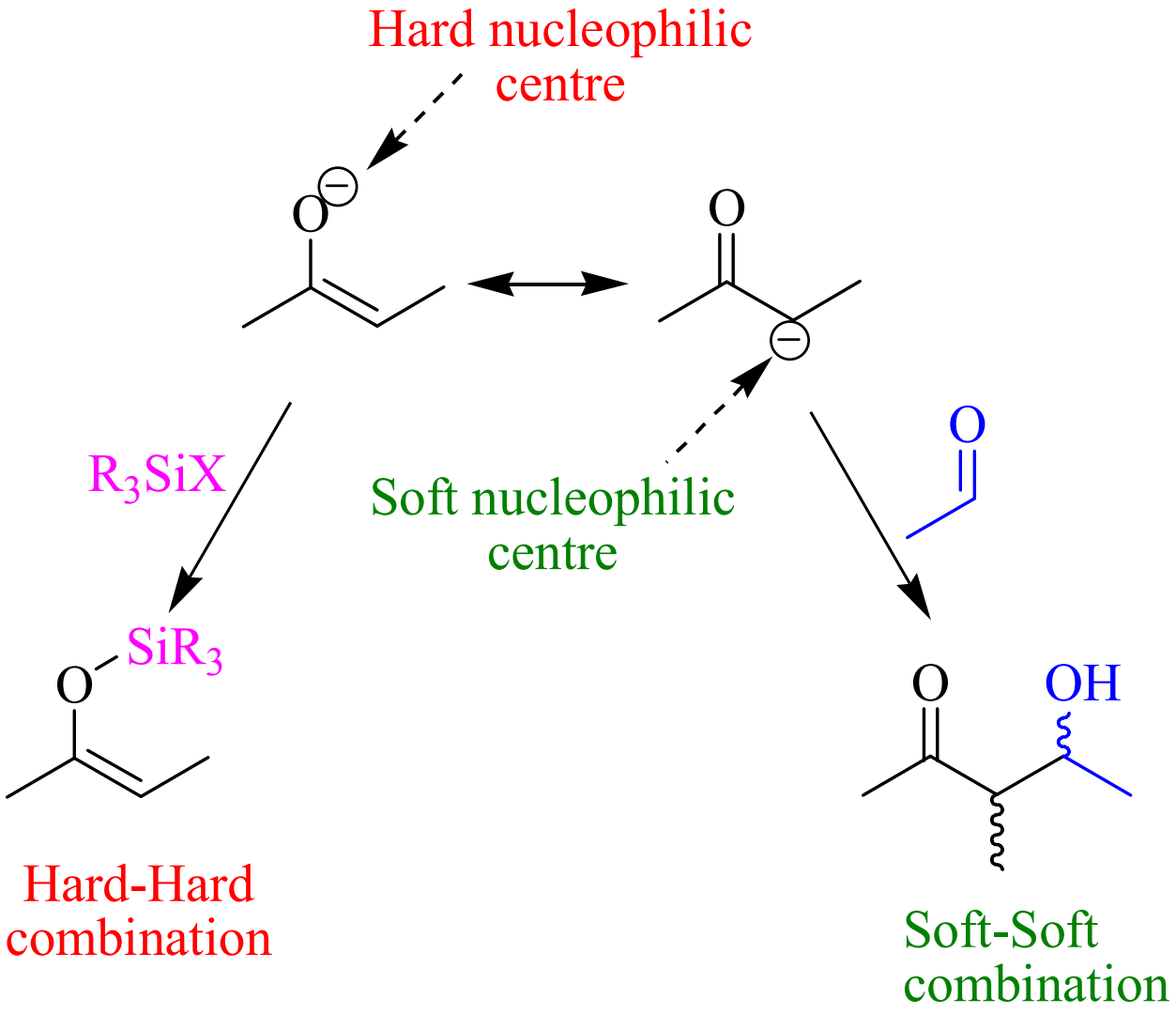
Addition Reactions



Soft *vs* Hard Electrophilic Centres

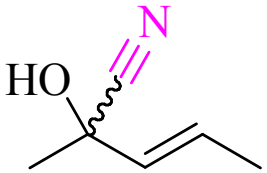


Factors Affecting 1,2/1,4-Addition

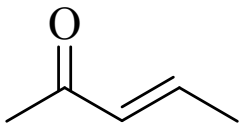
- The reaction conditions (Kinetically / Thermodynamically controlled reactions)
- Type of Nucleophile (Hard / soft)
- Nature (Functional group) of carbonyl
- Steric Factor
- Nature of Organometallic

Reaction Conditions

1,2 / direct addition

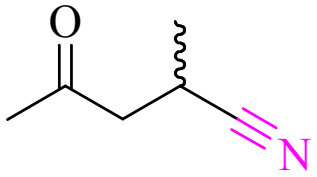


NaCN / HCN
5-10 °C
(60 min)



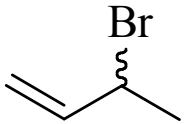
1,4 / conjugate addition

NaCN / HCN
80 °C (8 h)



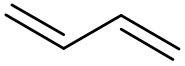
1. Fast but revirsible
2. Steric factor applies
3. Transition state is important

1. Slow but irrevirsible
2. Stability of reactants, product(s) or intermediate is important

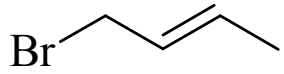


Monosubstituted C=C

HBr
25 °C (30 min)

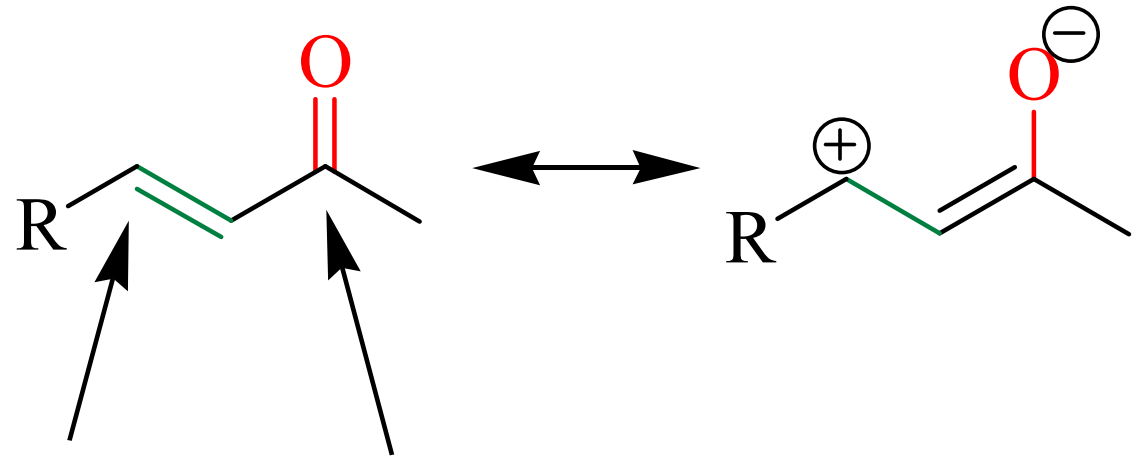


HBr
60 °C (5 h)



Disubstituted C=C

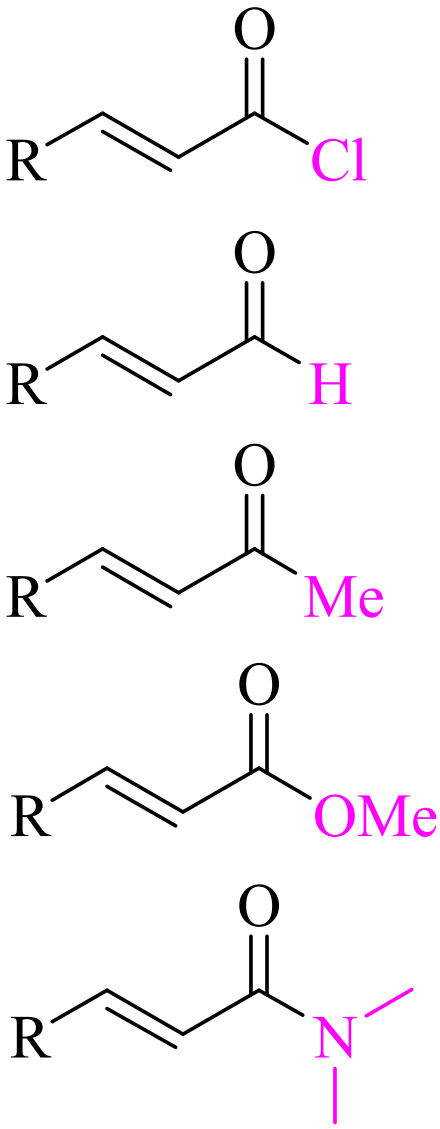
Type of Nucleophiles



Soft Nucleophiles
(I^-, RS^-, RSe^-, S^{2-}, RSH, R_3P, Aromatic rings)

Hard Nucleophiles
(F^-, ^-OH, OR, H_2O, ROH, ^-Cl, NH_3, RMgBr, RLi)

Nature of Carbonyl

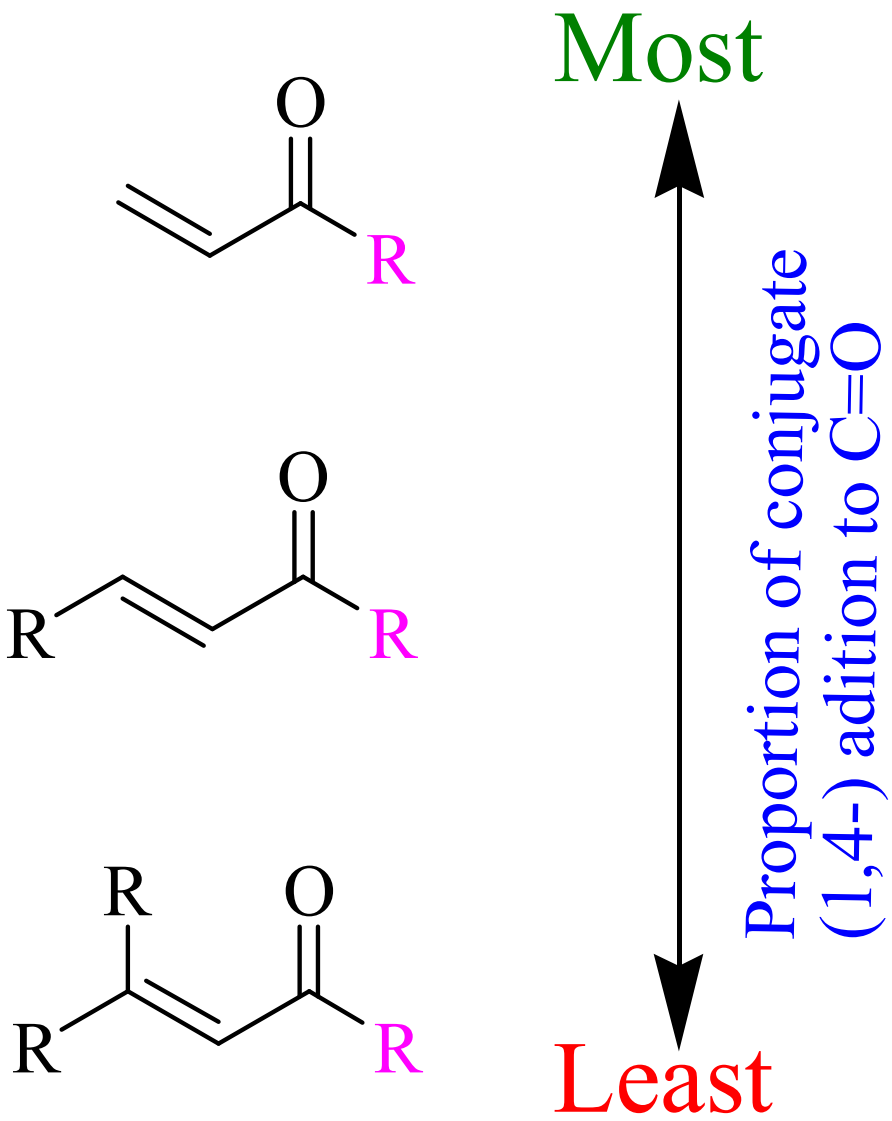


Most

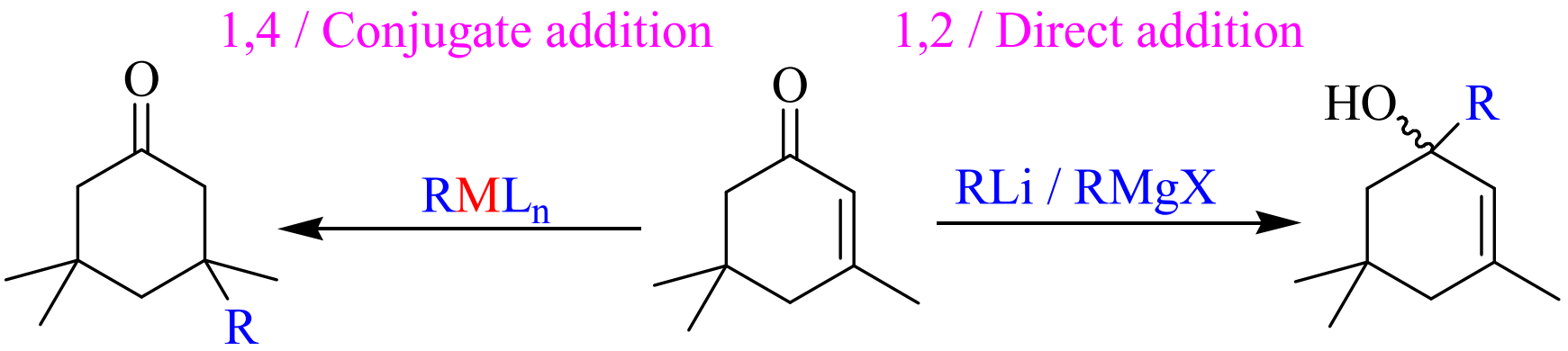
Proportion of direct (1,2-) adition to C=O

Least

Steric Factor

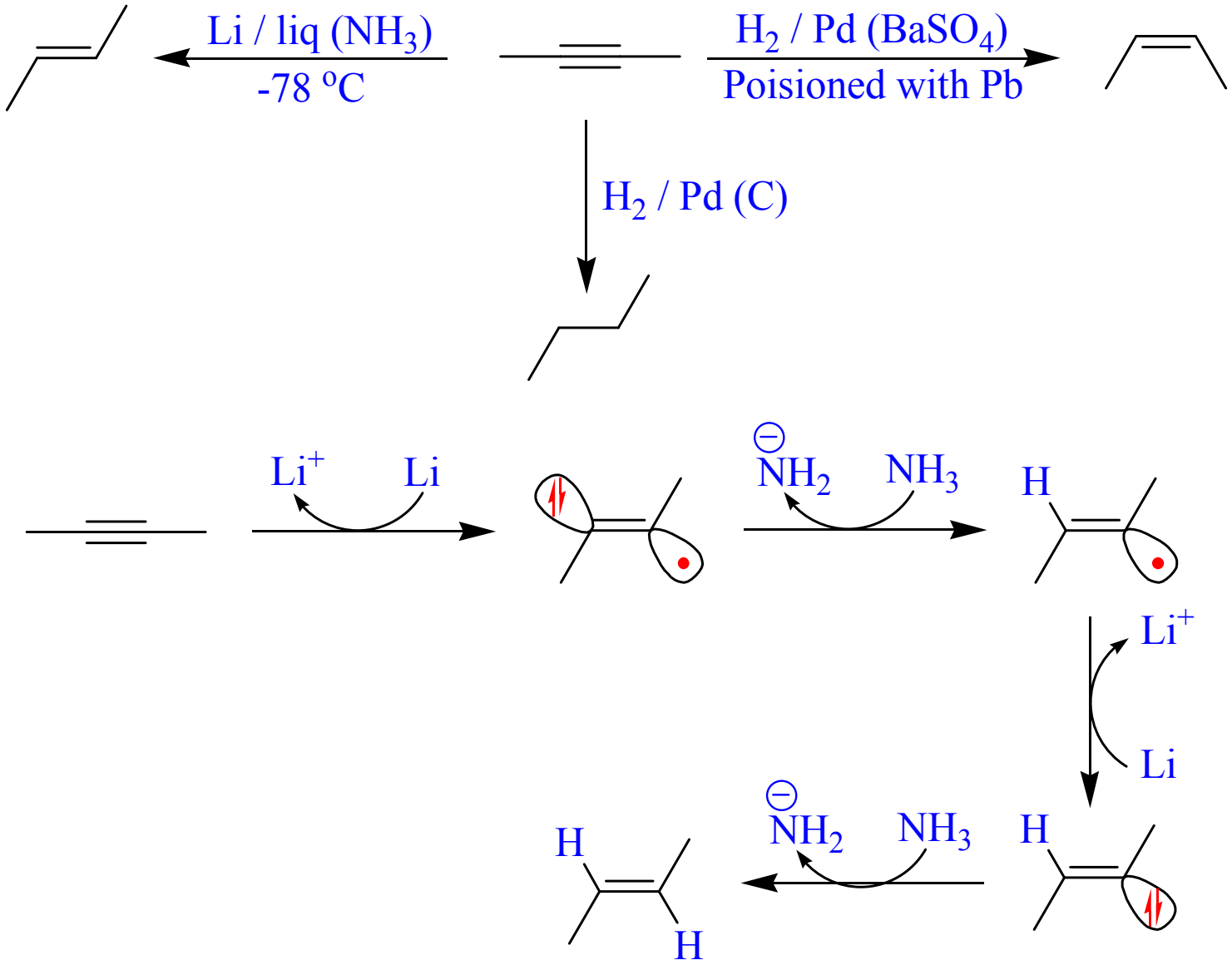


Nature of Organometallic



M = Cu^{1+}, Zn^{2+}, Pd^{2+}, Sn^{4+}
Ru^{2+}, Rh^{2+} etc.

Addition to Alkynes



Suggested Reading

i) Chapter 19 (Page 446 to 447)
ii) Chapter 20 (Page 449 to 459)
of "Organic Chemistry" by Clayden, J; Greeves, N; Warren, S., 2nd Edition, Oxford University Press, England (2008)