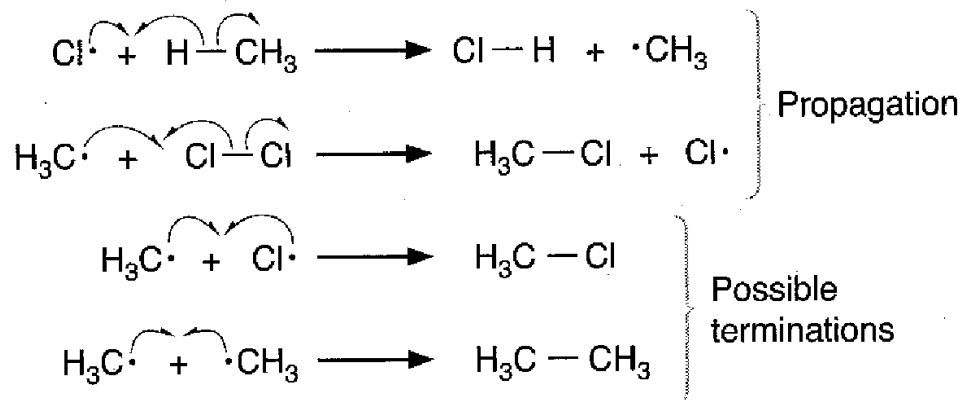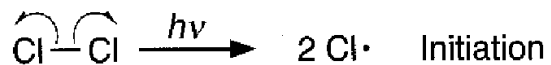# RADICAL SUBSTITUION REACTIONS

Mechanism

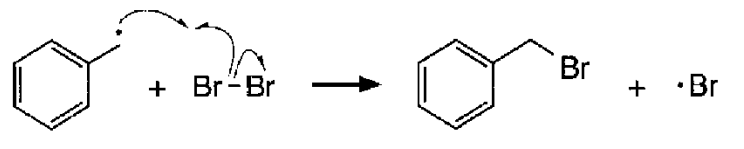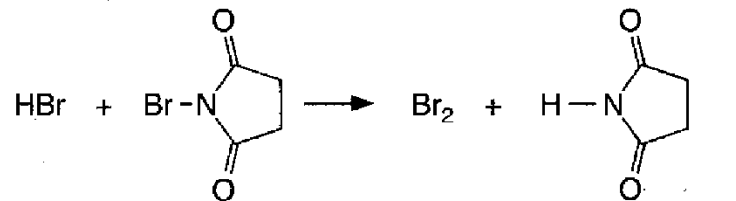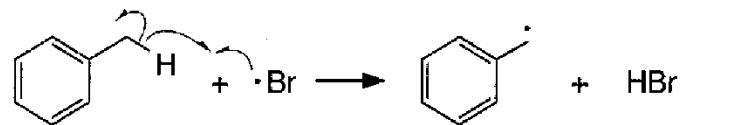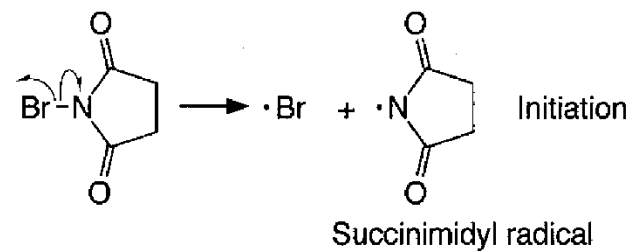**Relative Rates of Hydrogen Abstraction by Various Radicals***

Radical	Temperature (°C)	1° C–H	2° C–H	3° C–H
F•	25	1	1.2	1.4
Cl•	25	1	4	6
Br•	40	1	200	19000
H•	35	1	5	40
CH$_3$•	110	1	4	46
Ph•	60	1	9	47

Approximate Activation Energies for Free Radical Halogenations (kcal/mol)*

	1° C–H	2° C–H	3° C–H
Radical	E_a	E_a	E_a
F•	0	0	0
Cl•	1	0.5	0
Br•	13	10	7

Initiation

Succinimidyl radical

Propagation

PINACOL-PINACOLONE REARRANGEMENT

Mechanism
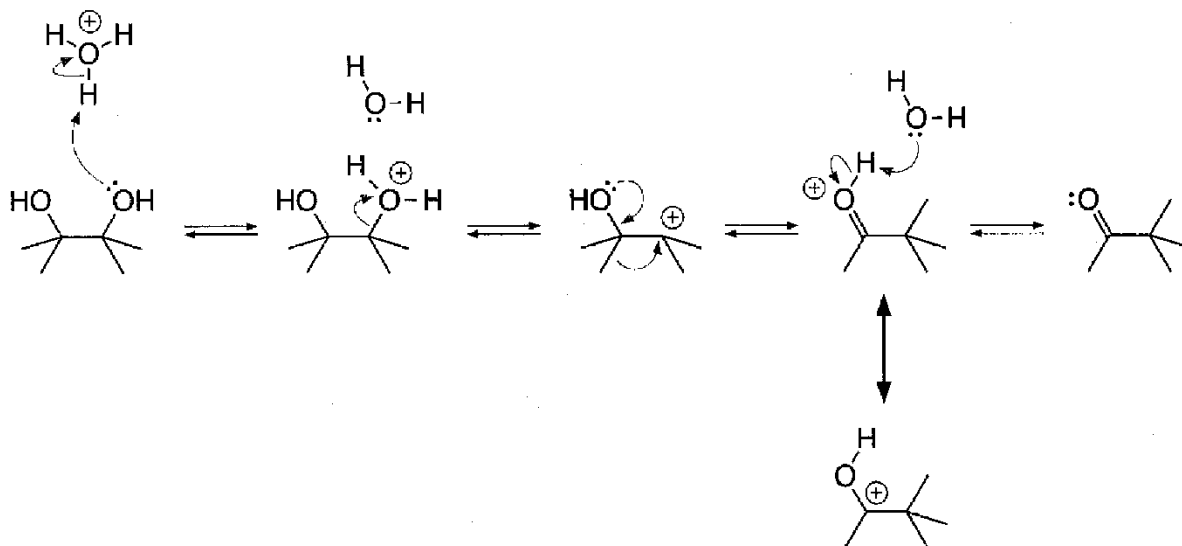
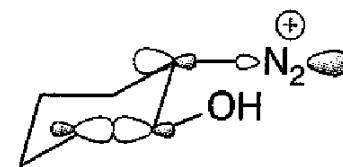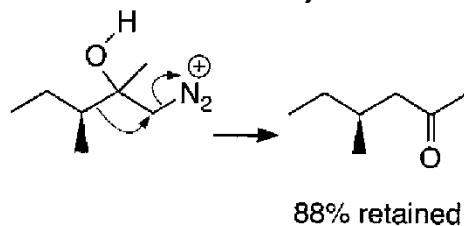
Migratory Aptitude

Relative Migratory Aptitudes in the Pinacol Rearrangement*

R group	Migratory aptitude
p-Methoxyphenyl	500
p-Tolyl	15.7
p-Biphenyl	11.5
m-Tolyl	1.95
m-Methoxyphenyl	1.6
Phenyl	1.0
p-Chlorophenyl	0.66

Stereochemistry

88% retained
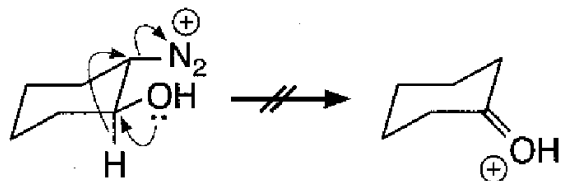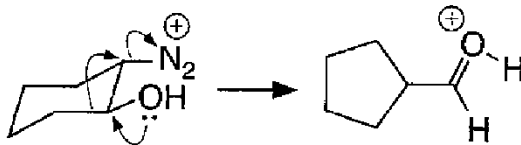
Orbital alignment

OXIDATIVE ADDITION

$$M \quad + \quad X-Y \quad \longrightarrow \quad X-M-Y$$

Stereochemistry of the Metal Complex
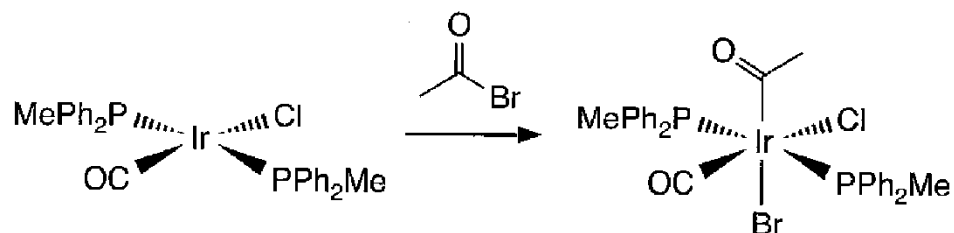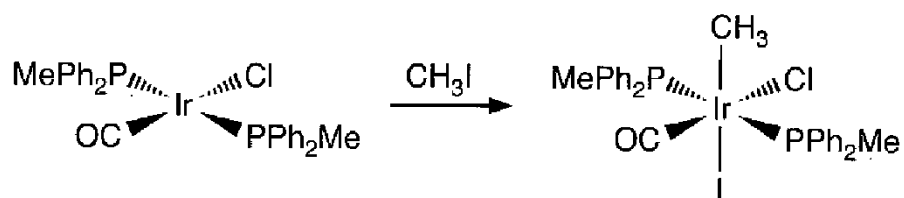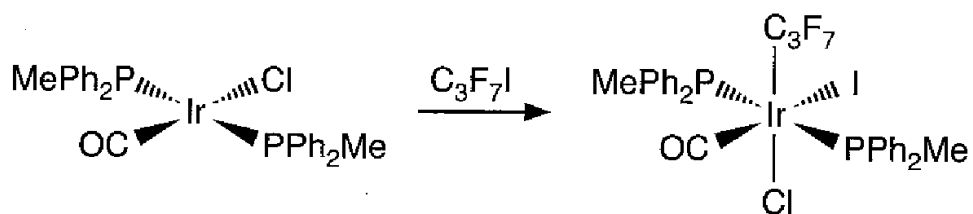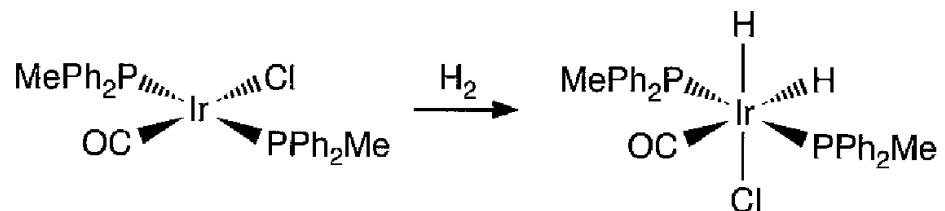
The kinetics as a function of ligands, R group, X group, and solvent can be very informative as to the mechanism. For example, the reaction given in Eq. 12.18 has been explored in detail. The reaction is second order, first order in both the metal complex and CH_3X for all concentrations of these reactants. Hence, both reactants are involved at or prior to the rate-determining step. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are 5–9 kcal/mol (depending upon X) and –50 eu, respectively. The very negative entropy of activation supports a highly ordered transition state with a loss of translational freedom, and is in the same range as that for S_N2 reactions.