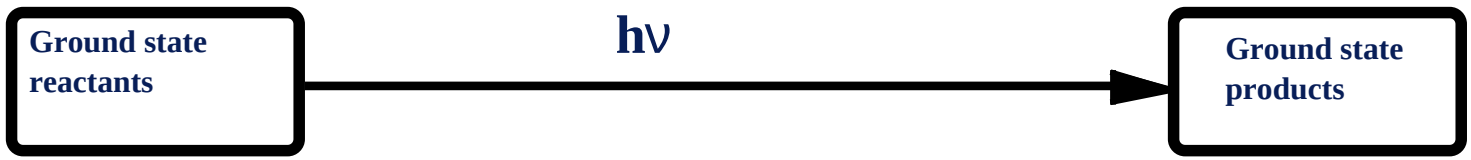
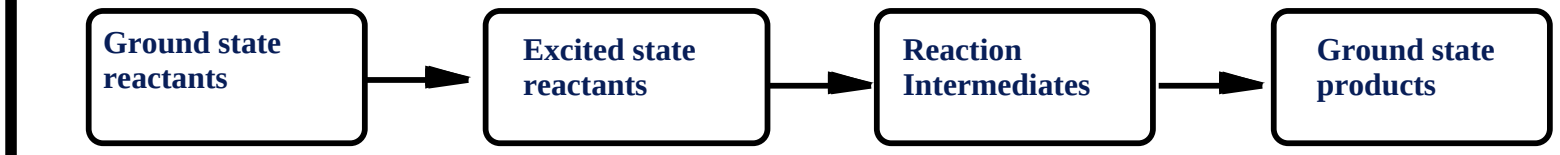
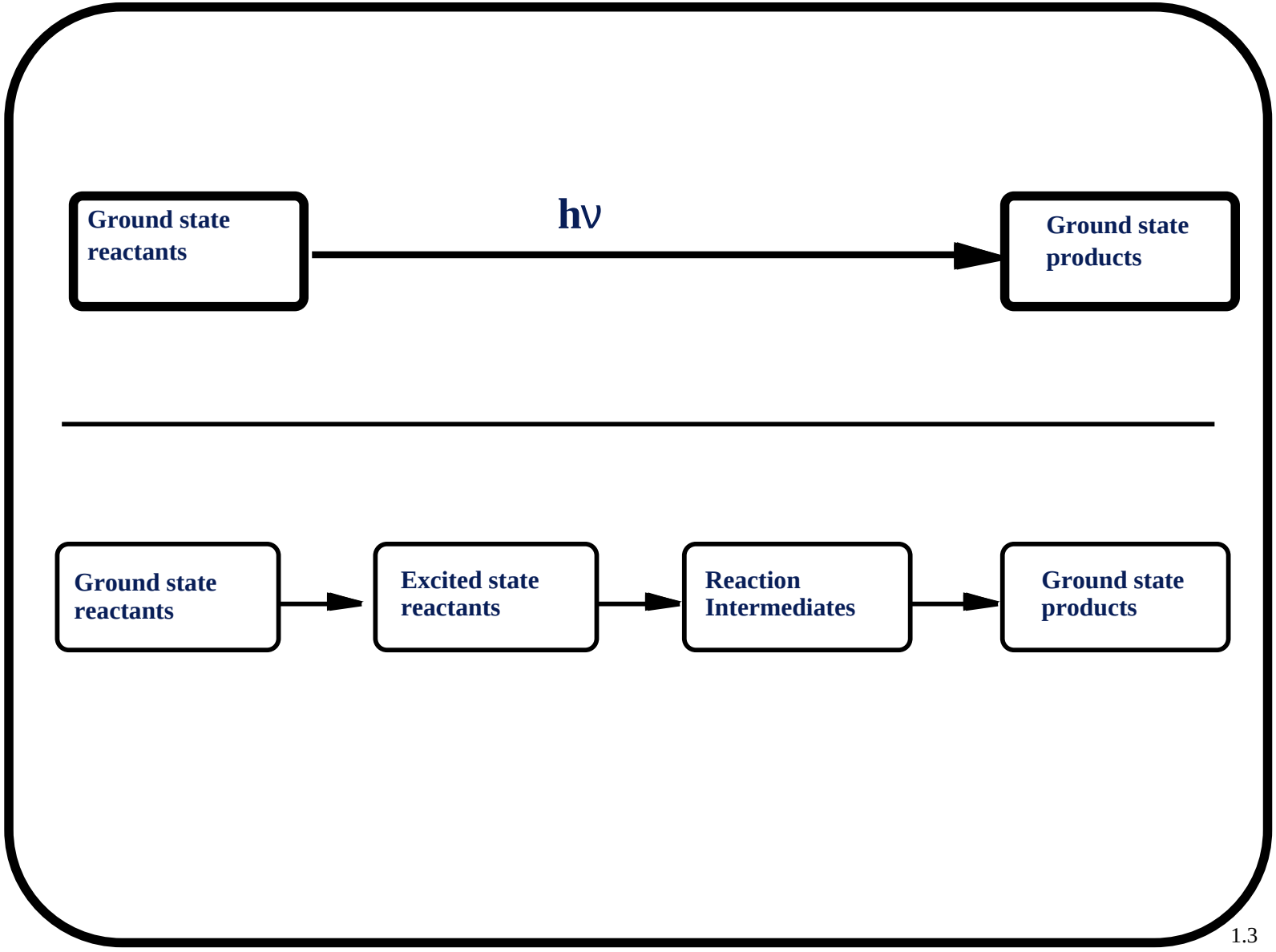
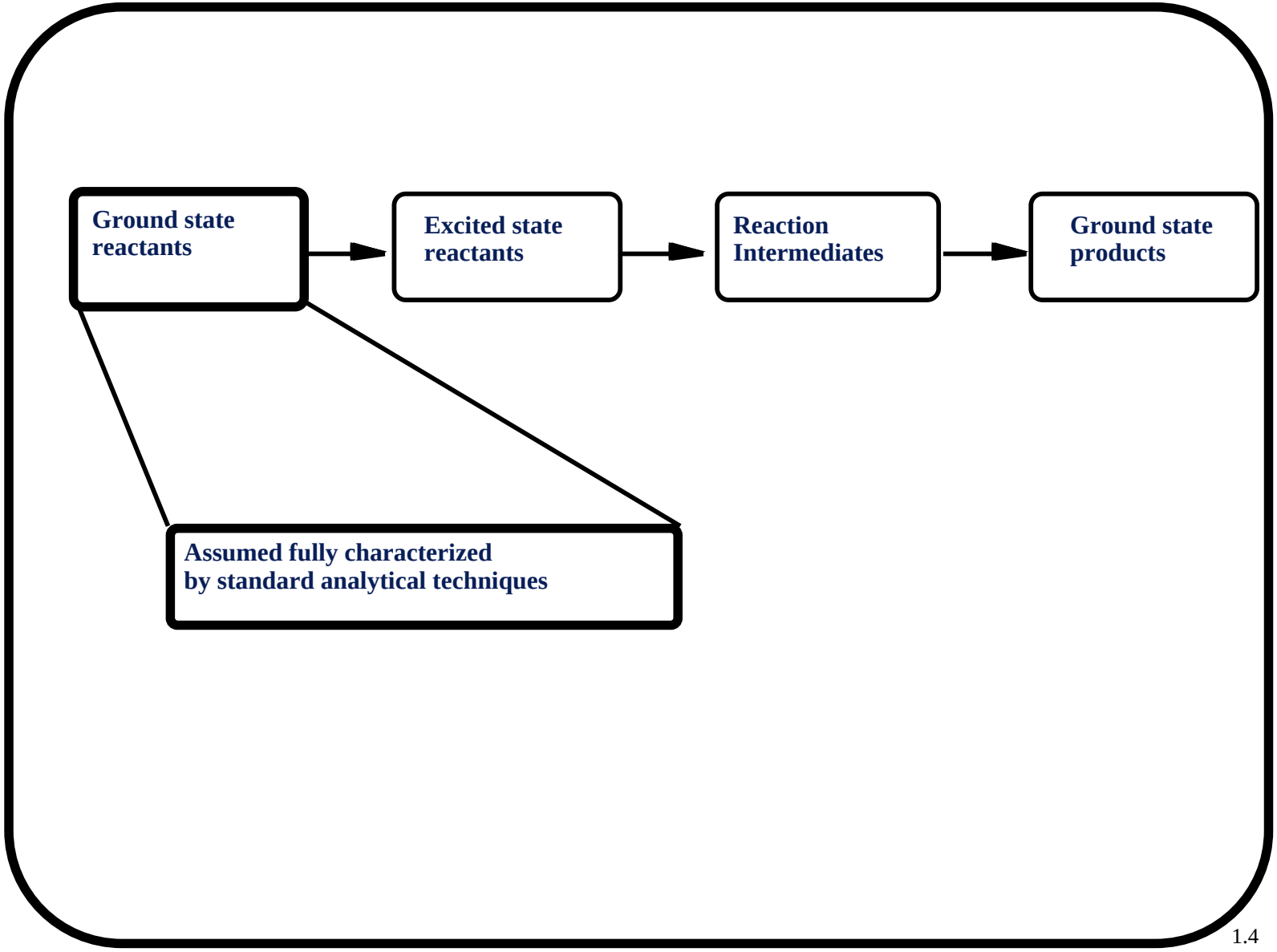


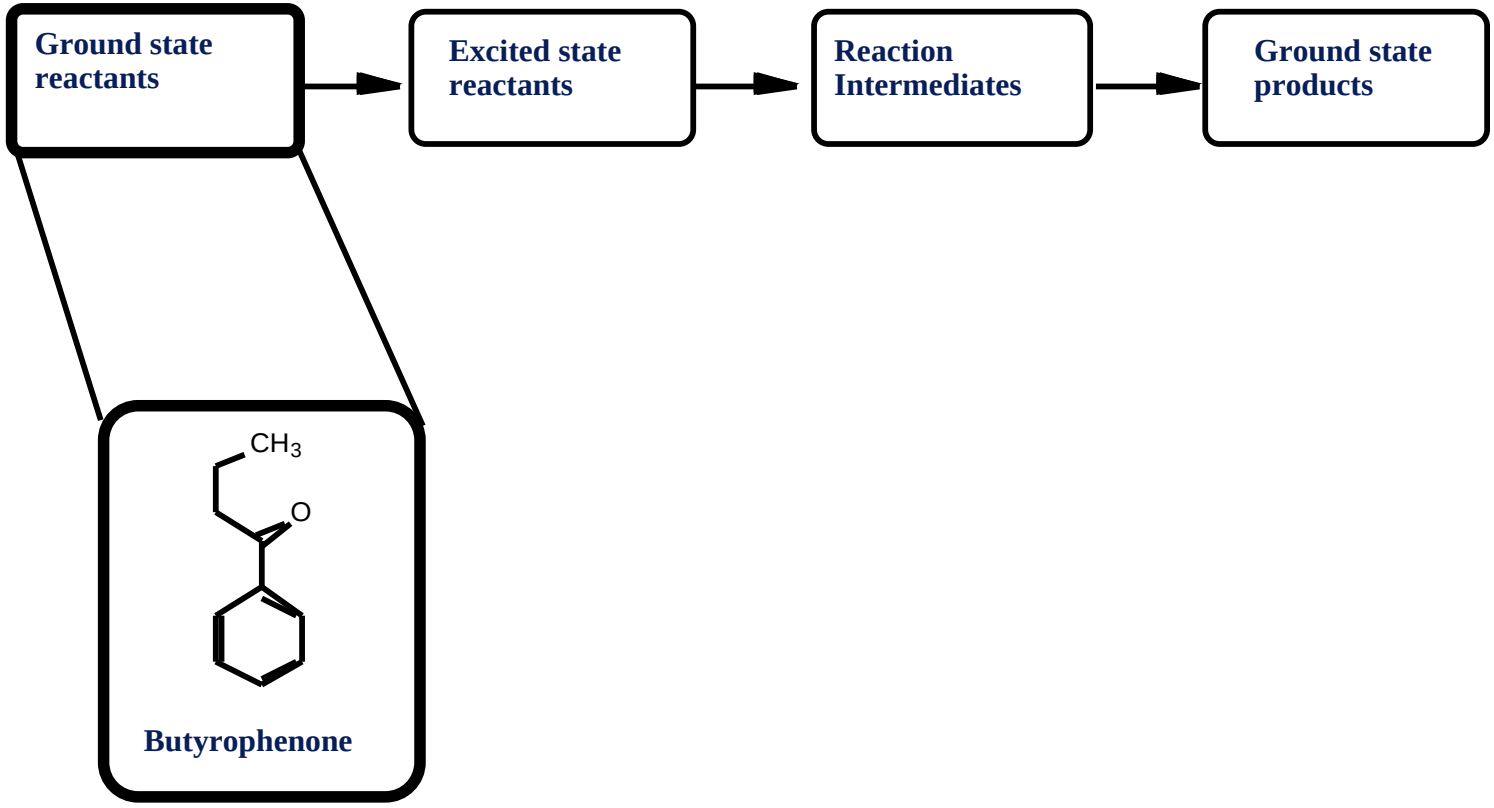
The overall reaction

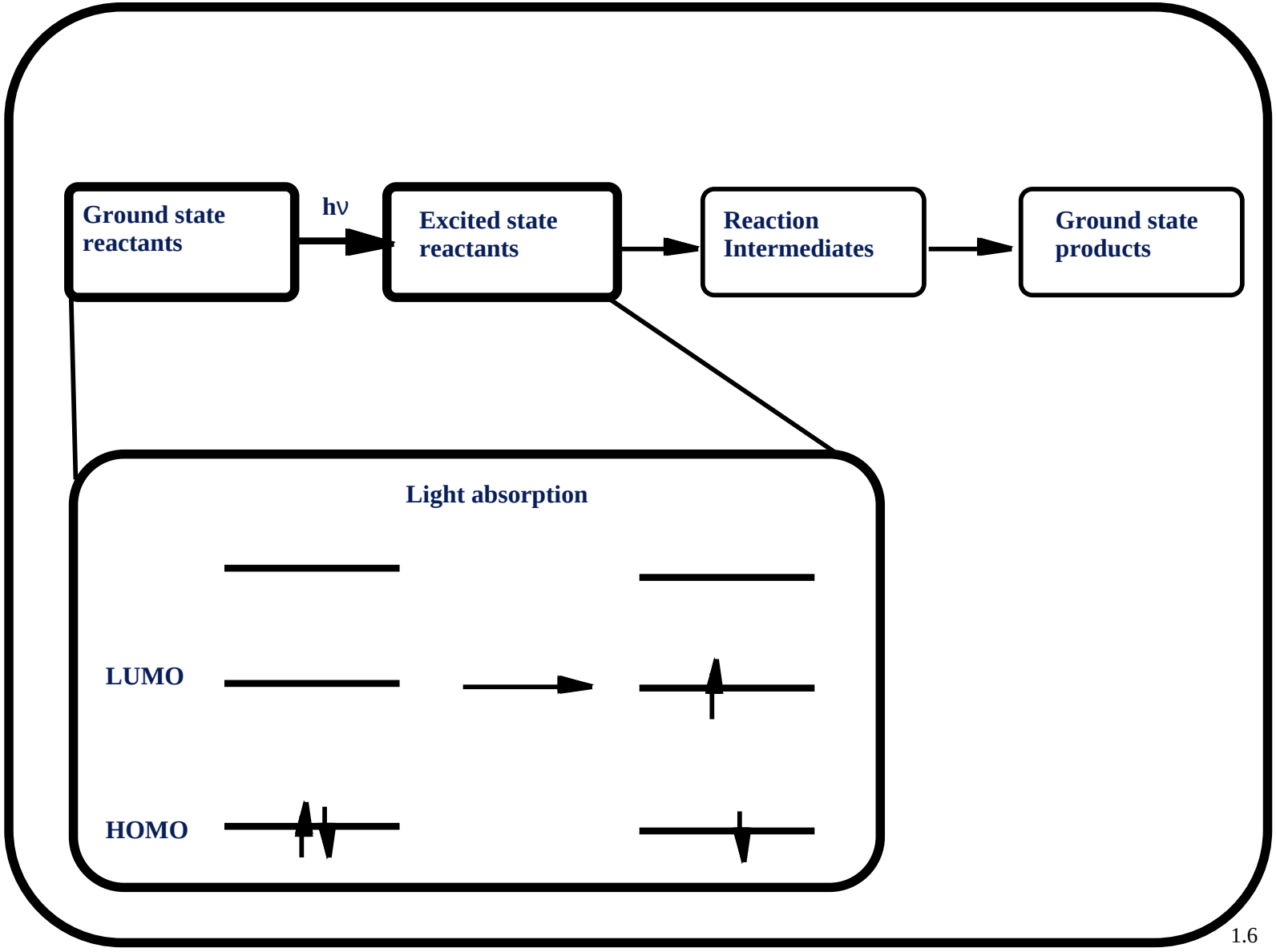

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products

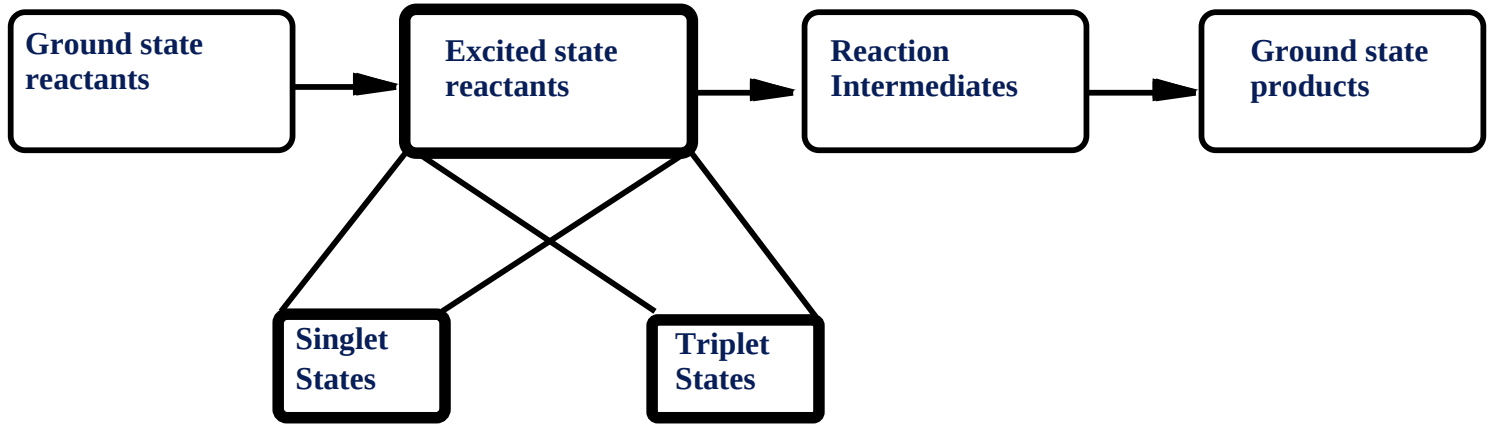

Ground state reactants
hν
Ground state products
Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products

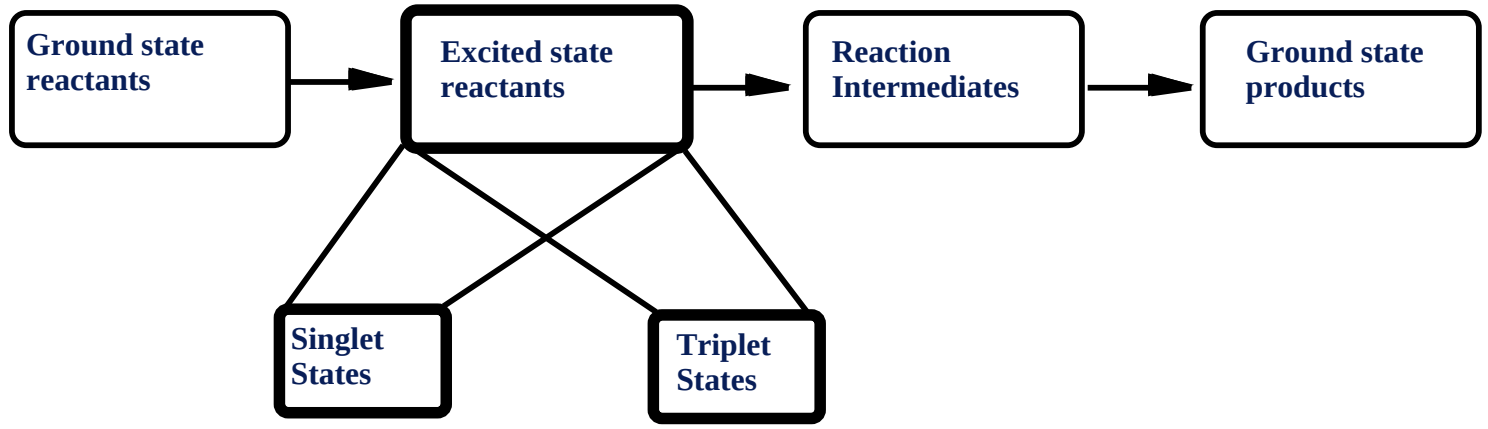

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Assumed fully characterized by standard analytical techniques

EXAMPLE

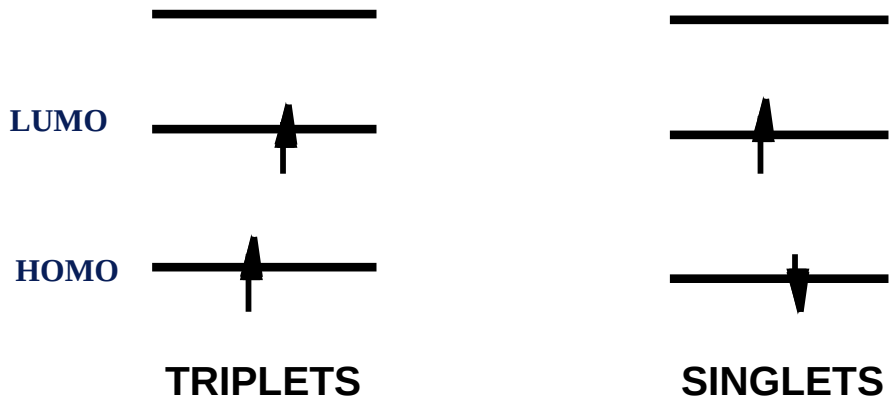

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
CH3
O
Butyrophenone

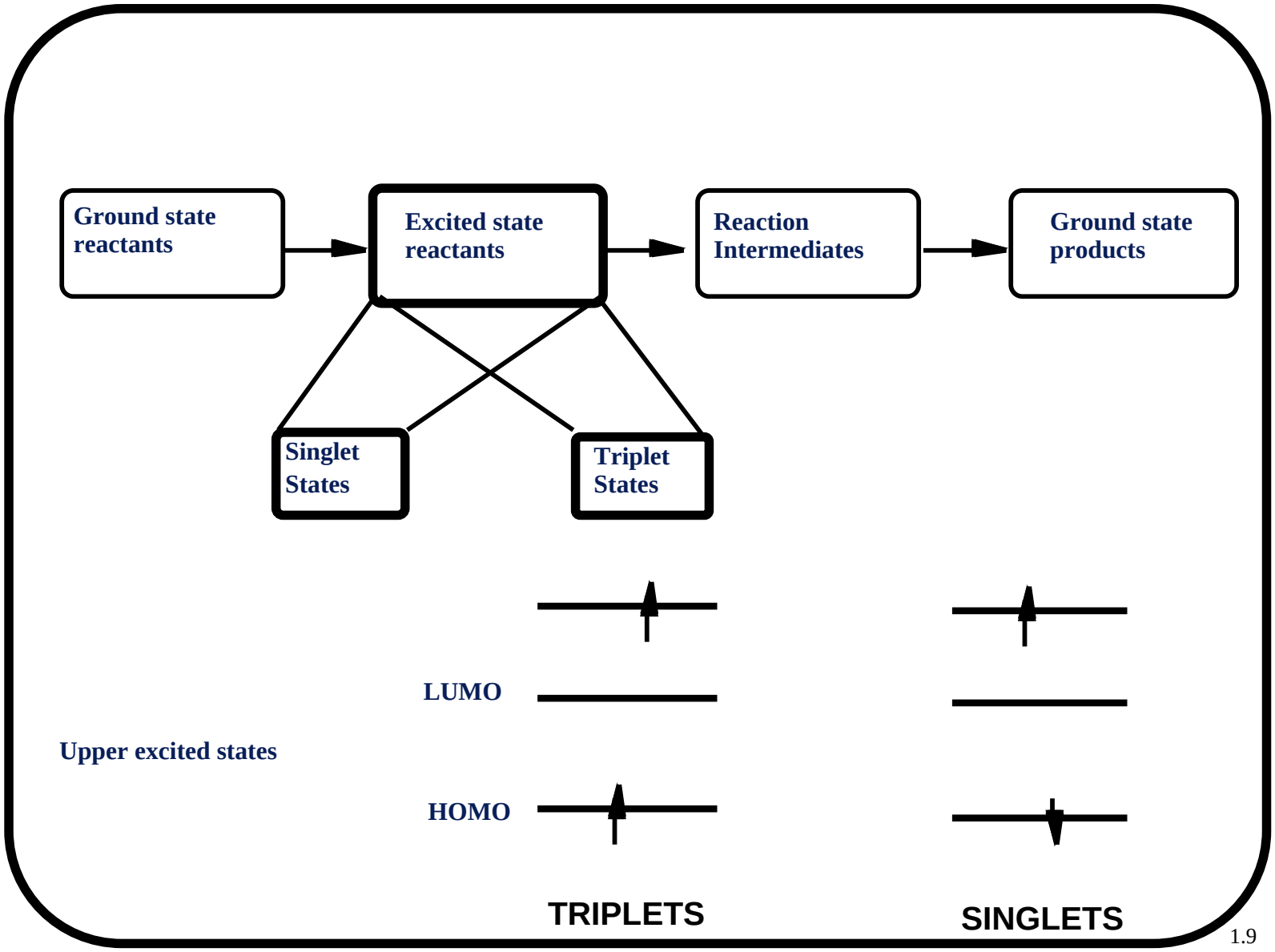

Ground state reactants
hν
Excited state reactants
Reaction Intermediates
Ground state products
Light absorption
LUMO
HOMO

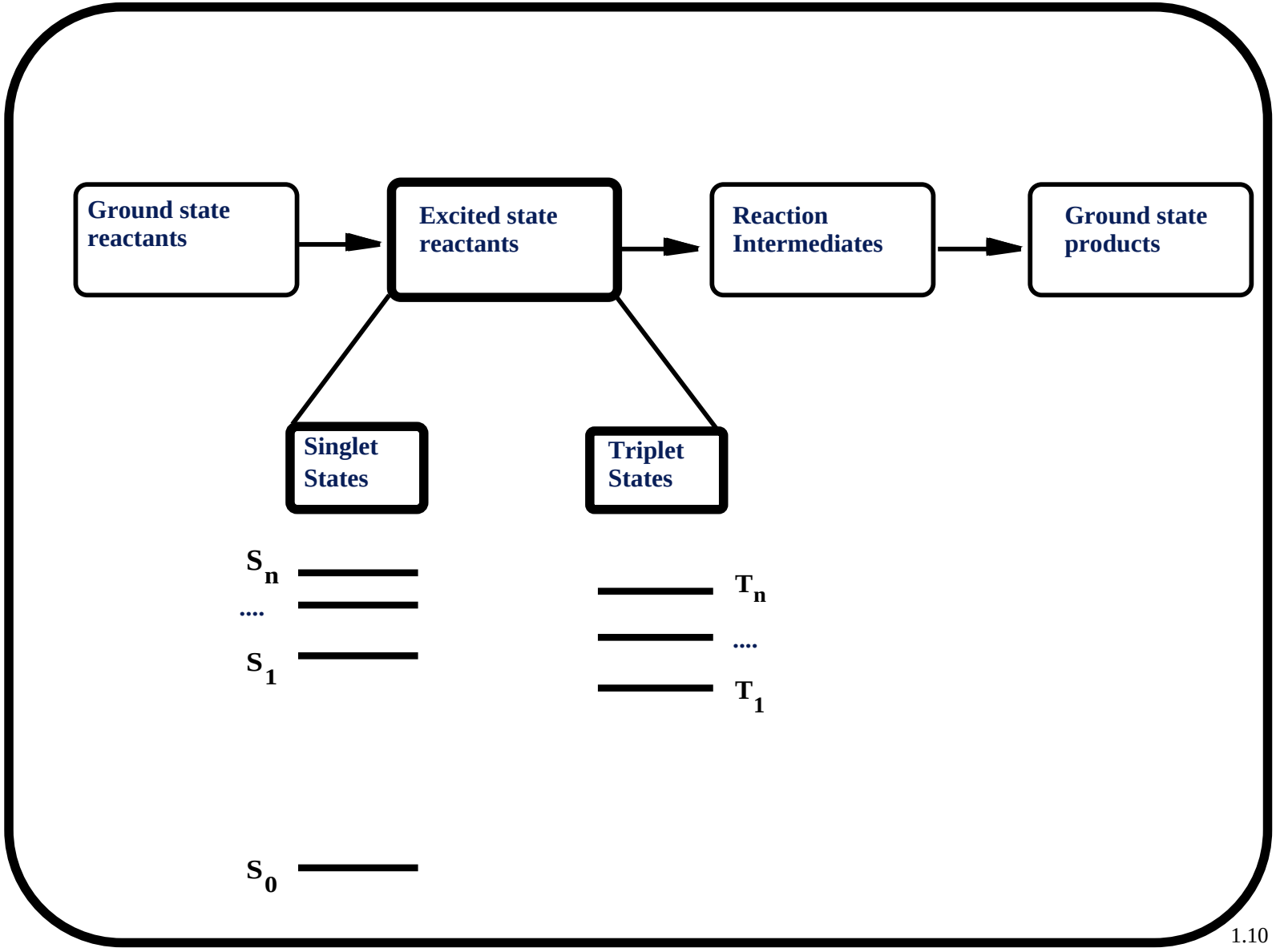

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Singlet States
Triplet States

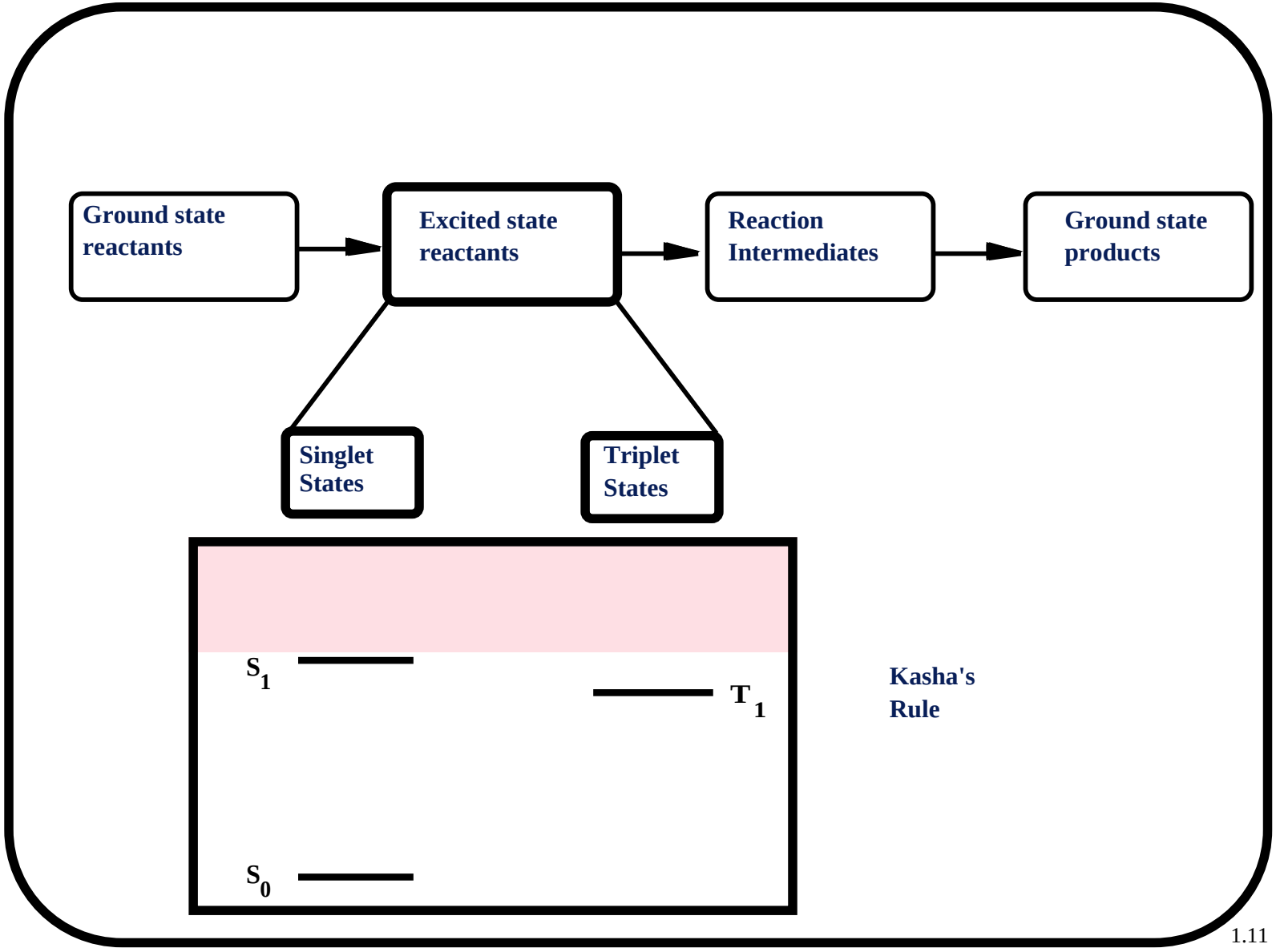


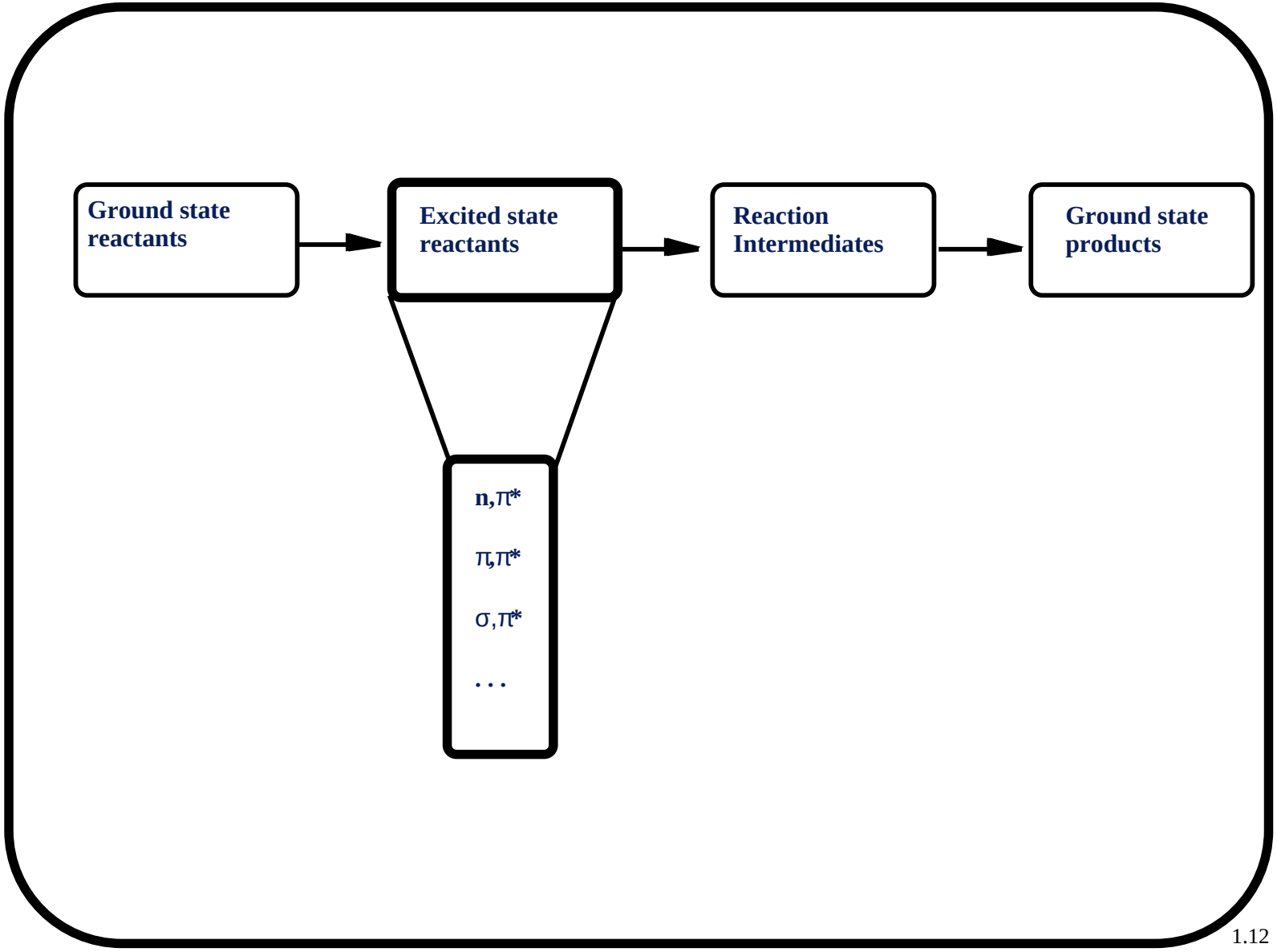
Lowest excited states

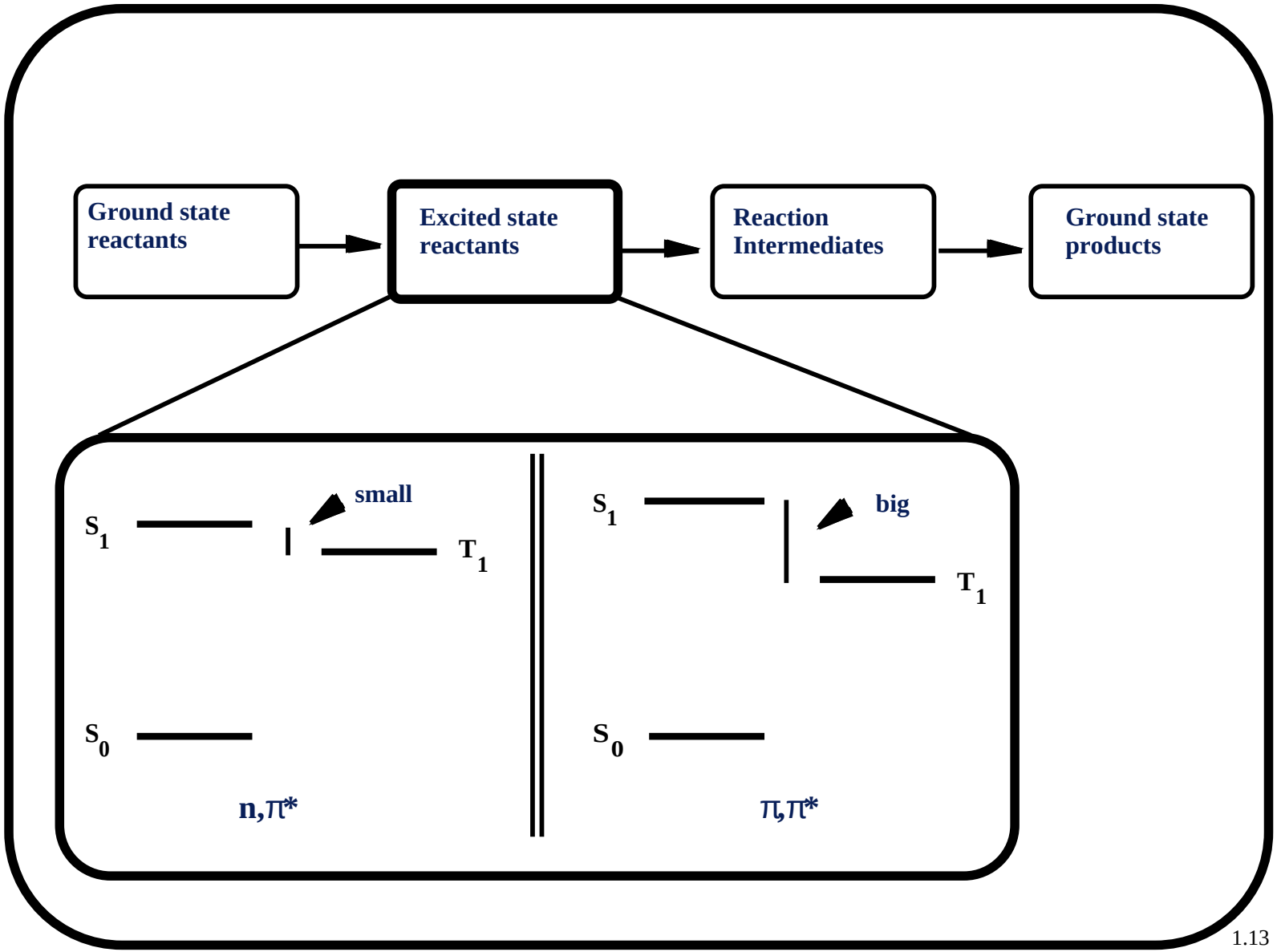


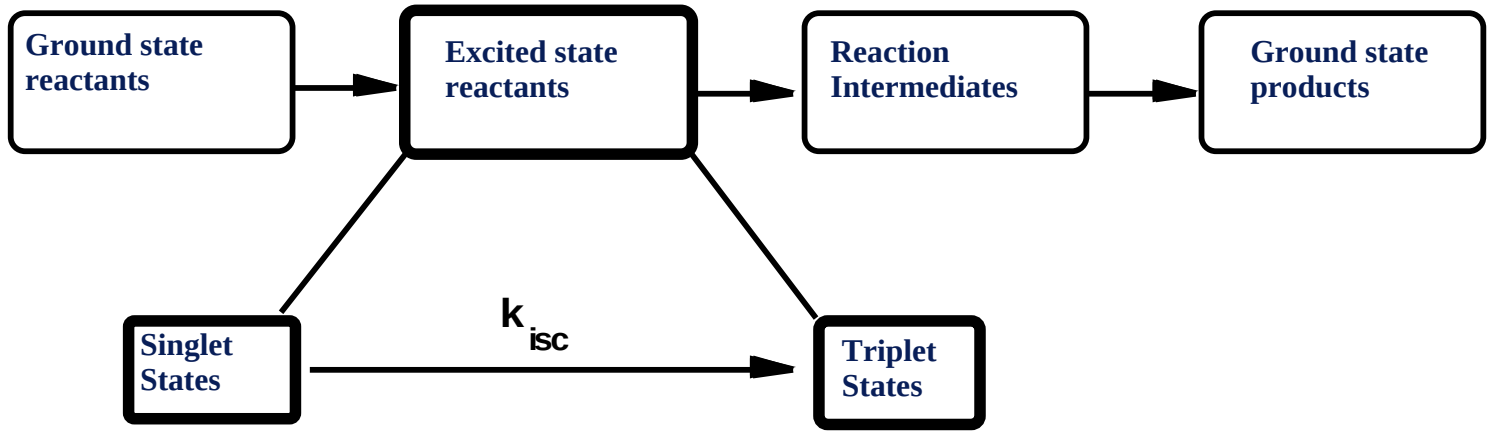

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Singlet States
Triplet States
LUMO
Upper excited states
HOMO
TRIPLETS
SINGLETS


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Singlet States
Triplet States
S_n
....
S_1
S_0
T_n
....
T_1


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Singlet States
Triplet States
S1
T1
S0
Kasha's Rule

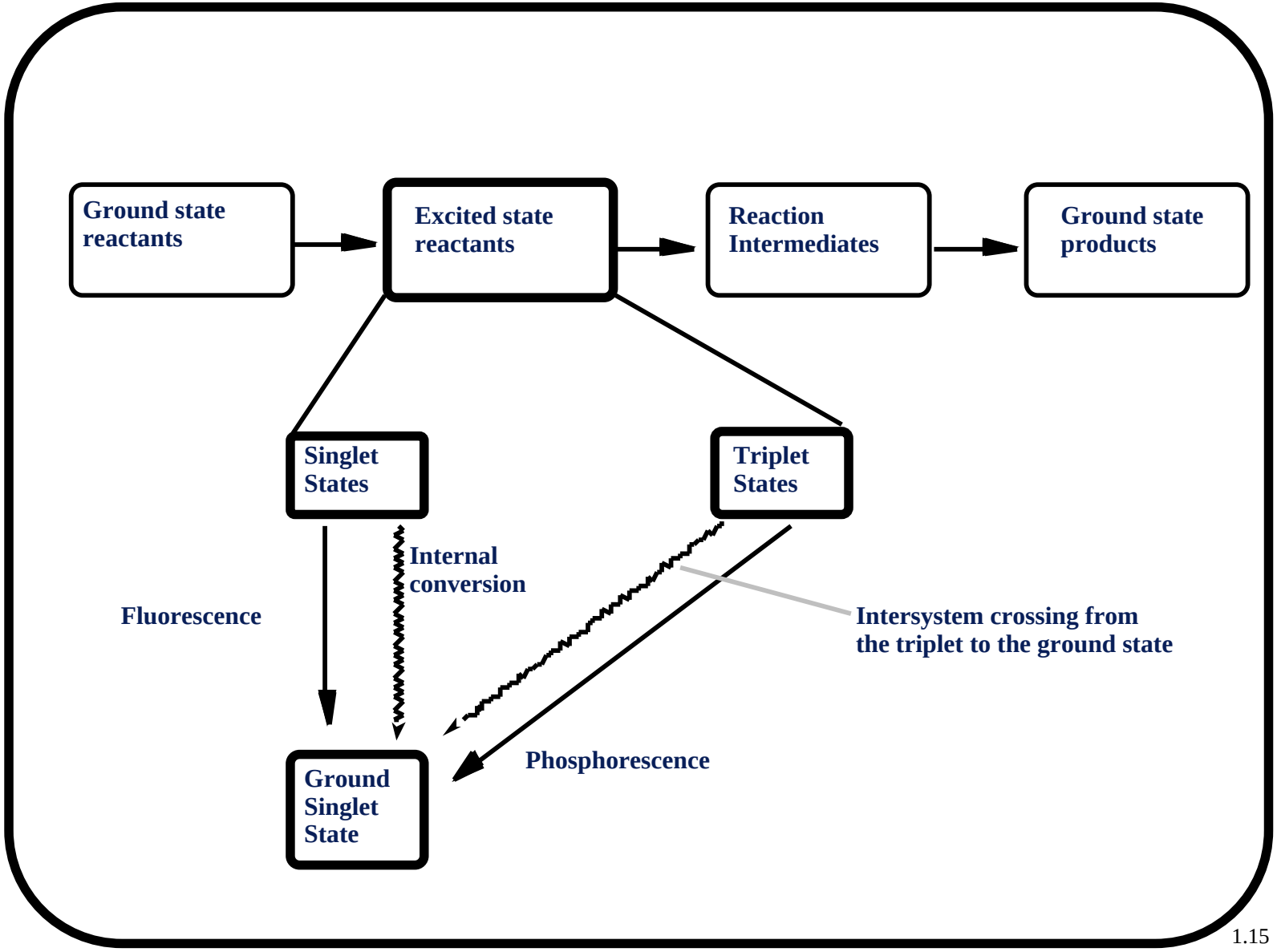

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
n,π*
π,π*
σ,π*
. . .


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
small
S_1
T_1
S_0
n,π*
S_1
big
T_1
S_0
π,π*

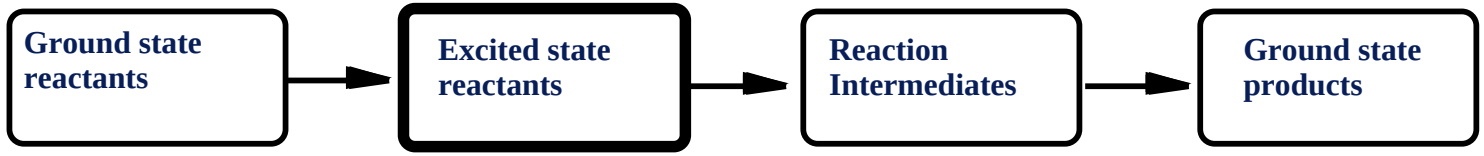


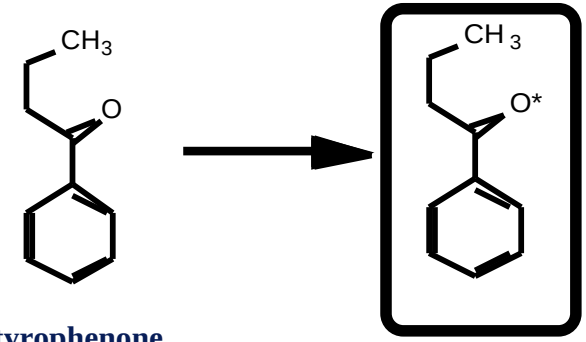
Intersystem crossing from the first excited singlet state to the lowest triplet state

The importance of spin


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Singlet States
Triplet States
Internal conversion
Fluorescence
Intersystem crossing from the triplet to the ground state
Phosphorescence
Ground Singlet State

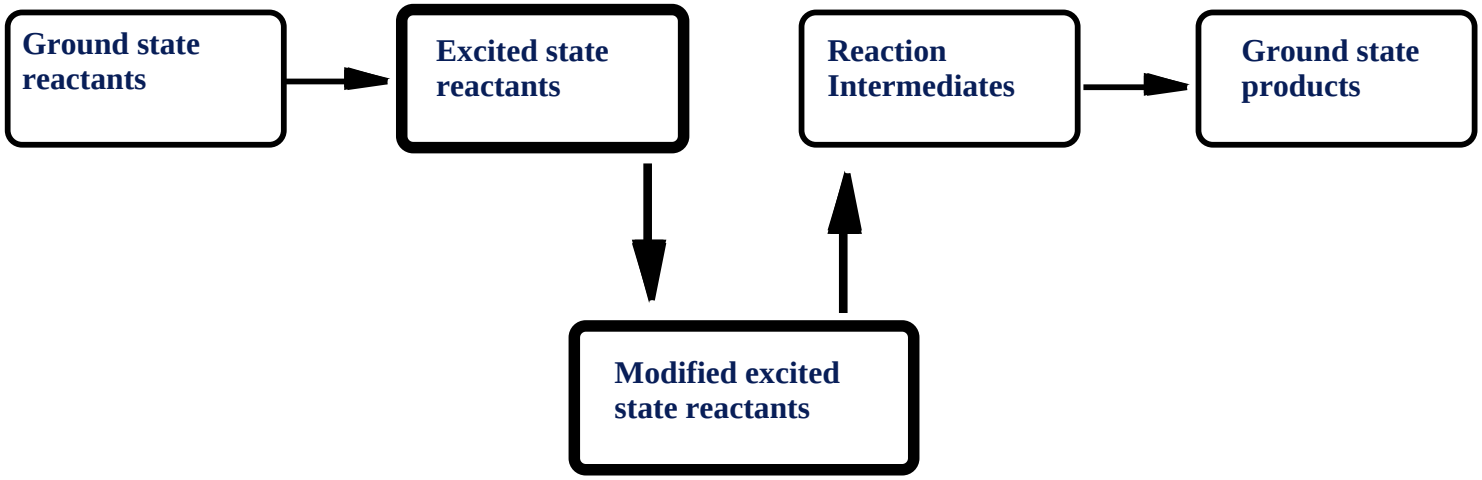
EXAMPLE





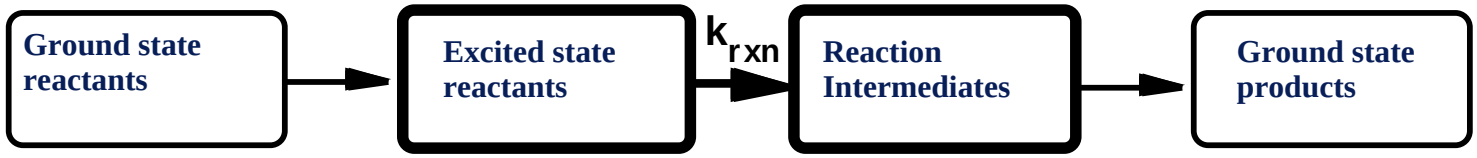
Butyrophenone

Triplet butyrophenone has n,π* character and is formed following very rapid intersystem crossing after excitation to the singlet state

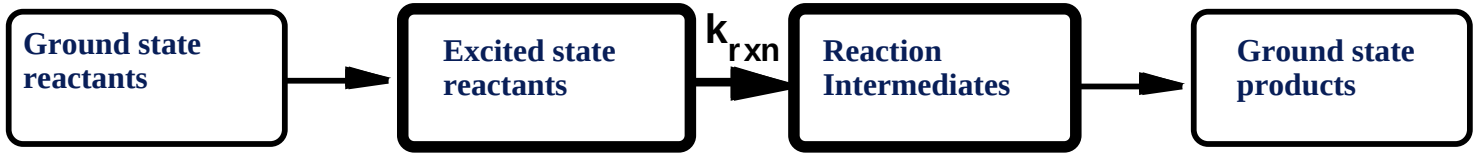


In some cases excited states may undergo significant *modifications* before they participate in the reaction of interest, e.g.:

- **Associative processes (excimer, exciplex)**
- **Structural (adiabatic) modifications**



The reactive excited state transforms into ground but short lived species which eventually yield the final products of reaction

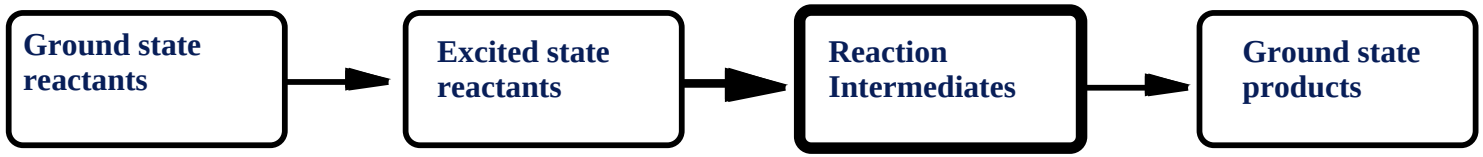


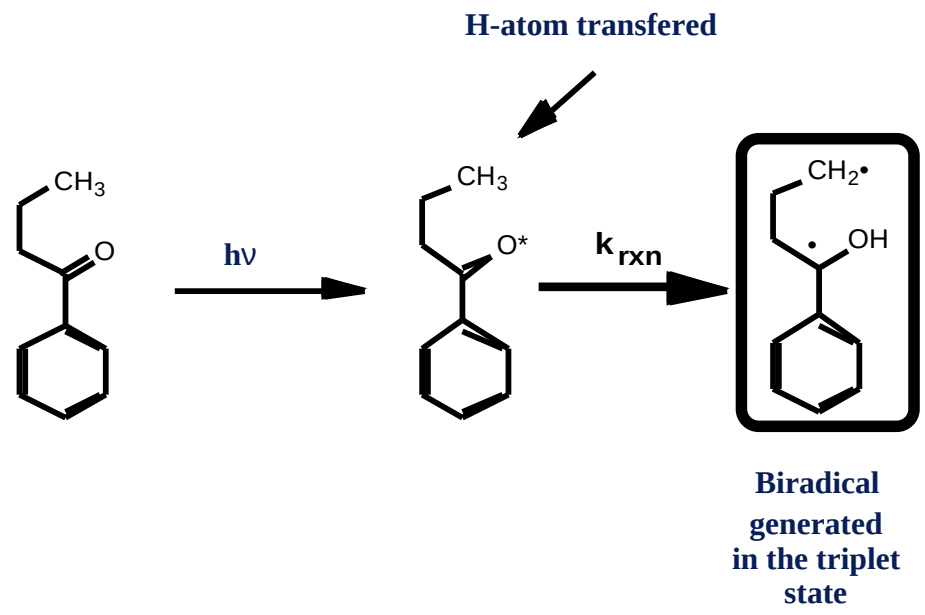
The transformation may involve atom or electron transfer or bond breaking or formation. It is usually an adiabatic process.

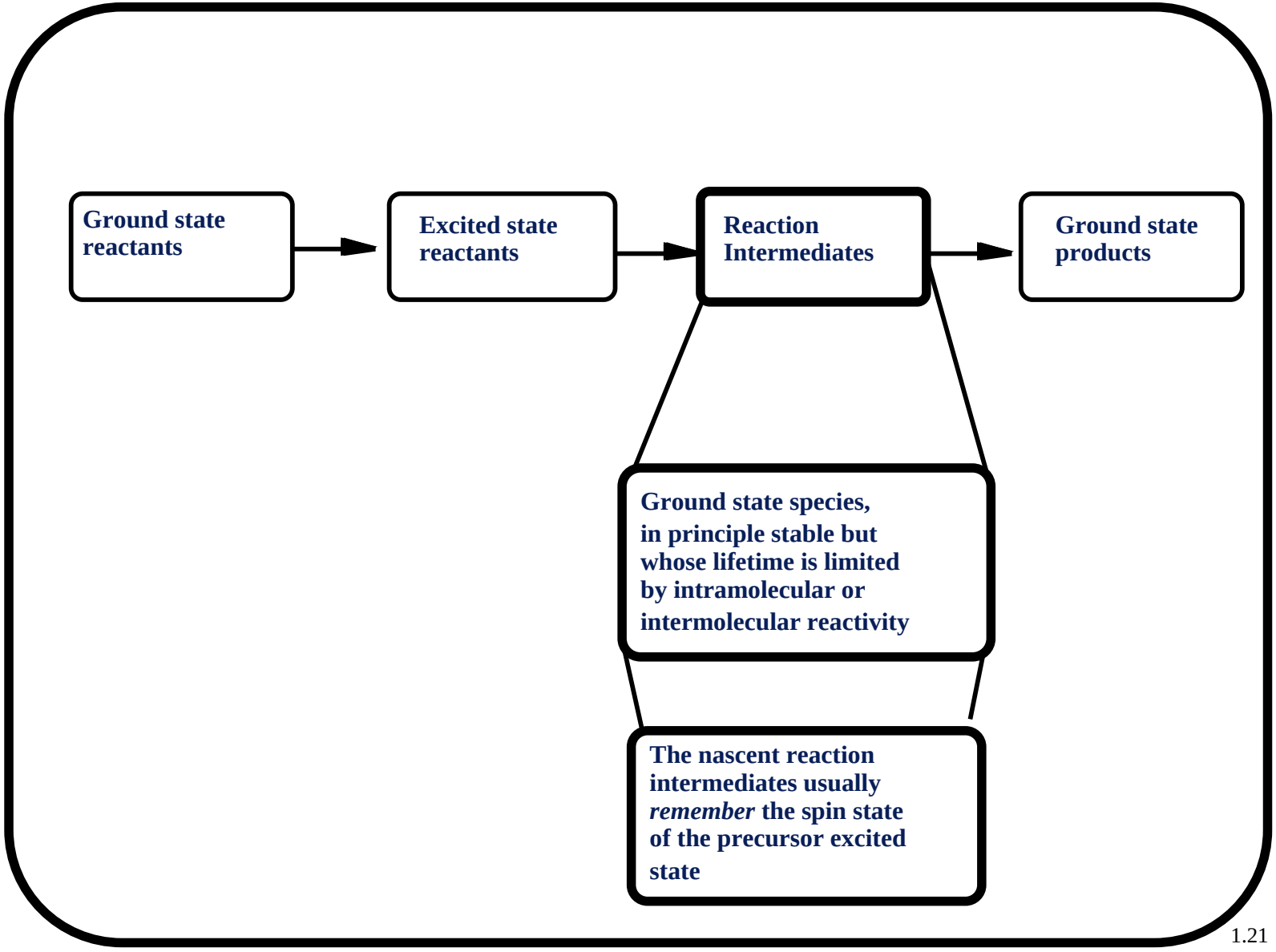
Spin is conserved

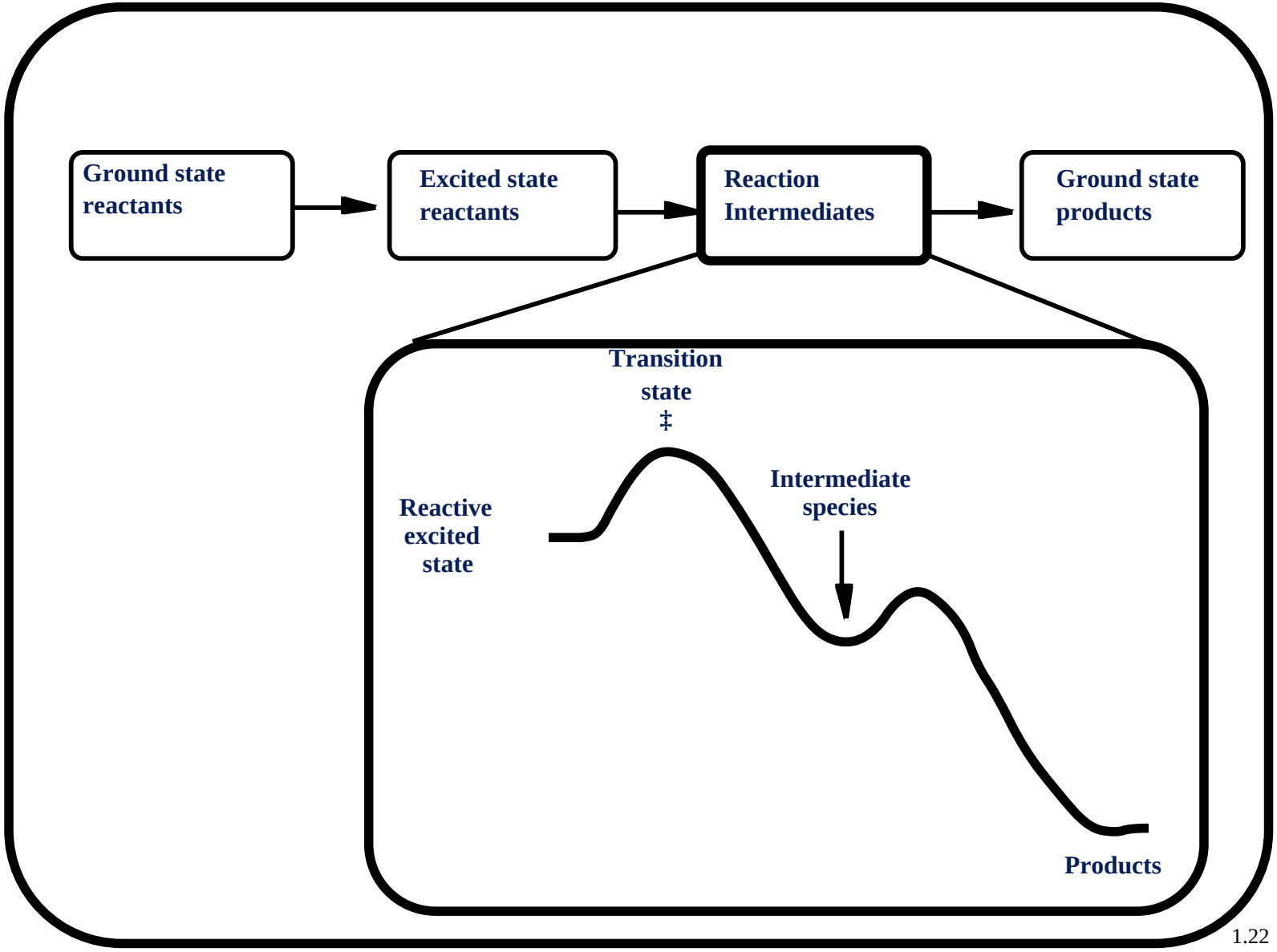
A small number of elementary transformations are normally sufficient to explain most photo-reactions, which may reflect combinations of this basic reaction set

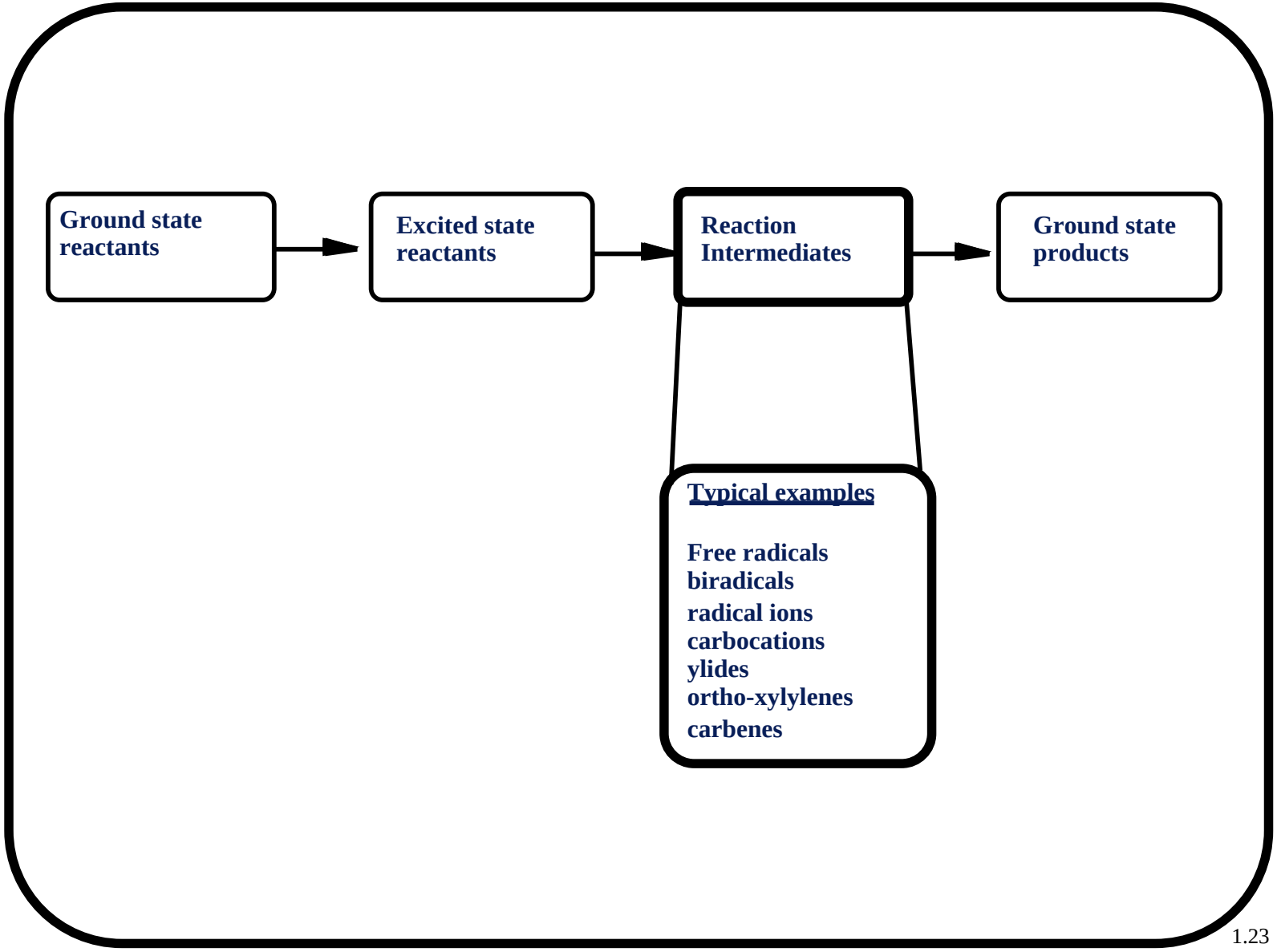
EXAMPLE


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products

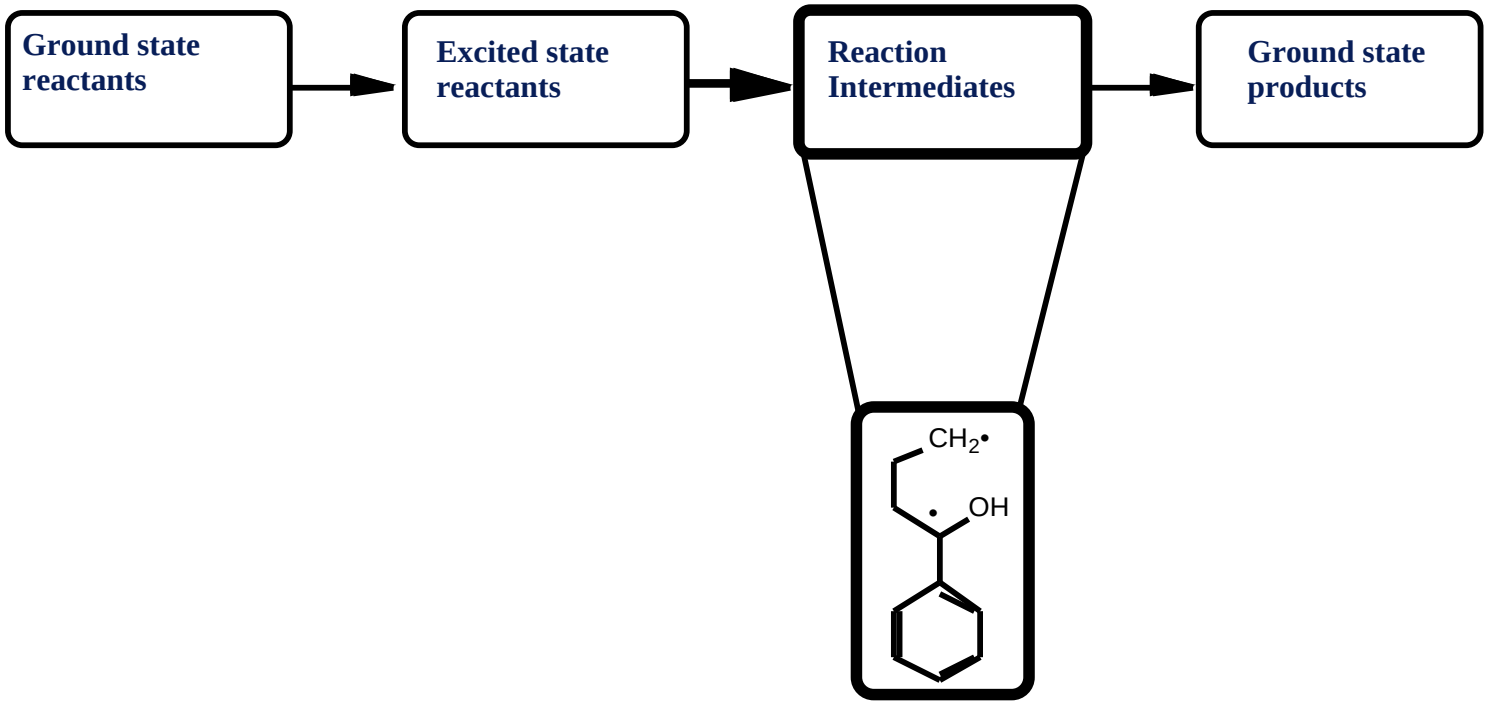

H-atom transfered
CH3
O
hν
CH3
O*
k rxn
CH2•
OH
Biradical generated in the triplet state

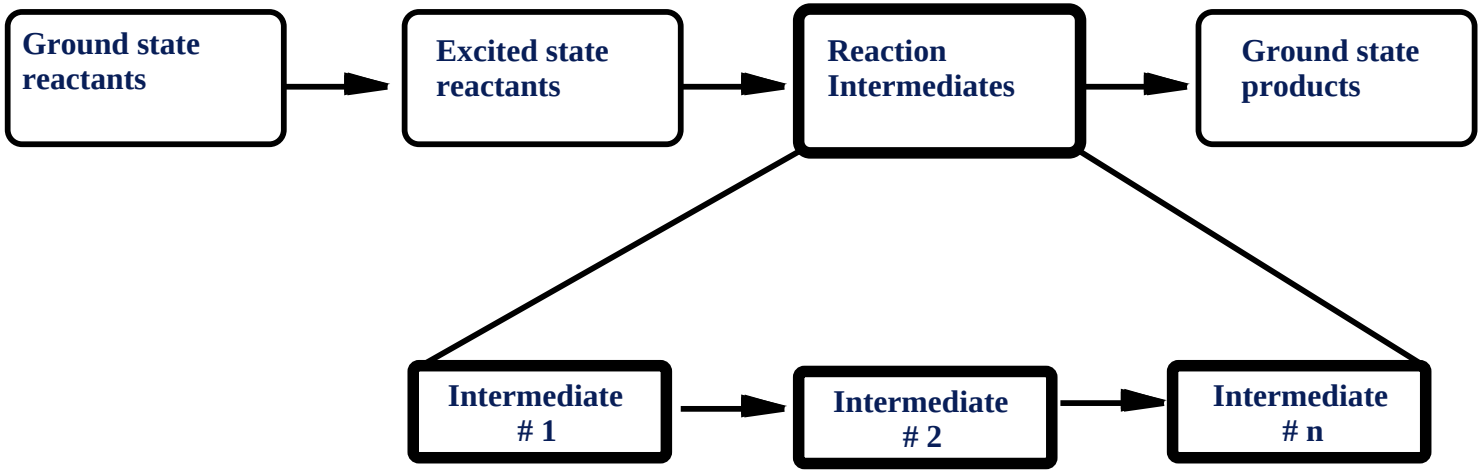

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Ground state species, in principle stable but whose lifetime is limited by intramolecular or intermolecular reactivity
The nascent reaction intermediates usually *remember* the spin state of the precursor excited state


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Transition state ‡
Reactive excited state
Intermediate species
Products

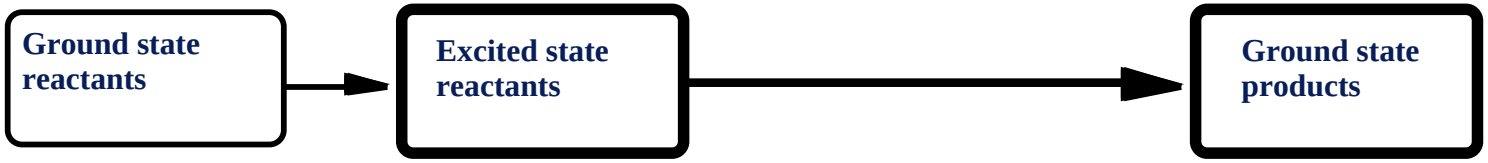

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Typical examples
Free radicals
biradicals
radical ions
carbocations
ylides
ortho-xylylenes
carbenes

EXAMPLE

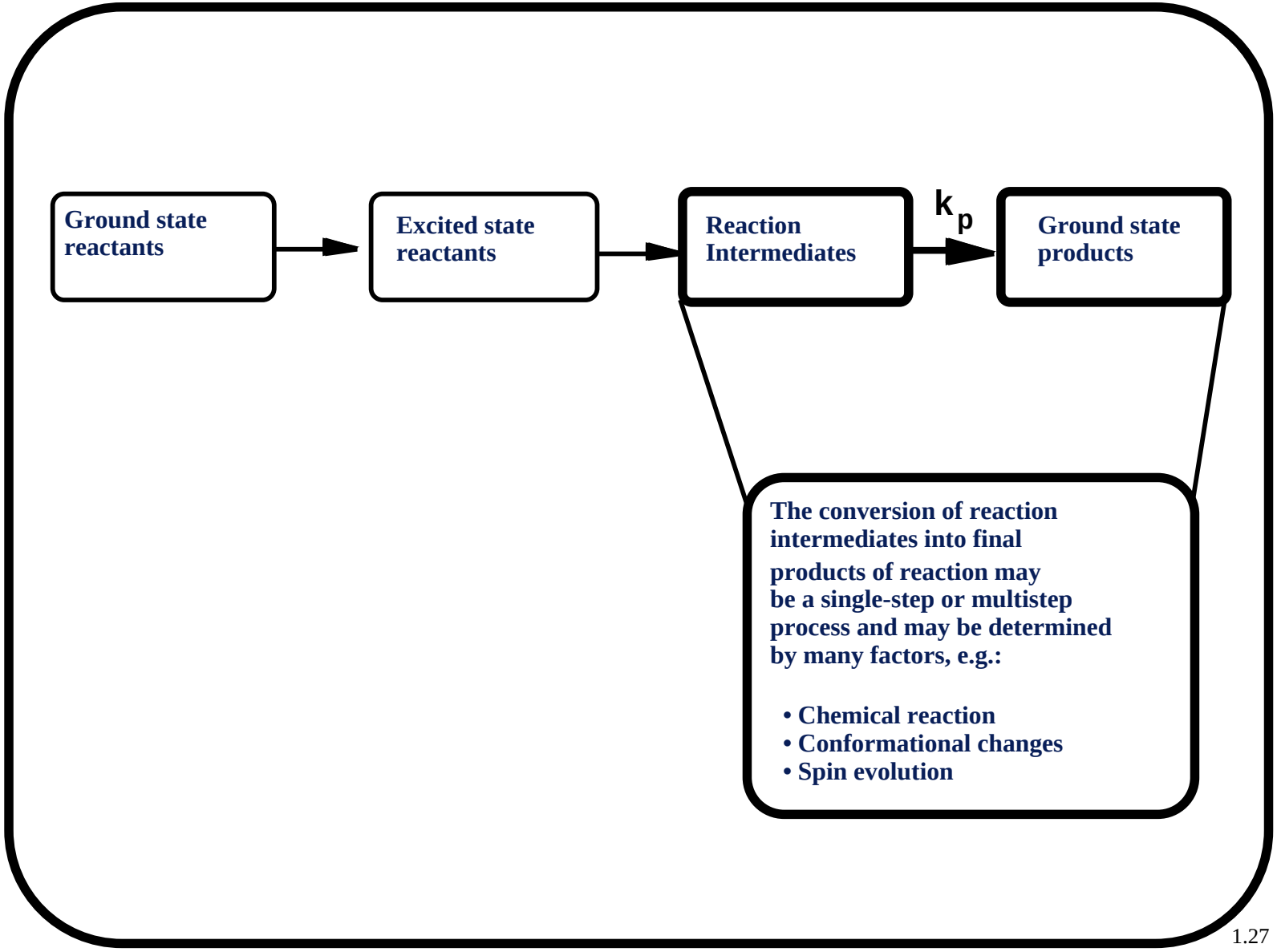

Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
CH2•
OH



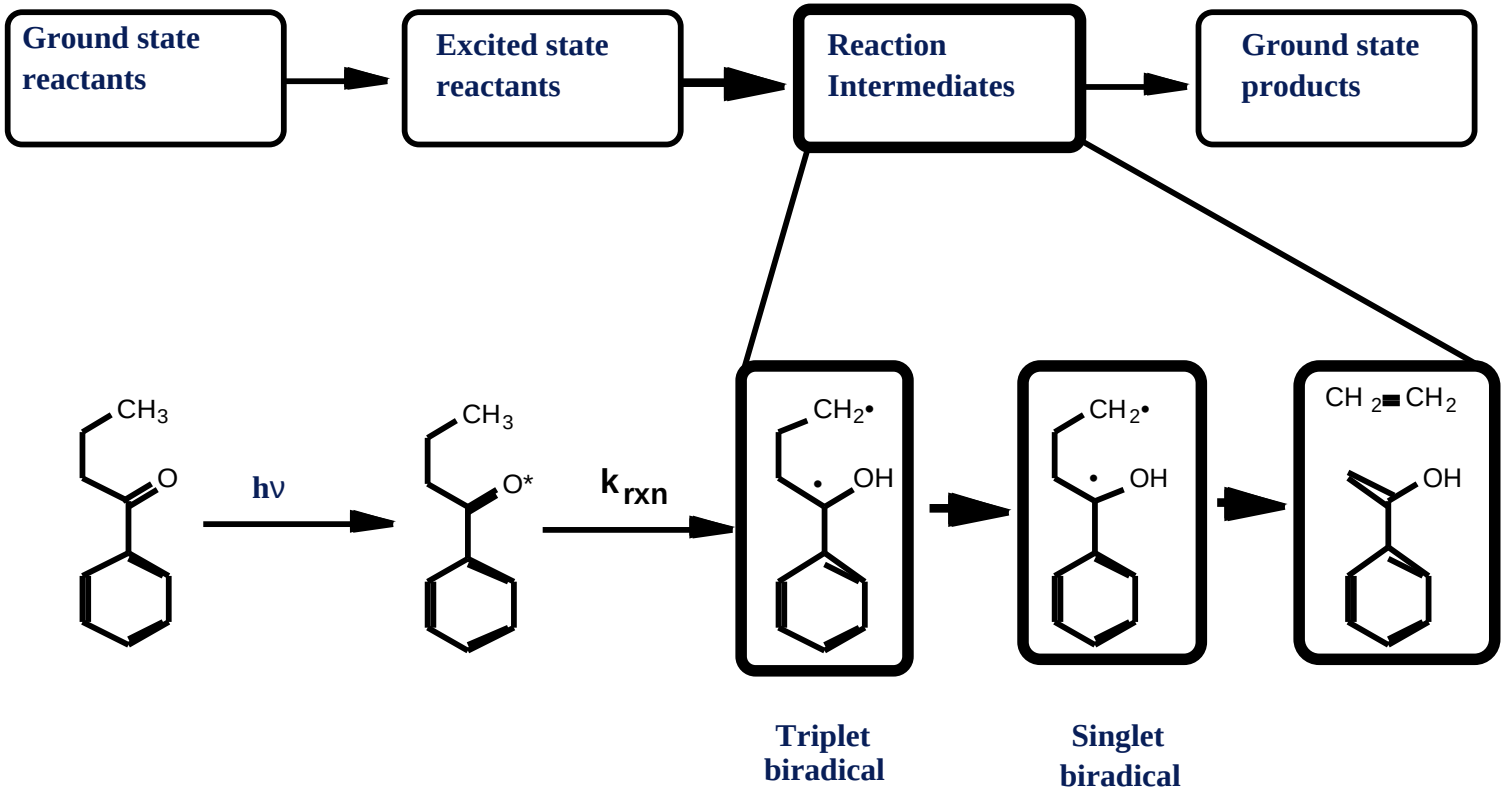
Several reaction intermediates may be involved between the precursor excited state and the final products

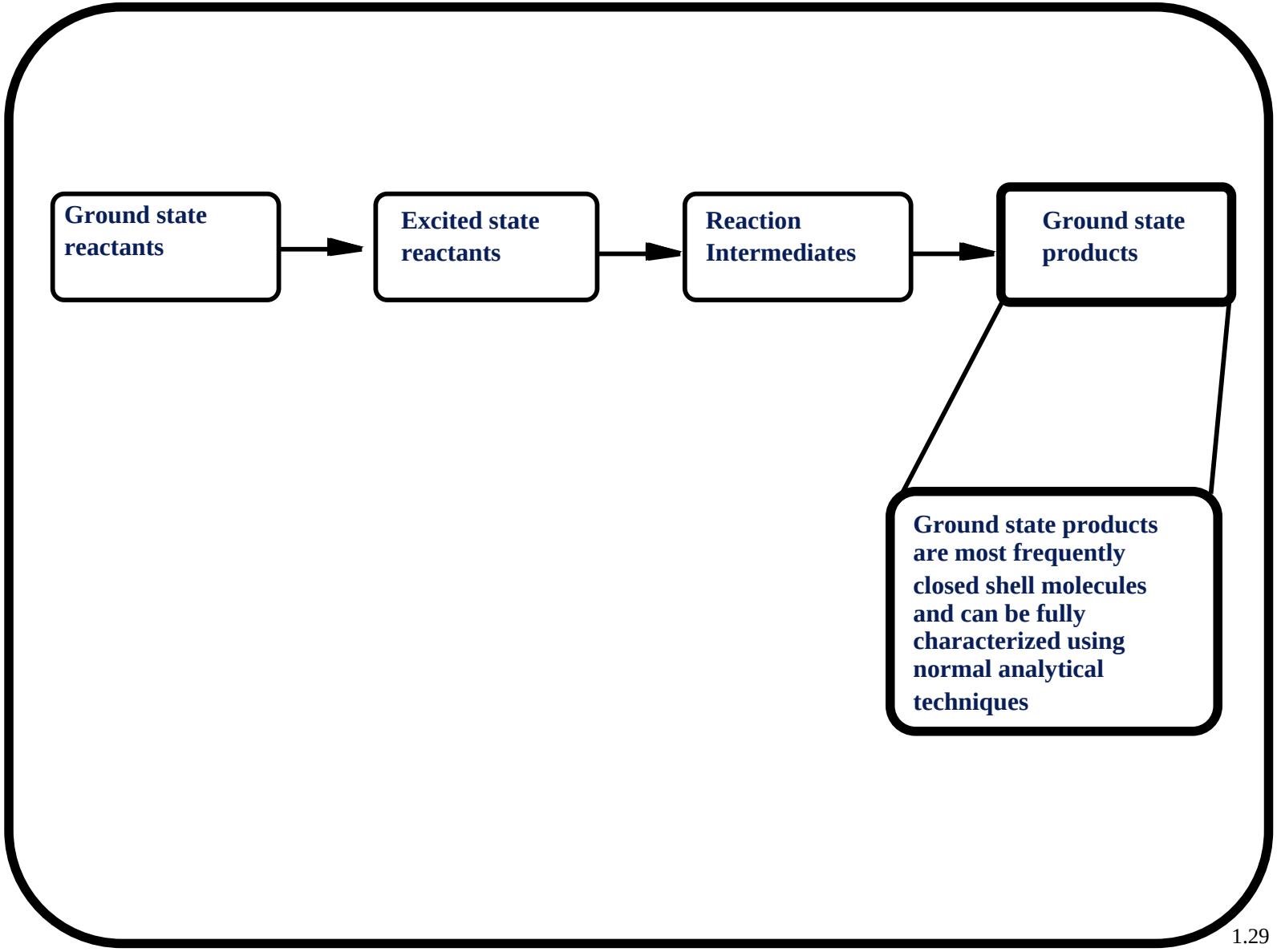


The involvement of reaction intermediates on the way between excited states and products is very common, but not essential

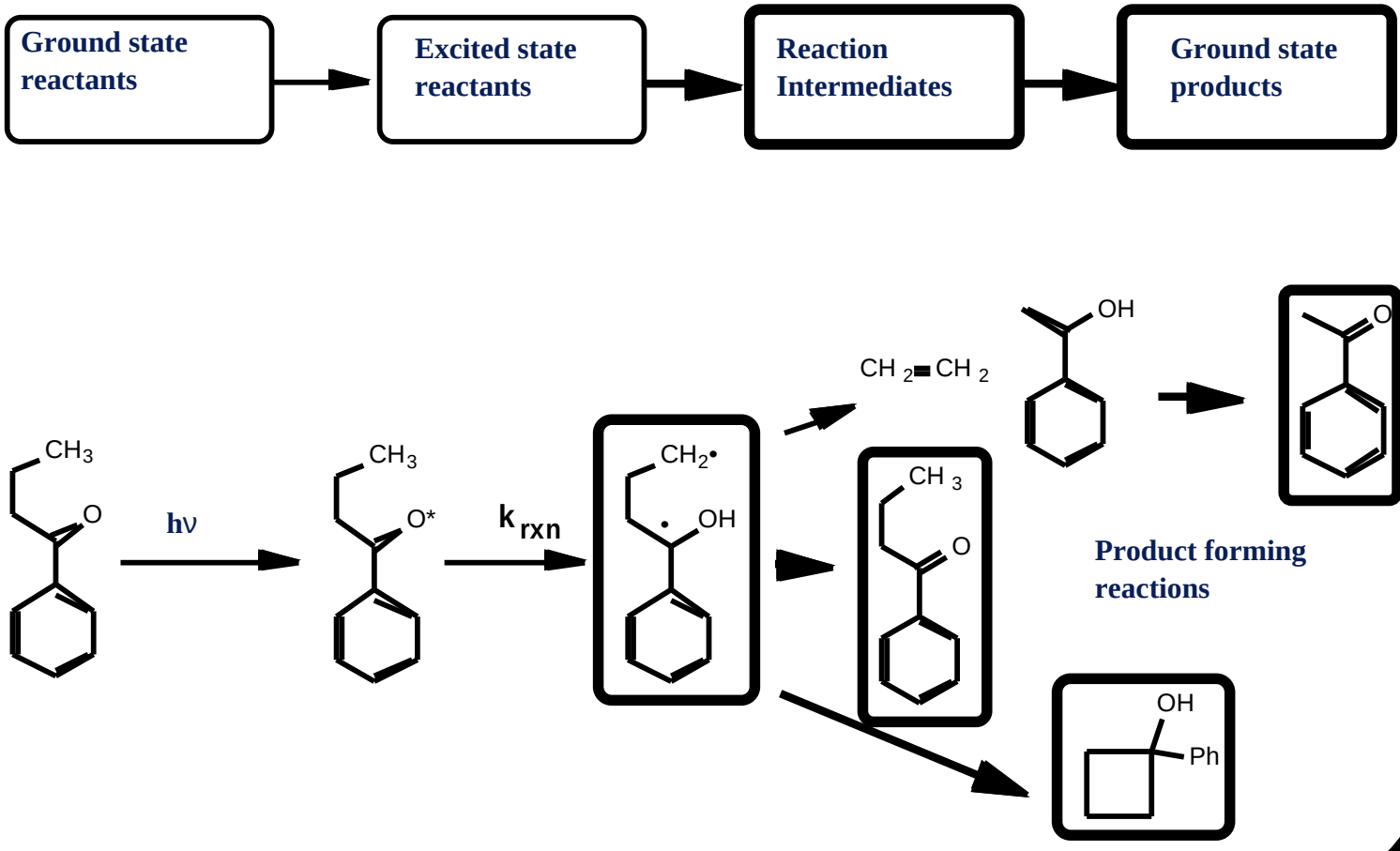

Ground state reactants
Excited state reactants
Reaction Intermediates
k_p
Ground state products
The conversion of reaction intermediates into final products of reaction may be a single-step or multistep process and may be determined by many factors, e.g.:
• Chemical reaction
• Conformational changes
• Spin evolution

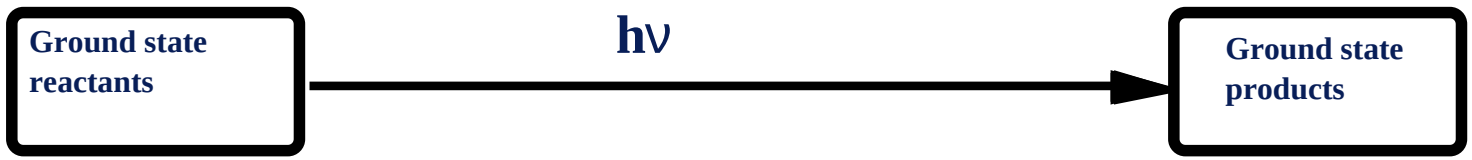
EXAMPLE


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
CH3
O
hν
CH3
O*
krxn
CH2•
OH
CH2•
OH
CH 2 CH2
OH
Triplet biradical
Singlet biradical


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Ground state products are most frequently closed shell molecules and can be fully characterized using normal analytical techniques

EXAMPLE


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
CH3
O
hν
O*
k rxn
CH2•
OH
CH 2 CH 2
CH 3
O
OH
O
OH
Ph
Product forming reactions

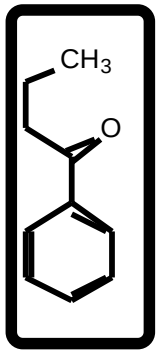


The overall reaction

EXAMPLE

The overall reaction

Ground state reactants —hν→ **Ground state products**



—hν→