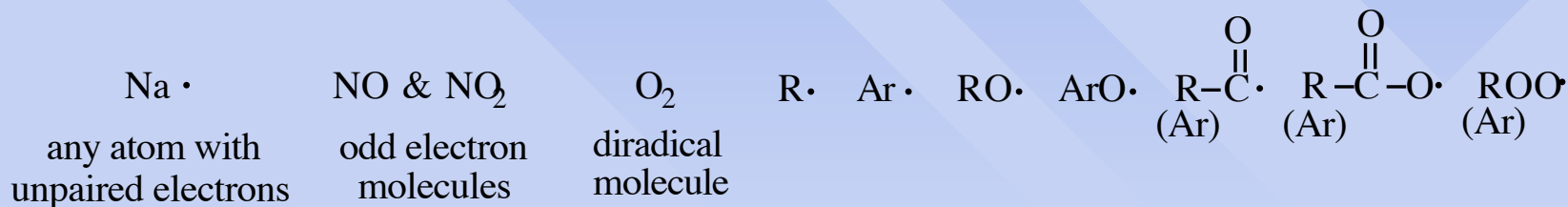


Free Radicals

Definition: Any chemical species with one or more unpaired electrons

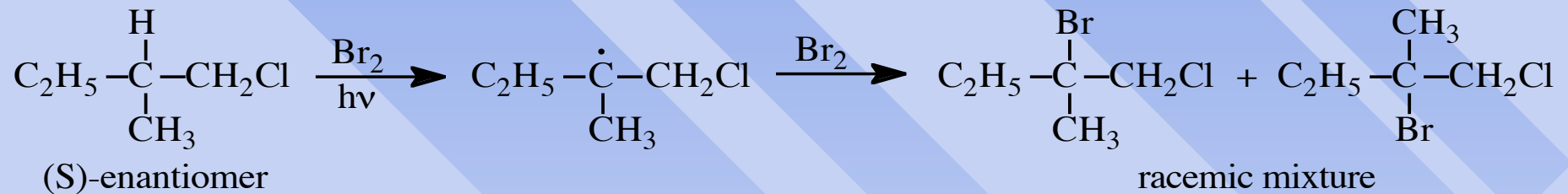
Examples of radical species



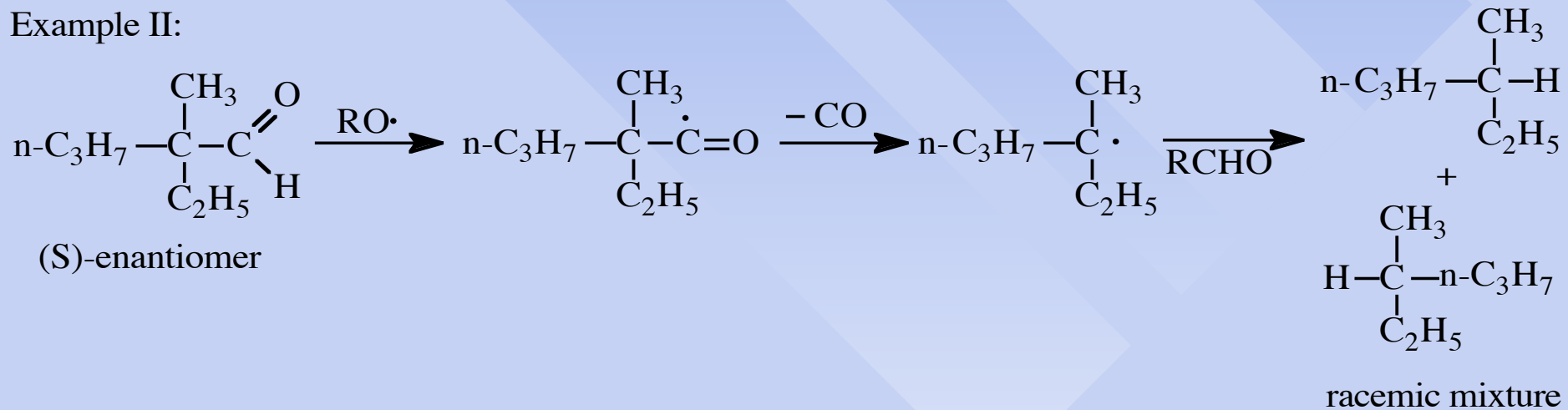
Nature of Free Radicals

Geometry

Example I:



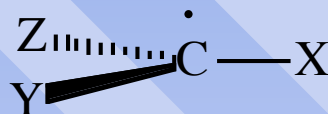
Example II:



RATIONALIZATION TO ACCOUNT FOR RACEMIZATION IN RADICAL REACTIONS

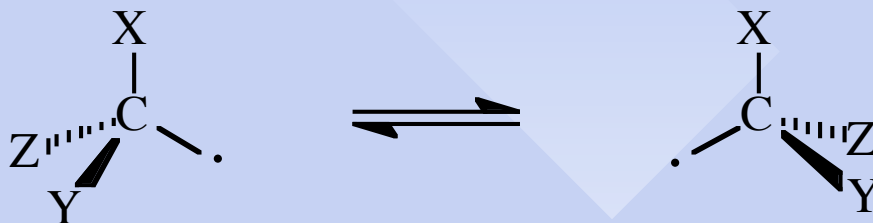
Explanation I:

Participation by a planar radical species capable of undergoing "top" or "bottom" attack with equal likelihood



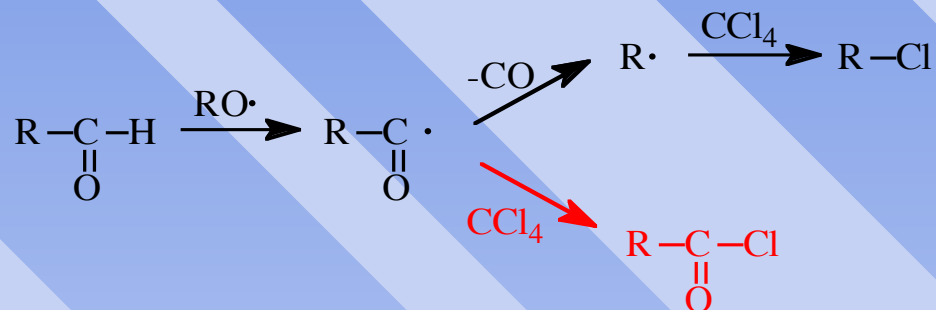
Explanation II:

Participation by a rapidly equilibrating pair of enantiomeric pyramidal radical species that would lead to racemic products

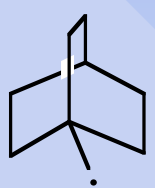
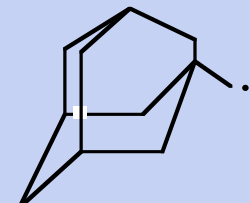


Evidence in favor of the “pyramidal” radical

Consider the following reaction:



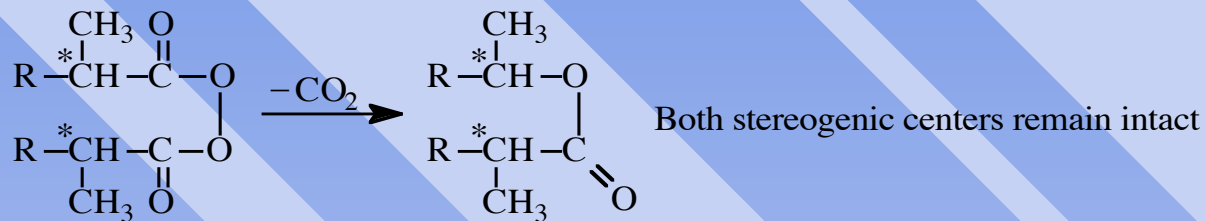
Object: Change R- from a group that can easily adopt a planar geometry to one that cannot. If planar geometry is favored for free radicals, that fact should be reflected in a low RCl:RCOCl ratio.

Observations: <u>R-group</u>	<u>RCl:RCOCl ratio</u>	<u>Stability of R·</u>
(CH ₃) ₃ C-	12.3:1.0	1.0 (ref.)
	15.2:1.0	1.2
	30.5:1.0	2.5

Conclusion: The formation of pyramidal radicals is **not** accompanied by adverse energy considerations. In fact, the opposite is true.

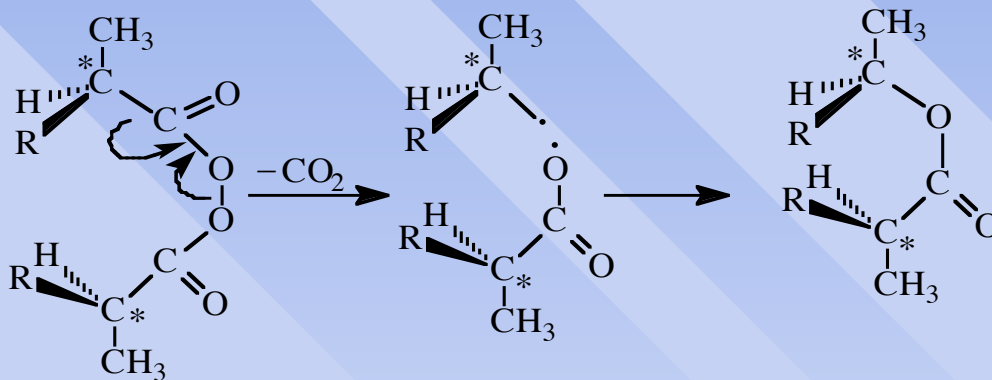
More evidence in favor of the "pyramidal" radical?

Consider the following observation:

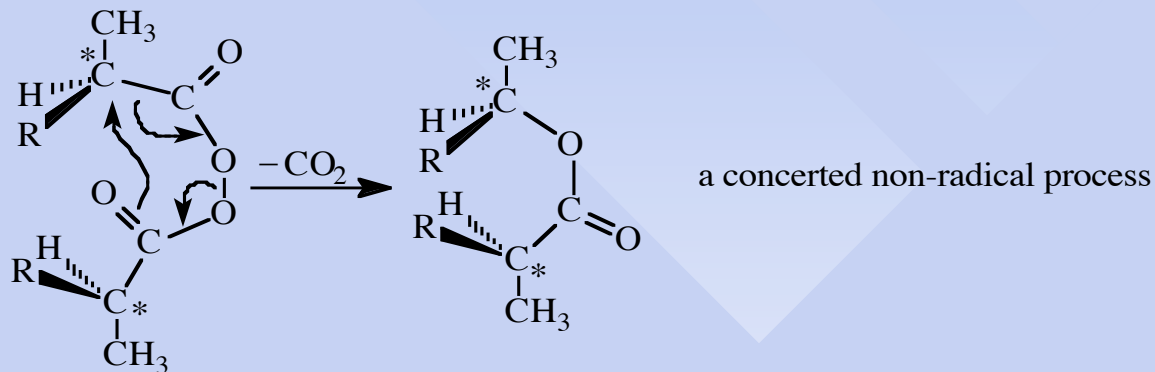


Plausible explanation

Loss of carbon dioxide leads to a pyramidal alkyl radical that rapidly recombines with incipient oxyradical before inversion of configuration can occur (an example of the "cage effect").

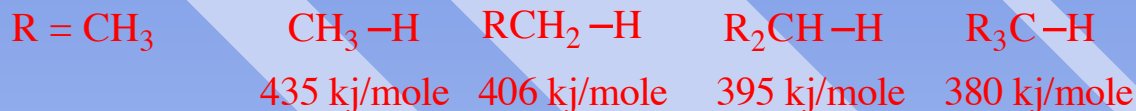


Alternate explanation



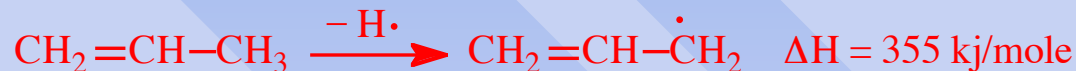
Stability of Free Radicals

Observation: Measurement of Bond Dissociation Energies



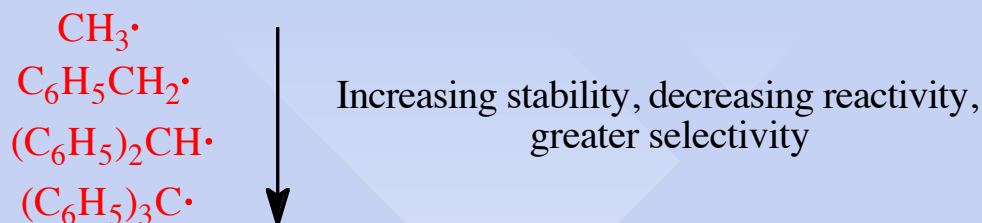
Conclusion: The order of radical stability is tertiary > secondary > primary > methyl

Observation:



Rationale: Abstraction of either benzylic or allylic hydrogen atoms to produce benzyl or allylic radicals is a lower energy process than that for corresponding saturated systems due to the possibility of π -delocalization of the odd electron in the former systems.

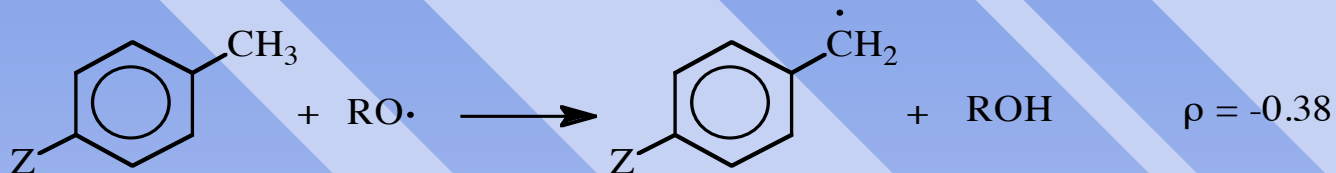
Observation:



Rationale: The greater the possibility for π -delocalization, the greater the stability of the radical species.

Stabilities of Substituted Benzyl Radicals

Observation:



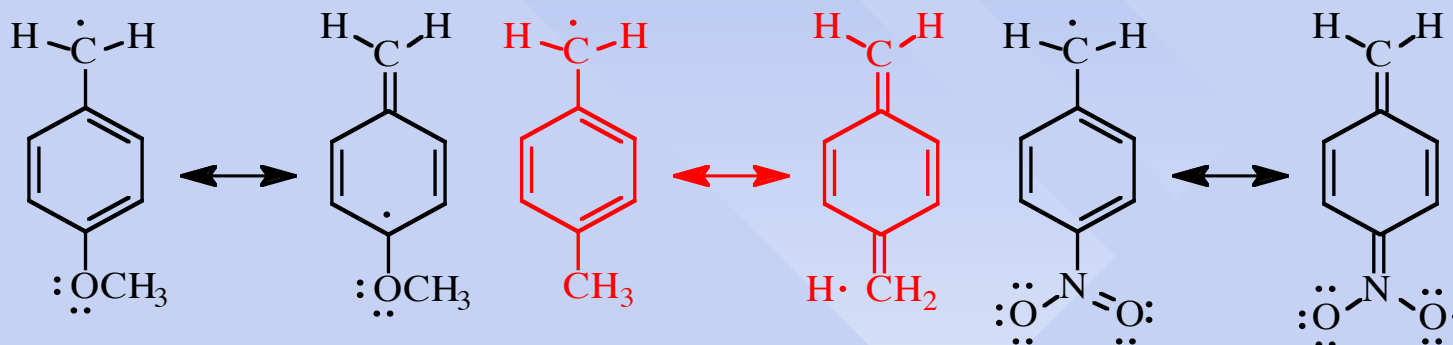
Relative stabilities:

Z =	CH ₃	OCH ₃	H	Br	CN	NO ₂
	1.9	1.2	1.0	1.8	3.7	4.0

Conclusions:

1. Based on the measured rho value for benzyl radical formation, the reaction is relatively insensitive to substituent electronic effects.
2. Both electron donating and electron withdrawing substituents stabilize the benzyl radical produced.

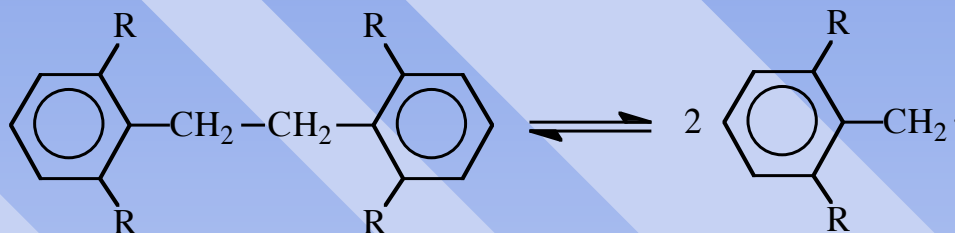
Rationale:



Substituted Benzyl radicals

Steric effects

Consider the following dissociation reaction:



Observations: As the size of R increases (methyl, ethyl, isopropyl, t-butyl),

- the magnitude of the equilibrium constant increases
- the reactivity of the resulting benzyl radical decreases
- the benzyl radical with the largest ortho-substituents forms fastest (at a fixed temp.)
- the benzyl radical with the largest ortho-substituents is formed under the mildest reaction conditions (under variable temp. conditions)

Rationale:

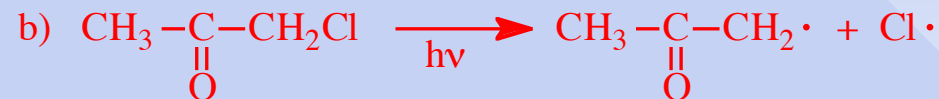
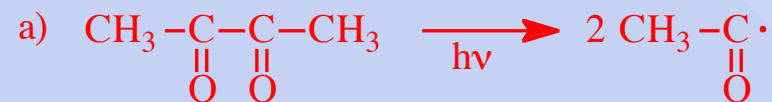
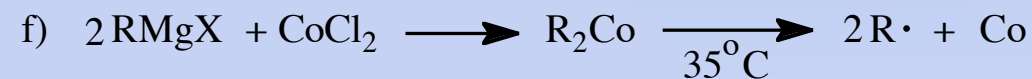
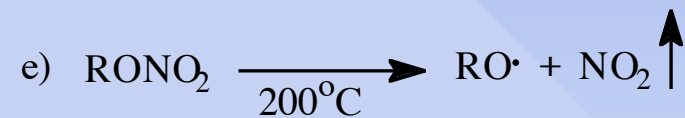
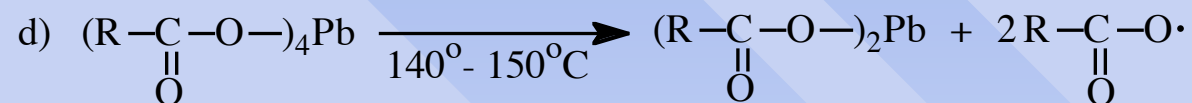
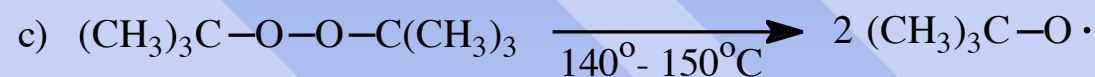
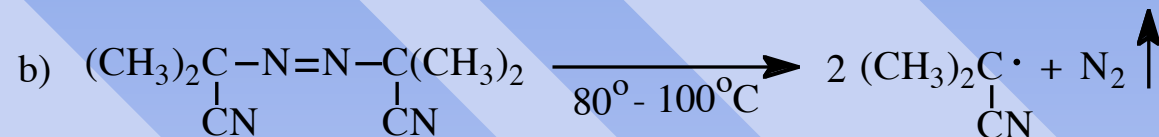
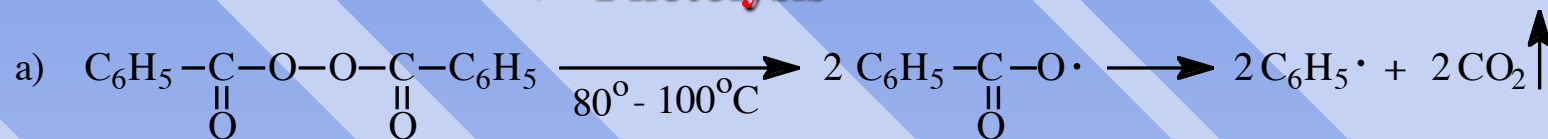
As R increases in size, the reactant is destabilized. Production of the substituted benzyl radical serves to relieve steric strain.

Once formed, the benzyl radical with the largest ortho-substituents will experience the greatest steric hindrance to recombination or to other reactions at the radical site.

Generation of Free Radicals

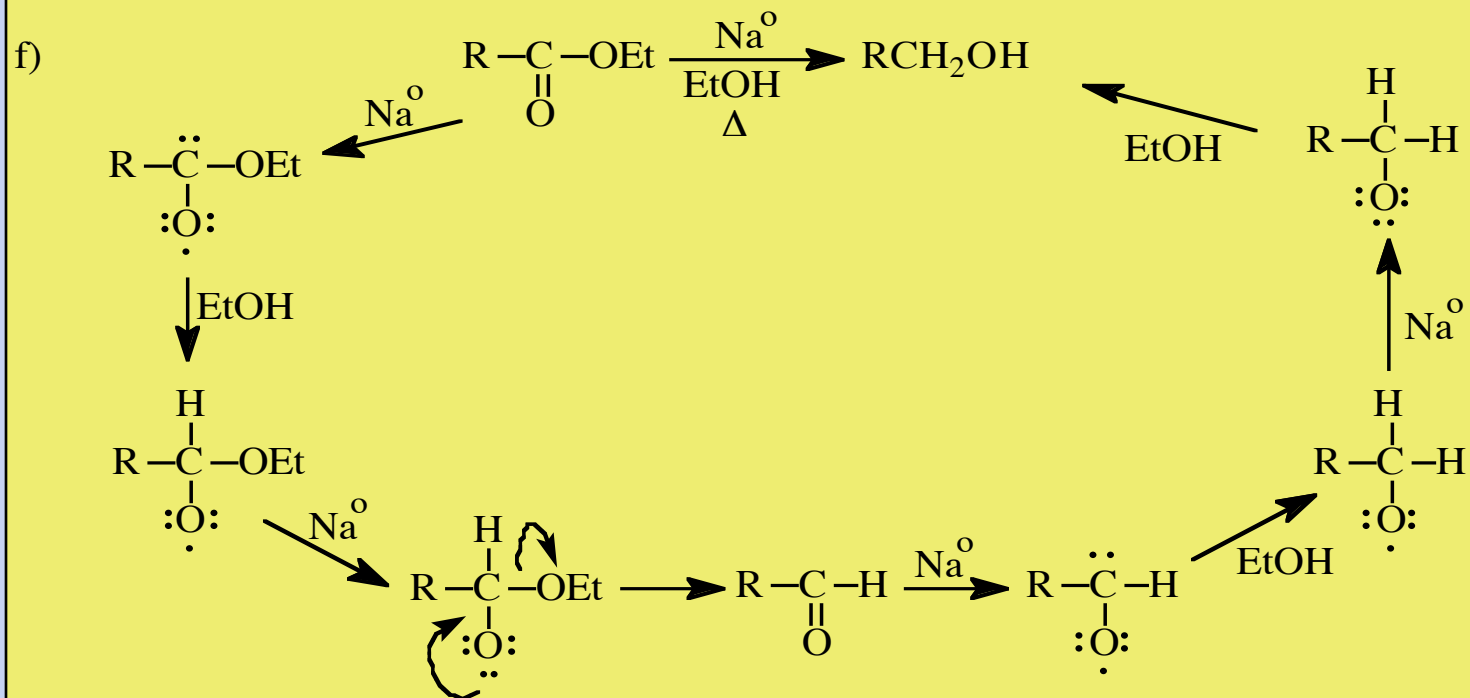
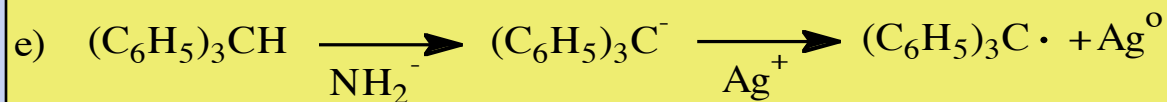
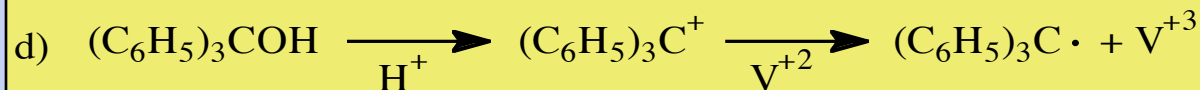
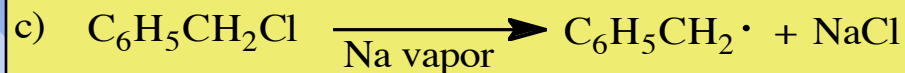
* **Thermolysis**

* **Photolysis**



GENERATION OF FREE RADICALS

Redox reactions

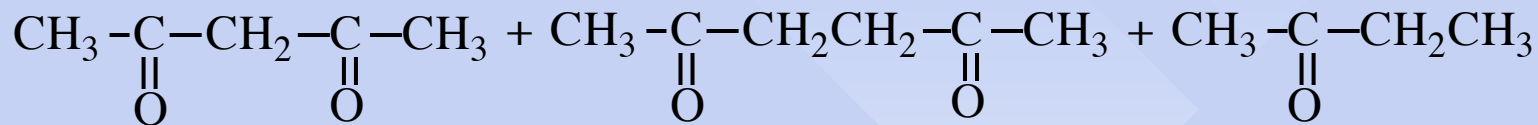
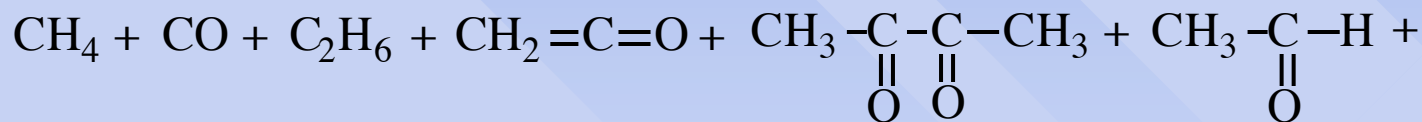
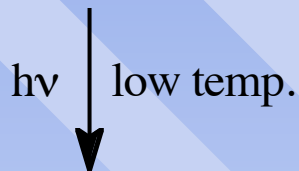
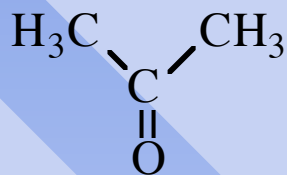


Characteristics of Radical Reactions

- ❖ Most radical reactions occur readily in the gas phase
- ❖ Radical reactions generally are not influenced by solvent polarity
- ❖ Radical reactions generally are not influenced by acid or base catalysis
- ❖ Unlike cations or anions, radicals generally are not influenced by electron-donating or electron-withdrawing substituents
- ❖ Radical reactions are often preceded by an induction period during which time they are subject to inhibition
- ❖ Radical reactions are frequently chain reactions
- ❖ Radical reactions generally are not accompanied by skeletal rearrangements

A Typical Radical Reaction

Overall reaction



A Typical Radical Reaction: Mechanism

