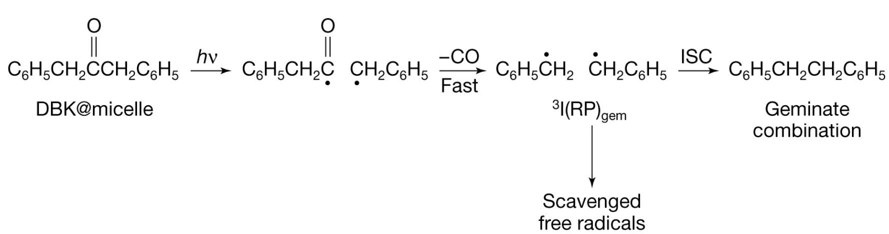
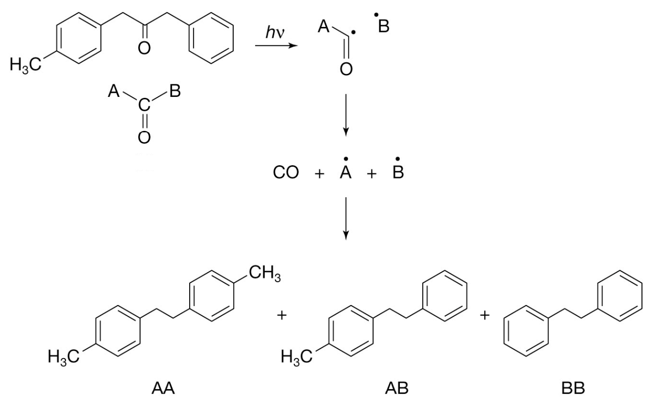
Cage effect

Conformational effect

Photochemistry of dibenzyl ketone as an exemplar of cage effect

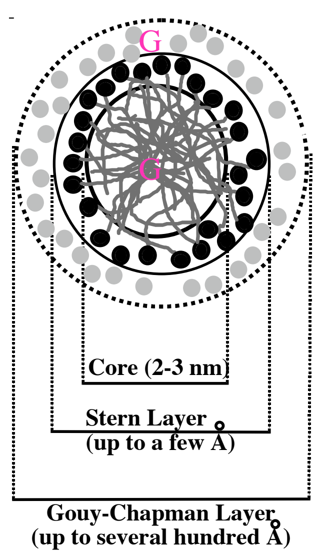


Definition of cage effect

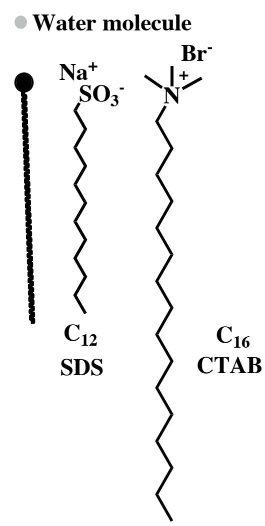


$$\text{Cage effect (\%)} = \frac{[AB] - ([AA] + [BB])}{([AB] + [AB] + [BB])} \times 100$$

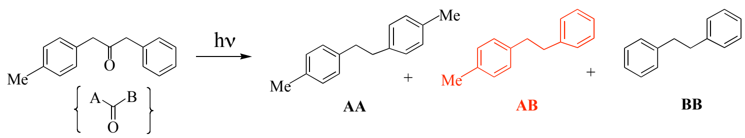
Schematic representation of a guest@micelle complex



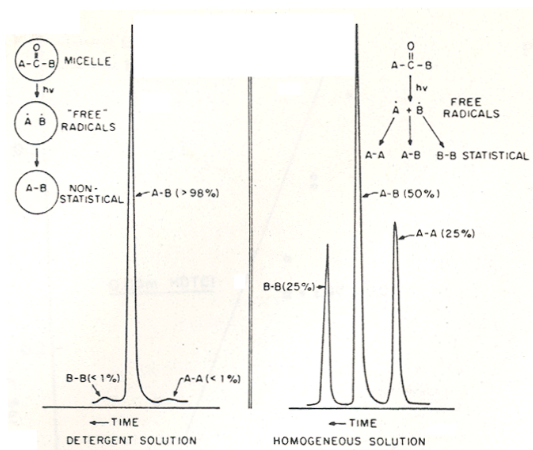
Surfactant monomers



A comparison between solution and micellar irradiations

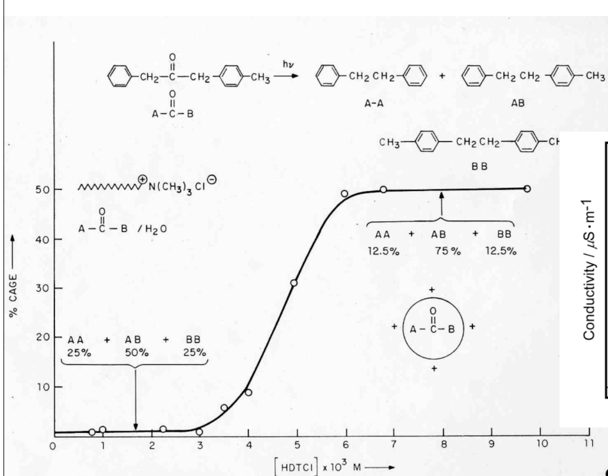


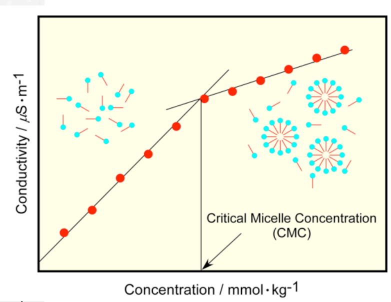
GC traces of product distributions upon irradiation in solution and in HDTCl micelle



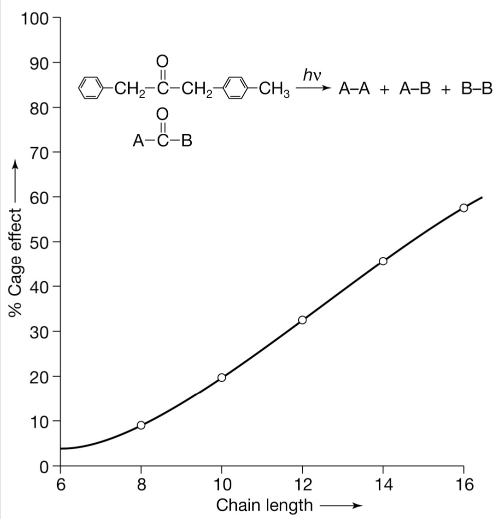
In micellar solutions the % cage depends on the surfactant concentration

Cage effect dramatically increases at a certain concentration of surfactant





In micellar solutions the % cage depends on the the cage size

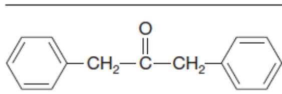
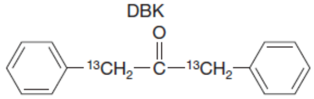
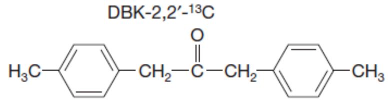
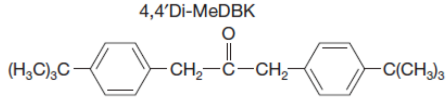


Sulfate surfactants
$CH_3(CH_2)_nOSO_3Na$

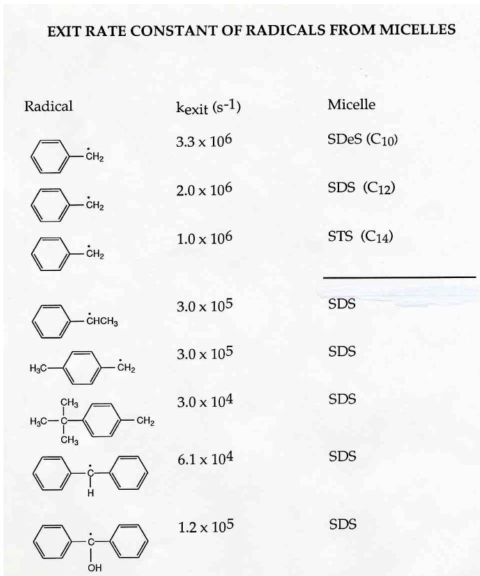
Reactive radicals escape from smaller cages more easily.

Bigger micelles, more hydrophobic cage. slower exit to water

In micellar solutions the % cage depends on the guest structure

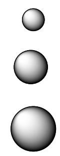
Ketone	Cage Effect
 DBK	31
 DBK-2,2′-^{13}C	46
 4,4′Di-MeDBK	59
 4,4′Di-*t*-BuDBK	95

Cage effect depends on the exit rate.



EXIT RATE CONSTANT OF RADICALS FROM MICELLES

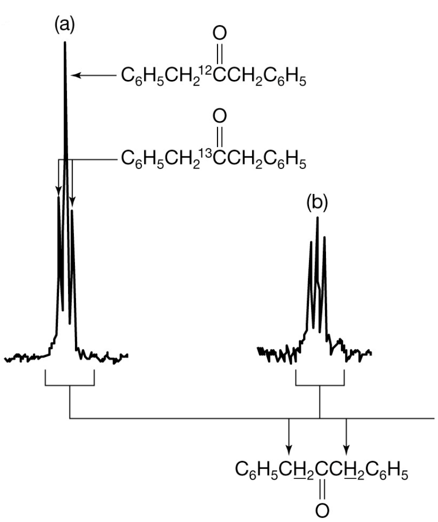
Radical	k_{exit} (s^{-1})	Micelle
$C_6H_5\dot{C}H_2$	3.3×10^6	SDeS (C_{10})
$C_6H_5\dot{C}H_2$	2.0×10^6	SDS (C_{12})
$C_6H_5\dot{C}H_2$	1.0×10^6	STS (C_{14})
$C_6H_5\dot{C}HCH_3$	3.0×10^5	SDS
$H_3C{-}C_6H_4\dot{C}H_2$	3.0×10^5	SDS
$(CH_3)_3C{-}C_6H_4\dot{C}H_2$	3.0×10^4	SDS
$C_6H_5\dot{C}(H)C_6H_5$	6.1×10^4	SDS
$C_6H_5\dot{C}(OH)C_6H_5$	1.2×10^5	SDS



For a given guest the rate of exit decreases with increasing micelle size.

For a given guest the rate of exit decreases with the hydrophobicity of the guest.

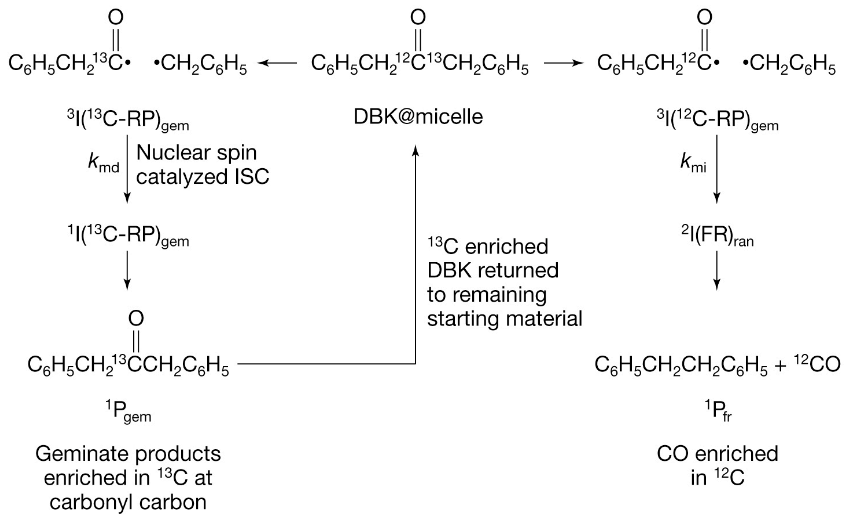
Nuclear isotope effect on triplet radical pairs



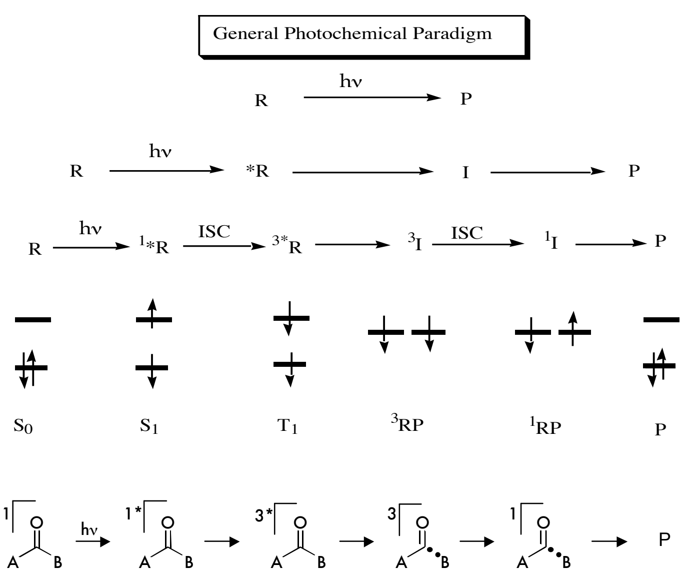
(a) Initial sample of $^{13}C{=}O$ enriched DBK

(b) The degree of $^{13}C{=}O$ in DBK increases with photolysis (90% conversion)

Origin of nuclear isotope effect

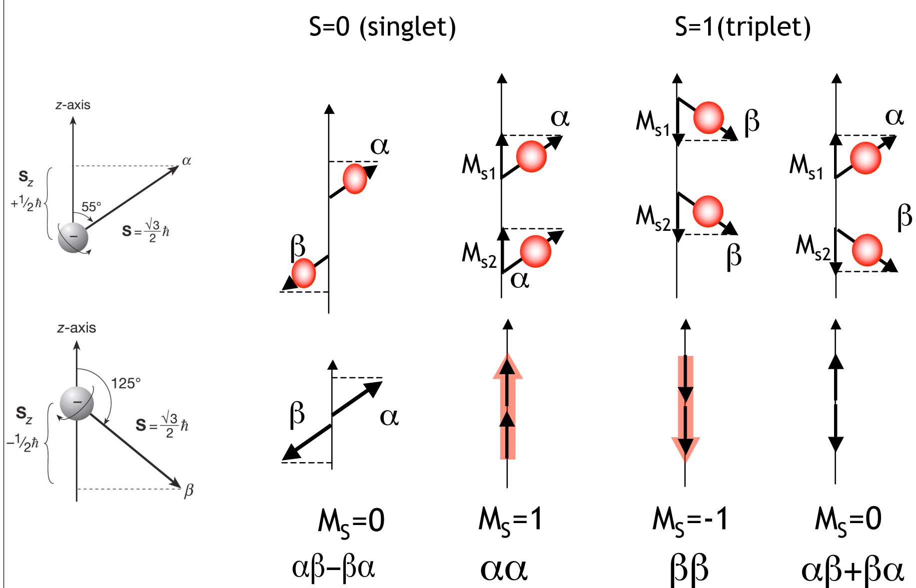


Understanding nuclear isotope effect

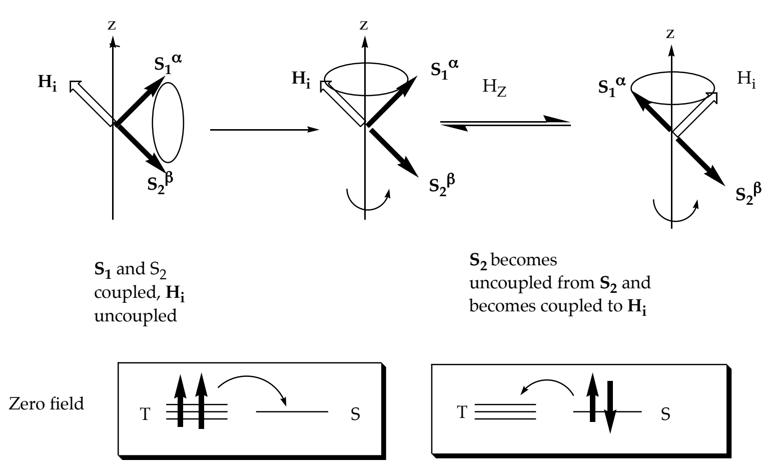


Spin ½ particles (electrons, ^{1}H, ^{13}C)

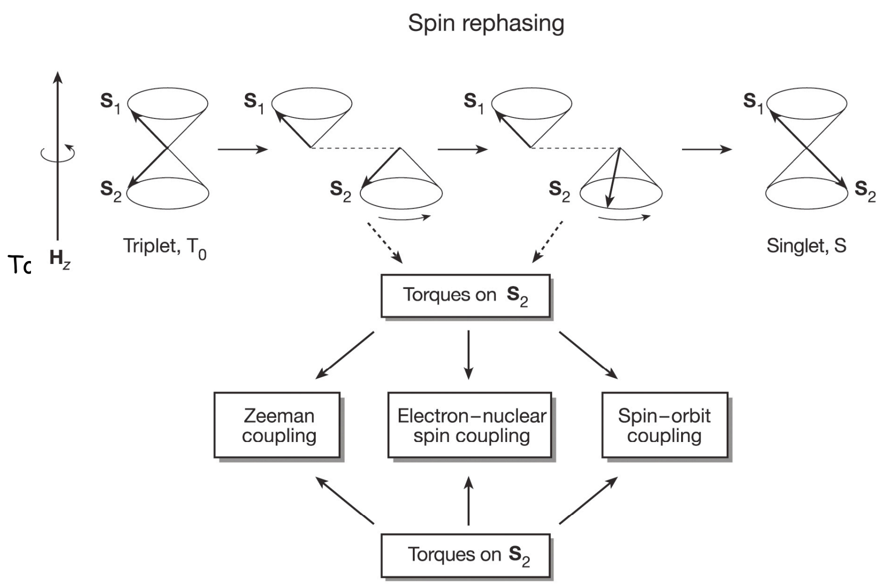
Spin 1 particles (two coupled electrons, two coupled protons)



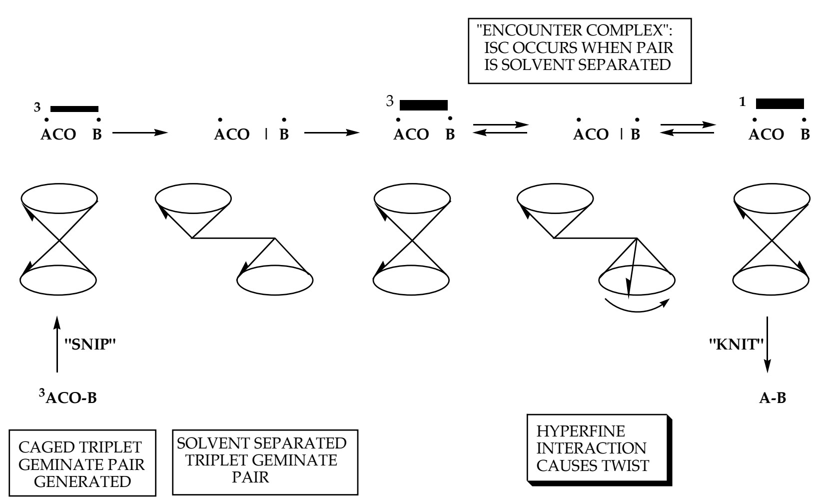
Vector representation of triplet-singlet conversions: intersystem crossing (ISC)



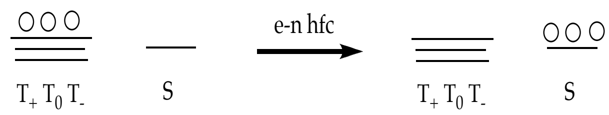
Mechanisms of crossing from T to S (intersystem crossing, ISC)



Vector representation of triplet-singlet conversions in I(RP) and I(BR): intersystem crossing (ISC)



The effect of electron-*nuclear* hyperfine coupling on T-S conversion

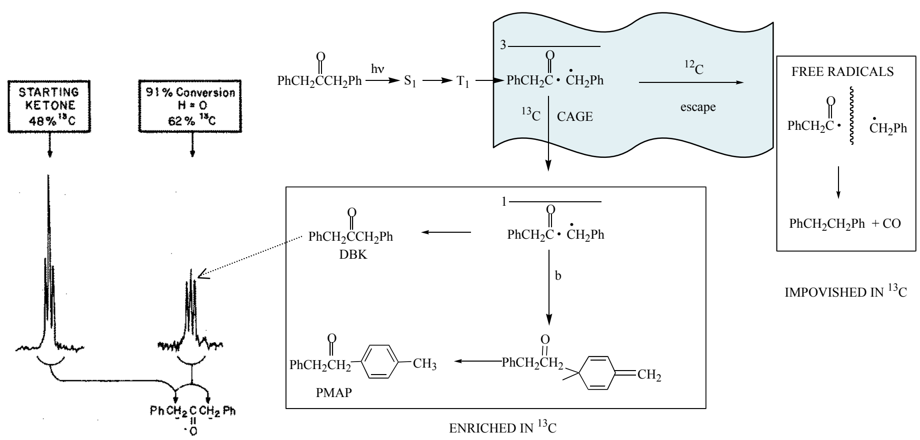


Triplets coupled to nuclei with spin will cross to the singlets faster than triplets coupled to nuclei without spins.

Triplet radical pairs coupled to ^{13}C will cross to singlets faster than triplets coupled to ^{12}C

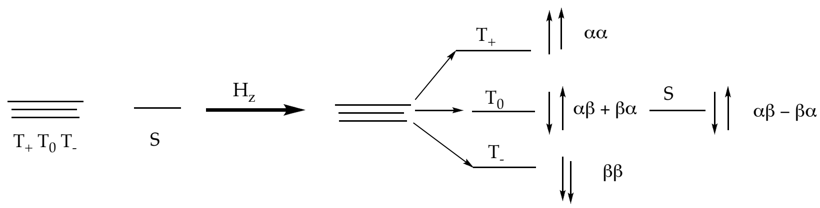
Result: Separation of ^{13}C radical pairs from ^{12}C radical pairs

Cage effect can be utilized for isotope enrichment



The competion is between cage escape and hyperfine induced ISC

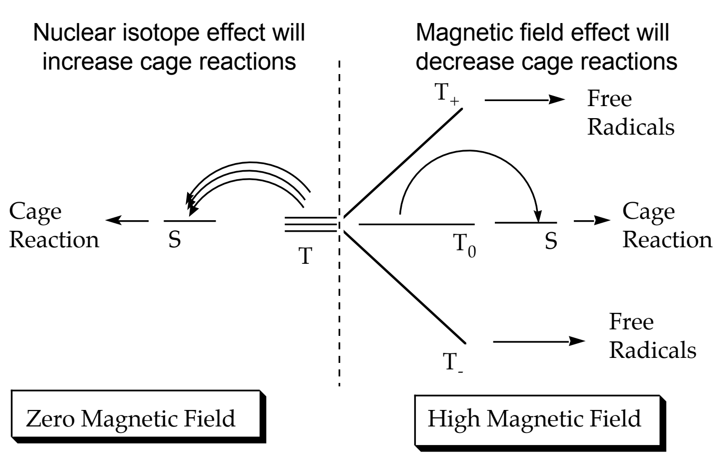
Effect of an applied magnetic field on the T splitting



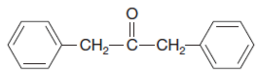
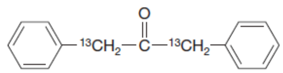
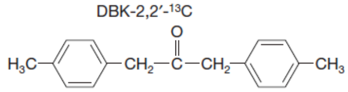
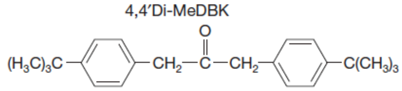
T levels split apart, T_0 has the same energy as S

Only $T_0 \rightarrow S$ ISC allowed

Spin chemistry of radical pairs in supramolecular systems



The effect of external magnetic field on the cage effect

Ketone	Cage Effect at 0 G	Cage Effect at 13,000 G
 DBK	31	16
 DBK-2,2′-^{13}C	46	22
 4,4′Di-MeDBK	59	31
 4,4′Di-*t*-BuDBK	95	76

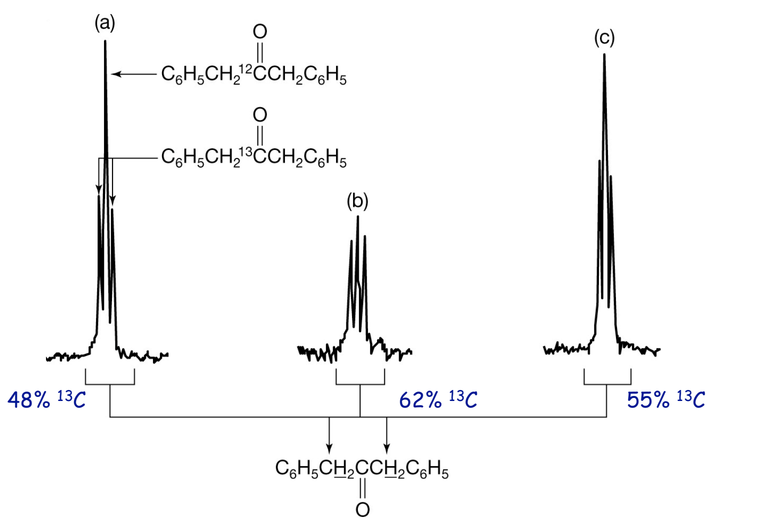
The cage effect decreases. More exit from host cage.

Isotope enrichment decreases in presence of applied magnetic field

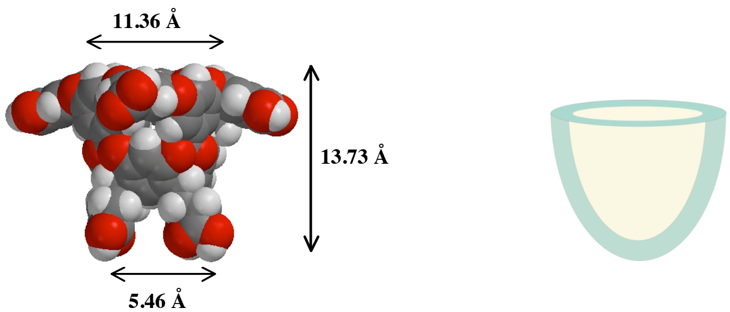
Initial

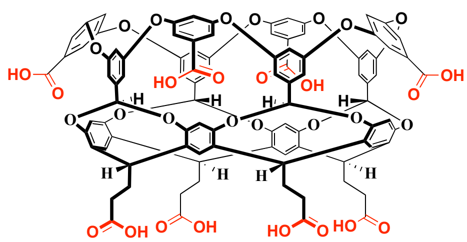
90% photolysis
at 0 applied mag. field

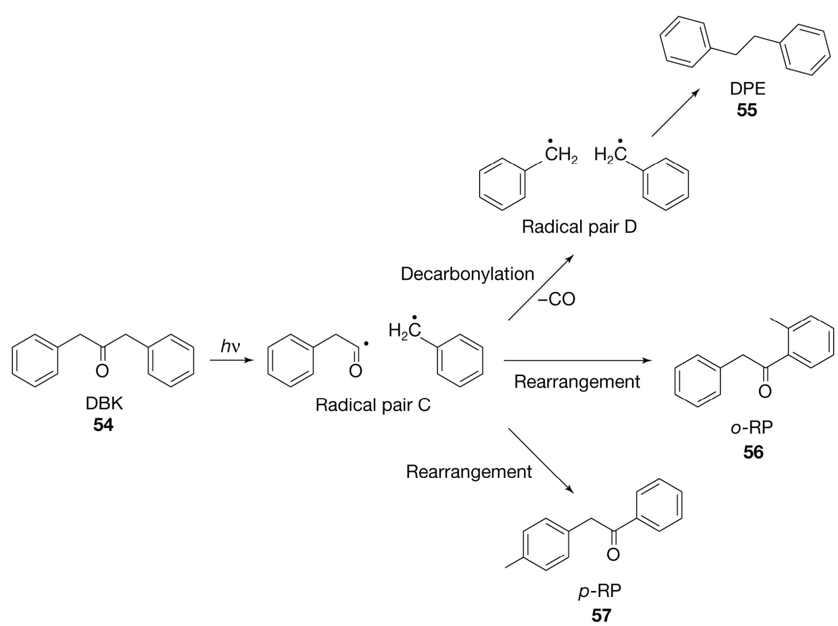
90% photolysis
at 15,000 G applied
mag. field



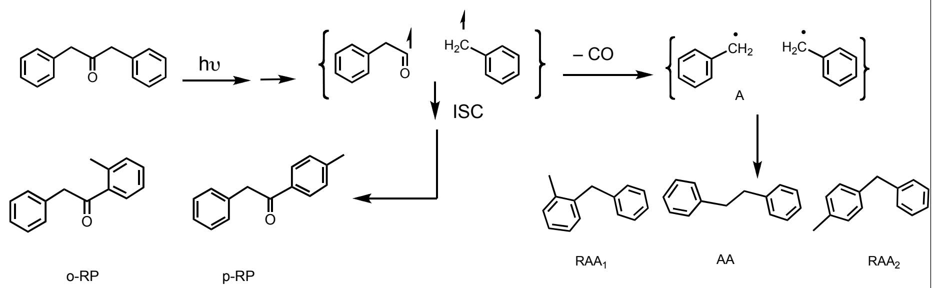
Octaacid as a Cage





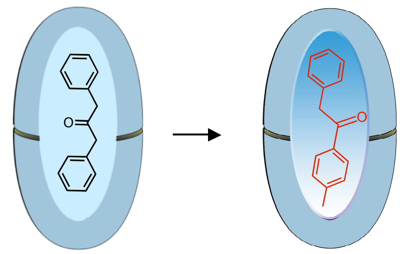


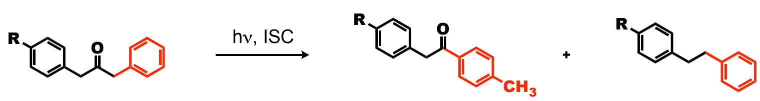
The primary radical pair prefers to rotate than decarbonylate

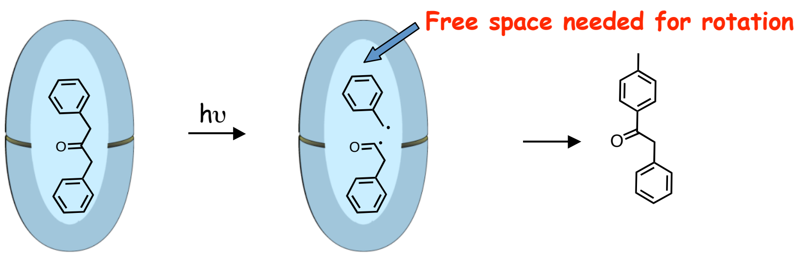


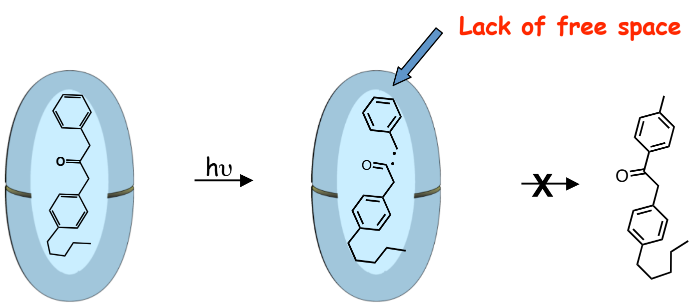
Relative product distribution (%)

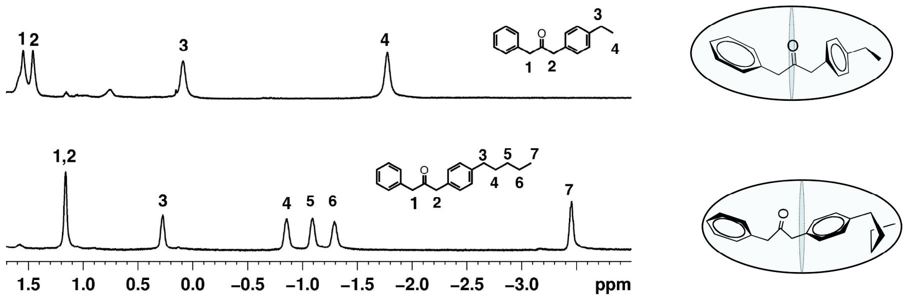
Medium	RAA1+RAA2	AA	p-RP
Hexane	--	>99	--
Octa acid	10	34	56

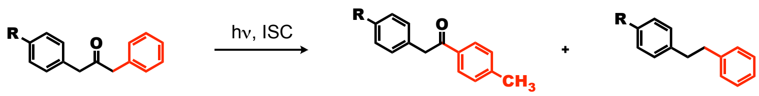


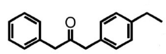
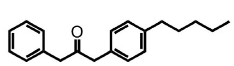




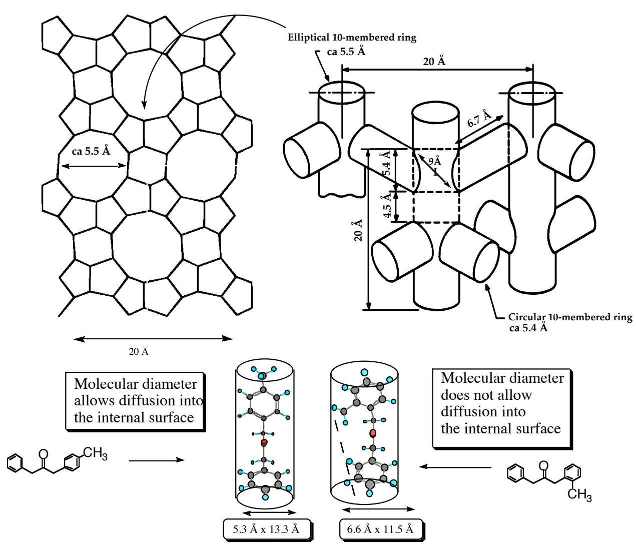


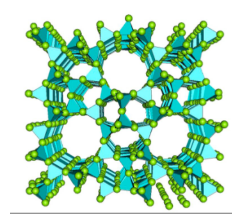


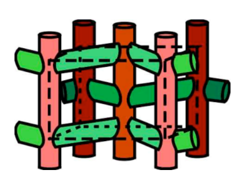


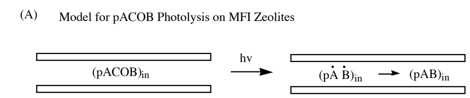
	49	51
	0	100

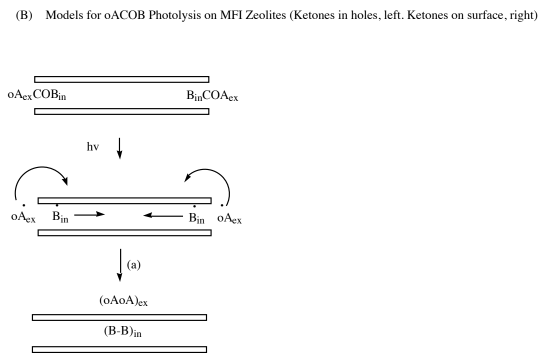
Structure of MFI zeolites

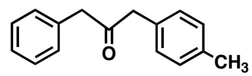






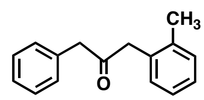






para ketone fits into the internal surface

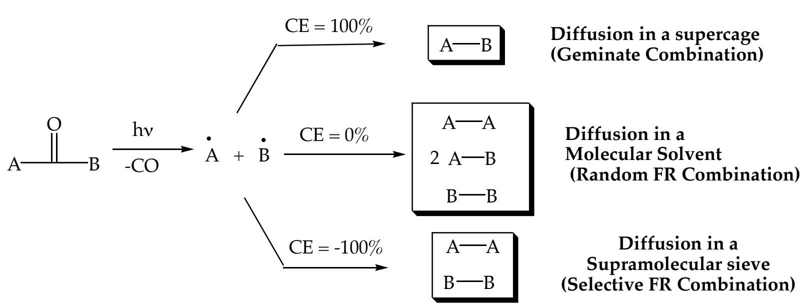
Ketone completely inside: 100 % cage

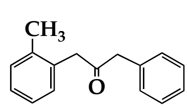


ortho ketone does not fit into the internal surface

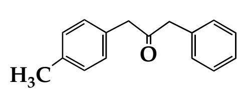
Ketone half inside,half outside: -100 % cage!!!

Molecular vs. supramolecular radical-radical combination

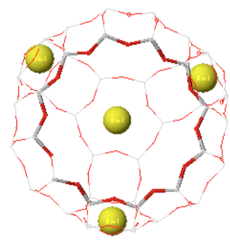


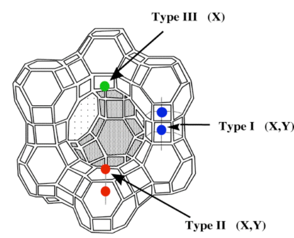


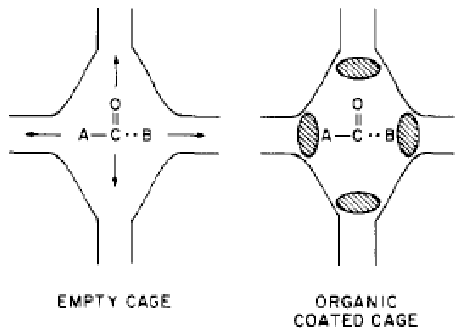
oMeDBK = oACOB

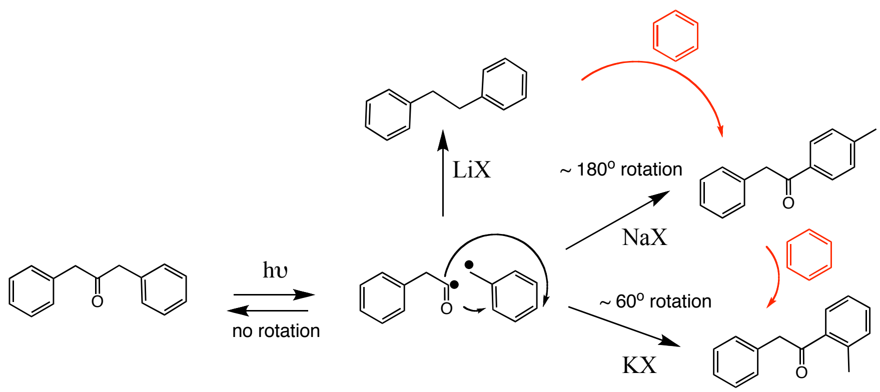


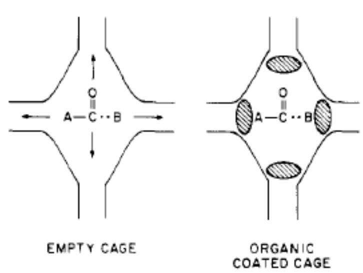
pMeDBK = pACOB



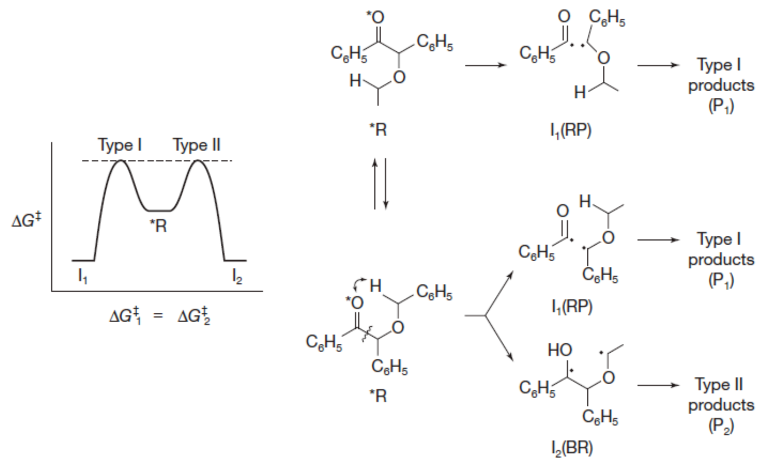

Type III (X)
Type I (X,Y)
Type II (X,Y)


O
A—C··B
EMPTY CAGE
ORGANIC
COATED CAGE

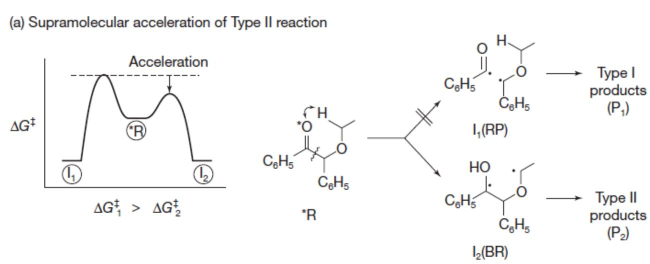

hυ
no rotation
LiX
~ 180° rotation
NaX
~ 60° rotation
KX


EMPTY CAGE
ORGANIC
COATED CAGE

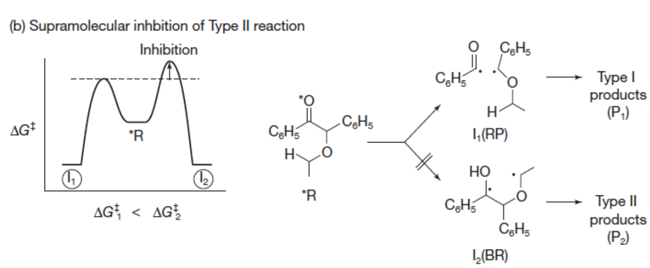
An schematic of supramolecular conformational control of a photoreaction with two competing paths: *R → I(BR) + *R → I(RP)



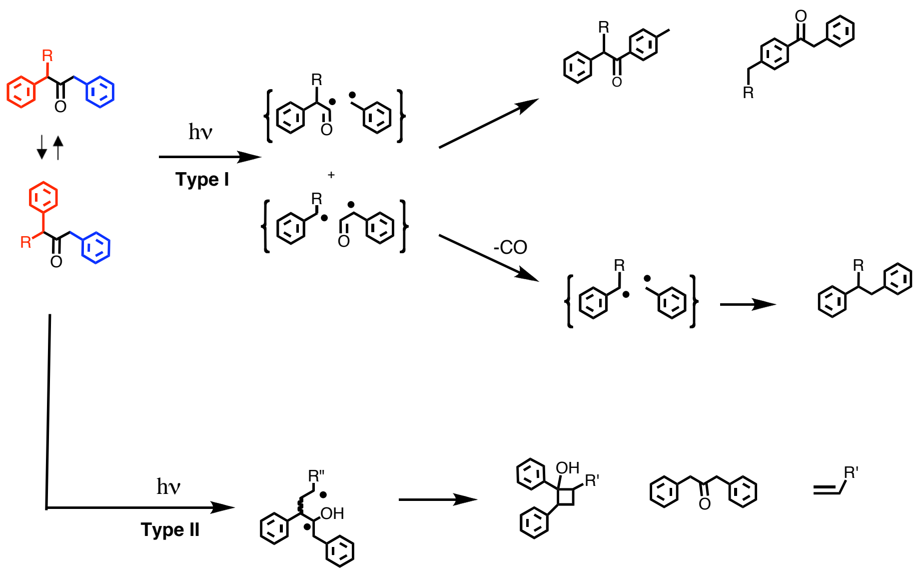
Controlling the competition between Type I and Type II products by controlling the *R → I(BR) of the Type II process

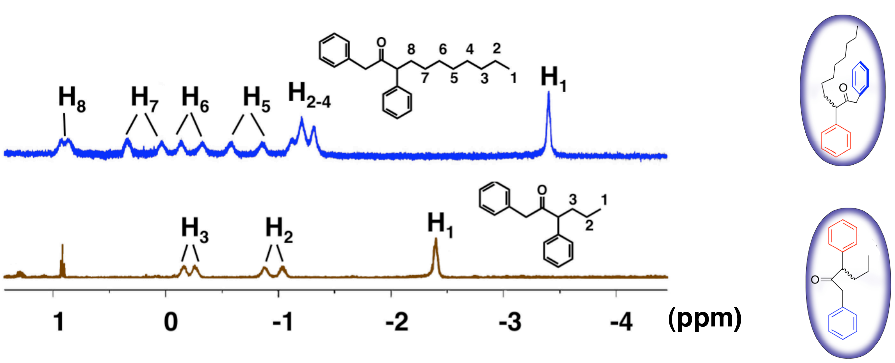


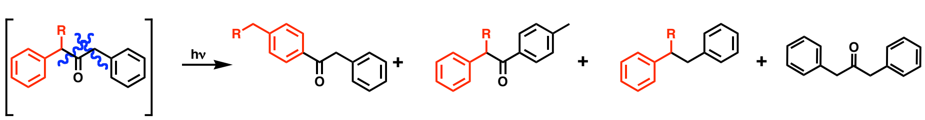
Type II Accelerated by preorganization



Type II Inhibited by preorganization



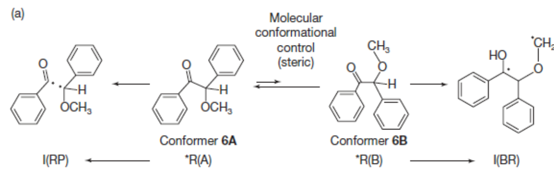




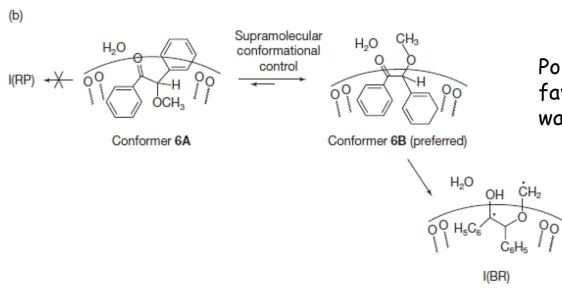
$-C_3H_7$	35	4	50	11
$-C_8H_{17}$	-	-	10	90

Supramolecular mechanistic rationalization of the micellar effect: Preorganization of the conformation of *R

*R → I(RP)



*R → I(BR)

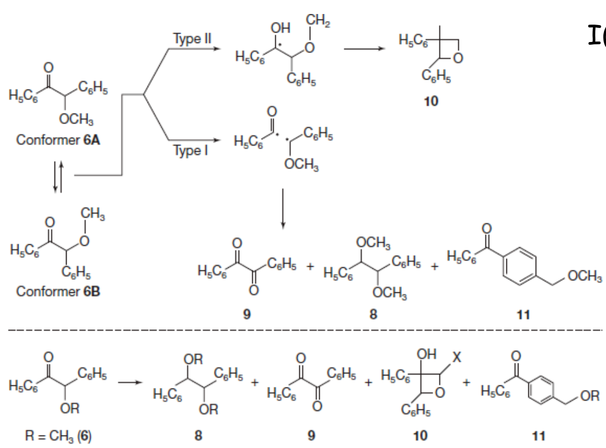


Polar group favored near water interface

*R → I(BR)

Exemplar of micellar control of ratio of Type I and Type products

I(BR) products



I(RP) Free radical products

R = CH$_3$ (6)	8	9	10 (X = H)	11
Benzene	39%	23%	—	—
Cetyltrimethyl ammonium chloride micelle	8%	7%	52%	—

I(RP) favored by fast diffusional separation

I(BR) favored by preorganization and enhanced cage effect in micelles