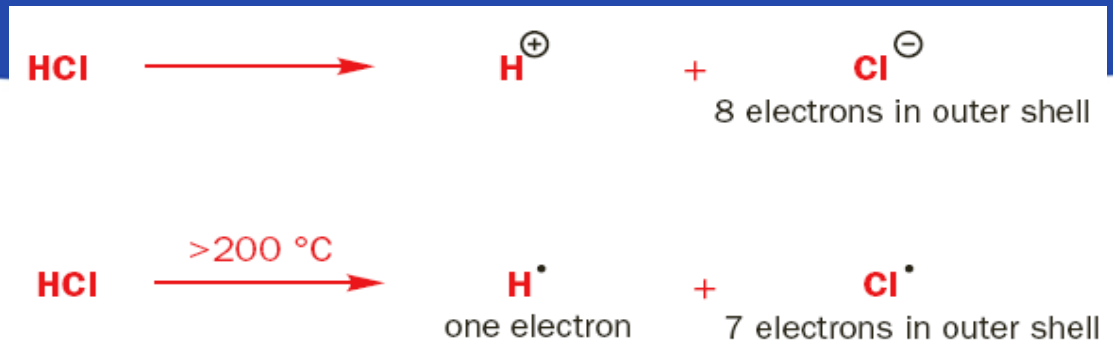
TÁMOP-4.1.1.F-14/1/KONV-2015-0006
SZTE TTIK, KTCS, 1a) Duális és moduláris képzésfejlesztés a mesterképzéshez

Gyökös reakciók

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020
MAGYARORSZÁG KORMÁNYA
Európai Unió
Európai Szociális Alap
BEFEKTETÉS A JÖVŐBE



ΔG = +1347 kJ mol^{-1}, 273 K

ΔG = +431 kJ mol^{-1}, 473 K

Heterolysis and homolysis

- When bonds break and one atom gets both bonding electrons, the process is called **heterolysis**

  The products of heterolysis are, of course, **ions**.

- When bonds break and the atoms get one bonding electron each, the process is called **homolysis**

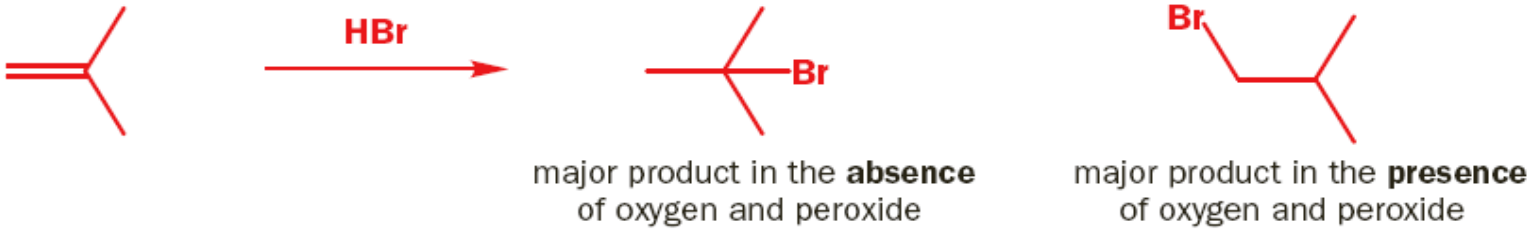
  The products of homolysis are **radicals**, which may be atoms or molecules, and contain an unpaired electron.

A gyökös reakciók jellemző közege:

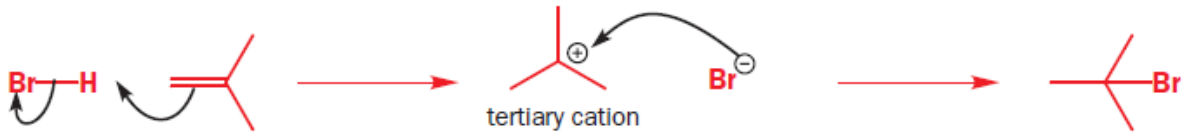
gázfázis

vagy

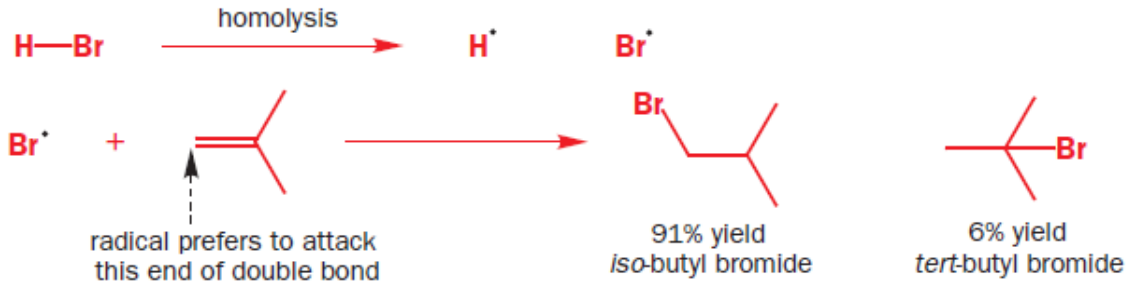
apoláris oldószer (például CCl_4)



ionos mechanizmus



gyökös mechanizmus (nem teljes)



Bond X–Y	ΔG for X–Y $\rightarrow X^{\bullet} + Y^{\bullet}$, kJ mol^{-1}	Bond X–Y	ΔG for X–Y $\rightarrow X^{\bullet} + Y^{\bullet}$, kJ mol^{-1}
H–OH	498	CH_3–Br	293
H_3C–H	435	CH_3–I	234
H_3C–OH	383	Cl–Cl	243
H_3C–CH_3	368	Br–Br	192
H–Cl	431	I–I	151
H–Br	366	HO–OH	213
H–I	298	MeO–OMe	151
CH_3–Cl	349		

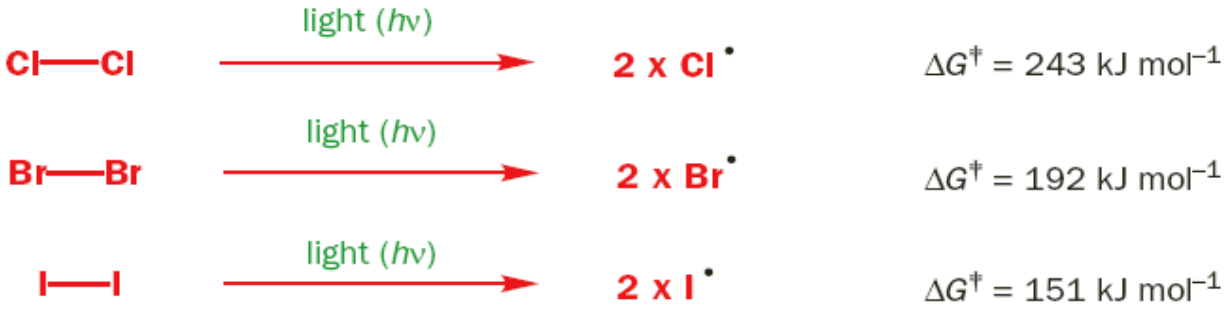
Hogyan csináljunk gyököket?

a kötési energiát kell befektetni (hő, fény, radioaktív sugárzás)

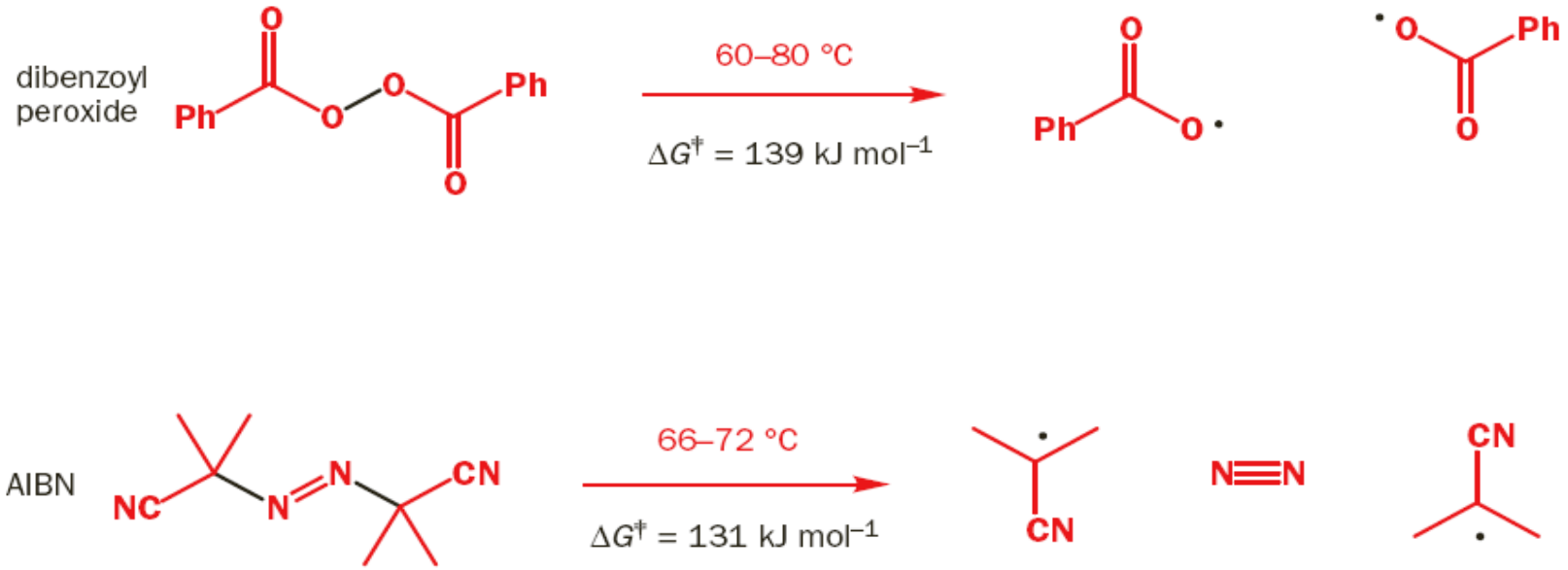
Ez azonban nem elég:

kell legyen egy mechanizmus, amely a homolízishez vezető rezgési módban gyűjti a befektetett energiát

fénybesugárzás



melegítés



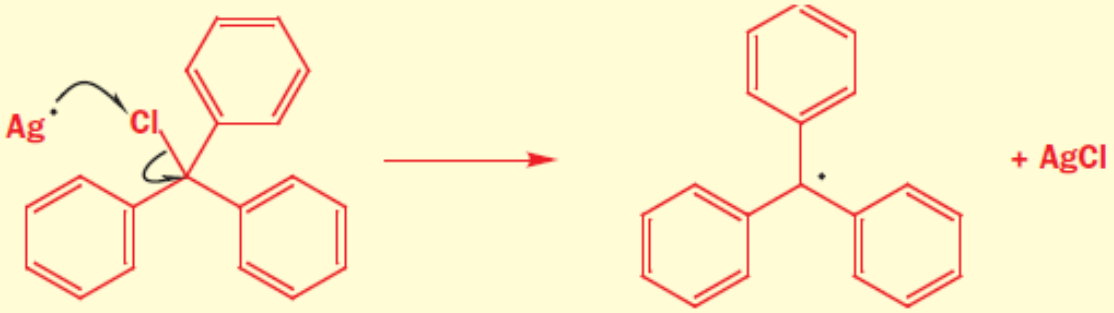
AIBN = azoizobutironitril

a legtöbb gyök eszméletlenül reaktív

de nem mindegyik

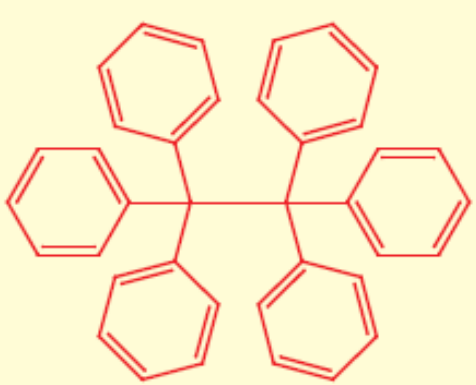
First radical detected

The very first radical to be detected, the triphenylmethyl radical, was made in 1900 by abstraction of $Cl^{\bullet}$ from Ph_3CCl by Ag metal.

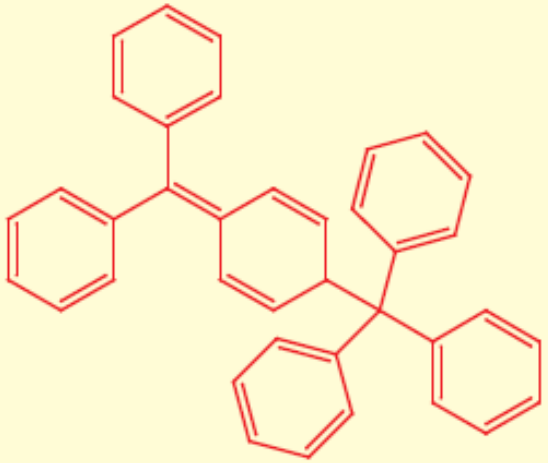


relatively stable triphenylmethyl radical

This radical is relatively stable (we shall see why shortly), but reacts with itself reversibly in solution. The product of the dimerization of triphenylmethyl was for 70 years believed to be tetraphenyl ethane but, in 1970, NMR showed that it was, in fact, an unsymmetrical dimer.

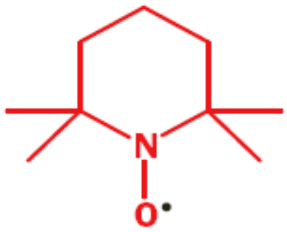


original suggested structure of triphenylmethyl dimer (1900)

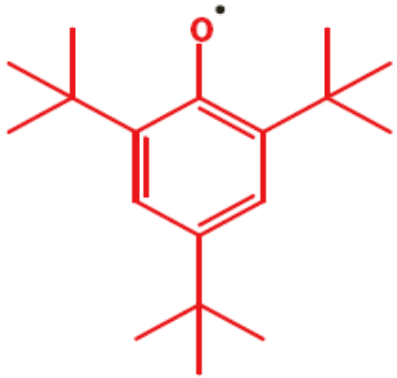


correct structure of dimer (1970)

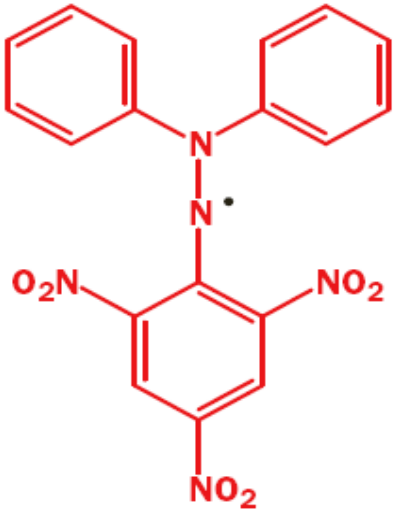
ezek is nagyon stabilisak



TEMPO
TEtraMethylPiperidine *N*-Oxide
m.p. 36–38°C



dark blue solid
m.p. 97°C



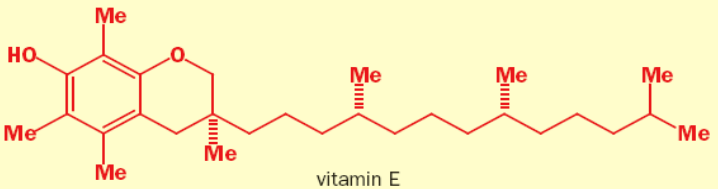
violet crystals

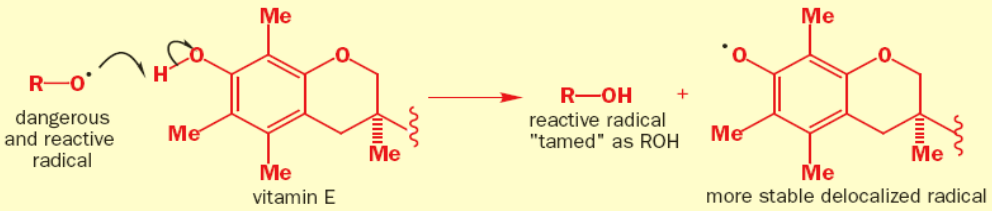
sztérikus és/vagy elektronikus (konjugáció) okok

gyökök és az öregedés

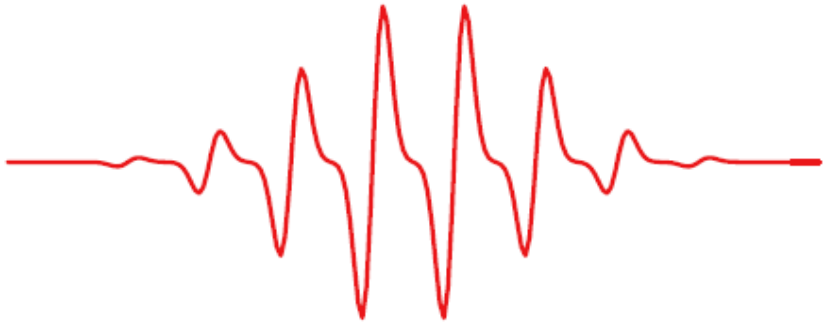
Vitamin E tames radicals

Many of the molecules that make up the structure of human tissue are susceptible to homolysis in intense light, and the body makes use of sophisticated chemistry to protect itself from the action of the reactive radical products. Vitamin E plays an important role in the 'taming' of these radicals: abstraction of H from the phenolic hydroxyl group produces a relatively stable radical that does no further damage.

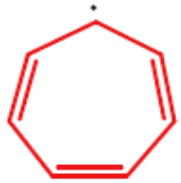




gyökök szerkezetvizsgálata (koncentrációmeghatározás): ESR spektroszkópia

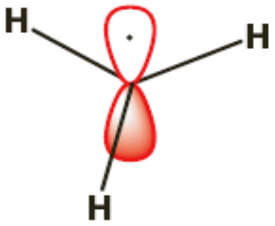


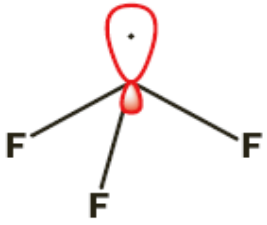
ESR spectrum of cycloheptatrienyl radical



cycloheptatrienyl radical

planar $CH_3^{\bullet}$ radical



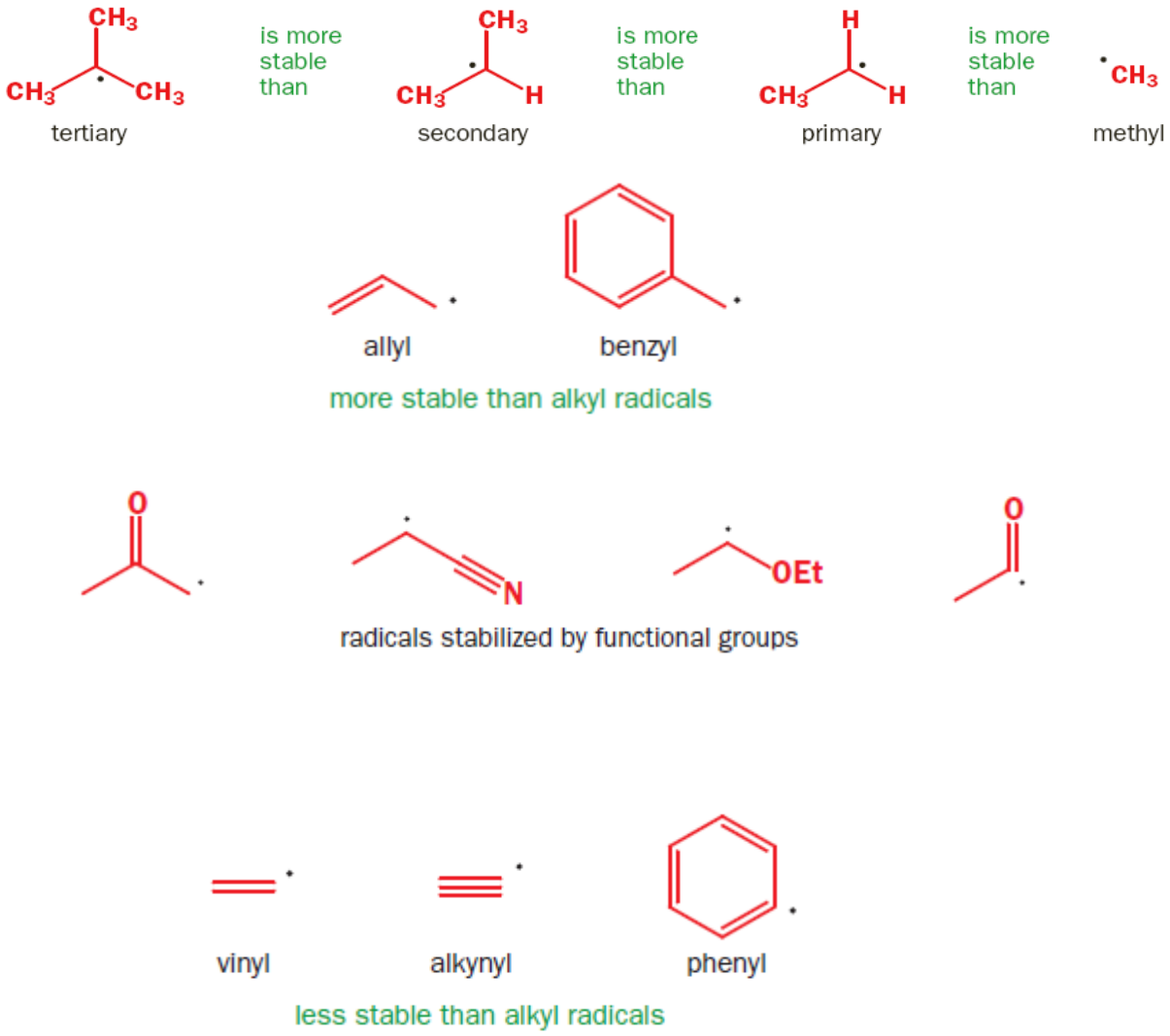


pyramidal $CF_3^{\bullet}$ radical

A gyökök stabilitása

Bond	Dissociation energy, kJ mol^{-1}
CH_3–H	439
$MeCH_2$–H	423
Me_2CH–H	410
Me_3C–H	397
HC≡C–H	544
H_2C=CH–H	431
Ph–H	464
H_2C=CH_2CH_2–H	364
$PhCH_2$–H	372
RCO–H	364
EtOCHMe–H	385
N≡CCH_2–H	360
$MeCOCH_2$–H	385

gázfázisban megmérve

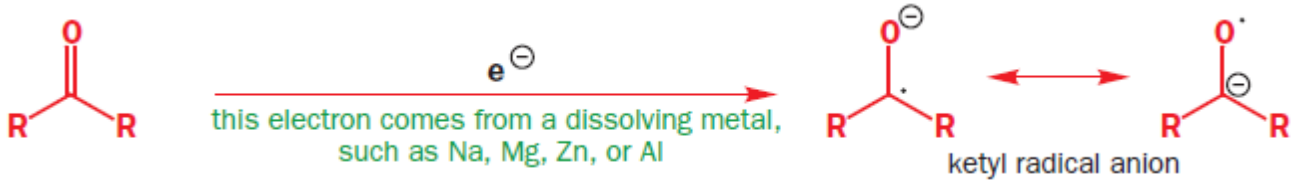


Hogyan reagálnak a gyökök?

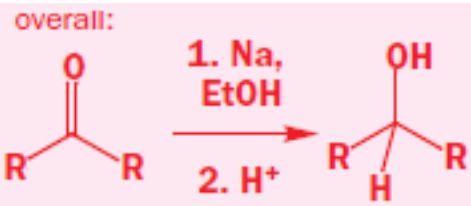
(1) gyök + gyök $\rightarrow$ molekula (viszonylag ritkák)
(2) gyök + molekula $\rightarrow$ másik gyök + másik molekula
(3) gyök $\rightarrow$ másik gyök + molekula

gyök + gyök

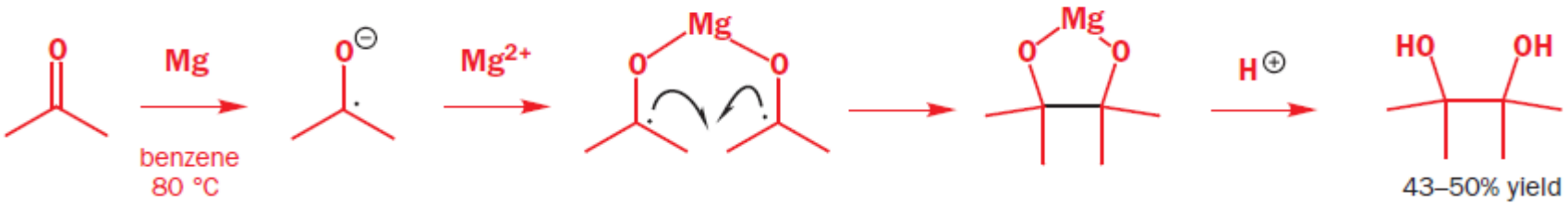
pinakol képződés



Bouveault–Blanc reduction



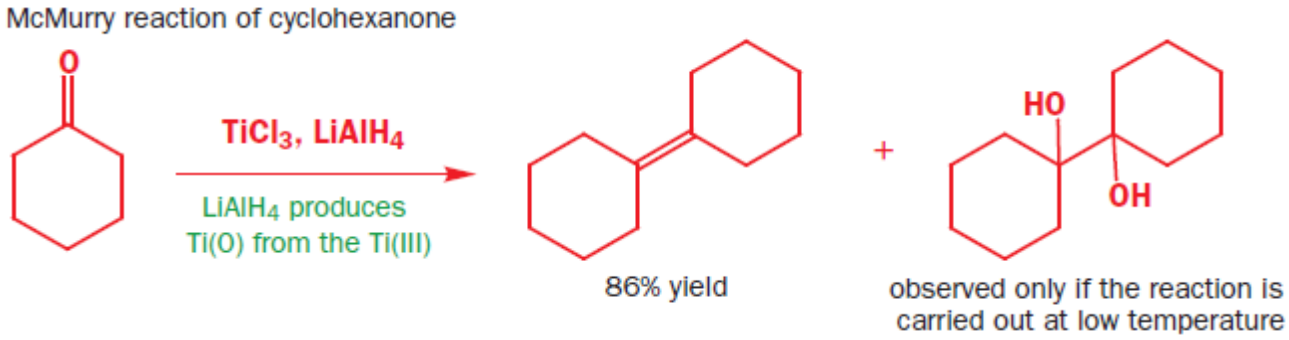
pinacol dimerization of acetone (ketyl radical reaction in hydrocarbon solvent)

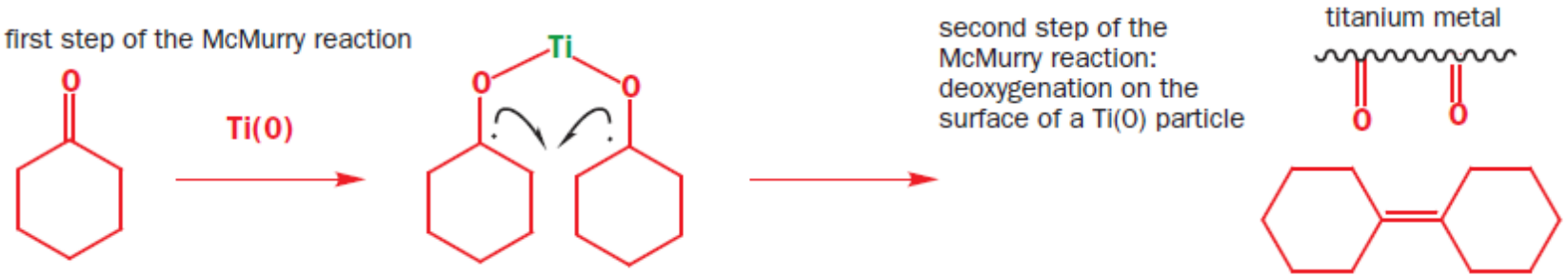


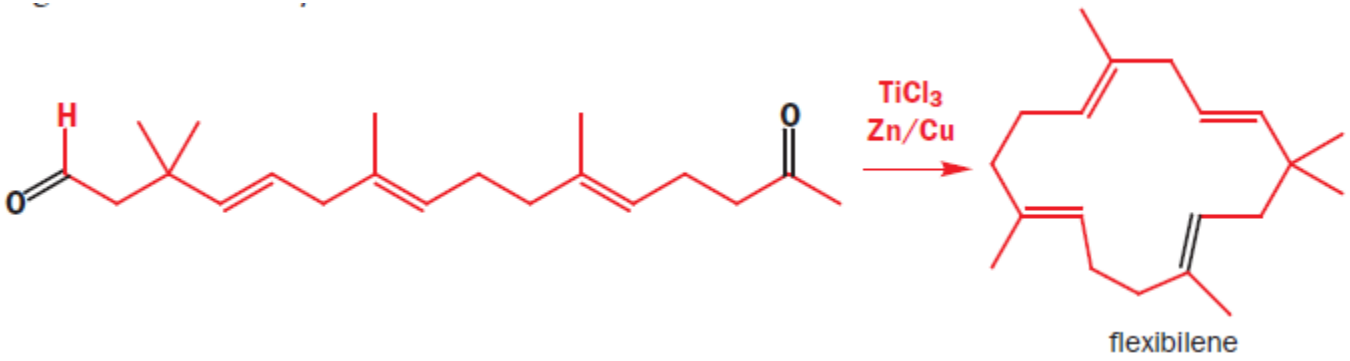
diol product known as "pinacol"

43–50% yield

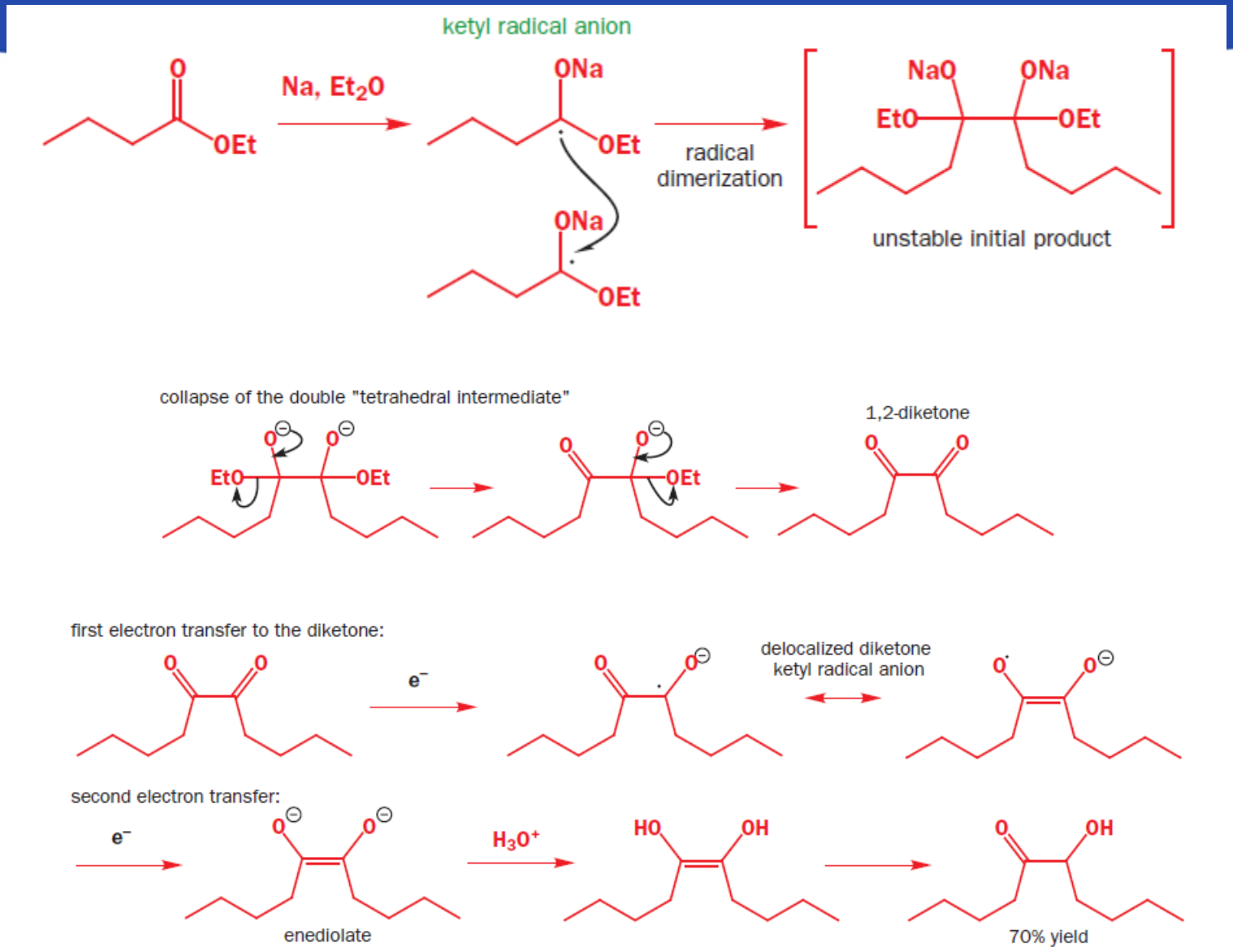
McMurry reakció







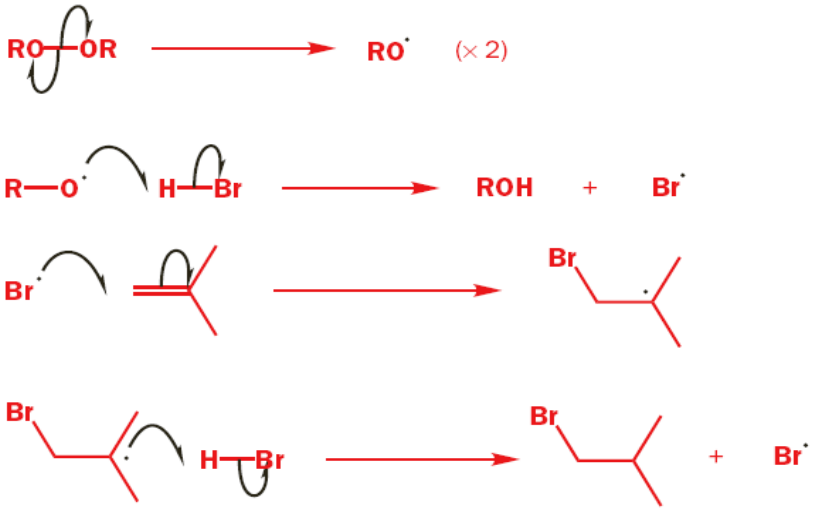
Észterek pinakol-típusú reakciója: aciloin képződés



gyök + molekula (gyökös láncreakció)

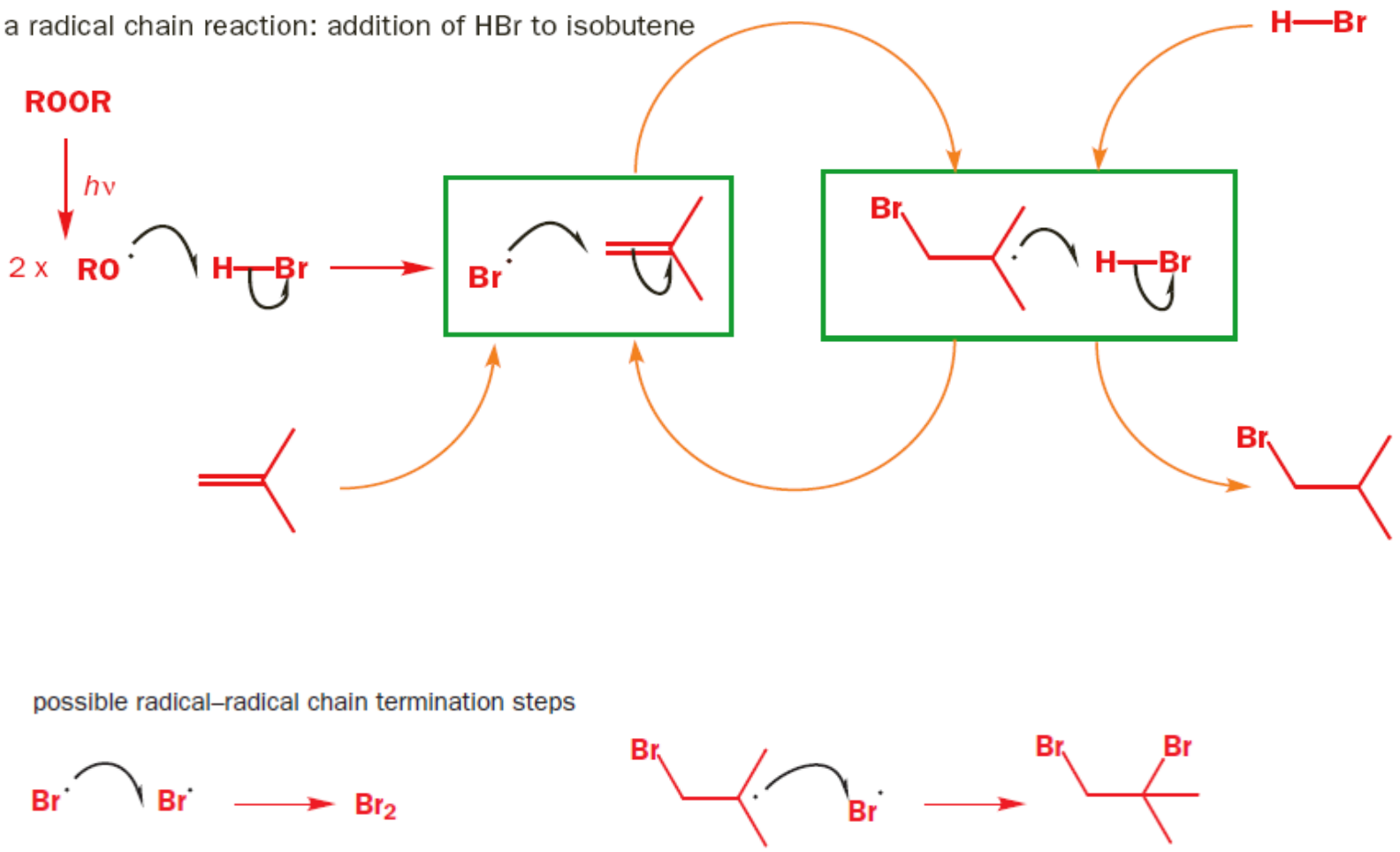
a bruttó reakció

a mechanizmus



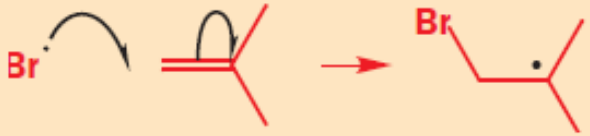
possible radical–radical chain termination steps

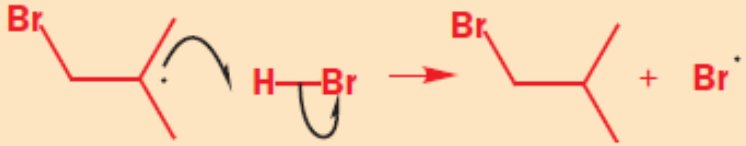
a mechanizmus másként ábrázolva



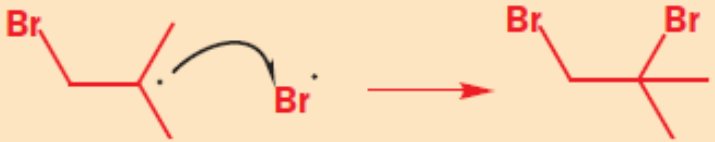
- Radical chain reactions consist of
  - **Initiation** steps

  - **Propagation** steps

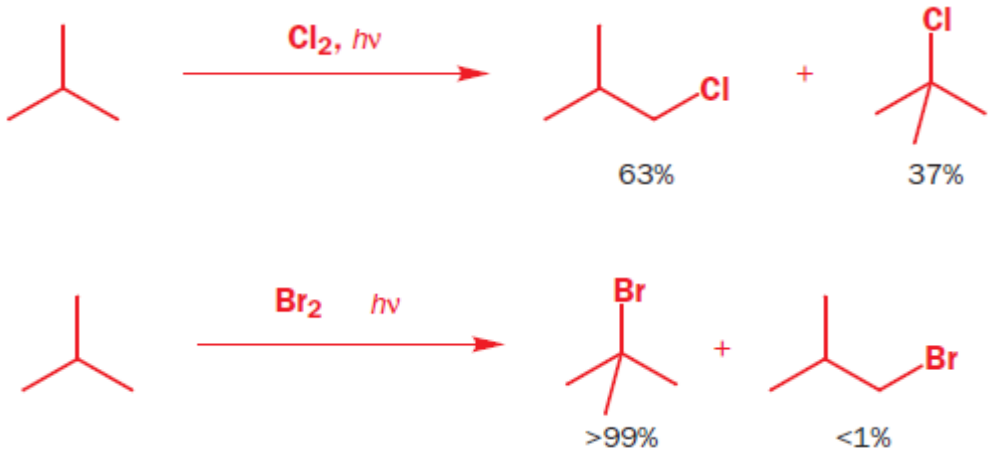




  - **Termination** steps



gyökös szubsztitúciók szelektivitása



a gyökös szubsztitúció fluórral kezelhetetlenül nagy sebességű

a jódos szubsztitúció nem gyökös folyamat (túlságosan endoterm lenne)

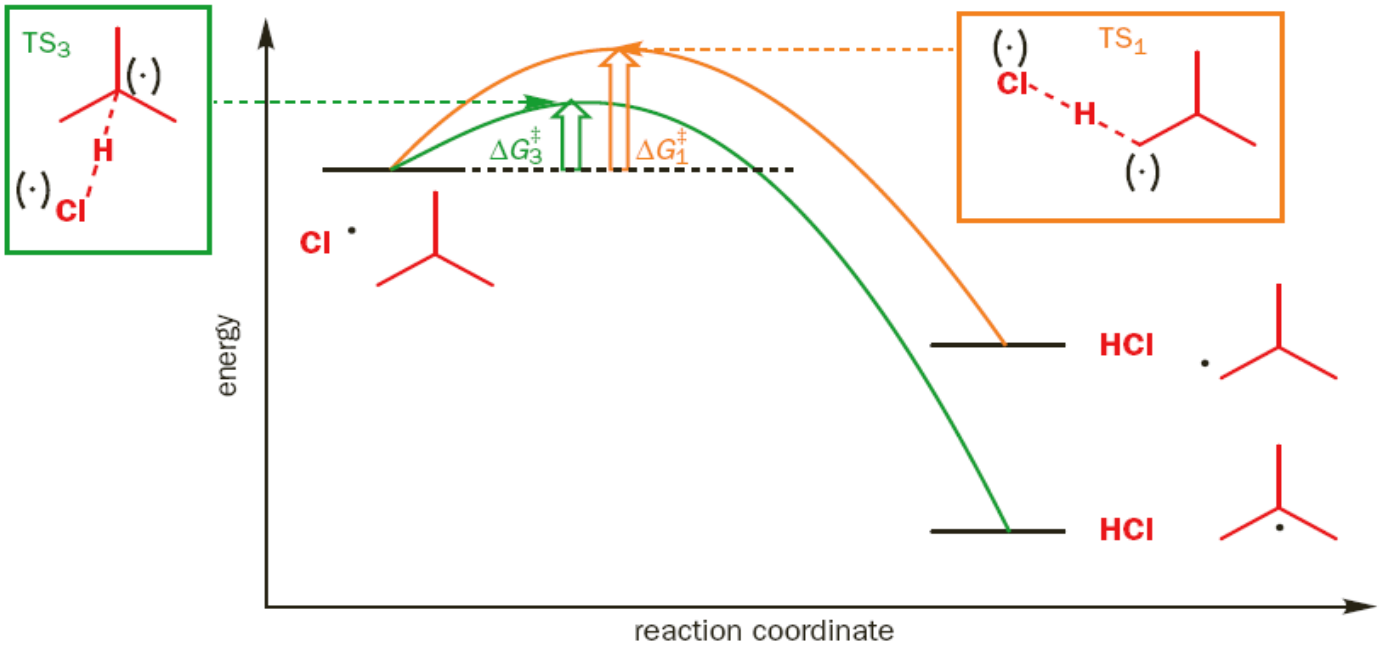
gyökös klórozás

abstraction of primary hydrogen

	ΔH, kJ mol^{-1}
one H–Cl bond formed	–431
one primary C–H bond broken	+423
total	–8

abstraction of tertiary hydrogen

	ΔH, kJ mol^{-1}
one H–Cl bond formed	–431
one tertiary C–H bond broken	+397
total	–34

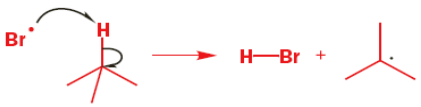


gyökös brómozás

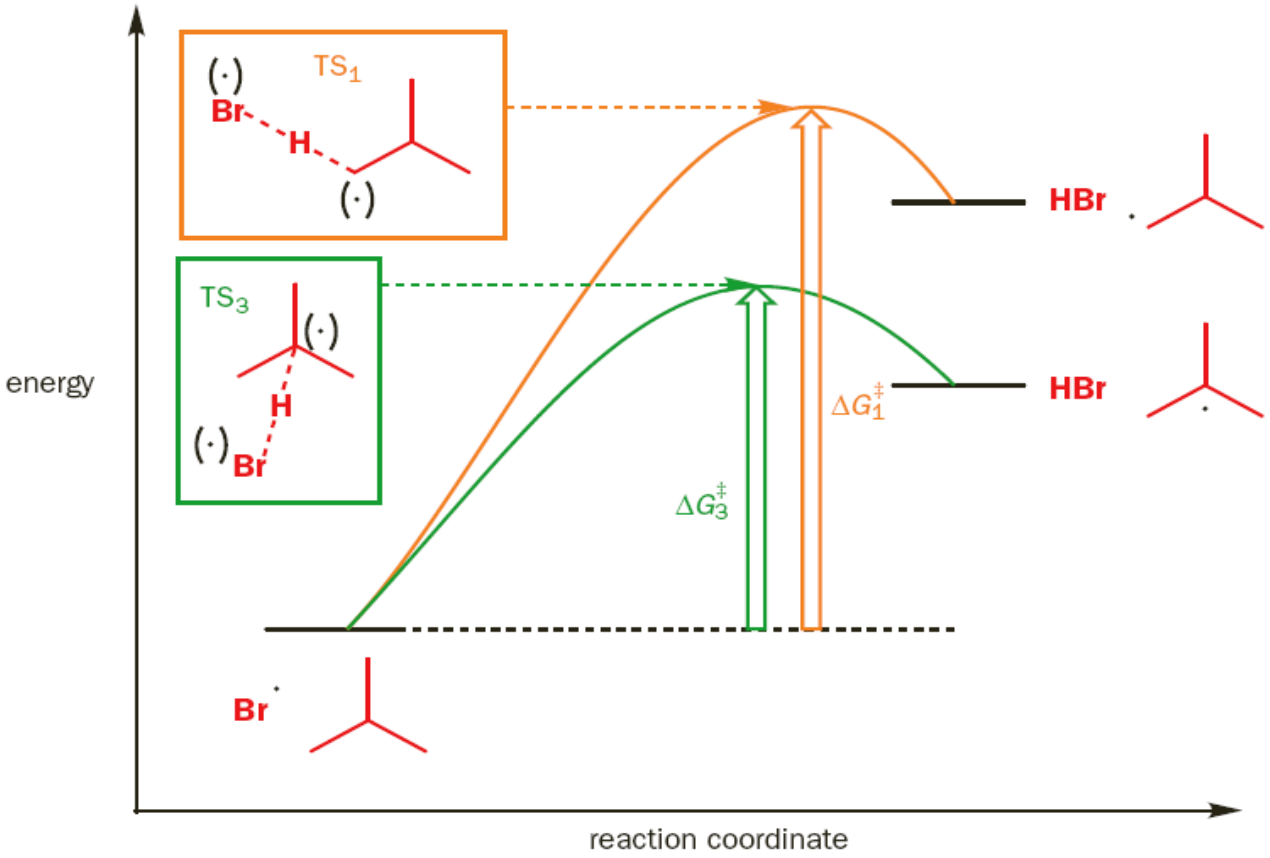
abstraction of primary hydrogen

	ΔH, kJ mol^{-1}
one H–Br bond formed	–366
one primary C–H bond broken	+423
total	+57

abstraction of tertiary hydrogen



	ΔH, kJ mol^{-1}
one H–Br bond formed	–366
one tertiary C–H bond broken	+397
total	+31

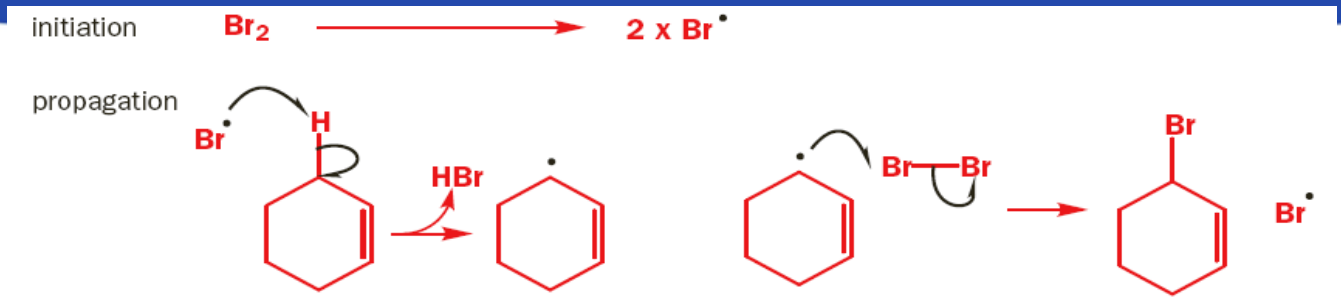


second step of the bromination reaction

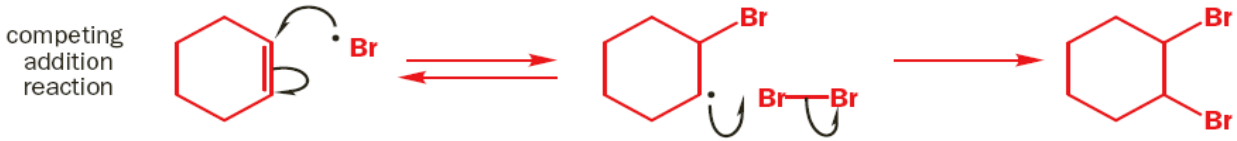
	ΔH, kJ mol^{-1}
one C–Br bond formed	–293
one Br–Br bond broken	+192
total	–101

The **Hammond postulate** gives information about the structure of transition states. It says that two states that interconvert directly (are directly linked in a reaction profile diagram) and that are close in energy are also similar in structure. So a transition state will be most like the starting material, the intermediate, or the product if it is close in energy to one of these observable structures.

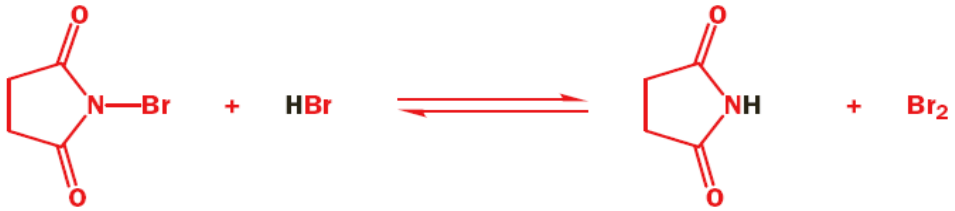
szintetikus alkalmazások – allil helyzetű brómozás

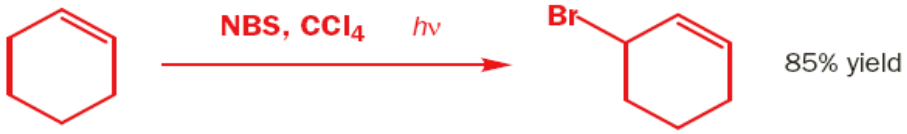


ha nagy a Br_2 koncentráció

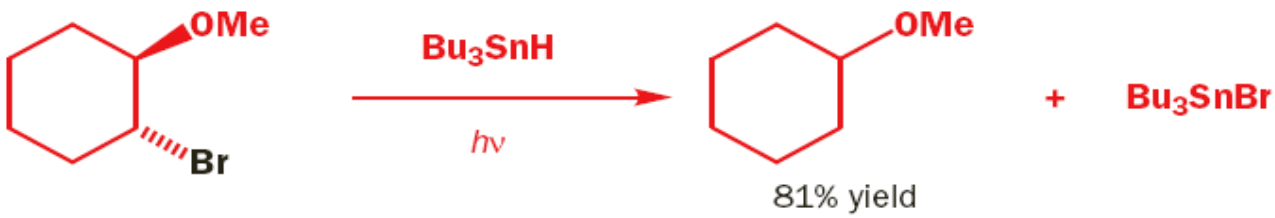


szelektivitásnövelés NBS-sel





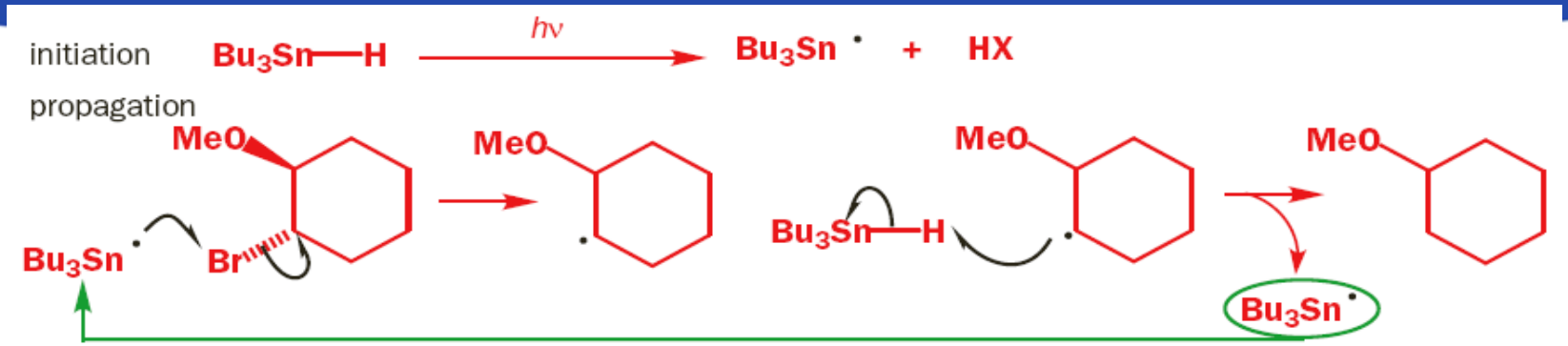
szintetikus alkalmazások – Br–H csere



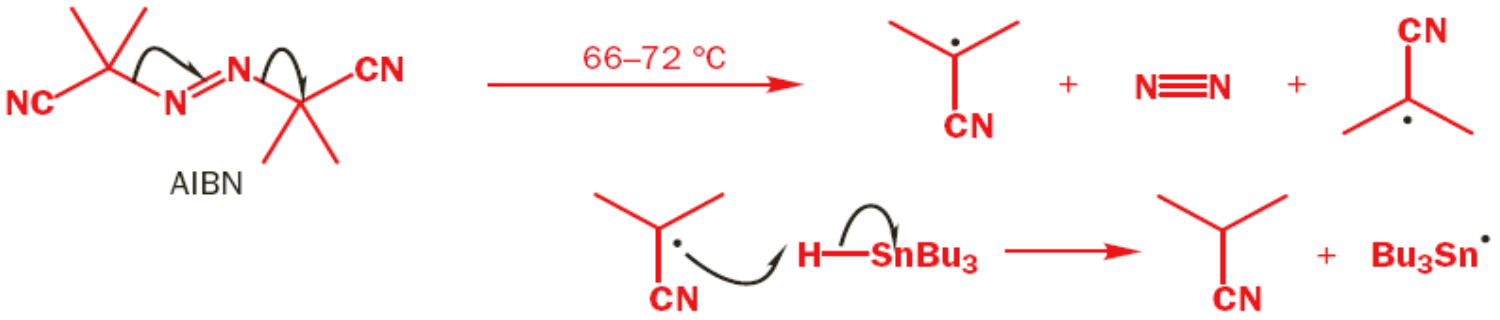
Bond	Representative bond energy, kJ mol^{-1}
C–Br	280
Sn–H	308
C–H	418
Sn–Br	552

a reakció könnyen megy bromid és jodid esetén, nagy gyökkoncentrációra van szükség kloridok esetén és nem megy fluoridokkal

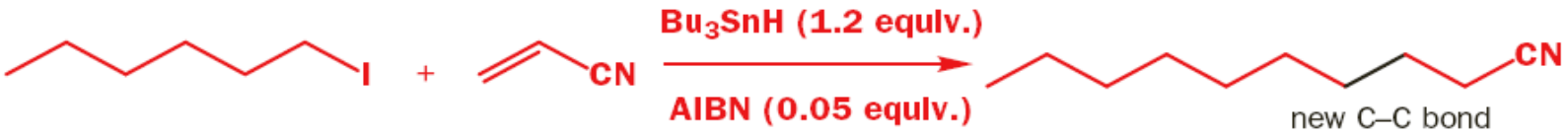
mechanizmus



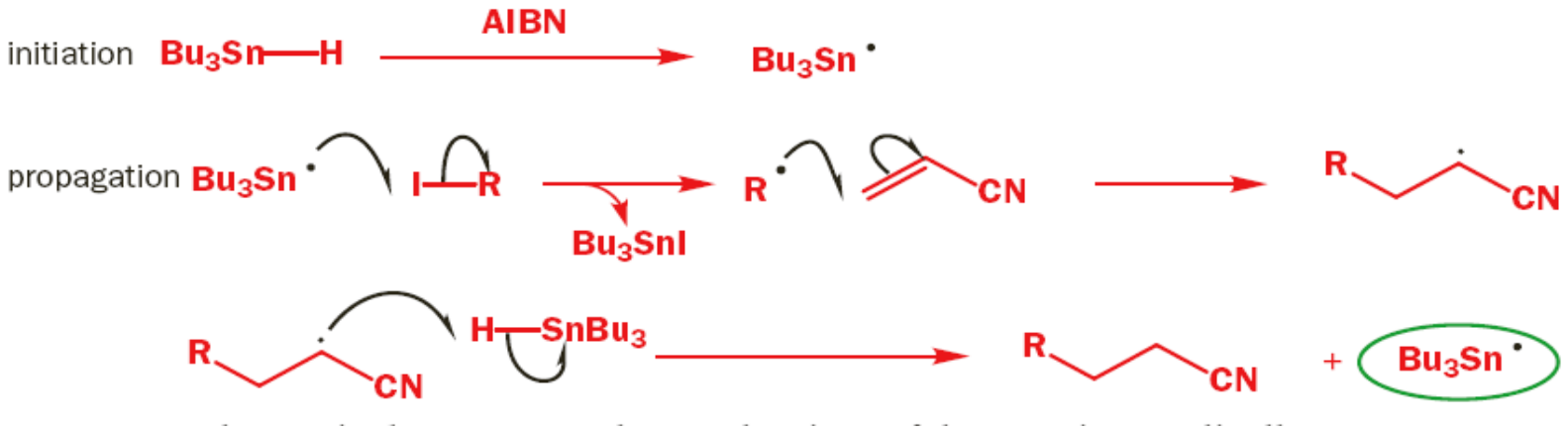
alternatív iniciálás (ha nagyobb mennyiségű gyökre van szükség – C–Cl kötésnél)



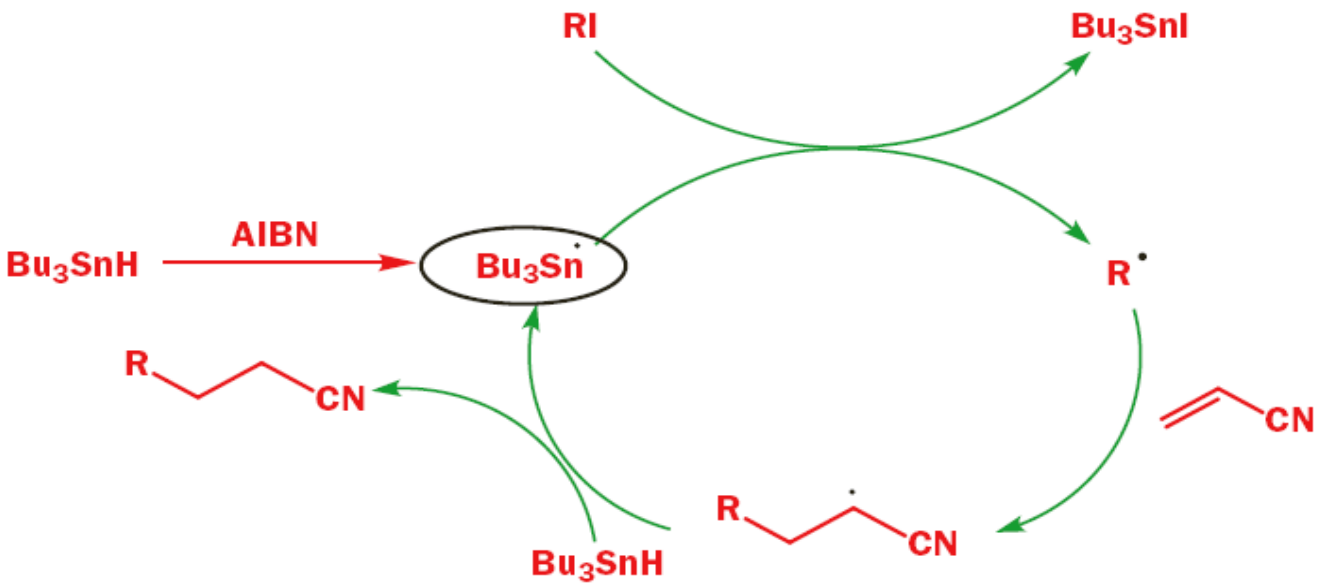
szintetikus alkalmazások – C–C kötés kialakítása



mechanizmus



a mechanizmus másként ábrázolva

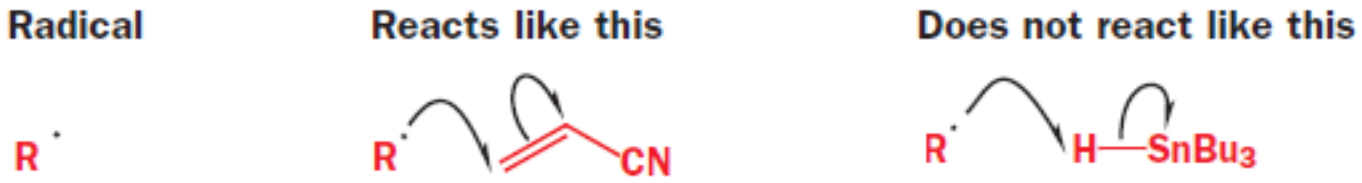


ezt szeretnénk

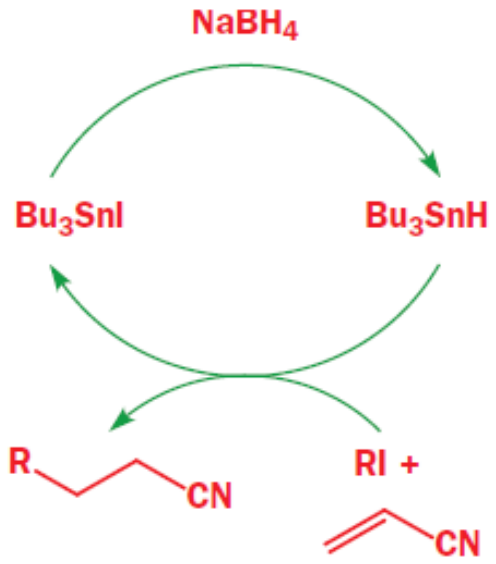
Radical	Reacts like this	Does not react like this
$Bu_3Sn^{\cdot}$		

szükséges: reaktív halogenid (jodid vagy bromid)

ezt szeretnénk



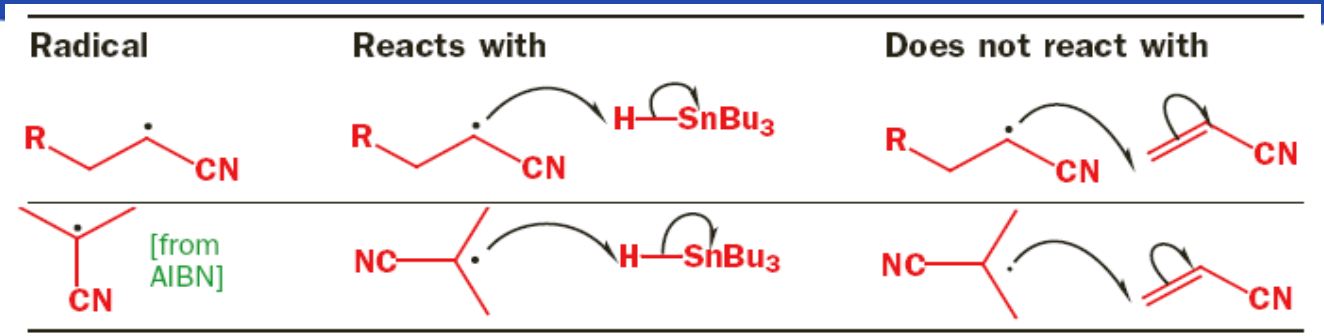
szükséges: óriási akrilnitril felesleg vagy alacsony H–$SnBu_3$ koncentráció (inkább)



0.1-0.2 ekvivalens Bu_3SnI-dal indulva

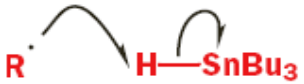
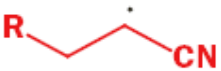
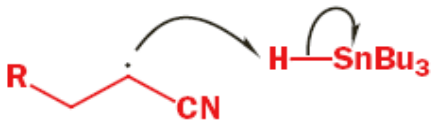
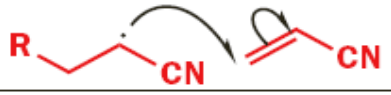
szükséges még: a telítetlen partneren elektronszívó csoport legyen

ezt szeretnénk



így lesz, mert az elektrofil gyökök (elektronszívó csoportok vannak rajtuk) nem szívesen reagálnak elektronszegény alkénekkel

mi, mivel reagál és mivel nem

Radical	Reacts like this	Does not react like this
$Bu_3Sn^{\cdot}$		
$R^{\cdot}$		
		
		

ha

Summary of requirements for the successful use of the tin method

• Bu_3SnH	must be added or generated slowly
• R–X starting material	must contain a weak C–X bond (C–I or C–Br)
• Radical trap	must be an electrophilic alkene
	must be present in a concentration at least 10 times that of Bu_3SnH

KÖSZÖNÖM A FIGYELMET!

SZÉCHENYI 2020

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