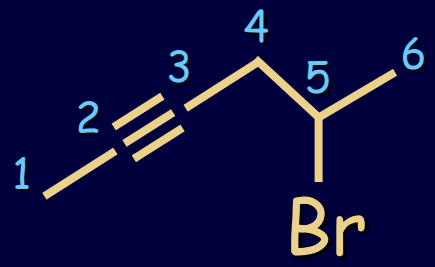
Bölüm 3.2 Alkinler: Üçlü Bağ

Adlandırma

Alkenlere benzer, ancak sonek -en yerine –in.

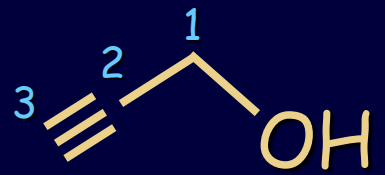
Etin

1-Pentin



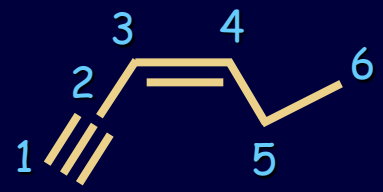
5-Brom-2-hekzin

Öncelik:
-ol > -in

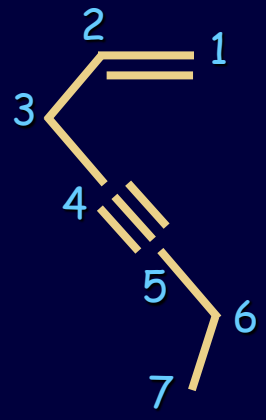


2-Propin-1-ol

Alkin çift bağlar da içerirse, enin olarak adlandırılır. Numaralandırma da ikili veya üçlü bağa yakın uçtan yapılır (küçük numaralar) :

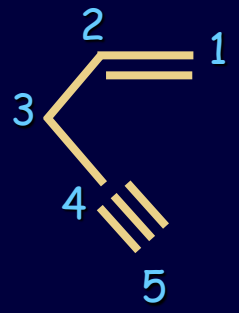


3-Hekzen-1-in



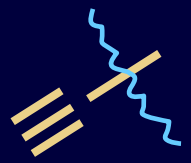
1-Hepten-4-in

İkili ve üçlü bağ eşit konumda ise öncelik ikili bağa verilir: En önce (alfabetik sıra!)

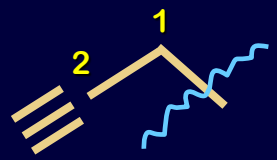


1-Penten-4-in

Sübstitüent olarak üçlü bağ:

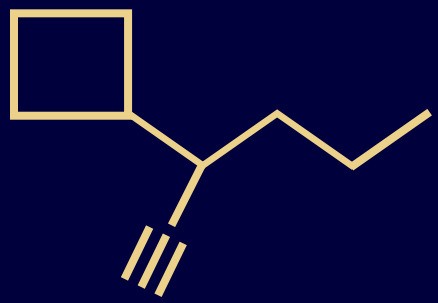


Etinil

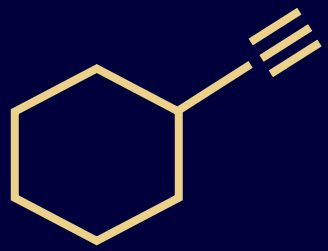


2-Propinil
(proparjil özel)

Halkalı yapılar: Adlandırma hidrokarbon kuralına göre: Küçük olan R sübstitüent, büyük olan R kök??

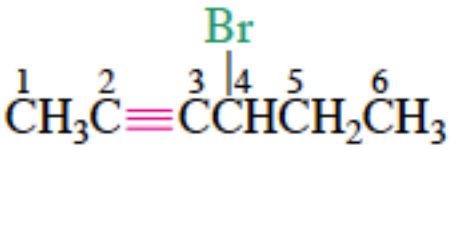


3-Siklobütil-1-hekzin



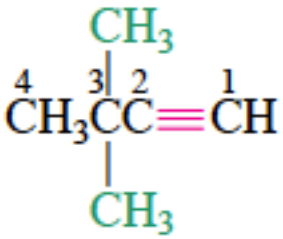
Etinilsiklohekzan mı

Siklohekziletin mi?



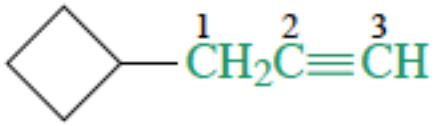
4-Brom -2-heksin

(Bir iç alkin)

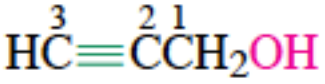


3,3-Dimetil-1-bütin

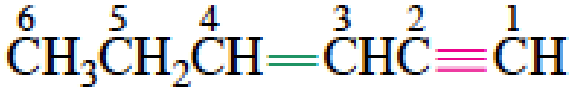
(Bir uç alkin)



2-Propinilsiklobütan
(Propargilsiklobütan)

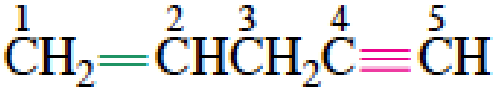


2-Propin-1-ol
(Propargil alkol)



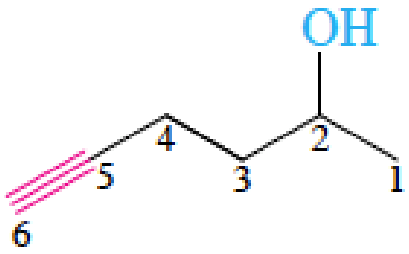
3-Heksen-1-in

(3-Heksen-5-in değil)



1-Penten-4-yne

(4-Penten-1-in değil)



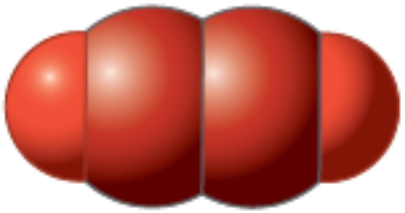
5-Hexyn-2-ol

(1-Heksin-5-ol değil)

R-C≡C-H; Uç Alkin, R-C≡C-R İç Alkin

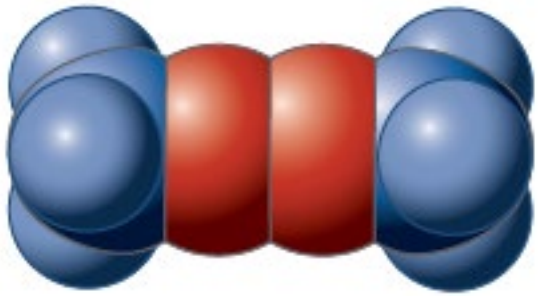
Alkinlerin Yaygın Adları

$HC{\equiv}CH$



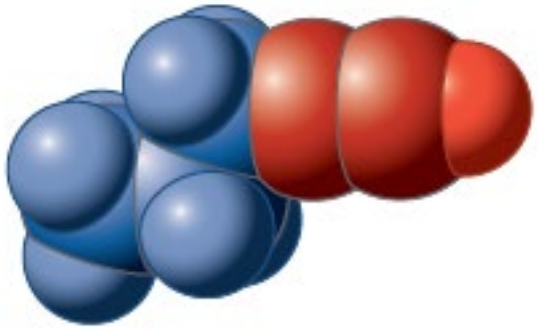
Asetilen

$CH_3C{\equiv}CCH_3$



Dimetilasetilen

$CH_3CH_2CH_2C{\equiv}CH$

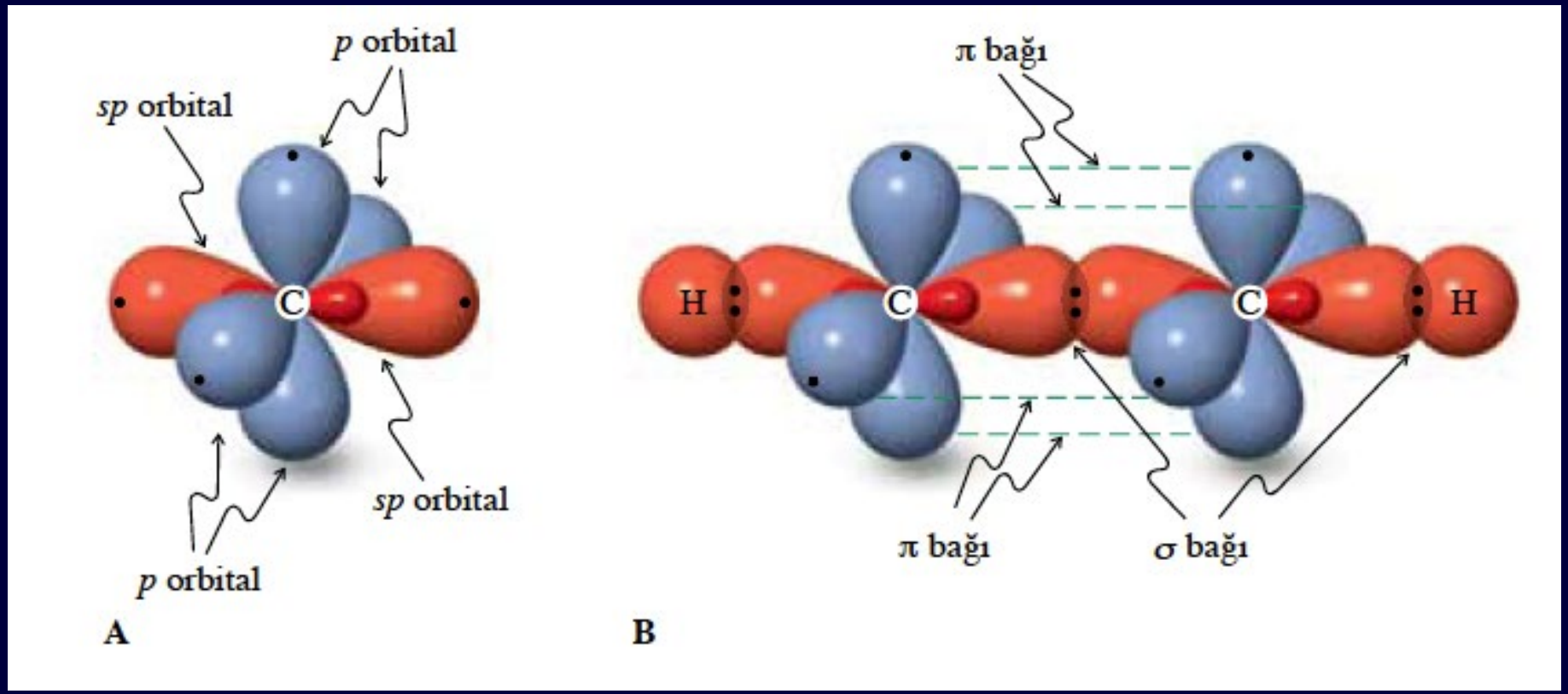


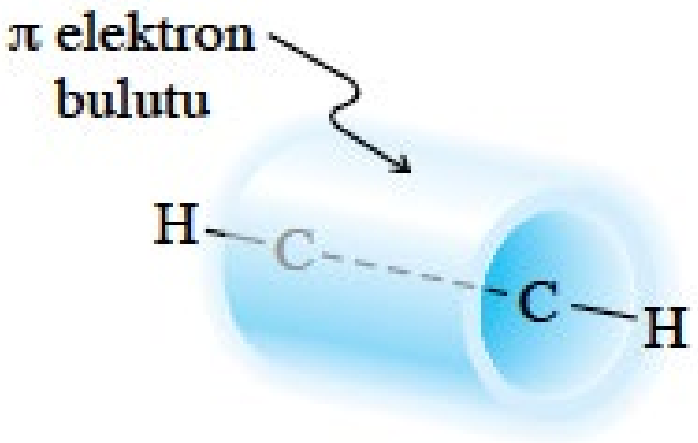
Propilasetilen

Alkinlerde Yapı ve Özellikler

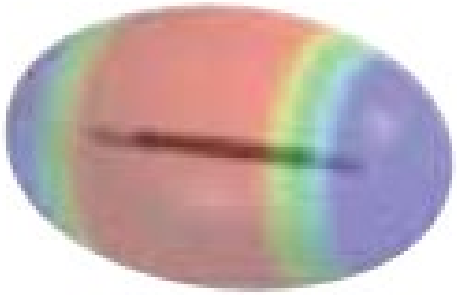
R—C≡C—R

Biribirine dik iki π bağı; *sp* hibritleşmesi

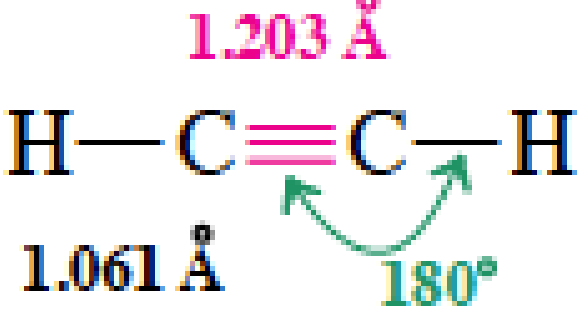




C



D



Doğrusal etin

Üçlü Bağın Enerjisi

$DH°$	$\equiv HC$	CH	$H_2C\equiv$	CH_2	$H_3C\equiv$
Kcal mol^{-1}	229	CH_3 173			90

Etinin yanması

$$HC{\equiv}CH + 2.5\ O_2 \longrightarrow 2\ CO_2 + H_2O \qquad \Delta H° = -311\ \text{kcal mol}^{-1}\ (-1301\ \text{kJ mol}^{-1})$$

Hidrojenlenme ısısı:

$$CH_3CH_2C{\equiv}CH + 2\ H_2 \xrightarrow{\text{Katalizör}} CH_3CH_2CH_2CH_3 \qquad \Delta H° = -69.9\ \text{kcal mol}^{-1}\ (-292.5\ \text{kJ mol}^{-1})$$

$$CH_3C{\equiv}CCH_3 + 2\ H_2 \xrightarrow{\text{Katalizör}} CH_3CH_2CH_2CH_3 \qquad \Delta H° = -65.1\ \text{kcal mol}^{-1}\ (-272.4\ \text{kJ mol}^{-1})$$

Asitlik : $RC\equiv C-H + :\bar{B} \overset{K}{\rightleftharpoons} R-C\equiv C:^{-} + HB$

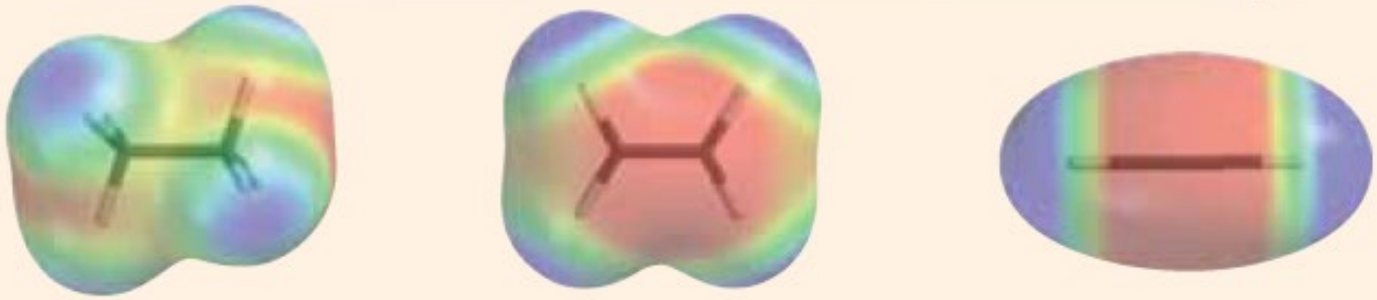
$pK_a \sim 25!$ cf. $CH_2=CH_2$ 44, CH_3-CH_3 50

Niçin? 50% s-karakter

Alkan, Alken ve Alkinlerin Göreceli Asitlikleri

	H_3C-CH_3	<	H_2C-CH_2	<	$HC\equiv CH$
Melezleşme:	sp^3		sp^2		sp
pK_a:	50		44		25

Artan asitlik

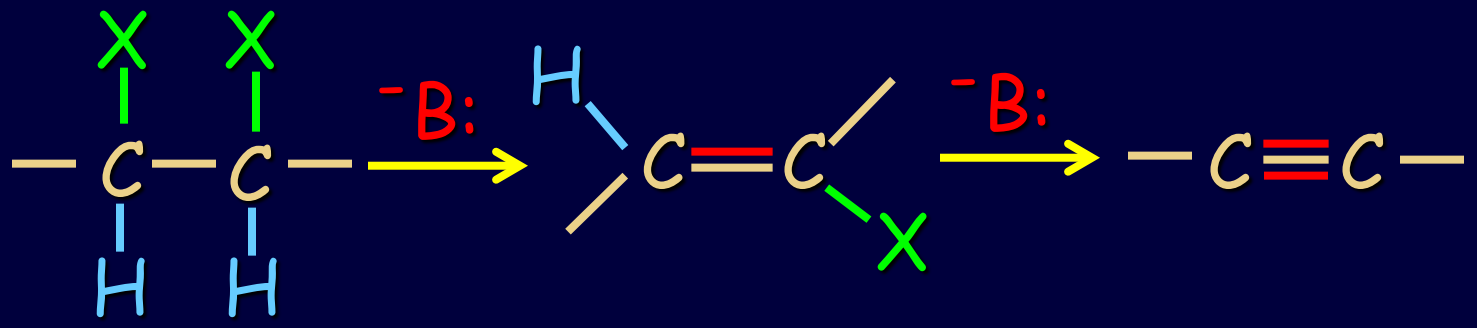


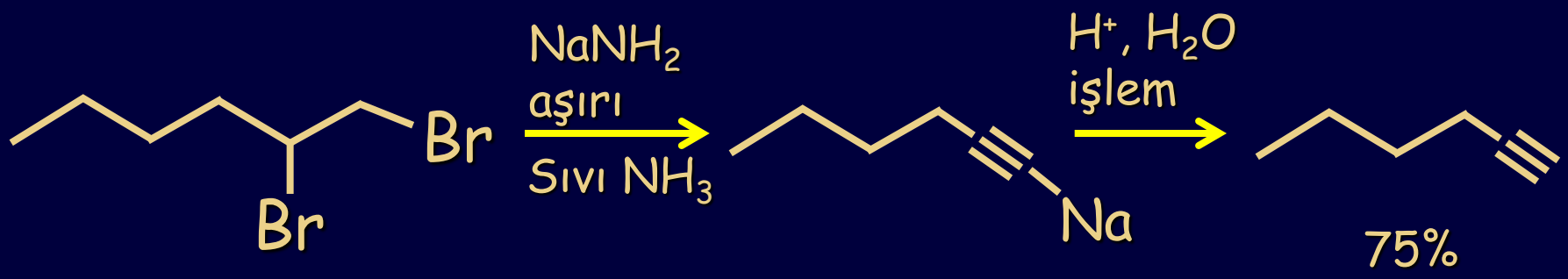
İç alkinler, uç alkinlerden daha kararlıdır

Alkenlere benzer davranış.
Aynı neden: hiperkonjugasyon.

Alkinlerin Elde Yöntemleri

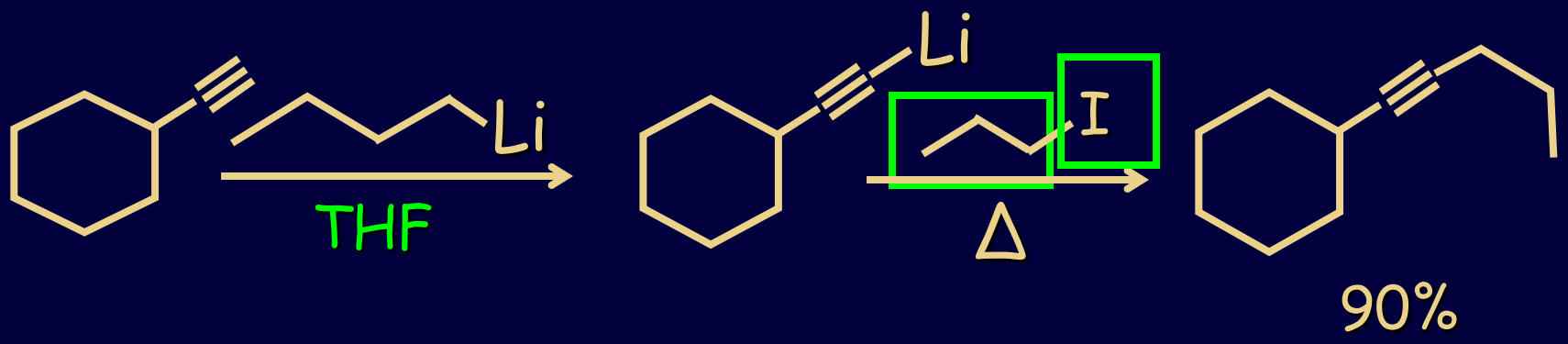
1. Dihaloalkanların Eliminasyonu E2





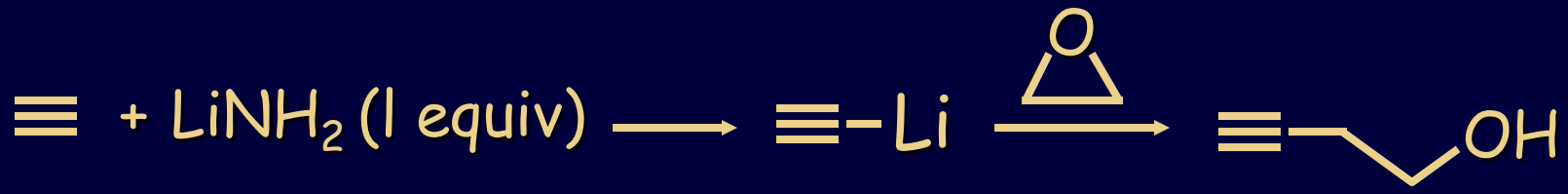
2. Alkinil Anyonlarının Alkillenmesi

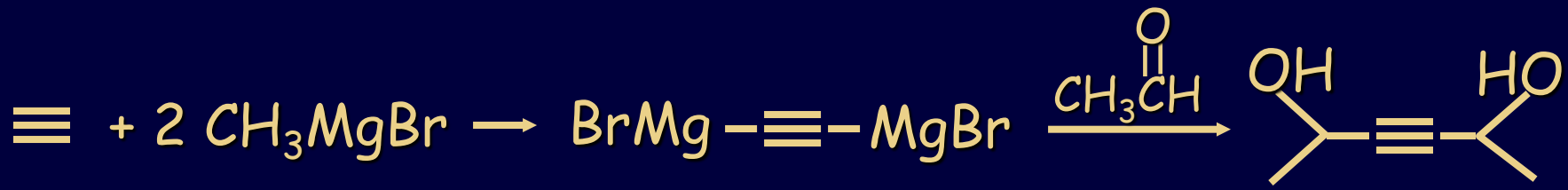
S_N2 kuralları geçerli

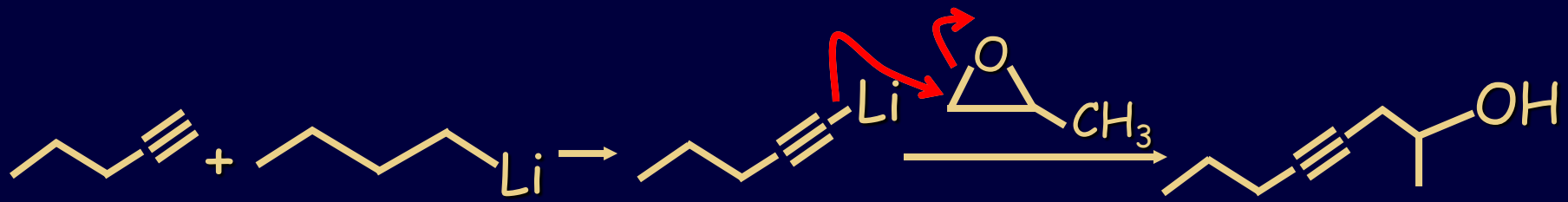


En iyi: RI, THF, Δ.
RBr veya RCl için "koordine olabilen" katkı maddesi: H_2N⌒⌒NH_2; veya HMPA.
Grignard reaktifi RX ile eşleşmez, fakat epoksit veya karbonil ile reaks. verir.


+ CH3MgBr
MgBr
CH2=O
OH


+ LiNH2 (1 equiv)
Li
O
OH

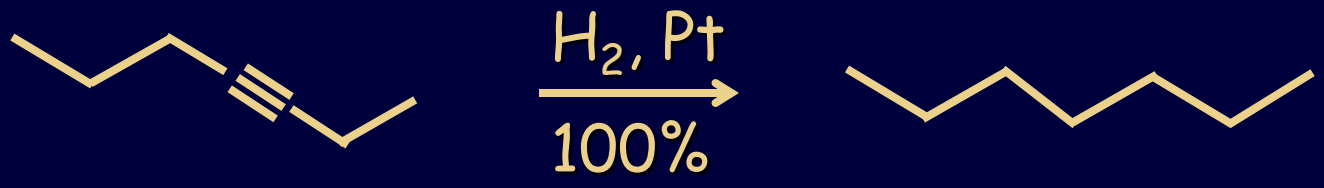

+ 2 CH3MgBr
BrMg
MgBr
O
CH3CH
OH
HO


+
Li
Li
O
CH3
OH

Alkinlerin Reaksiyonları

İndirgenme

a. Tam hidrojenasyon

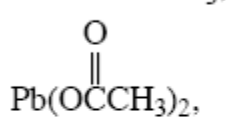


b. Kısmi hidrojenasyon:

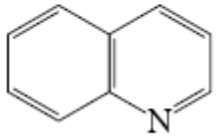
Lindlar katalizörü: cis ürün!

Lindlar Katalizörü

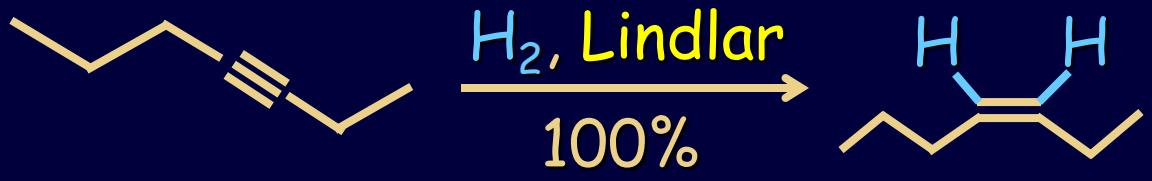
5% Pd–$CaCO_3$,



$Pb(OCCH_3)_2$,

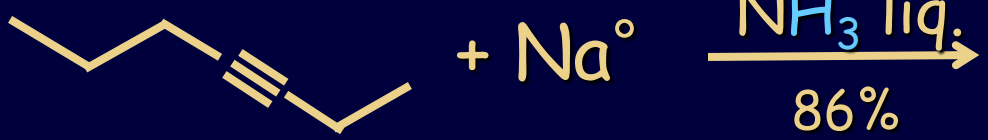


Kinolin



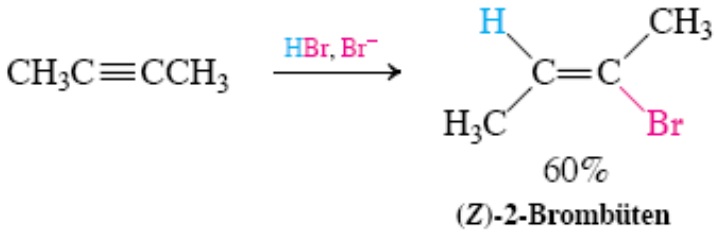
Cis-3-heptene

c. Na ile ind.: trans! 2e transferi

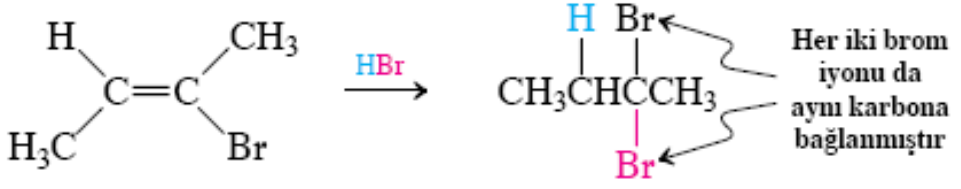


trans-3-hepten

Bir İç Alkene Hidrojen halojenür Katılması

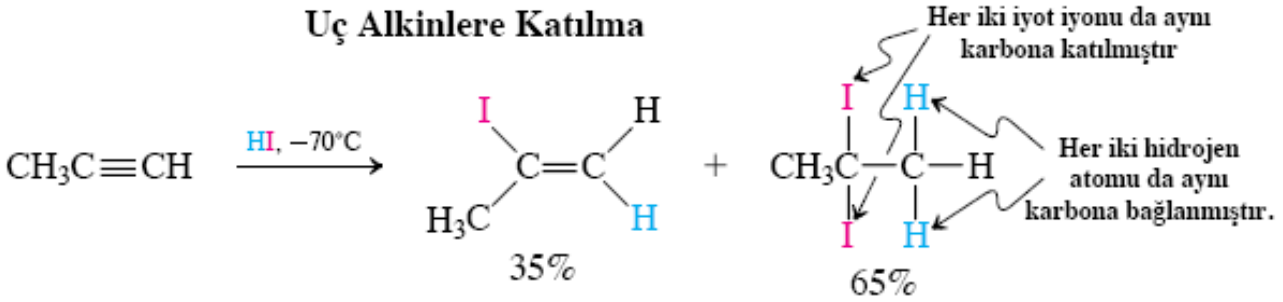


(*Z*)-2-Brombüten

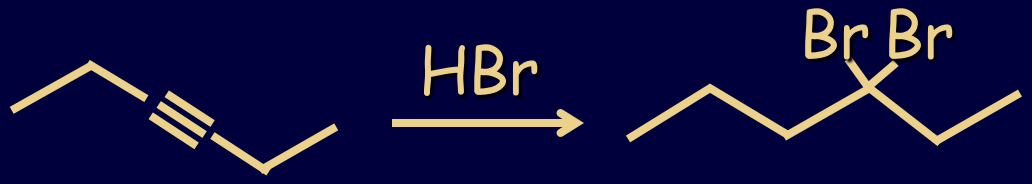


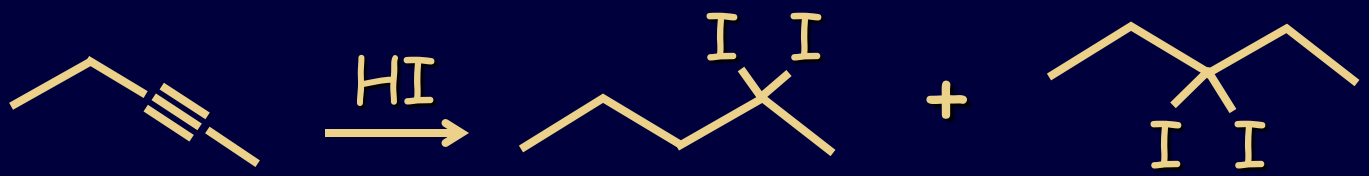
2,2-Dibromobütan

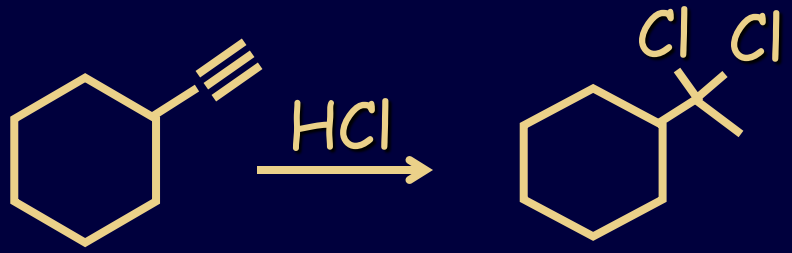
Uç Alkinlere Katılma

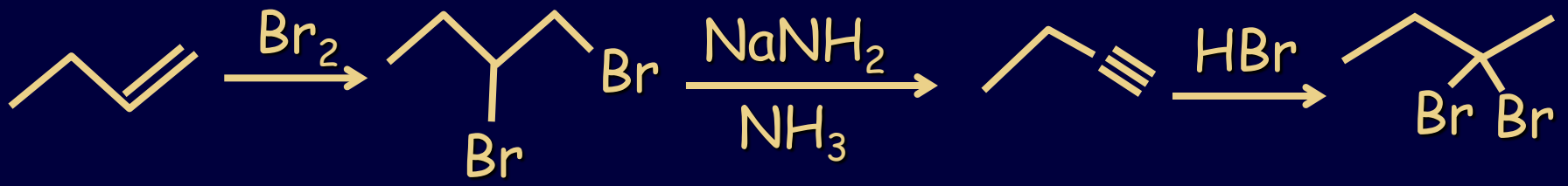


Örnekler:





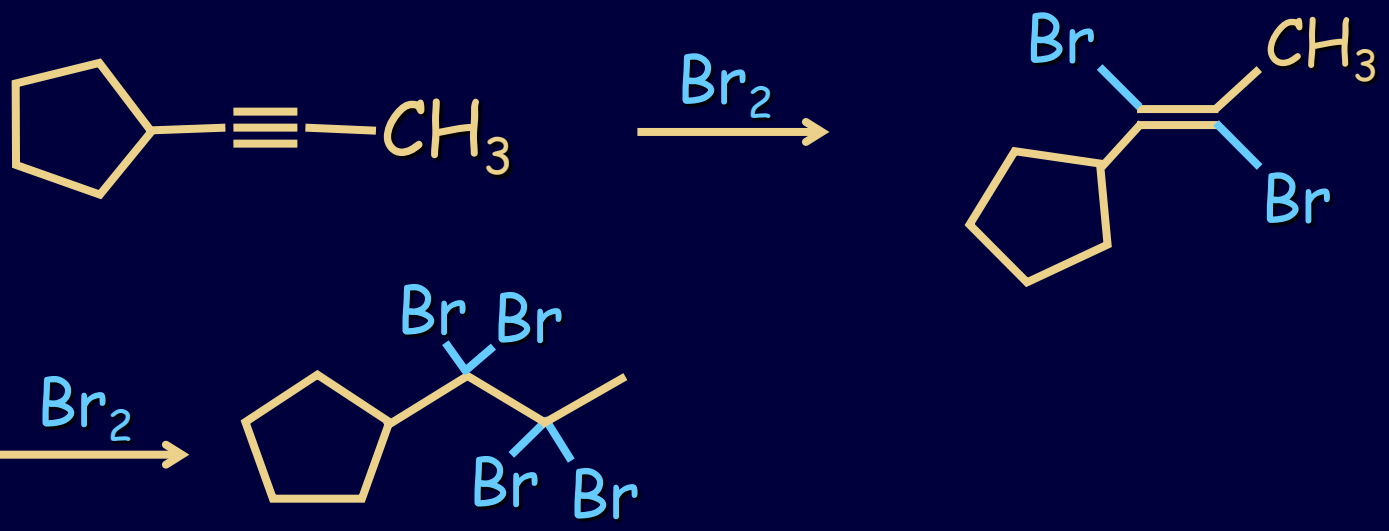




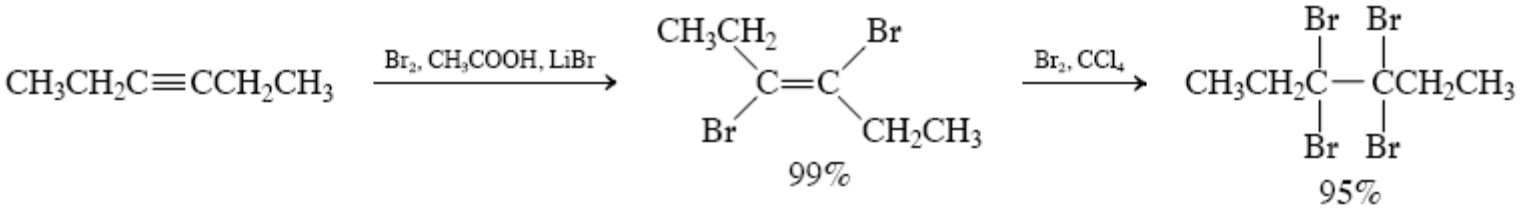
Visinal

Geminal

b. X_2katılması: Anti katılma, alkenler gibi



Alkinlerin İki Kez Halojenlenmesi



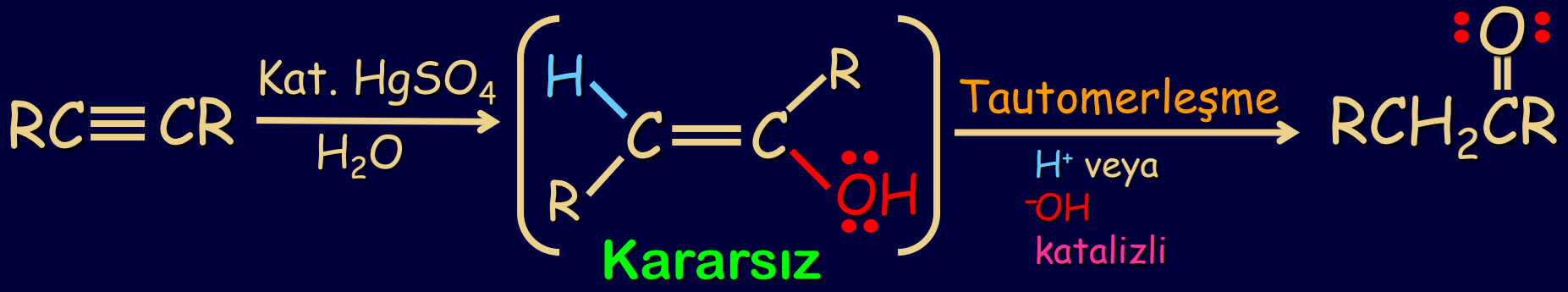
3-Heksin | (*E*)-3,4-Dibrom-3-heksen | 3,3,4,4-Tetrabromheksan

Alıştırma 13-16

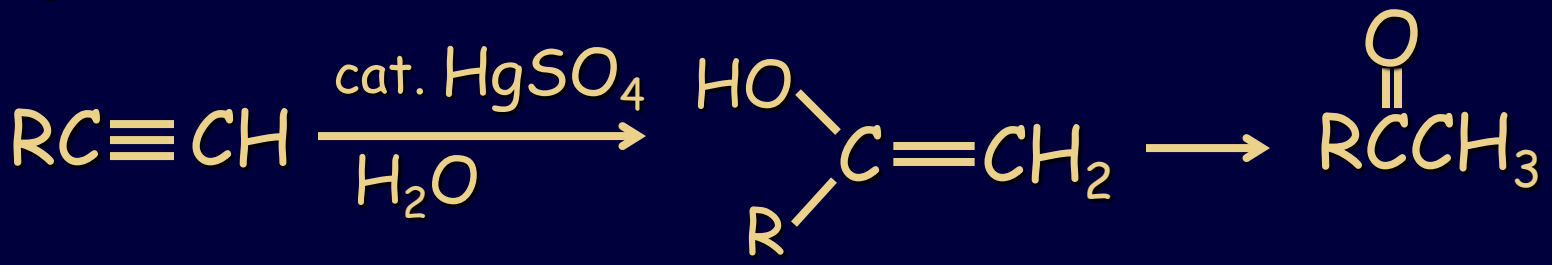
1-Bütine bir ve iki molekül Cl_2 katılımı ile oluşacak ürünleri belirtiniz.

c. Su Katılması Kat. $HgSO_4$, Markovnikov

İç alkin



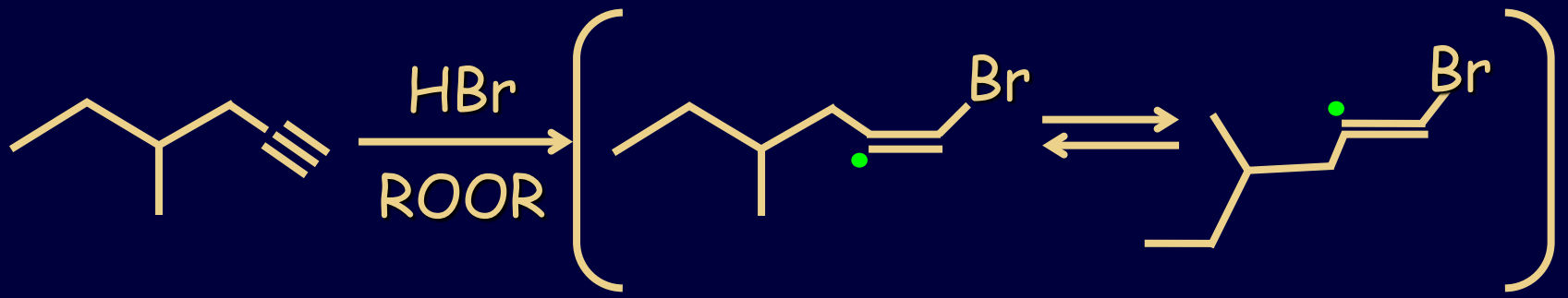
Uç alkin

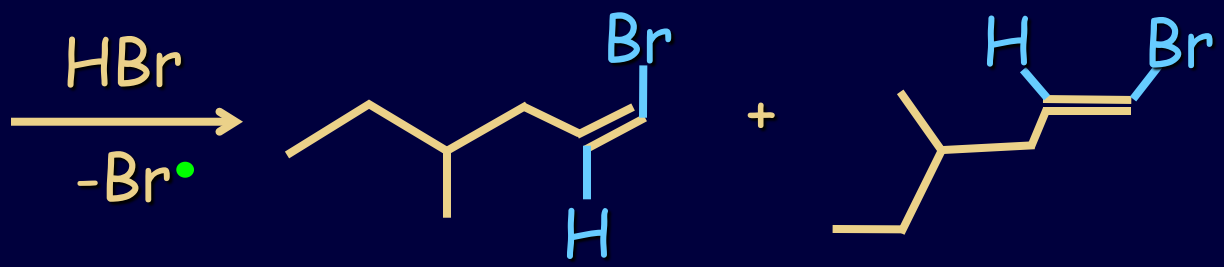


Metil keton

d. Radikalik HBr katılması:

Anti-Markovnikov - Alkenil halojenürlerin eldesi





Z- ve E- ürünler karışımı