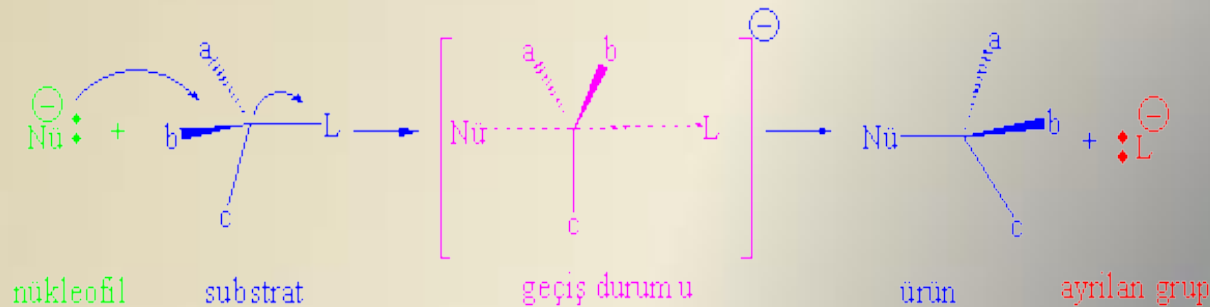
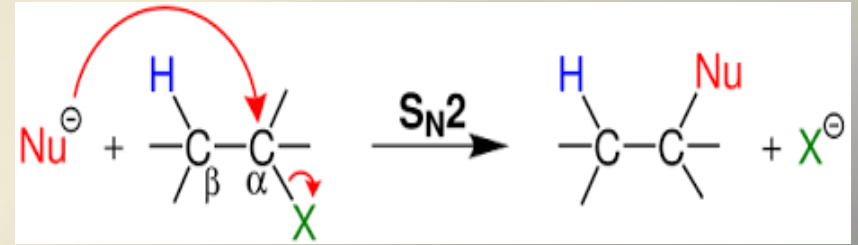
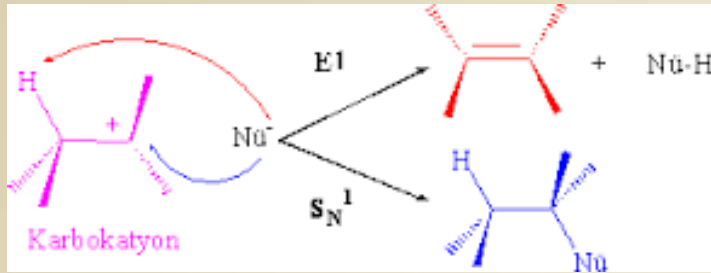


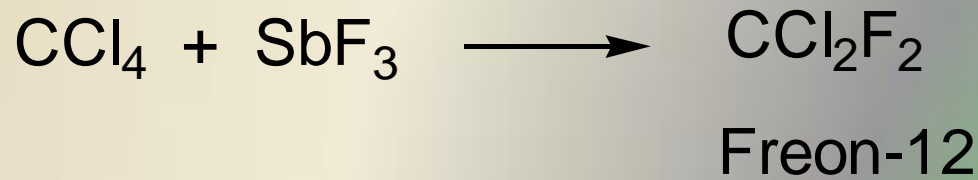
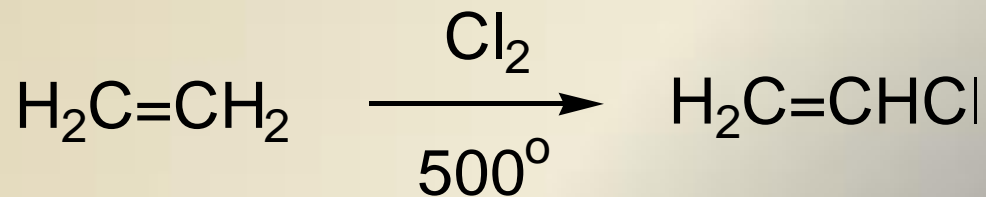
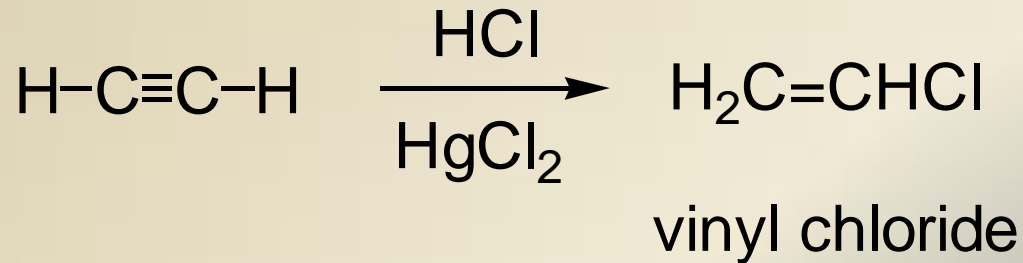
# KİM213 ORGANİK KİMYA I (E GRUBU)

## BÖLÜM 2: ALKİL HALOJENÜRLER VE NÜKLEOFİLİK YER DEĞİŞTİRME (SÜBSTİTÜSYON) REAKSİYONLARI

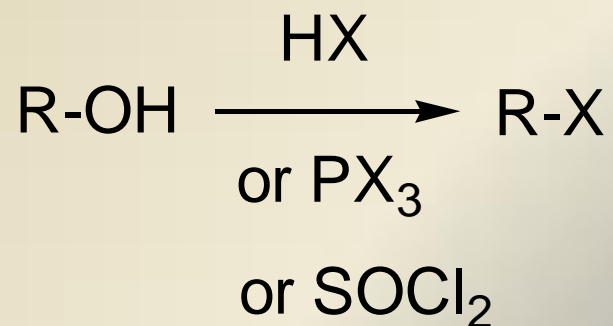


[http://w3.balikesir.edu.tr/~hnamli/okdn7/okdn7\\_dosyalar/image008.gif](http://w3.balikesir.edu.tr/~hnamli/okdn7/okdn7_dosyalar/image008.gif)

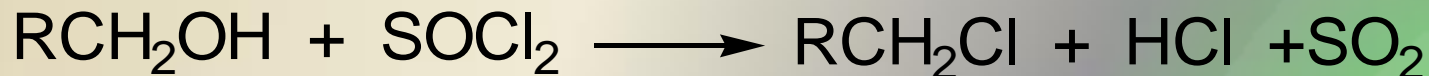
# Alkil halojenürlerin endüstriyel olarak eldesi



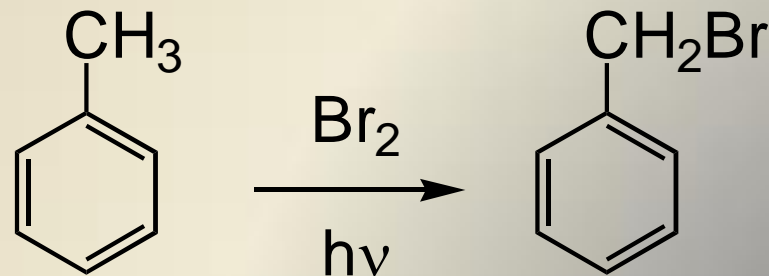
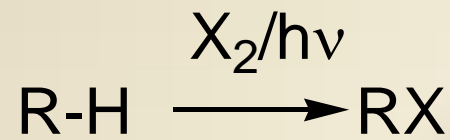
# Alkollerden eldesi



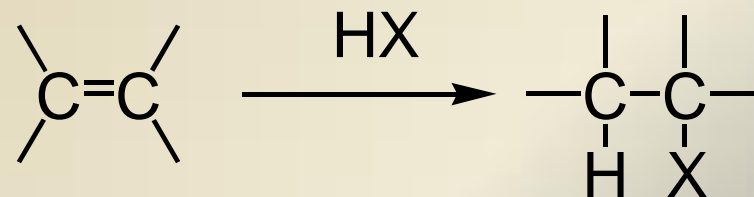
SOCl<sub>2</sub> – tiyonil klorür



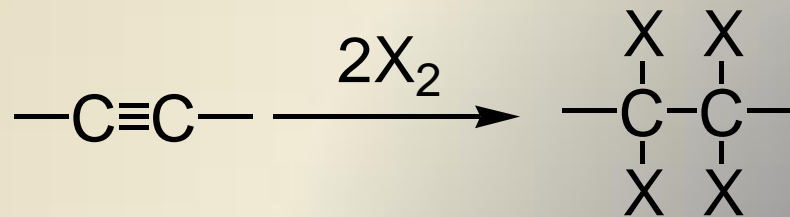
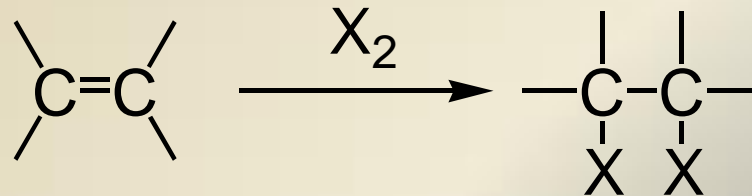
# Hidrokarbonların halojenlenmesiyle eldesi



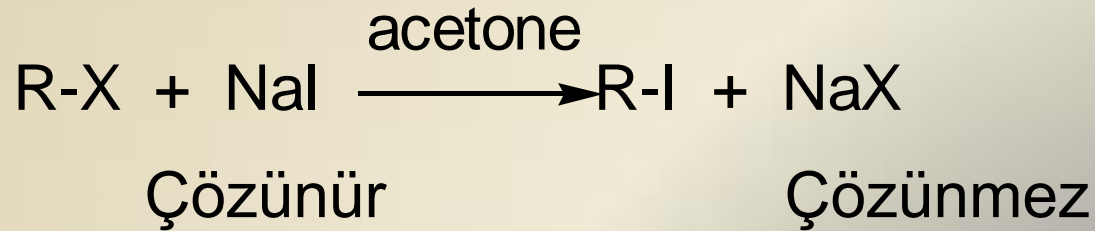
# Alkenlere hidrojen halojenür katılmasıyla



# Alken ve alkinlere halojen katılmasıyla eldesi



# Finkelstein reaksiyonu ile eldesi

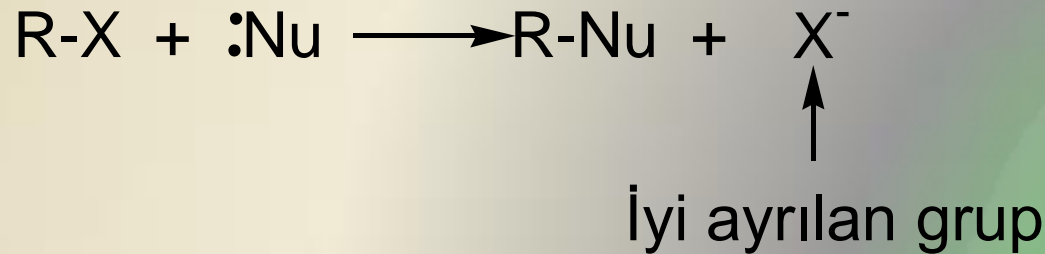


# Nükleofilik yer deęiřtirme (Sübstitüsyon) reaksiyonu

Halojenür iyonu kuvvetli asidin konjüge bazıdır. Bundan dolayı zayıf bazdır ve elektronlarını paylaşmaya istekli deęildir.

Karbona baęlı olduęunda halojen, kuvvetli nükleofiller tarafından halojenür iyonu olarak kolaylıkla yer deęiřtirebilir. Halojenür iyonu iyi bir ayrılan gruptur

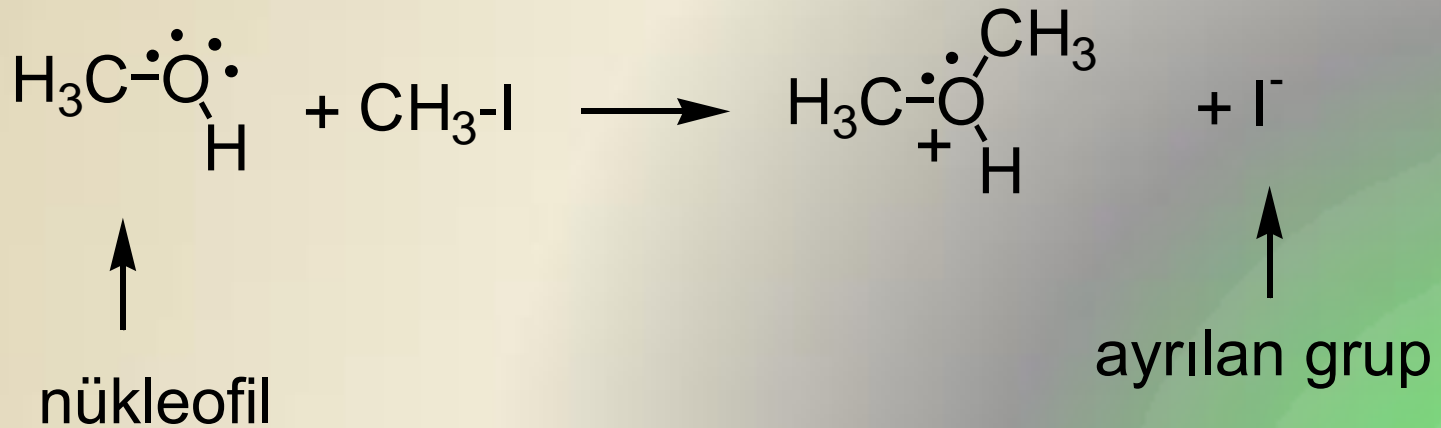
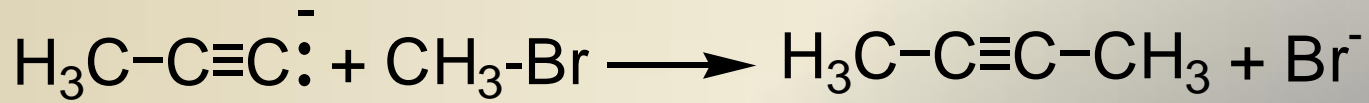
Bir alkil halojenürün yer deęiřtirme reaksiyonu basitçe ařaęıda gibi gösterilebilir:





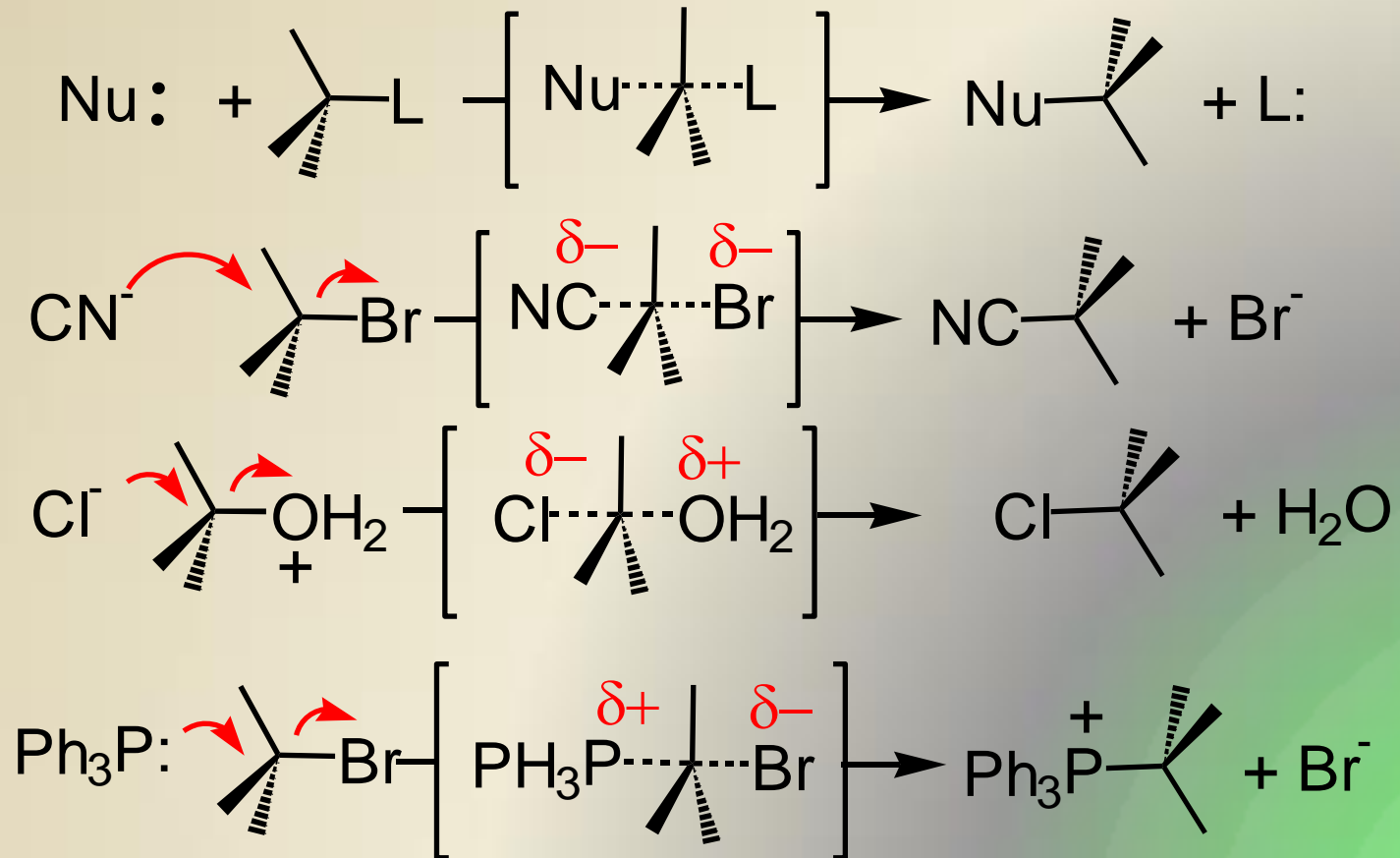
# Nükleofiller

- elektron eksikliği olan merkeze katılan reaktiflerdir.
- negatif iyonlar veya üzerinde bir çift paylaşılmamış elektrona sahip nötral moleküllerdir.



# Ayrılan gruplar

- zayıf bazik molekül veya iyonlar şeklinde ayrılan sübstitüentlerdir.



# Nükleofilik yer deęiřtirme



Reaksiyon hızlarının reaktif deriřimiyle nasıl deęiřtięinin bilinmesi, reaksiyon mekanizması aısından ok nemlidir.

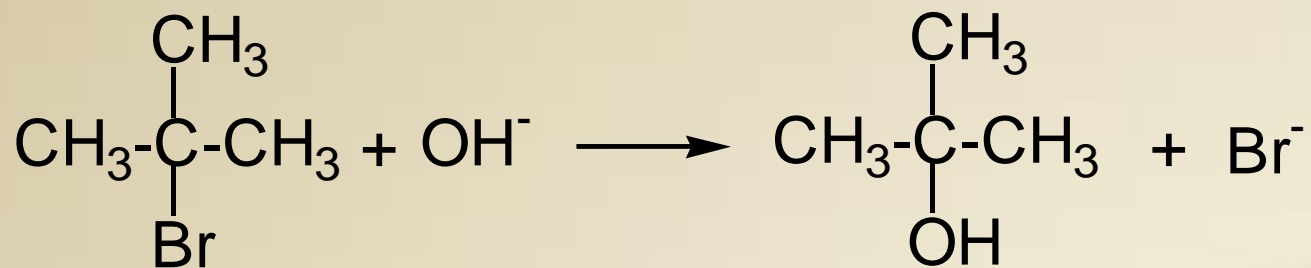
Buna gre, bu reaksiyonlar hakkında ne syleyebiliriz?



$[\text{CH}_3\text{Br}]_i$	$[\text{OH}^-]_i$	initial rate
0.001 M	1.0 M	$3 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
0.002 M	1.0 M	$6 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
0.002 M	2.0 M	$1.2 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

$$\text{rate} \propto [\text{CH}_3\text{Br}][\text{OH}^-]$$

$$\text{rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$



$[(\text{CH}_3)_3\text{CBr}]_i$	$[\text{OH}^-]_i$	initial rate
0.001 M	1.0 M	$4 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
0.002 M	1.0 M	$8 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
0.002 M	2.0 M	$8 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

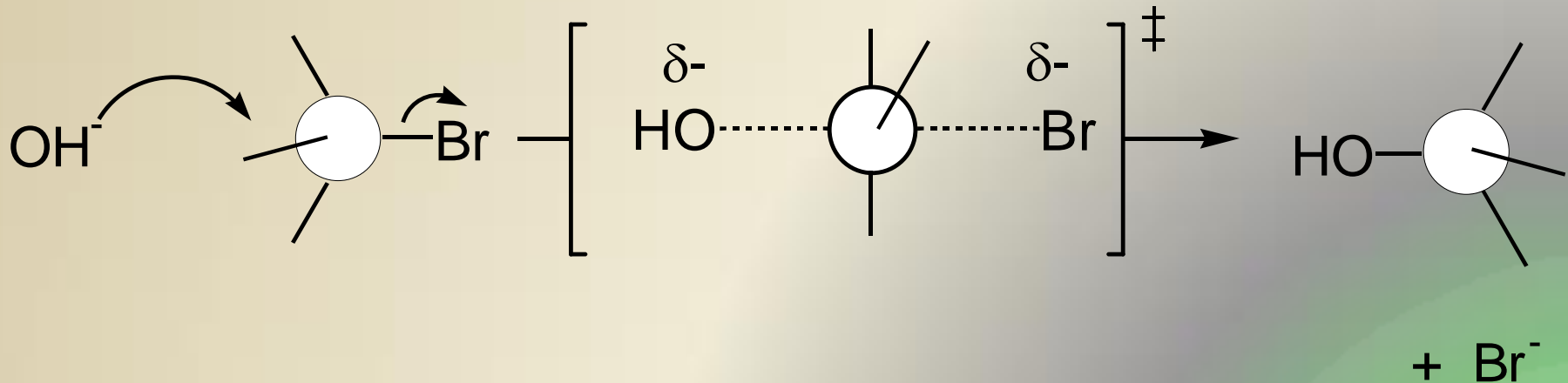
$$\text{rate} \propto [(\text{CH}_3)_3\text{CBr}][\text{OH}^-]^0$$

$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$$

# $S_N2$ mekanizması



$$\text{rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

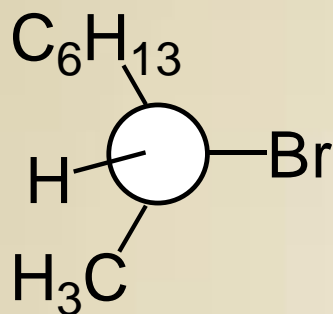
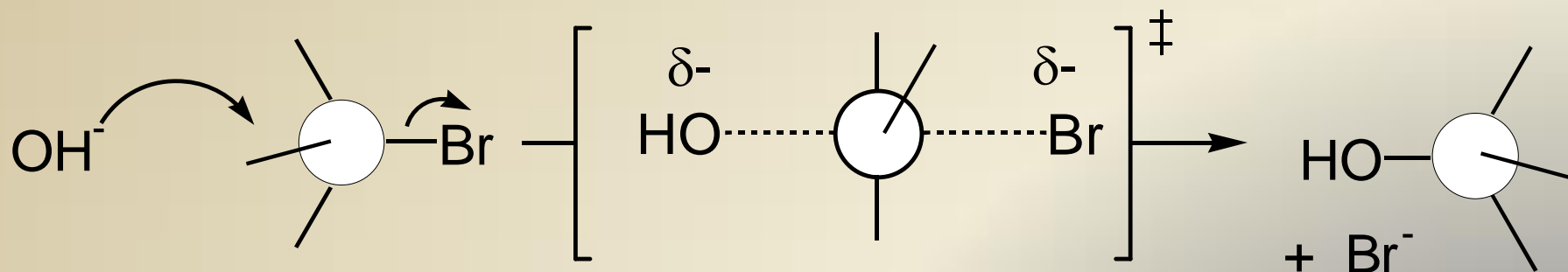


ilgili kaynaklar:

E.D. Hughes, C.K. Ingold, and C.S. Patel, *J. Chem. Soc.*, 526 (1933)

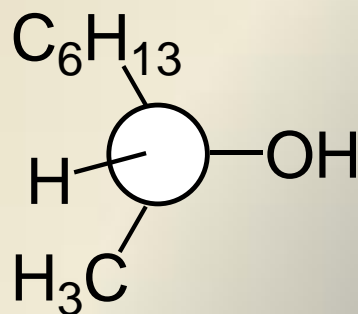
J.L. Gleave, E.D. Hughes and C.K. Ingold, *J. Chem. Soc.*, 236 (1935)

# $S_N2$ reaksiyonunun stereokimyası



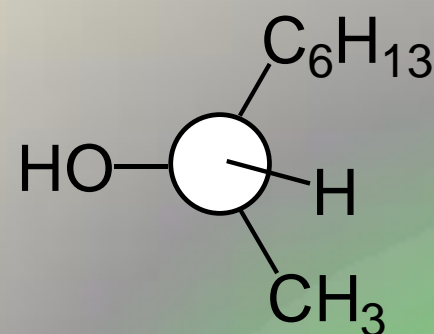
(-)-2-bromooctane

$$[\alpha] = -34.6^\circ$$



(-)-2-octanol

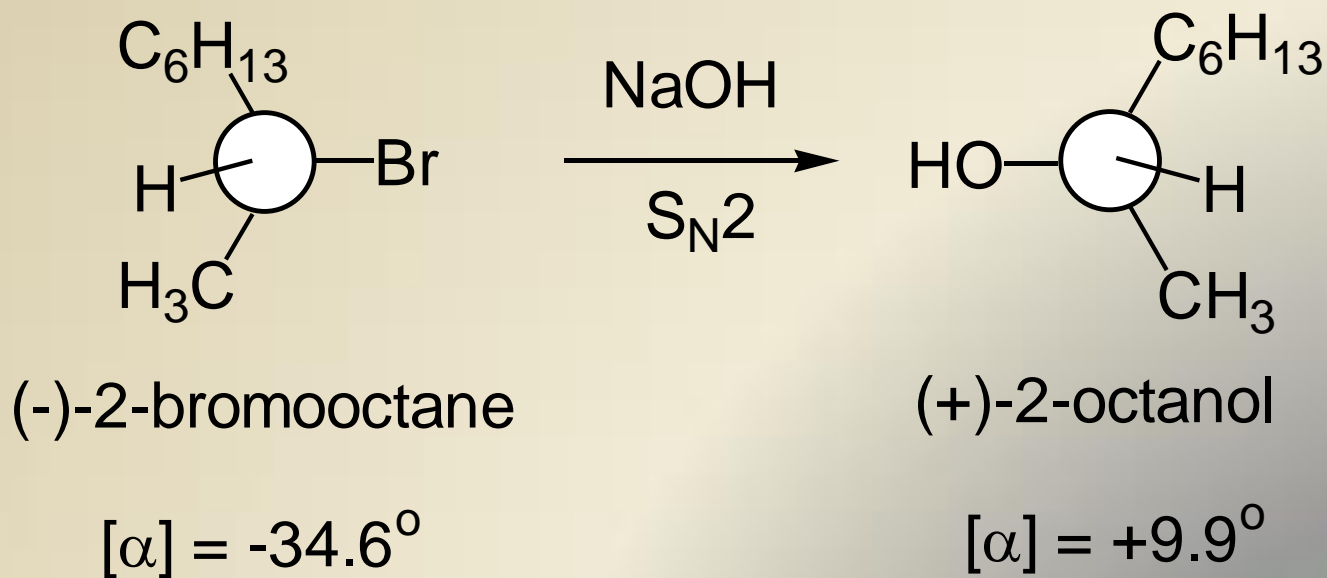
$$[\alpha] = -9.9^\circ$$



(+)-2-octanol

$$[\alpha] = +9.9^\circ$$

# Stereochemistry of the S<sub>N</sub>2 reaction



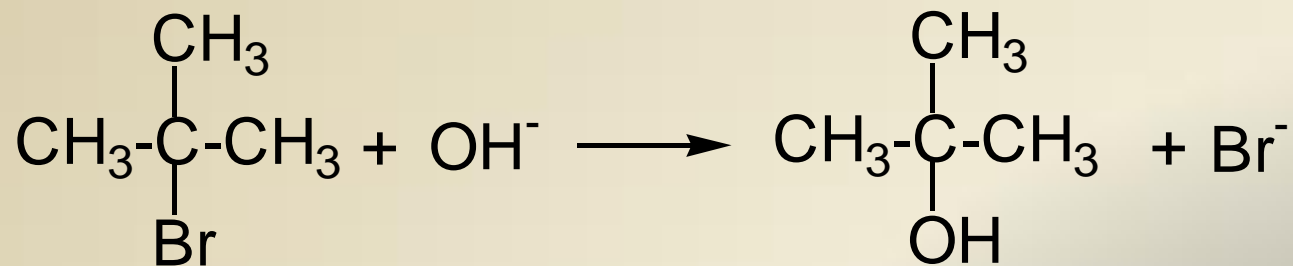
optical purity = 100%

A **Walden** inversion.

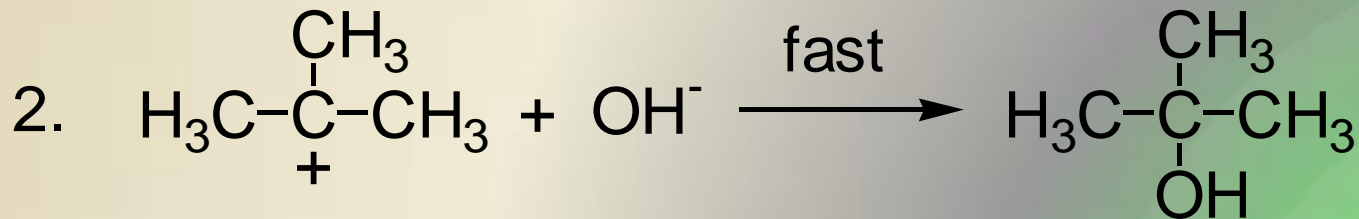
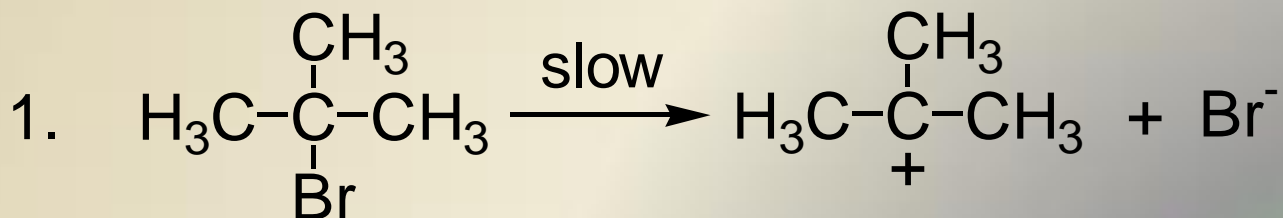
P. Walden, *Über die vermeintliche optische Activität der Chlorumarsäure und über optisch active Halogenbernsteinsäure*, *Ber.*, 26, 210 (1893)



# $S_N1$ reaksiyon mekanizması

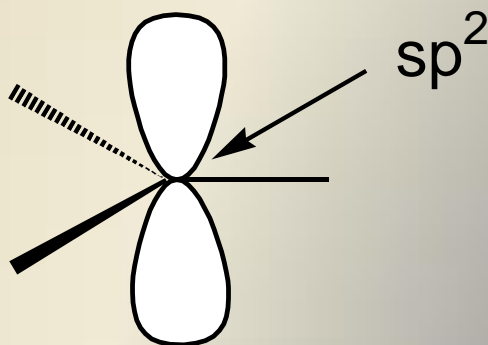
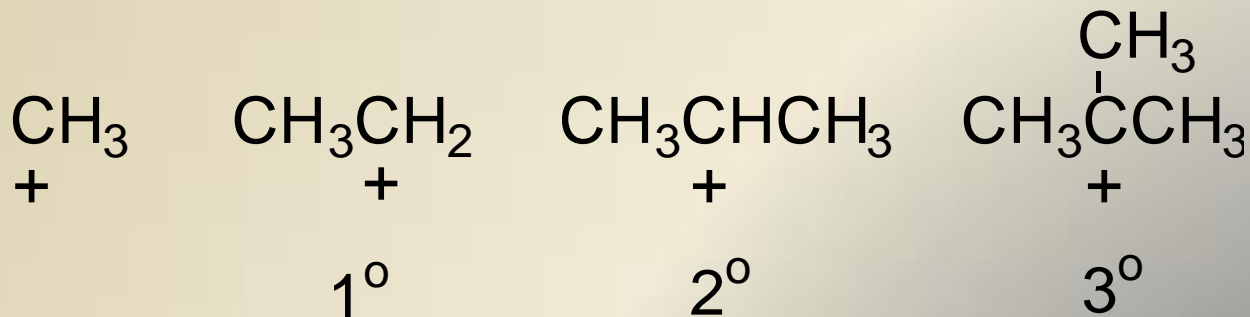


$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$$

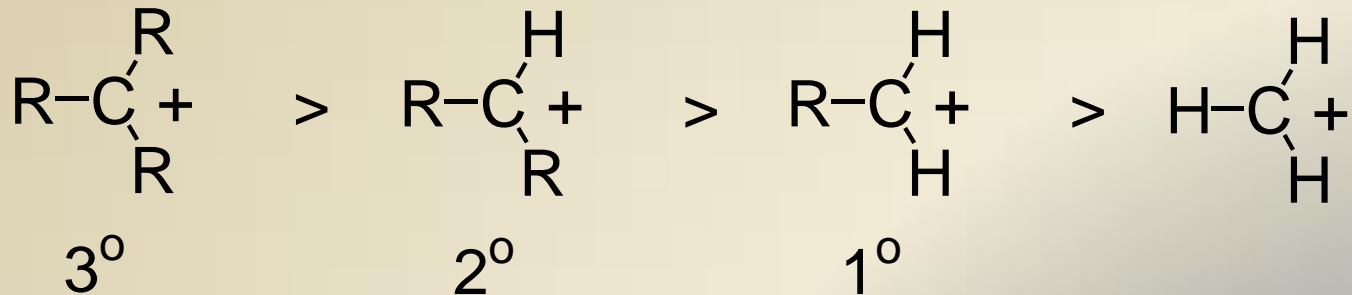


# Karbokatyonlar

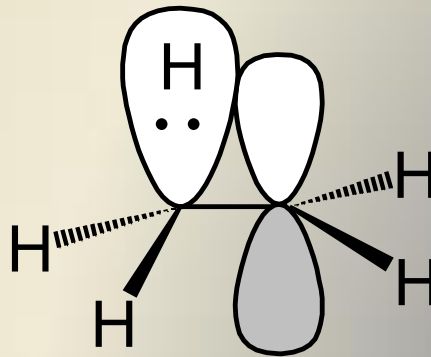
G.A. Olah, *J. Amer. Chem. Soc.*, 94, 808 (1972)



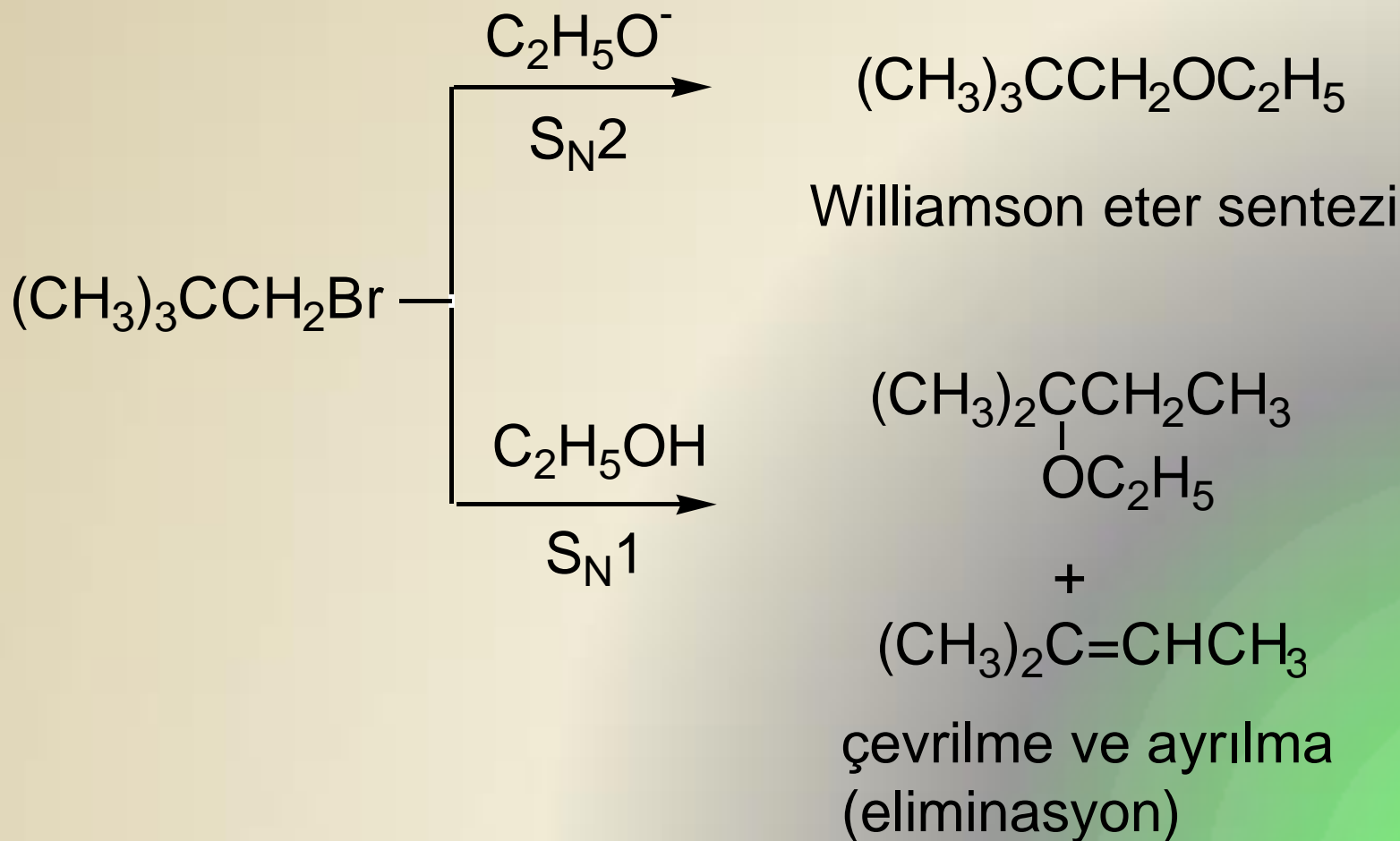
# Karbokatyonların kararlılığı



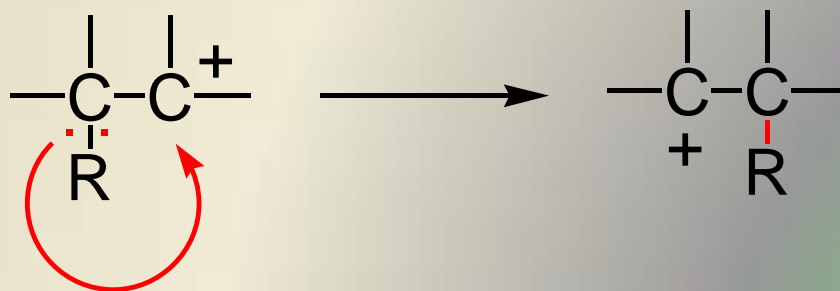
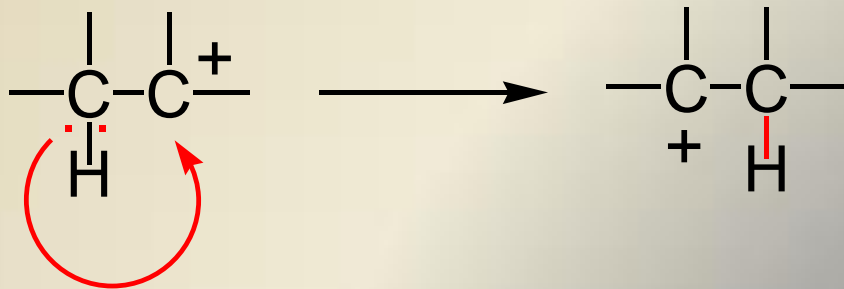
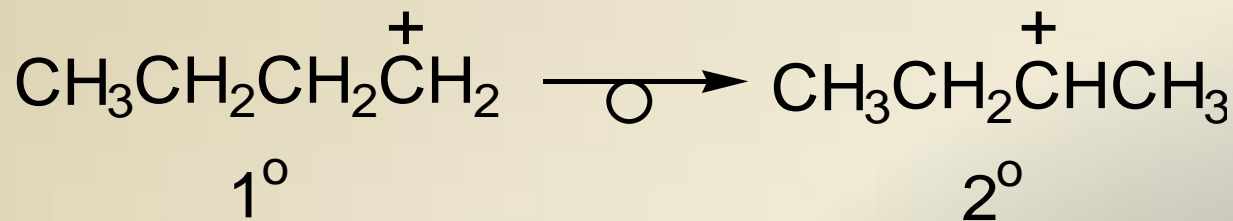
Hiperkonjügasyon pozitif yükü kararlı kılar.



# karbokatyon çevrilmeleri

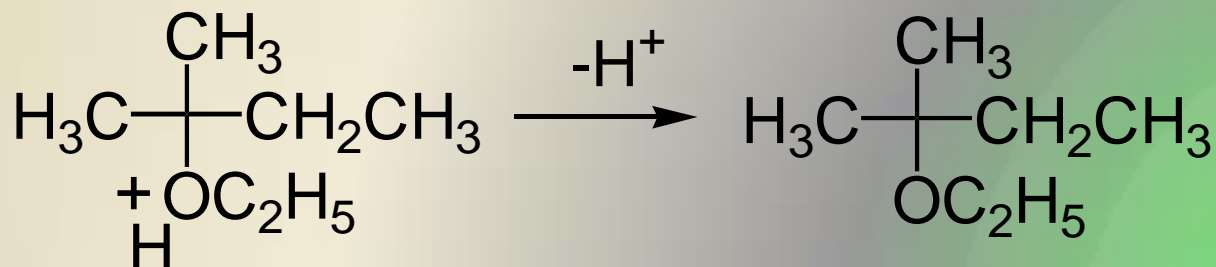
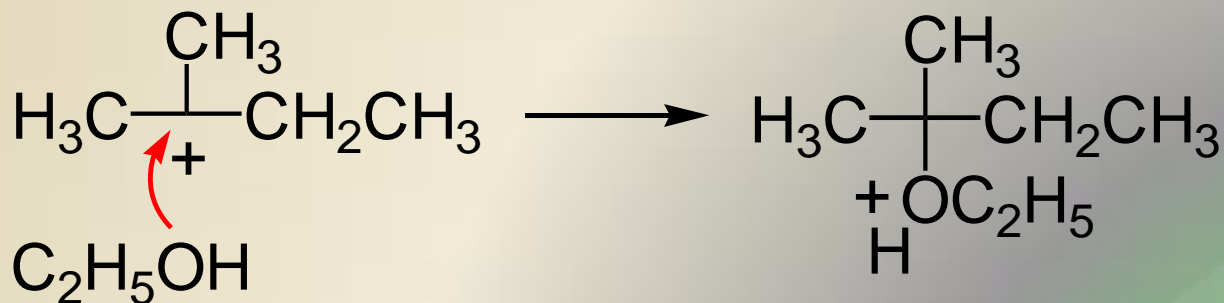
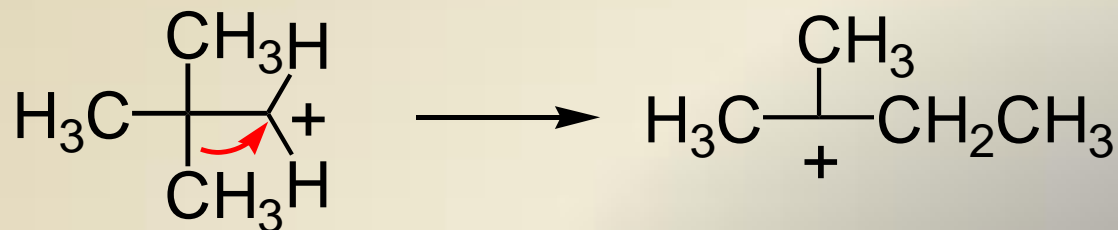


# Karbokatyon çevrilmeleri

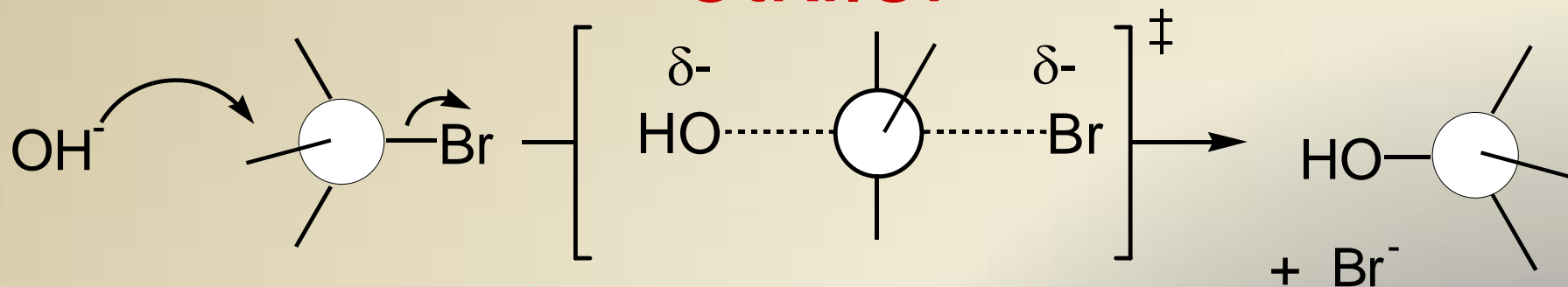


1,2 hydride and alkyl shifts

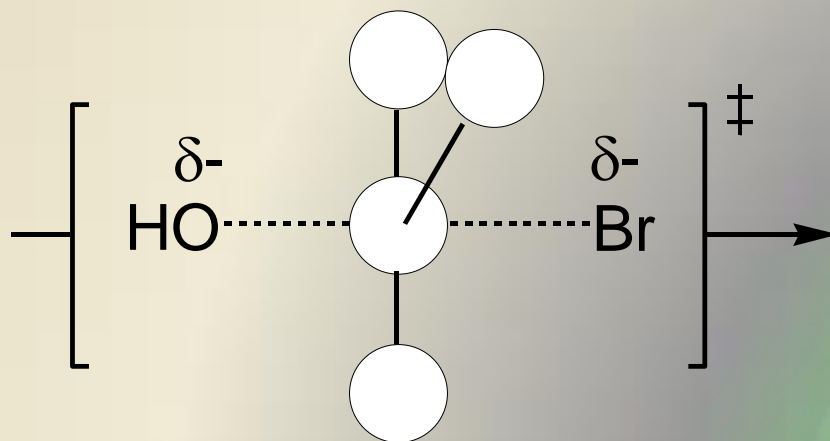
# karbokatyon çevrilmeleri

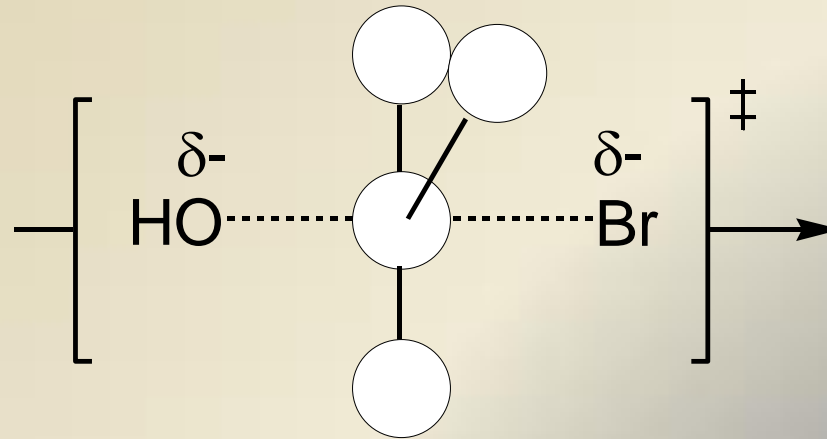


# $S_N2$ reaksiyonunda sterik etkiler

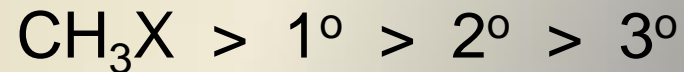


Look at the transition state to see how substituents might affect this reaction.

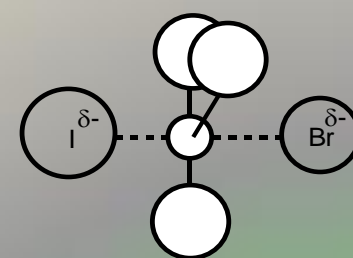
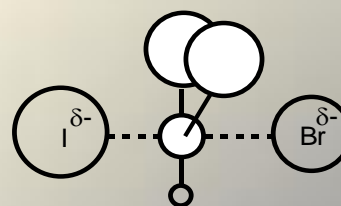
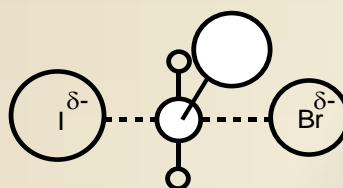
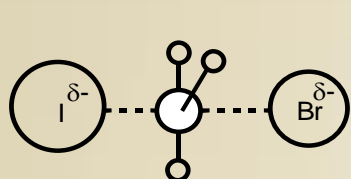
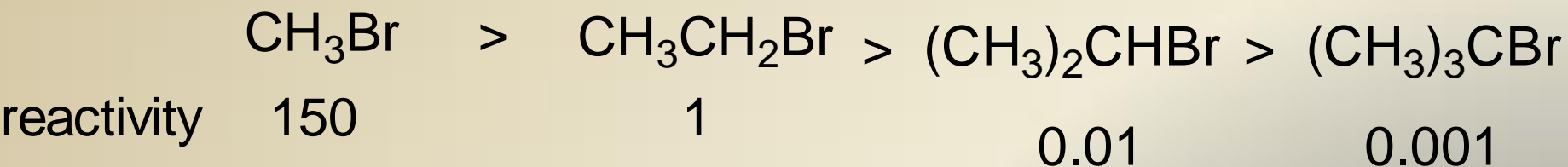




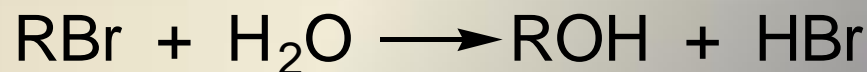
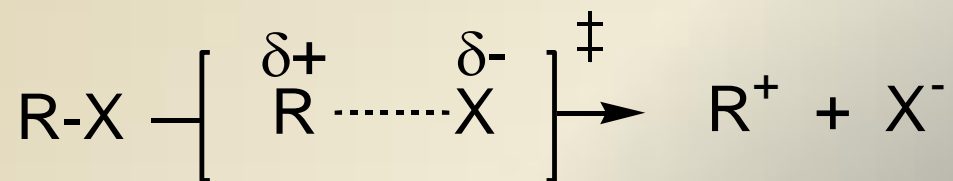
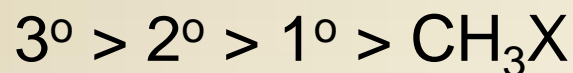
$S_N2$  reaksiyonlarında alkil halojenürlerin etkinlik sırası







# $S_N1$ reaksiyonlarında yapısal etkiler



100,000,000

45

1.7

1

# Nükleofilik güç

$S_N2$  reaksiyonlarının hızı, nükleofilin derişimine ve gücüne bağlıdır.

Bir baz, konjüğe asidinden daha güçlü nükleofildir:

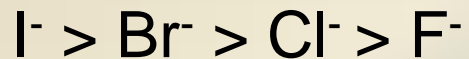


Aynı nükleofilik atoma sahip olan nükleofillerin nükleofilik güçleri bazlık güçleri ile paraleldir:



Nükleofilik atomları farklı olduğunda, nükleofilik güç ile baziklik her zaman paralellik göstermez

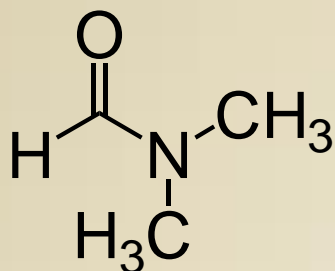
Protik çözücülerde, daha büyük nükleofilik atoma sahip olan atomlar iyi nükleofildir.



Protik bir çözücüde anyon ne kadar küçük ise hidrojen bağından dolayı solvatize olur. Bu şekilde çözücü moleküllerinin oluşturduğu tabaka bu iyonların etkisini azaltır.

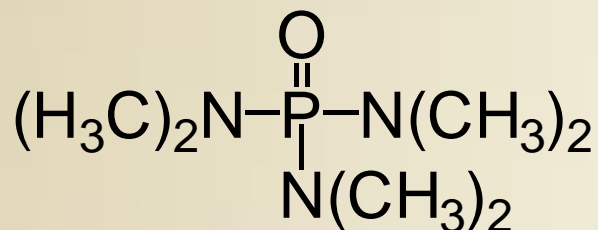
Aprotik çözücü anyonları değil katyonları sarmaya meyillidir. Böylece çözücü molekülleri ile sarılmamış anyonun nükleofilik gücü artar.

# Polar aprotik çözücüler



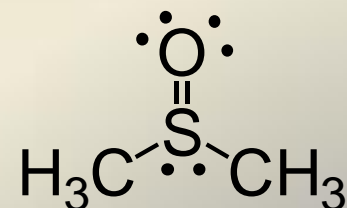
*N,N*-dimethylformamide

DMF



hexamethylphosphoramide

HMPA

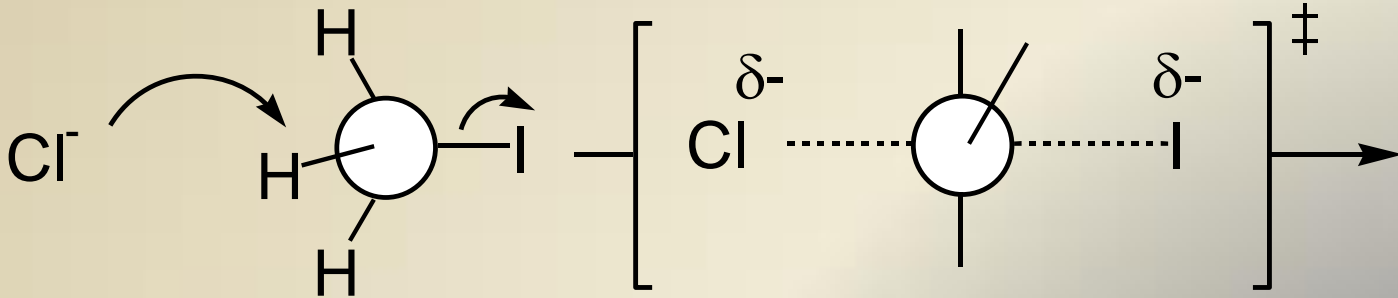


dimethyl sulfoxide

DMSO

Bu çözücüler iyonik bileşikleri çözer.

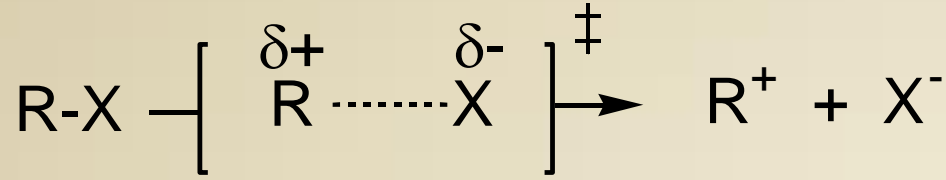
# Çözücü polaritesi



Daha polar

Geçiş basamağı reaktife göre daha az solvatizedir

Protik çözücü bu reaksiyonun hızını azaltır bu reaksiyon DMF içinde metanole göre 1,200,000 kat daha hızlı olur.



Daha az polar      daha polar

Çözücü molekülleri  
kararlılığı artırır.

Geçiş basamağı oldukça polarizedir.

Bundan dolayı bu reaksiyonun hızı çözücü polaritesi ile artar.

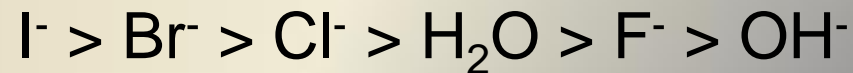
Protik çözücü özellikle ayrılan grup ile hidrojen bağı oluşturarak geçiş basamağını karırlı kılar.

# Ayrılan grubun etkisi

Zayıf bazlar iyi ayrılan gruptur.

Bunlar negatif yüklerini üzerinde taşımaya meyilli oldukları için geçiş basamağını kararlı kılar.

Buna göre  $I^-$  ,  $Br^-$  'dan daha iyi ayrılan bir gruptur.





# $S_N1$ ve $S_N2$

$S_N1$

$S_N2$

Kinetik : 1. derece

2. derece

Reakteflik :  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{X}$

$\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$

Çevrilme olur

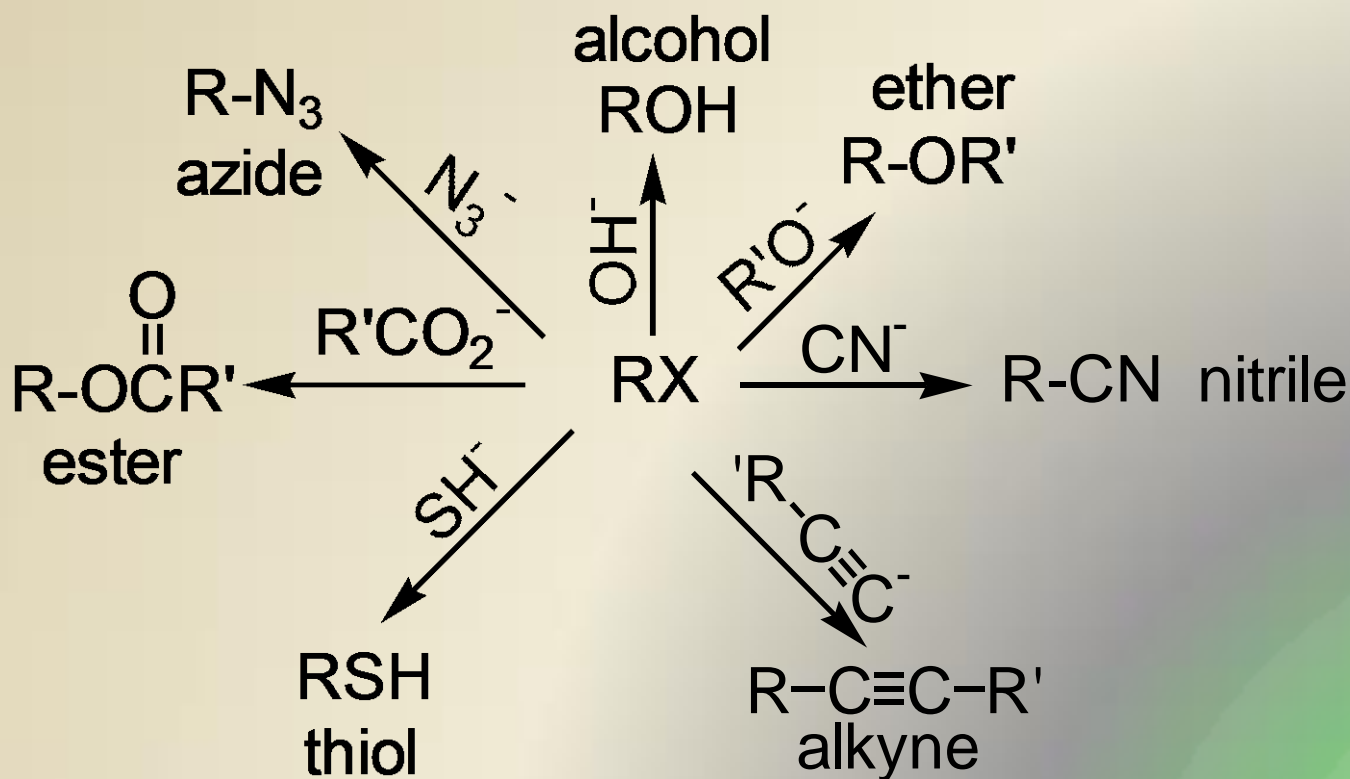
çevrilme olmaz

kısmi inversiyon

konfigürasyonun inversiyonu

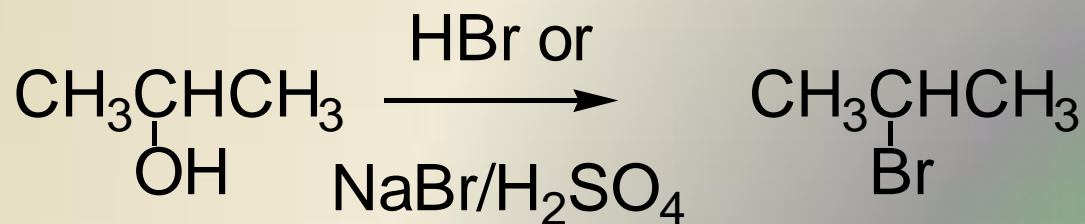
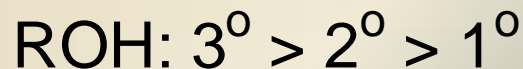
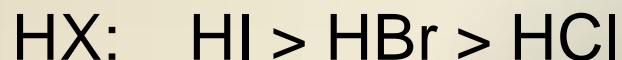
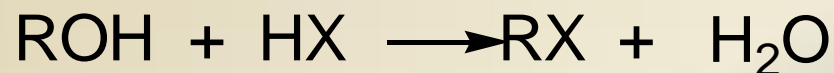
Eliminasyonlar olabilir

# $S_N2$ reaksiyonları ile fonksiyonlu grup dönüşümleri



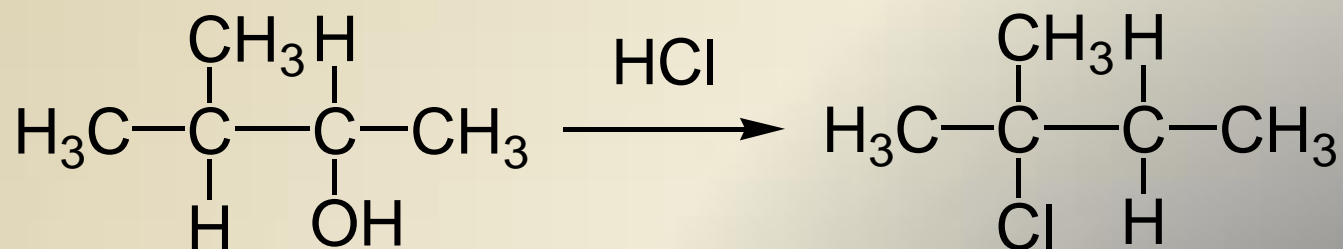
R = Me, 1°, or 2°

# ROH + HX - Bir S<sub>N</sub> reaksiyonu



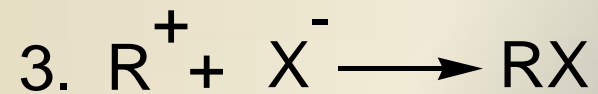
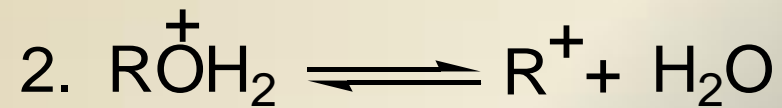
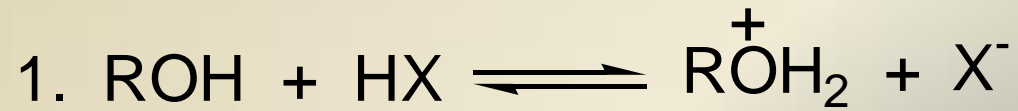
# Deneysel örnek

1. Reaksiyon asit katalizlidir.
2. Çevrilmeler mümkündür.

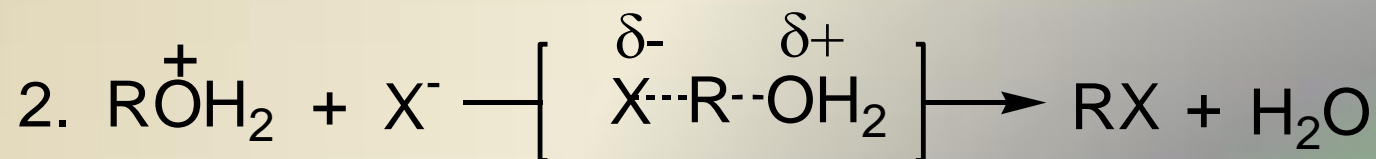
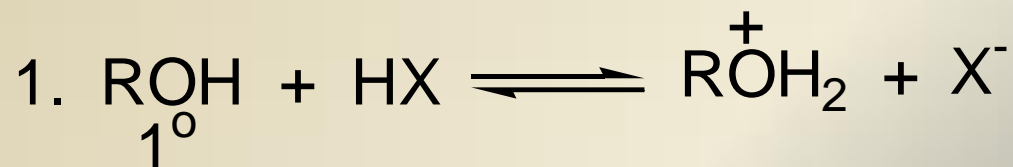


3. Alkolün reaktivliği:  $3^\circ > 2^\circ > 1^\circ < \text{CH}_3\text{OH}$

# Mekanizma



# Primer alkollerin HX ile reaksiyonu



$\text{S}_{\text{N}}2$

HX:  $\text{HI} > \text{HBr} > \text{HCl}$