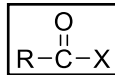


KARBOKSİLİK ASİT TÜREVİ BİLEŞİKLER

1. **Açıl halojenürler** $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$
2. **Asit anhidritleri** $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$
3. **Esterler** $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$
4. **Amidler** $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHR}'$

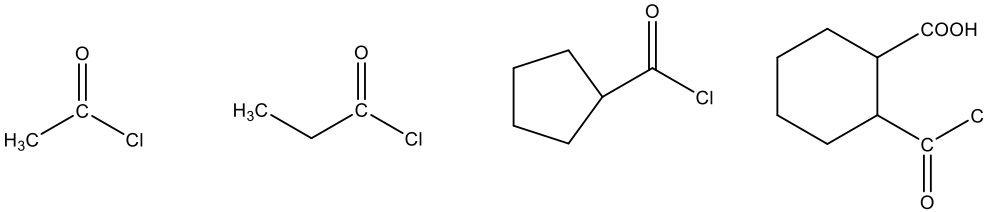
AÇIL HALOJENÜRLER



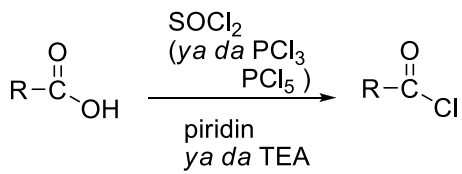
Kararlılığı en az, etkinliği en fazla olan asit türevleridir. X = Cl (Br)
Asit özellik kaybolmuştur, assosiasyon yoktur.

Aşağıdaki bileşiklerin kimyasal formülleri derste verilmiştir.

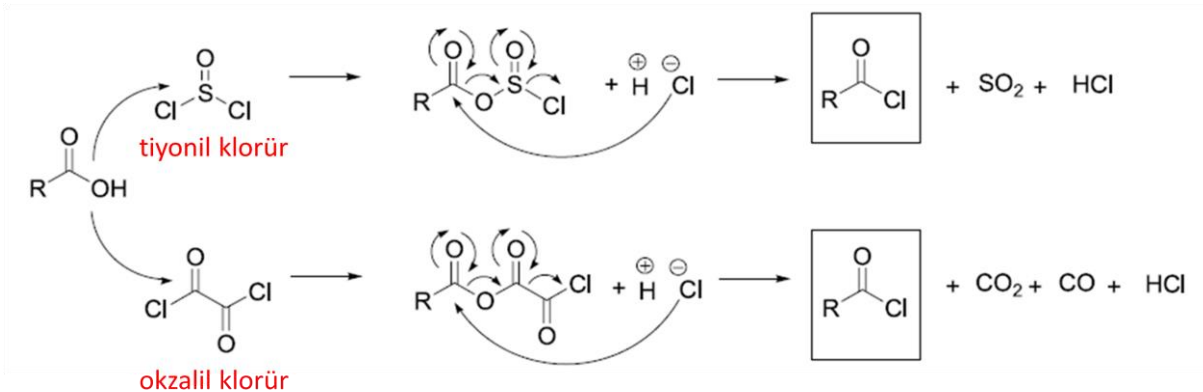
- Asetil klorür (etanoil klorür)
- Propanoil klorür
- Siklopentan karbonil klorür
- 2-kloroformilsikloheksan karboksilik asit

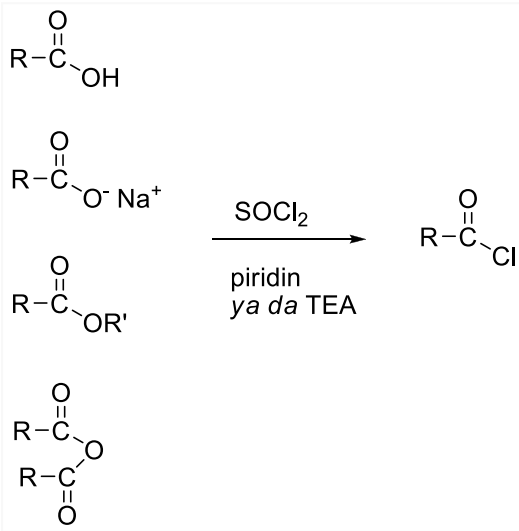


Elde edilişleri



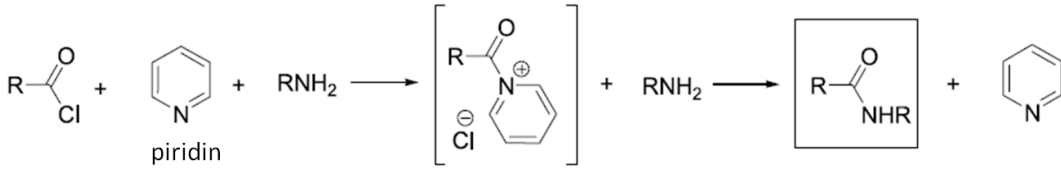
Reaksiyon mekanizması:





Piridin niin kullanılır?

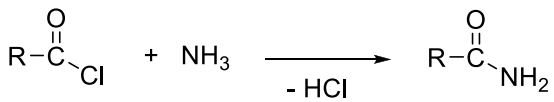
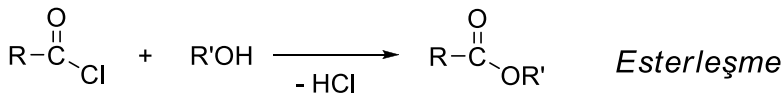
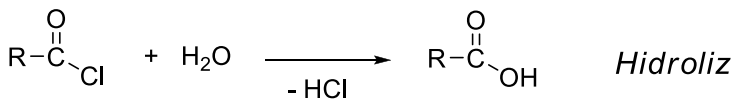
örnek reaksiyon:



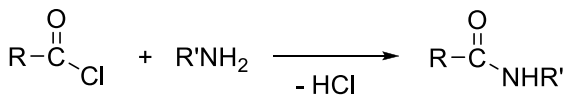
Reaksiyonları

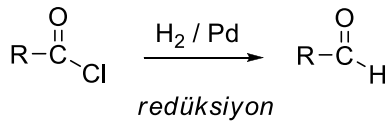
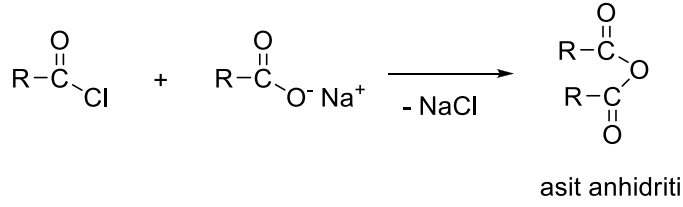
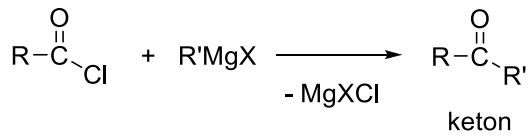
ok kolay SN verirler.

Bir ail klorürün C=O grubu, Cl atomunun indüktif etkisini (-I) hisseder ve sonuta ail klorürün C=O karbonu nu⁻ ataklara aık hale gelir.

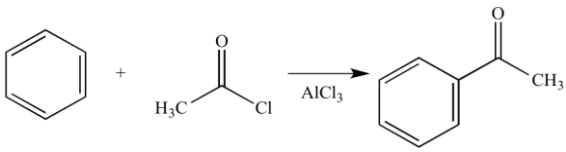
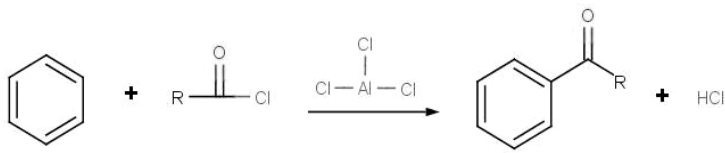


Amidleşme

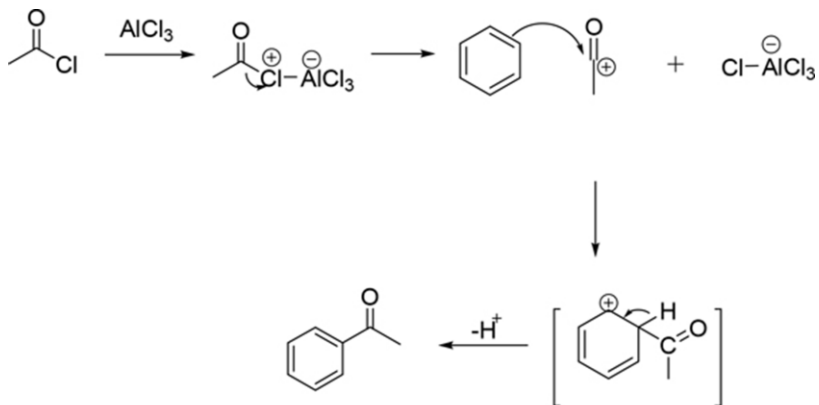




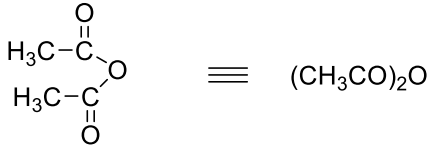
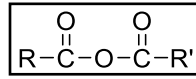
Friedel-Crafts açılması



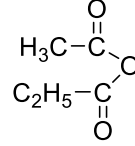
Reaksiyon mekanizması:



ASİT ANHİDRİTLERİ

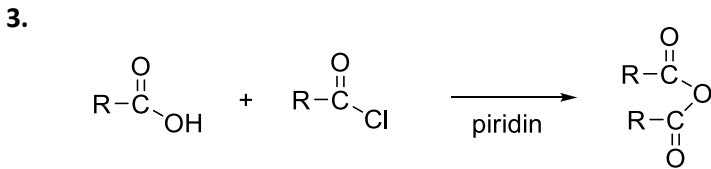
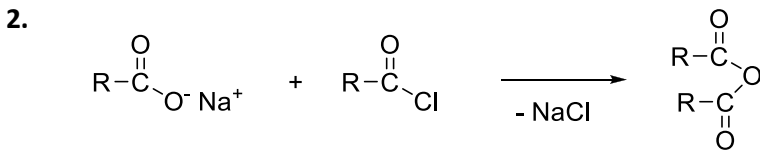
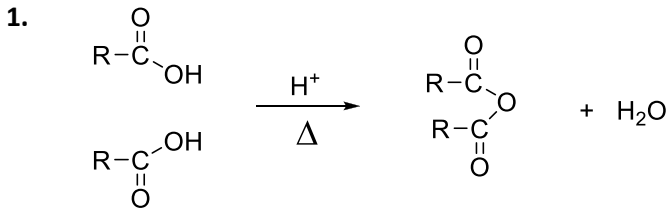


asetik asit anhidriti
= asetik anhidrit
= etanoik anhidrit

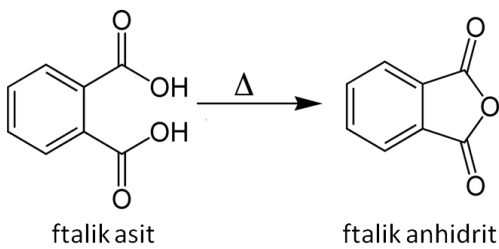
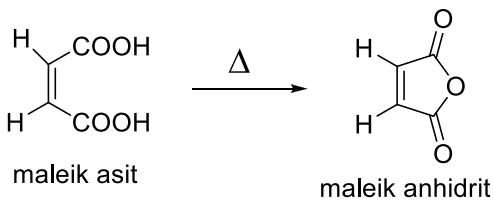


asetik propionik anhidrit

Elde edilişleri

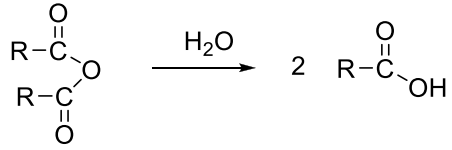


R grupları aynı ise basit, farklı ise karışım anhidritler elde edilir.

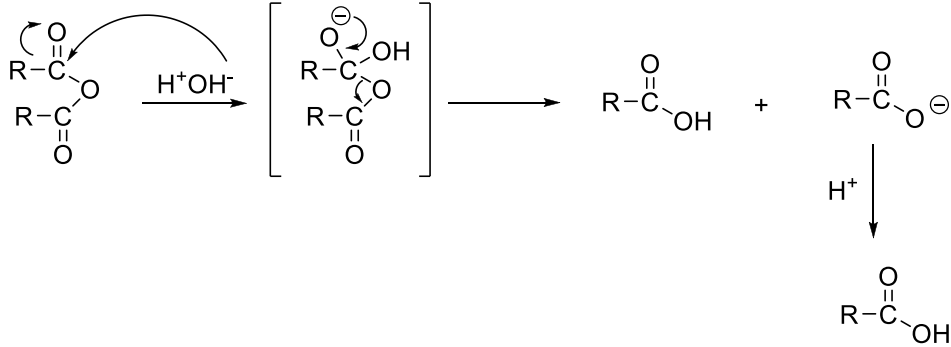


Reaksiyonları

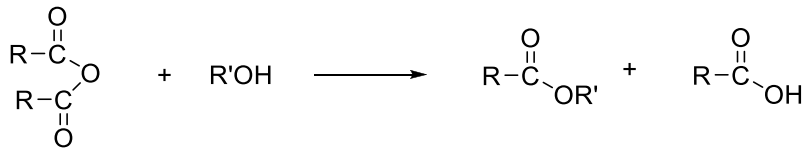
a. Hidroliz



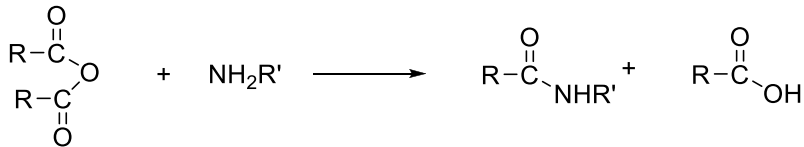
Reaksiyon mekanizması:



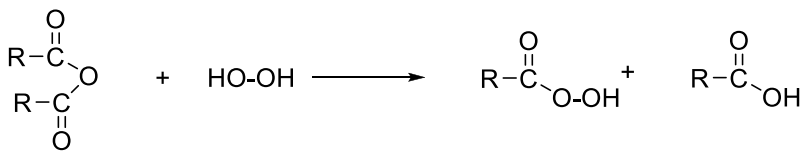
b. Esterleşme



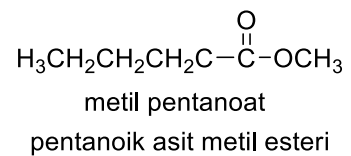
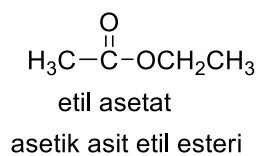
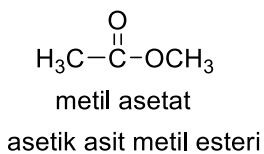
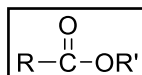
c. Amidleşme

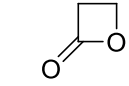


d. Perasit oluşumu

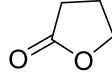


ESTERLER

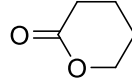




β -propiolakton



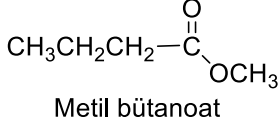
γ -butirolakton



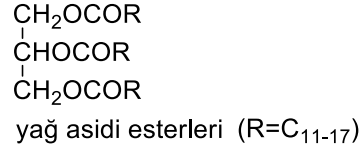
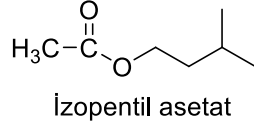
δ -valerolakton

Esterler yapıları, çeşitli meyve ve çiçeklere hoş ve güzel kokularını verirler.

Ananas yağında

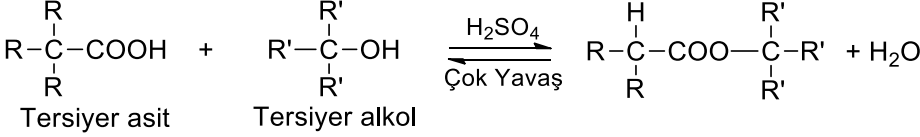
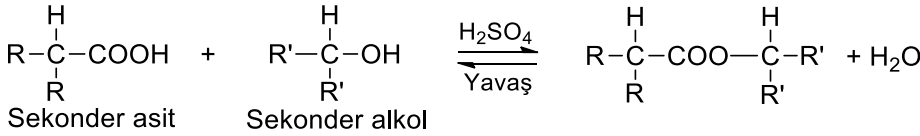
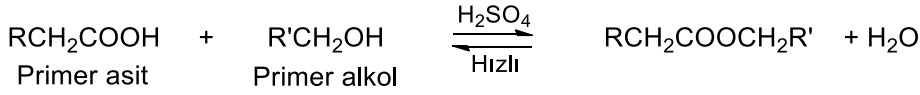


Muz yağında



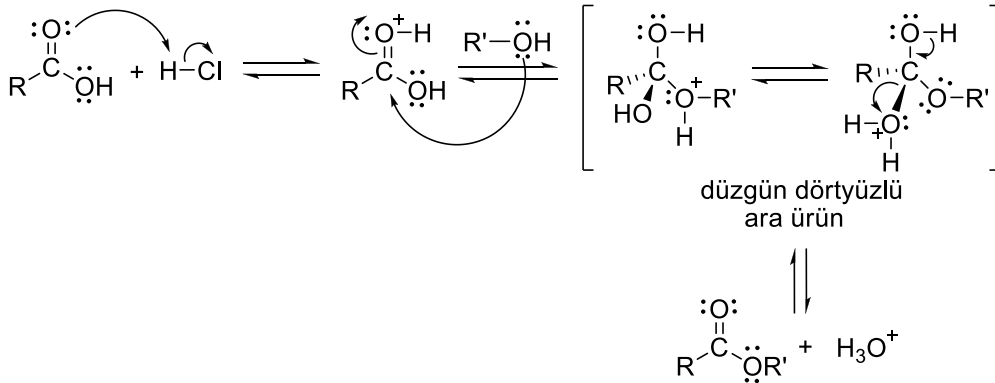
Esterlerin elde edilişi

1. Fischer esterifikasyonu



Asit katalizli nükleofilik açıl sübstitüsyonu (S_N). Karboksilik asidin C=O grubunun elektrofilik gücü alkol oksijeni ile etkileşmeye yeterli olmadığı için, asit kataliz ile bu grubun protonlanması sonucunda nükleofilik atak oluşur.

Reaksiyon mekanizması:



Esterleşme hızına etki eden faktörler

İndüktif Etki

Karboksilik asit molekülünde elektronegatif bir atom varsa, indüktif etki ile -COOH grubu C=O karbonunun elektrofil gücü artar ve buna alkolün bağlanması daha kolay olur. Reaksiyon hızı artar.

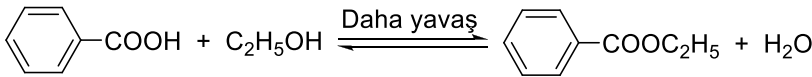
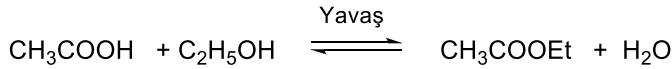
Moleküldeki elektronegatif atom -COOH grubuna ne kadar yakınsa etki o kadar artar.

Aşağıdaki moleküllerin esterleşme hızlarını karşılaştırınız.



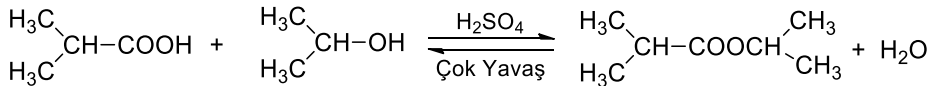
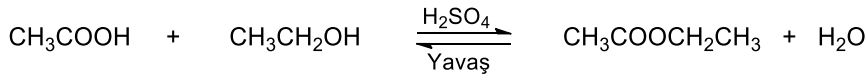
Mezomerik Etki

Benzoik asidin -COOH grubu C=O karbonundaki + yükün, konjuge sistemde olduğu aromatik halkanın mezomerik etkisi ile elektrofil gücü azalır. Alkolün alkoksi grubu (-OR) ile reaksiyonu daha zor olur ve esterleşme reaksiyonu daha yavaş yürür.



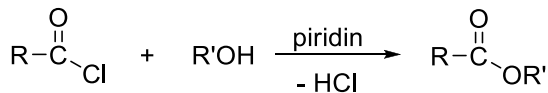
Sterik Etki

Karboksilik asidin -COOH grubuna komşu büyük hacimli gruplar varsa veya alkol molekülü dallanmışsa, sterik engel nedeniyle katyonik merkeze bağlanma engellenir ve esterleşme hızı düşer.

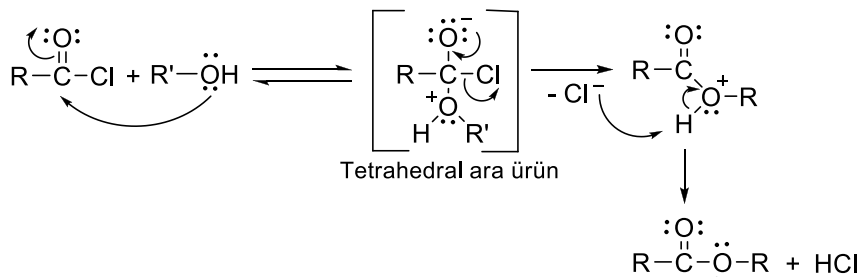


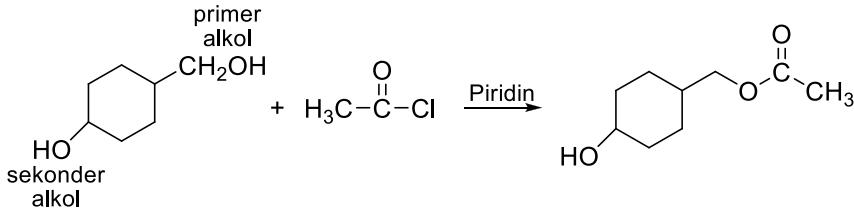
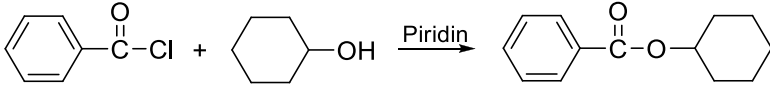
2. Açıl klorürlerin alkollerle reaksiyonu ile;

- Halojenler iyi ayrılan grup.
- Reaksiyon hızı alkolün yapısına göre; primer > sekonder > tersiyer

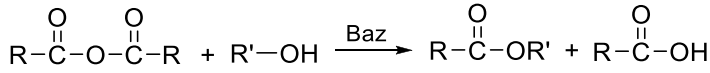


Reaksiyon mekanizması:

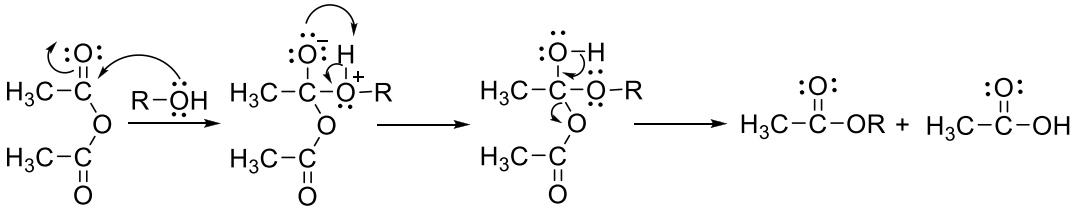




3. Asit anhidritlerinin alkollerle reaksiyonu ile;

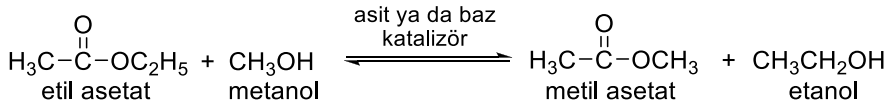


Reaksiyon mekanizması:

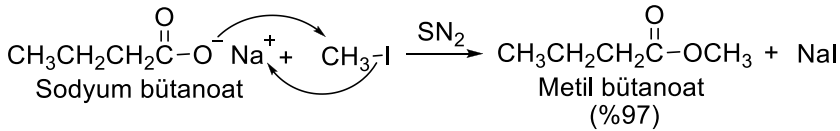
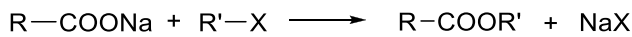


4. Transesterifikasyon ile;

Bir esterden bir alkol aracılığı ile başka bir ester sentezidir. Yeni ester yanında ilk esteri oluşturan alkol de serbest hale geçer.

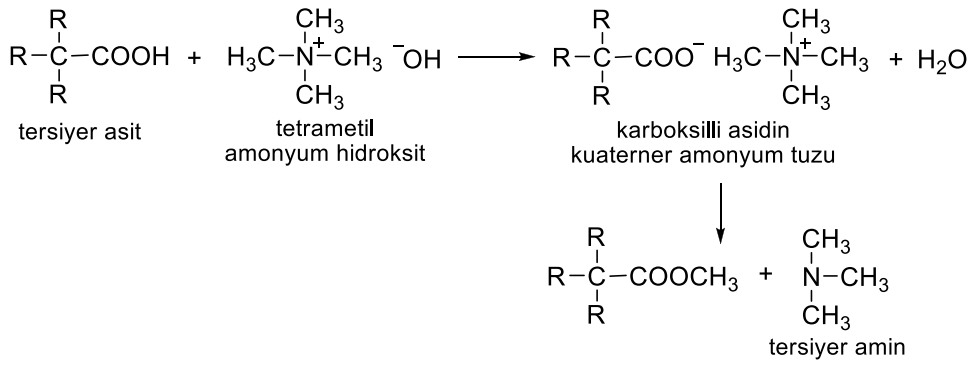


5. Karboksilli asitlerin alkali metal tuzlarının alkil halojenürlerle reaksiyonu ile;



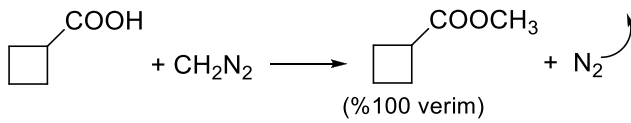
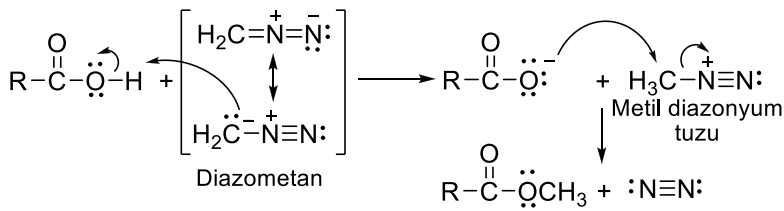
6. Kuaterner amonyum hidroksitlerin kullanıldığı esterleştirme yöntemleri ile;

Karboksil grubu tersiyer bir karbona bağlı olduğunda esterleşme engellenir. Bu durumda kuaterner amonyum hidroksitle oluşturulan tuz, ısı ile dekompoze olur ve ester oluşur.



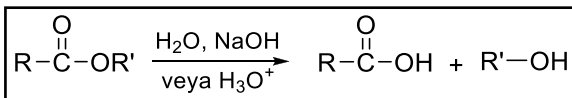
7. Diazometan ile;

- Karboksilik asitlerin **metil** esterleri elde edilebilir.
- Reaksiyon kantitatif; saflaştırma kolay.
- *Diazometan toksik ve patlayıcı !*

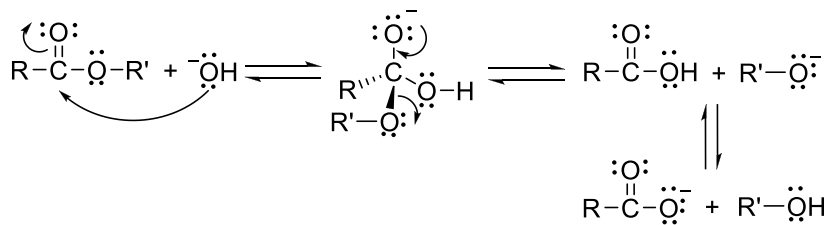


Esterlerin reaksiyonları

1. Hidroliz

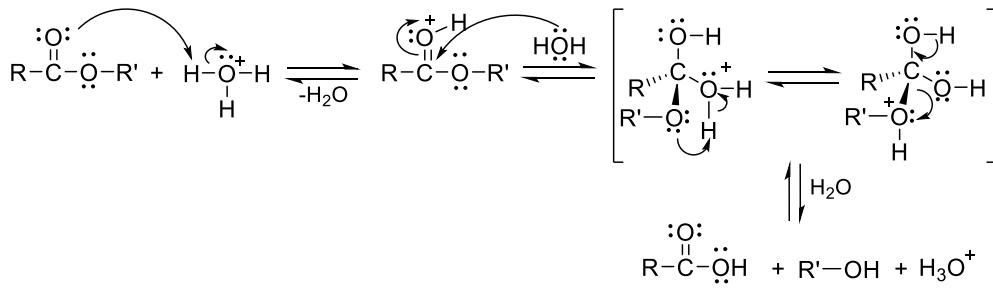


Bazik hidroliz (Esterlerin baz katalizli hidrolizi = Saponifikasyon = sabunlaştırma)

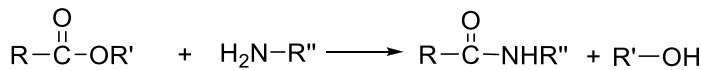


Yağ asitlerinin gliserin esterlerinin alkali hidrolizi ile SABUN elde edilir.

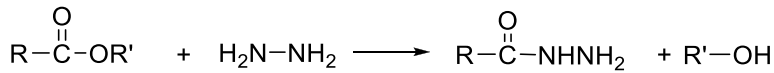
Asit hidroliz



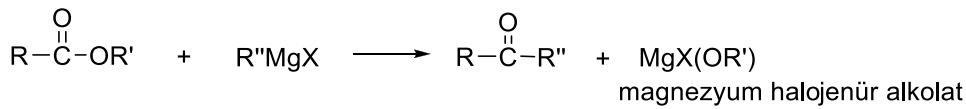
2. Amidleştirme



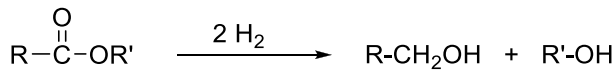
3. Hidrazin ile reaksiyon



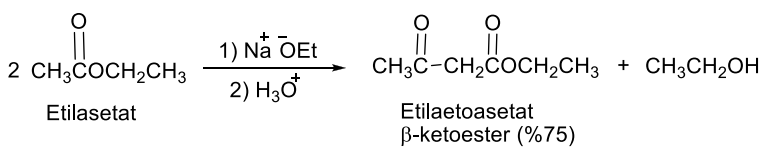
4. Organomagnezyenler ile reaksiyon



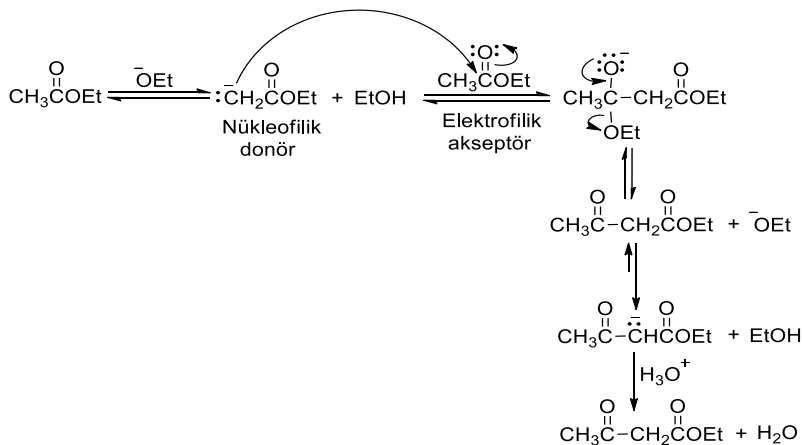
5. Redüksiyon



Claisen kondensasyonu

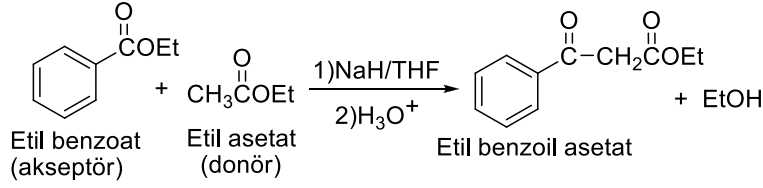


Reaksiyon mekanizması:

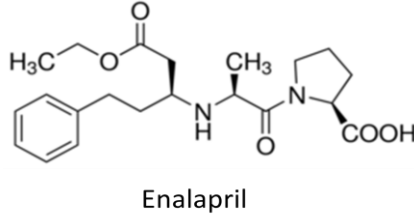
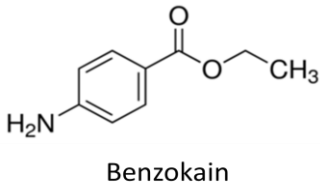
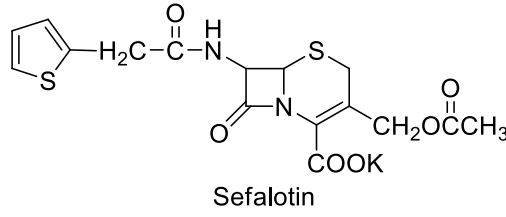
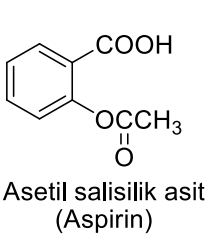


Karışık Claisen kondensasyonu

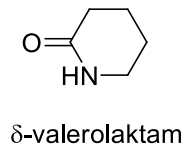
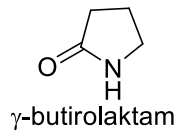
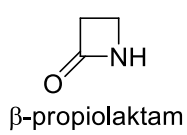
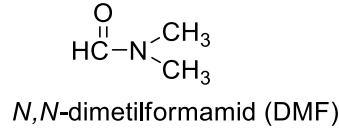
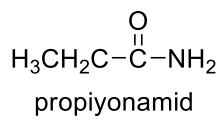
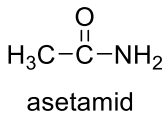
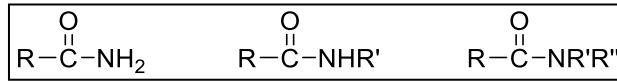
- Farklı 2 ester türevi
- Ester komponentlerinden birisi α -hidrojen taşımaz ve enolat iyonu oluşamaz.



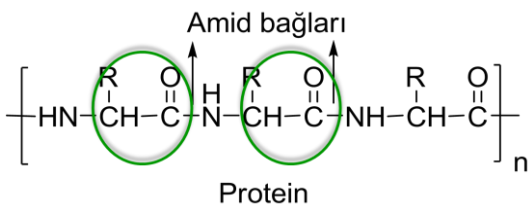
Ester grubu taşıyan bazı bileşikler



AMİDLER



β -laktam

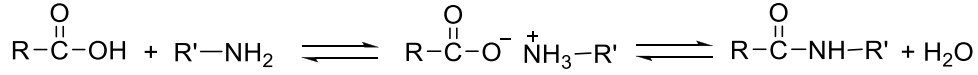


Amidlerin elde edilişi

1. Karboksilik asitlerin aminlerle reaksiyonu ile;

- Karboksilik asitler aminlerle reaksiyona girerek, amonyum tuzları üzerinden su çıkışı ile amid türevleri elde edilebilir.
- *karboksilik asit anyonları* → *en az etkin !!!*

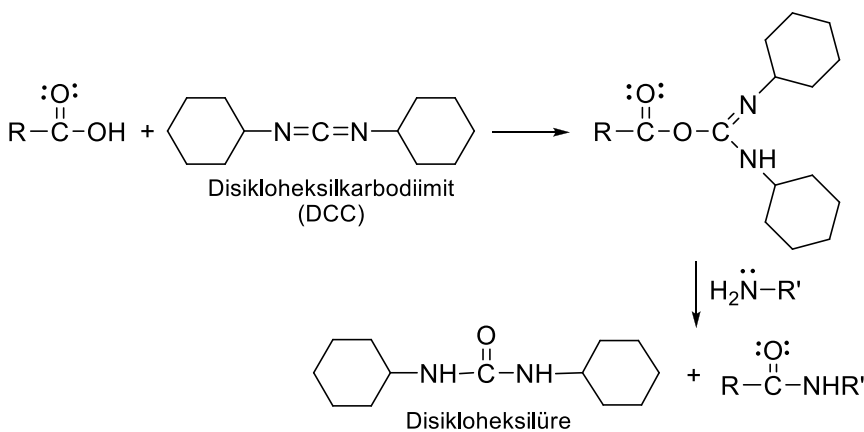
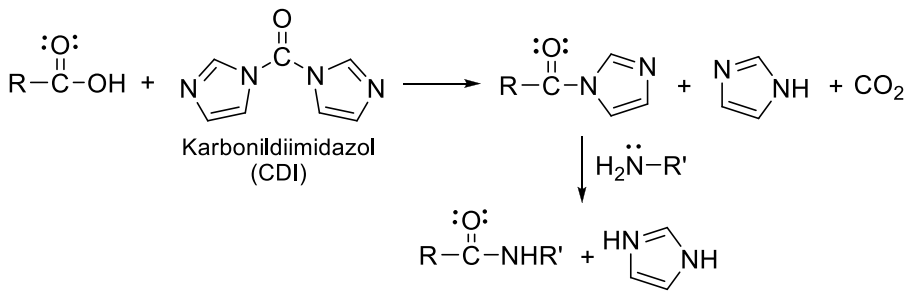
Tercih edilmeyen bir yöntem...



Amid sentezinde kullanılan bazı reaktifler

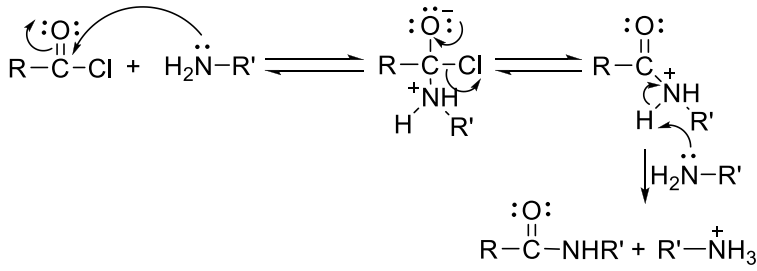
Karboksilik asitler bazı reaktiflerle aktive edilerek aminlerle reaksiyonu ile amidler elde edilir.

- **N,N'-Karbonildiimidazol (CDI)**
- Disikloheksilkarbodiimid (DCC)
- Diizopropilkarbodiimid (DIC)
- 1-Etil-3-(3-dimetilaminopropil)karbodiimid (EDCI)
- N,N-Dimetilaminopiridin (DMAP) / 1-Hidroksibenzotriazol (HOBT)
- Benzotriazol-1-il-oksitris-(dimetilamino)-fosfonyum hekzafluorofosfat (BOP)

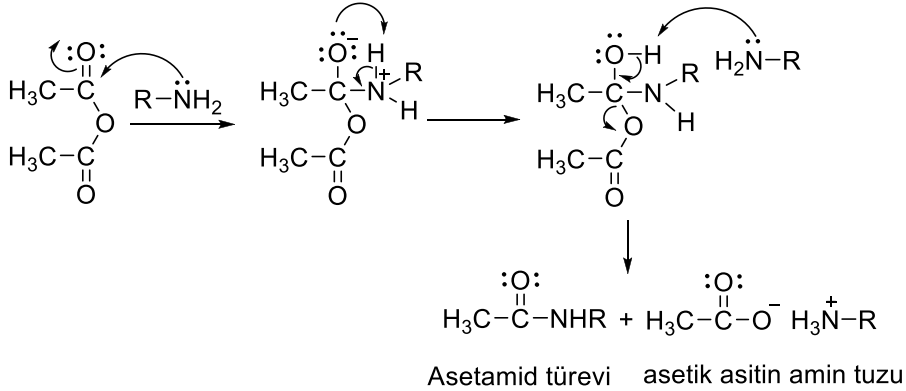


2. Açıl klorürlerin aminlerle reaksiyonu ile;

açıl klorürler → *en etkin*

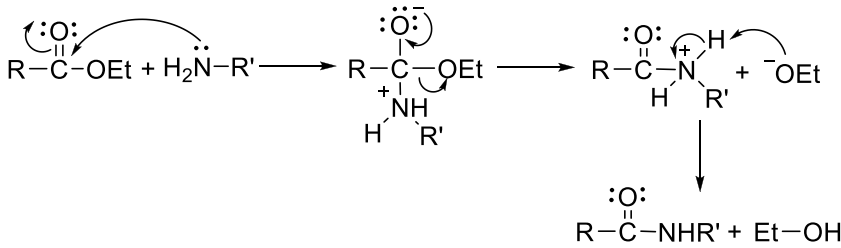


3. Asit anhidritlerin aminlerle reaksiyonu ile;



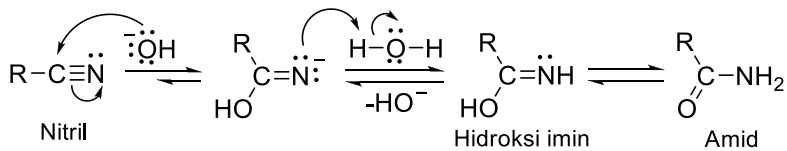
4. Esterlerin aminlerle reaksiyonu ile;

Açıl klorürler ve asit anhidritlerin aminlerle reaksiyonuna göre daha yavaştır.

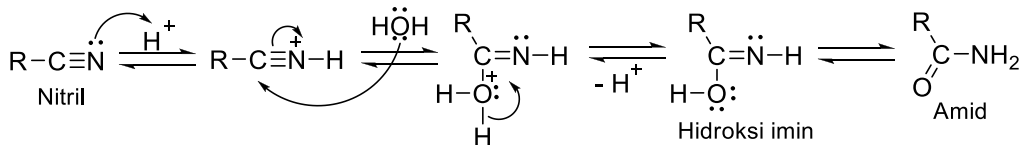


5. Nitrillerin hidrolizi ile;

Bazik hidroliz



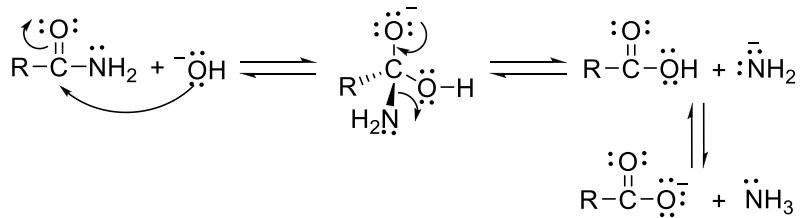
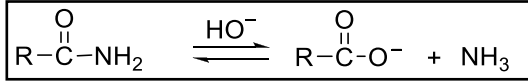
Asit hidroliz



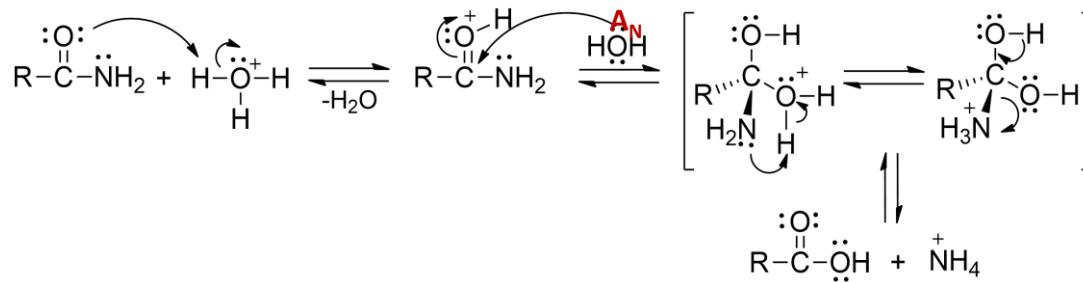
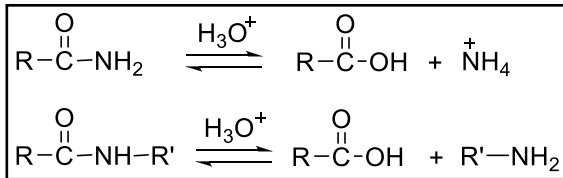
Amidlerin reaksiyonları

1. Hidroliz

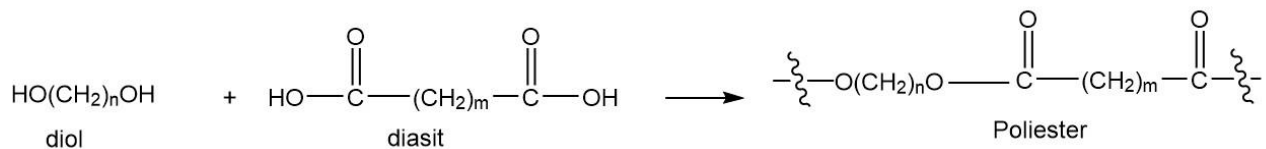
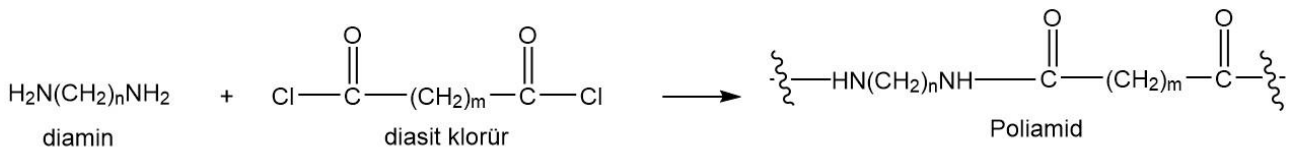
Bazik hidroliz



Asit hidroliz

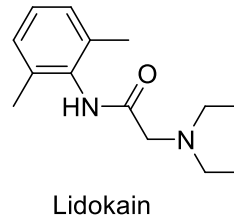
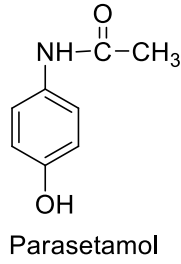
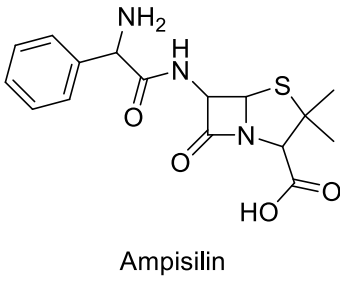
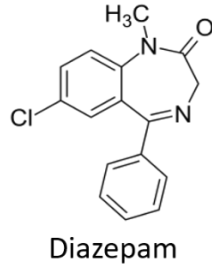
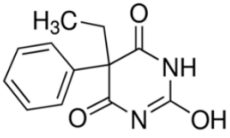
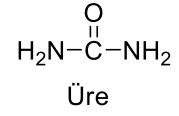
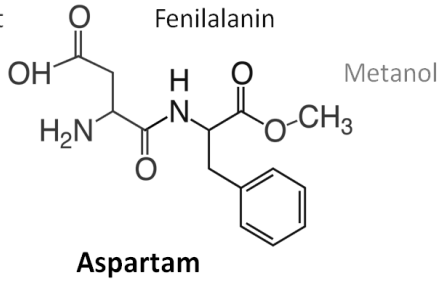


Polimerleşme



Amid grubu taşıyan bazı bileşikler

Aspartik
asit



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- Organic Chemistry, L.G. Wade, Jr., 6th Edition, 2005.
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