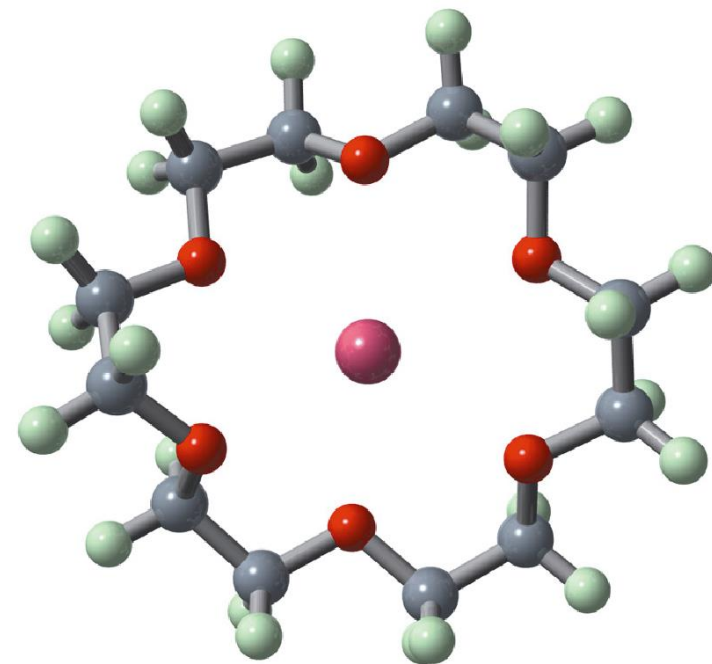




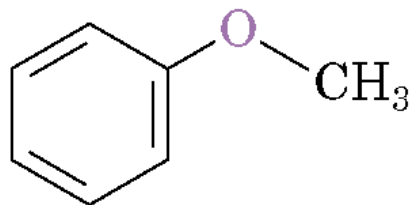
ΚΕΦ.18. ΑΙΘΕΡΕΣ ΚΑΙ ΕΠΟΞΕΙΔΙΑ
ΘΕΙΟΛΕΣ ΚΑΙ ΣΟΥΛΦΙΔΙΑ



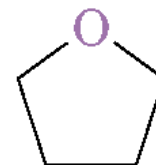
ΗΡΑΚΛΕΙΟ 2023



Διαιθυλο αιθέρας



Ανισόλη
(Μεθυλο φαιnyλο αιθέρας)



Τετραϋδροφουράνιο
(κυκλικός αιθέρας)

As a General ANESTHETIC

ETHER
*is by far the SAFEST FOR CHILDREN **

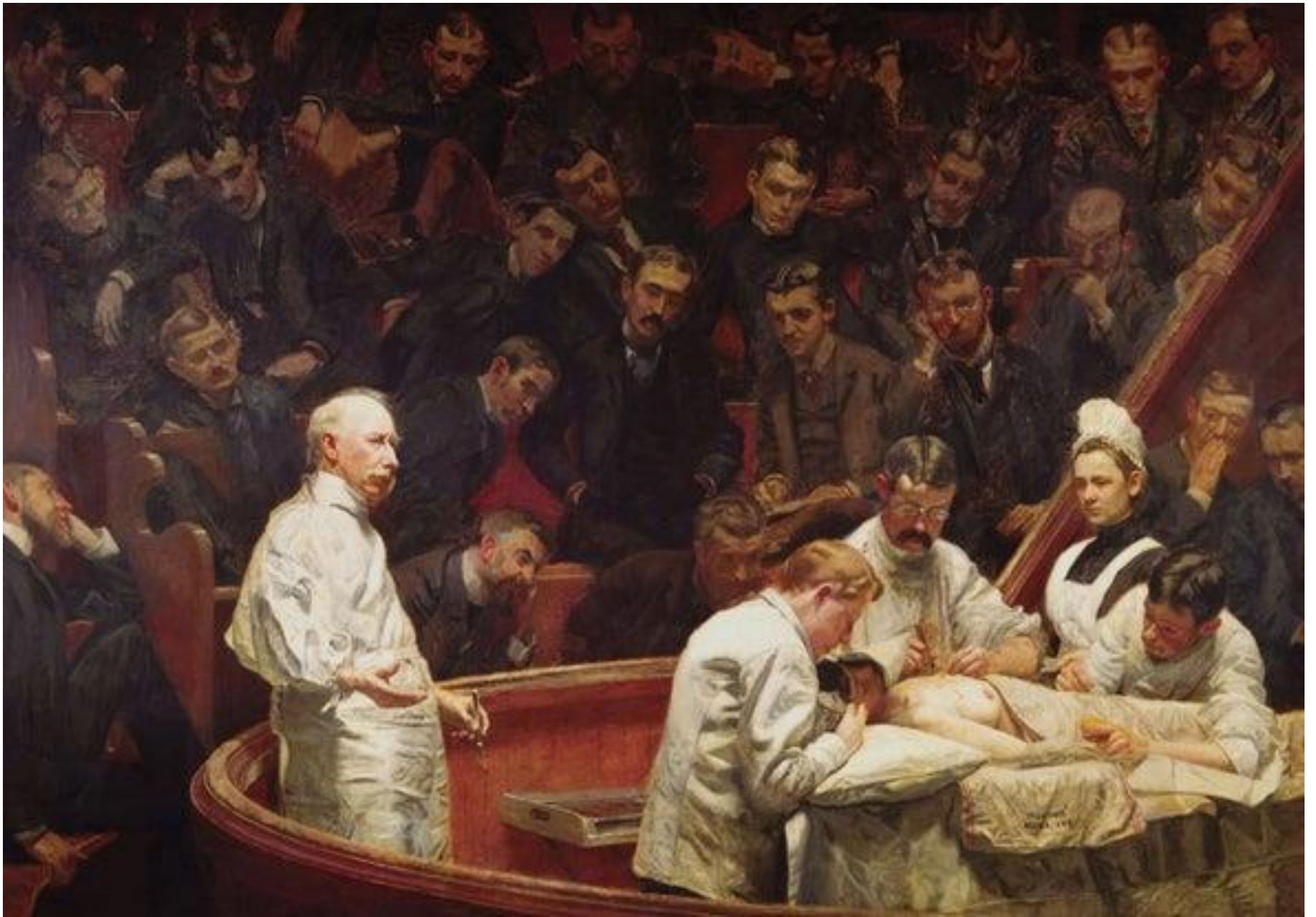
Ether is generally recognized as the anesthetic of choice because of completeness of relaxation and its greater margin of safety. MALLINCKRODT ETHER ANESTHESIA is dependably pure. Freedom from aldehyde, peroxide and all other toxic impurities affording absolute assurance against any toxic effect due to impurities in the anesthetic. Smooth induction, almost natural awakening, and minimum nausea or respiratory irritation characterize the administration of MALLINCKRODT ETHER ANESTHESIA. Manufactured from ethyl alcohol by the aliphatic acid process. Exceedingly tested by U. S. P. and extra sensitive Mallinckrodt tests, and sealed with the Mallinckrodt patented mechanical closure, MALLINCKRODT ETHER ANESTHESIA merits the confidence that it has been accorded by the medical profession. MALLINCKRODT ETHER ANESTHESIA is packed in 1/4 pound, 1/2 pound, 1 pound and 5 pound, chemically treated, hermetically sealed containers.

Mallinckrodt
CHEMICAL WORKS

ST. LOUIS
CHICAGO
PHILADELPHIA

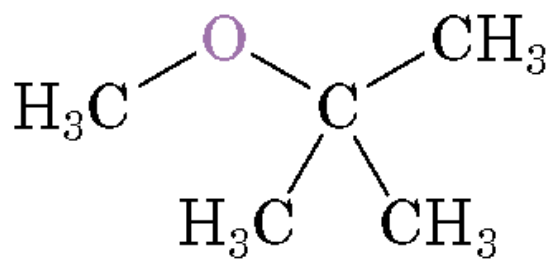
NEW YORK
TORONTO
MONTREAL



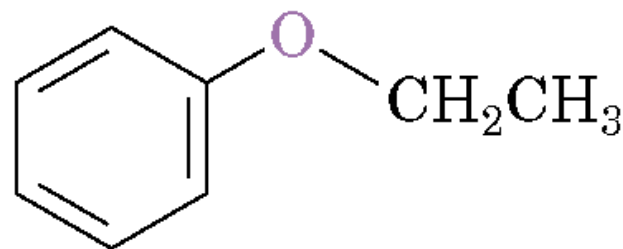


THE AGNEW CLINIC, 1889
Thomas Eakins

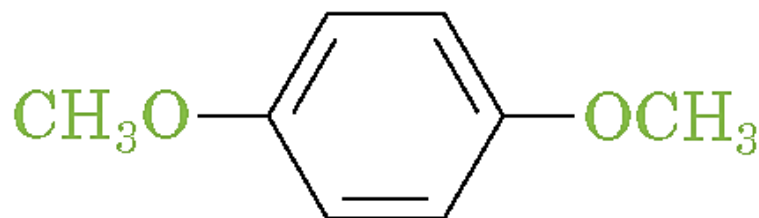
18.1



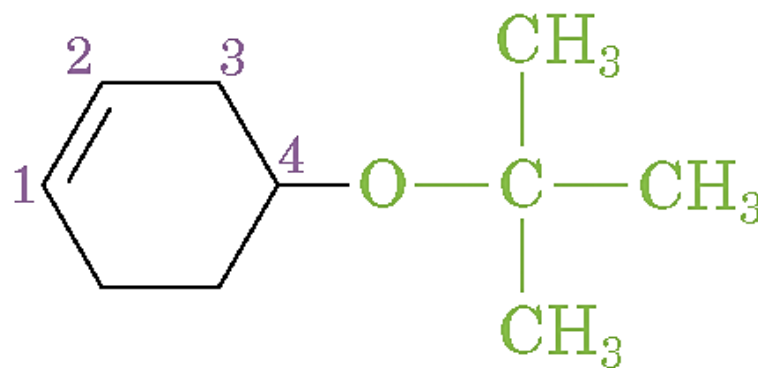
tert-Βουτυλο μεθυλο
αιθέρας



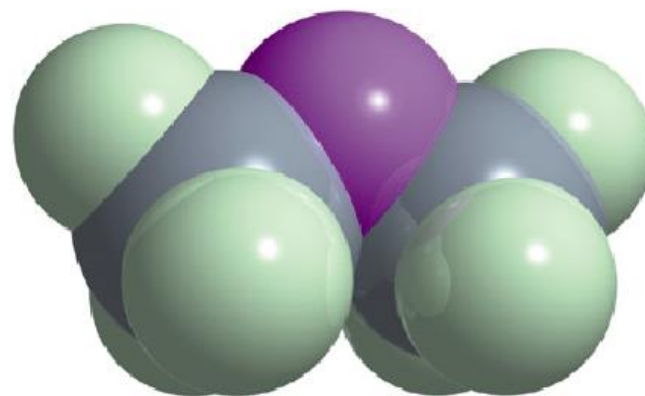
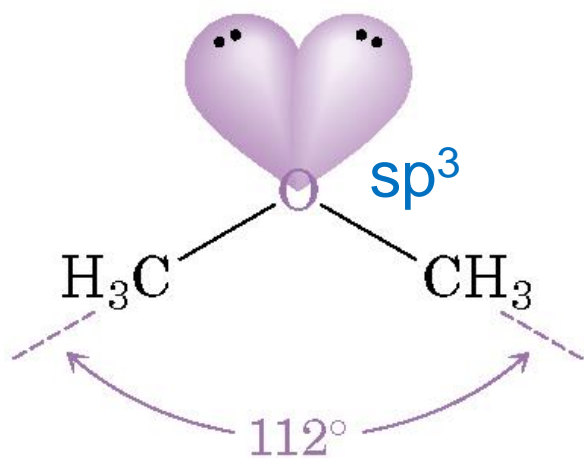
Αιθυλο φαινυλο αιθέρας



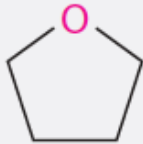

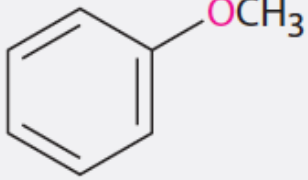
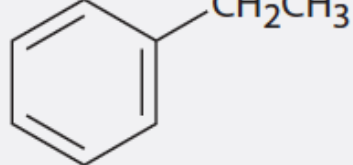
p-Διμεθοξυβενζόλιο

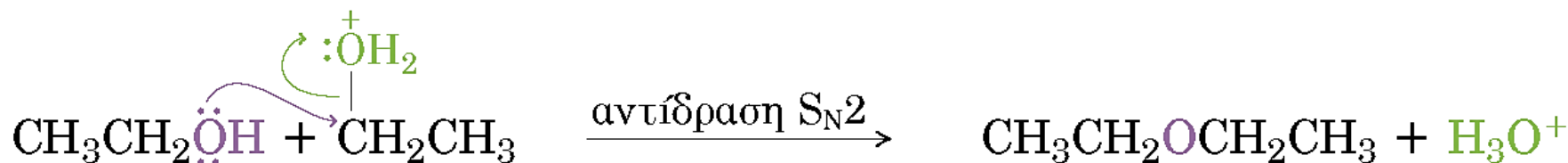
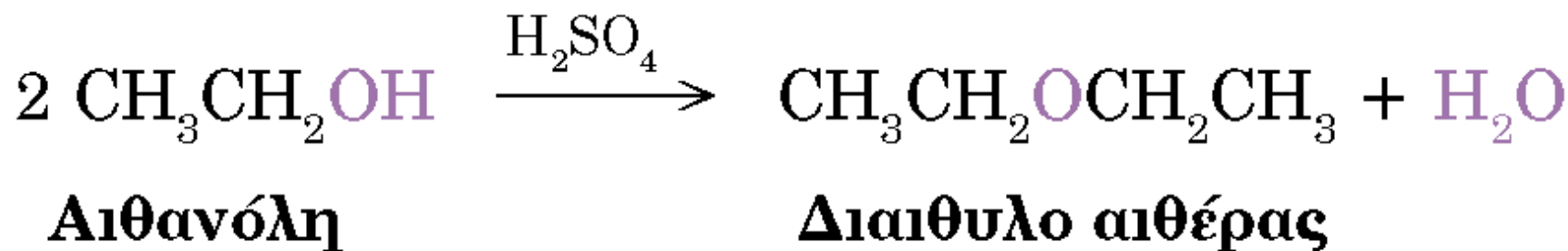


4-*tert*-Βουτοξυ-1-κυκλοεξένιο

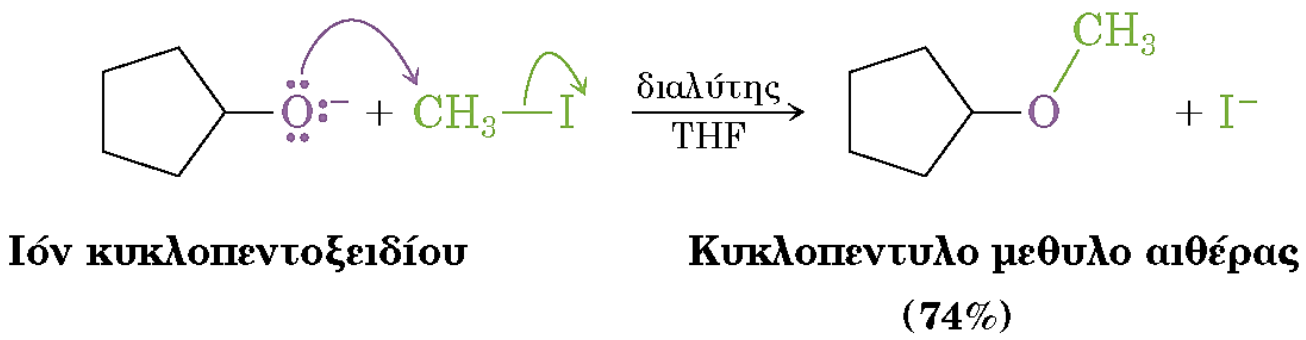
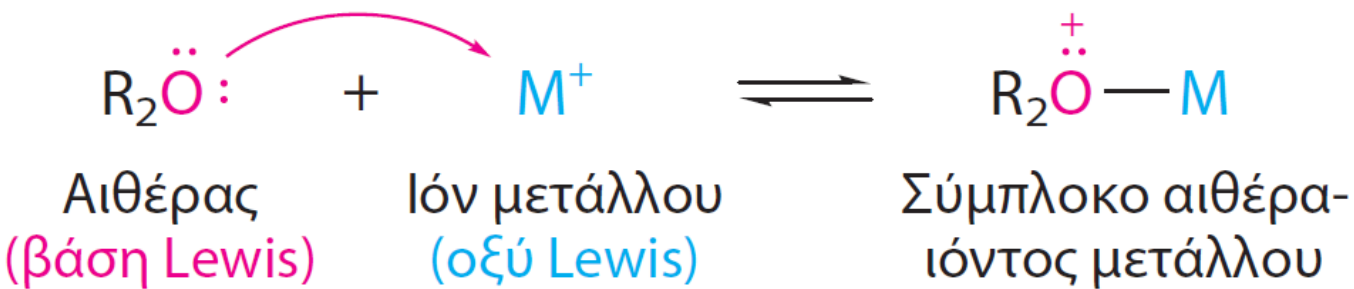


ΠΙΝΑΚΑΣ 18-1 Σύγκριση των σημείων ζέσεως αιθέρων και υδρογονανθράκων

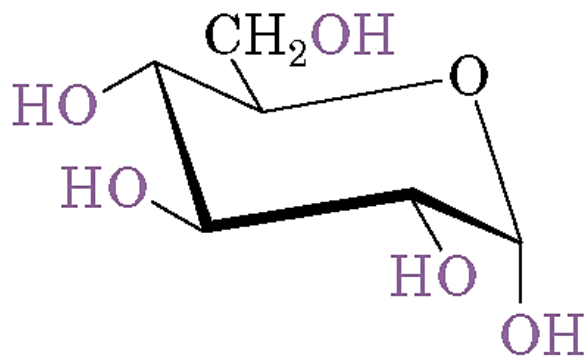
Αιθέρας	Σημείο ζέσεως °C	Υδρογονάνθρακας	Σημείο ζέσεως °C
CH_3OCH_3	-25	$\text{CH}_3\text{CH}_2\text{CH}_3$	-45
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	34,6	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	36
	65		49
	158		136



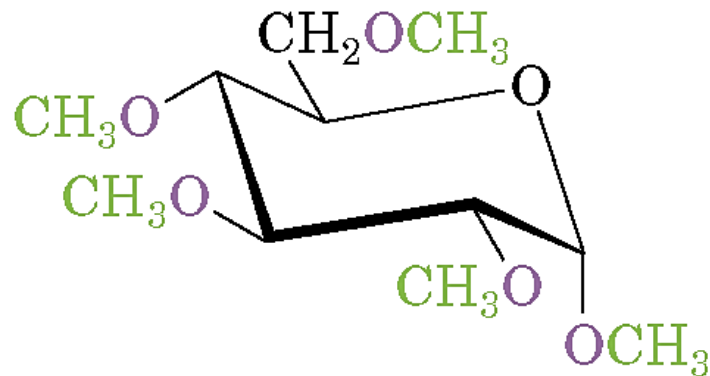
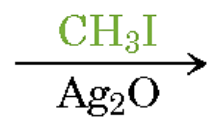
Σύνθεση κατά Williamson



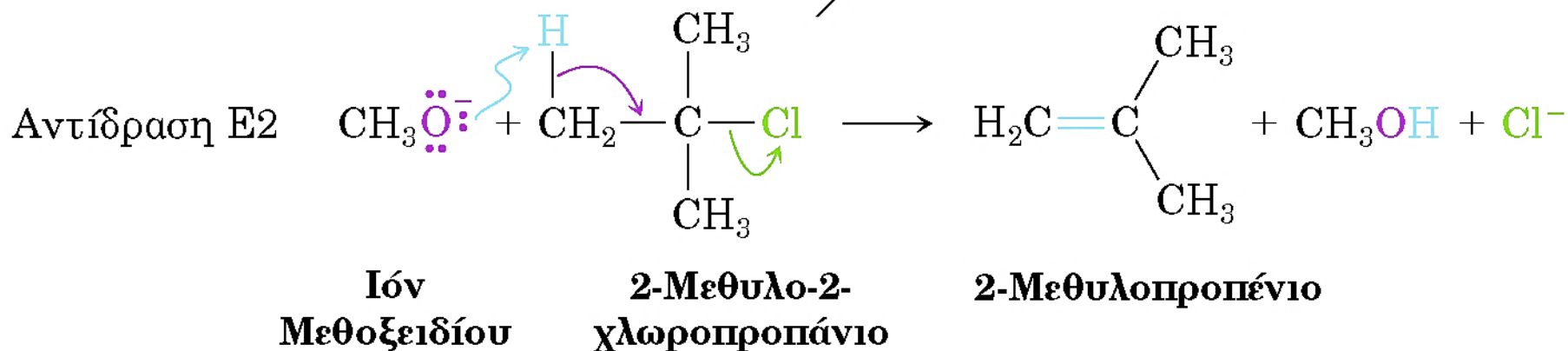
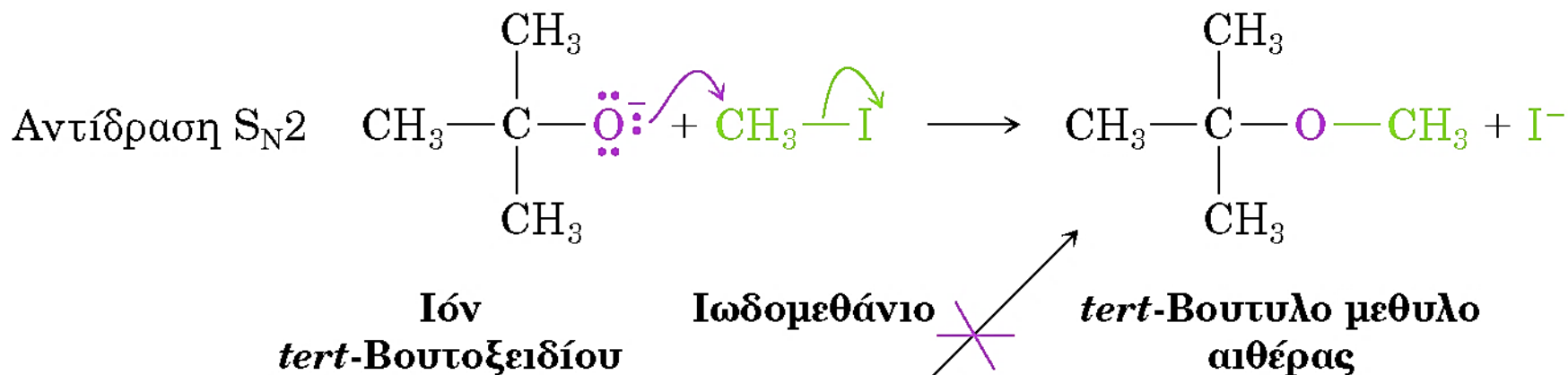
Alexander William Williamson (1824-1904)



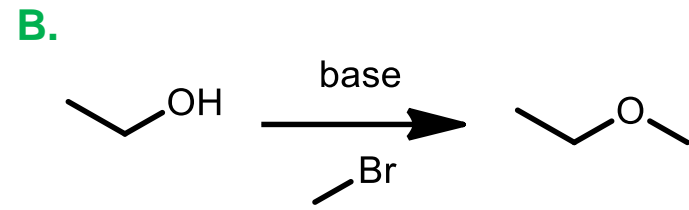
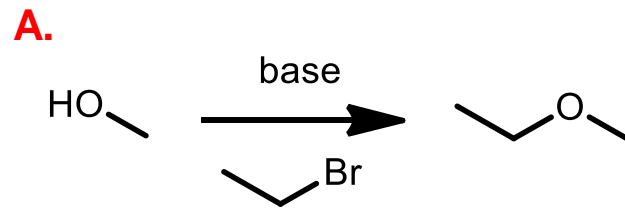
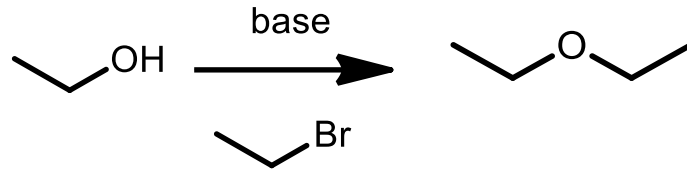
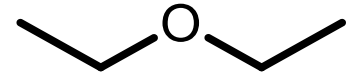
***α*-D-Γλυκόζη**



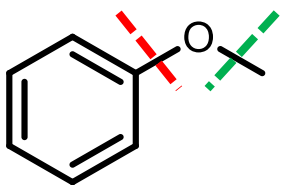
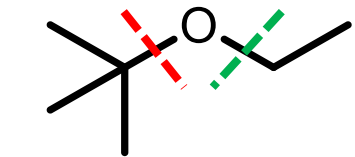
**Πενταμεθυλο αιθέρας
της *α*-D-γλυκόζης**



➤ Ρετροσύνθεση



Τι θα κάνετε;



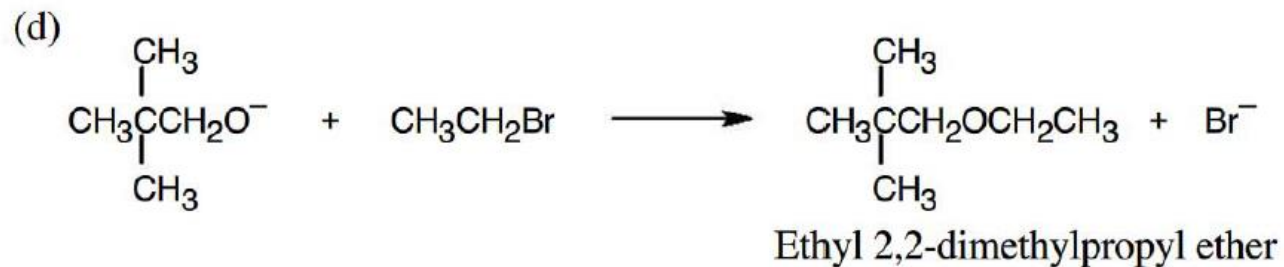
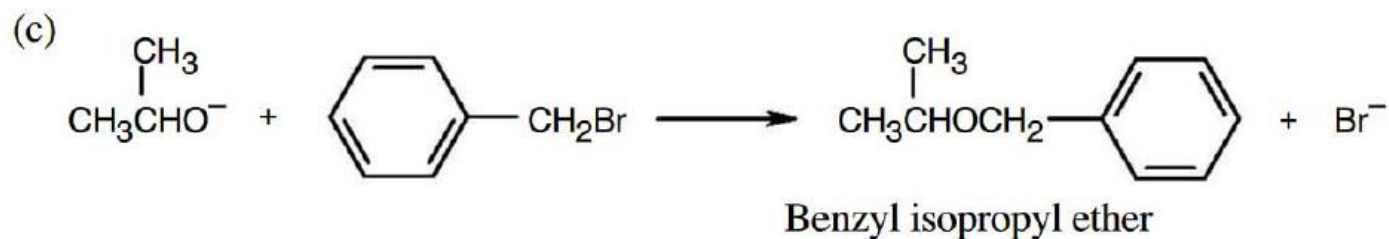
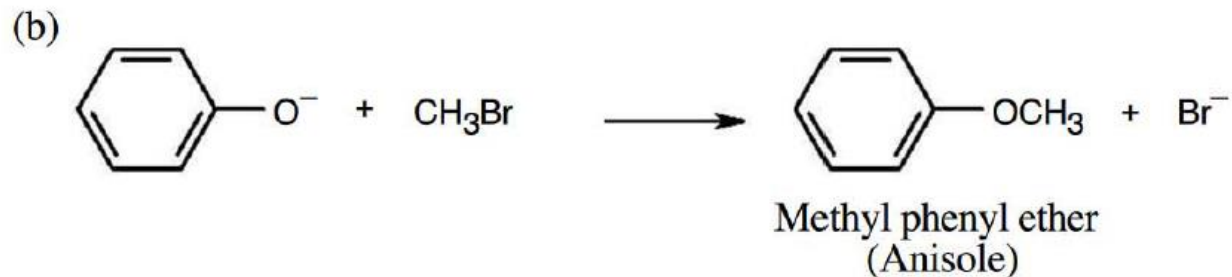
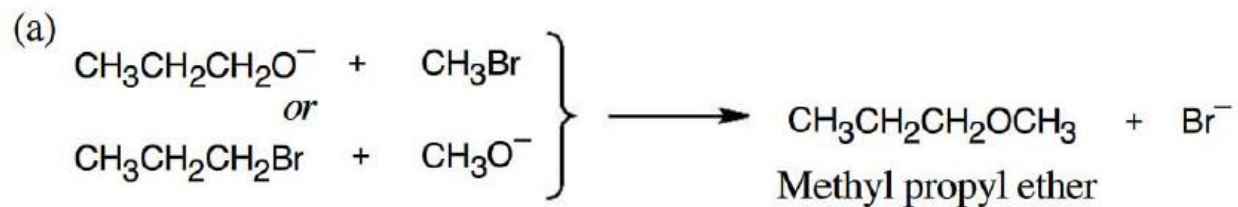
18-3 Πώς θα παρασκευάσετε τους παρακάτω αιθέρες με τη σύνθεση Williamson;

(α) Μεθυλο προπυλο αιθέρας

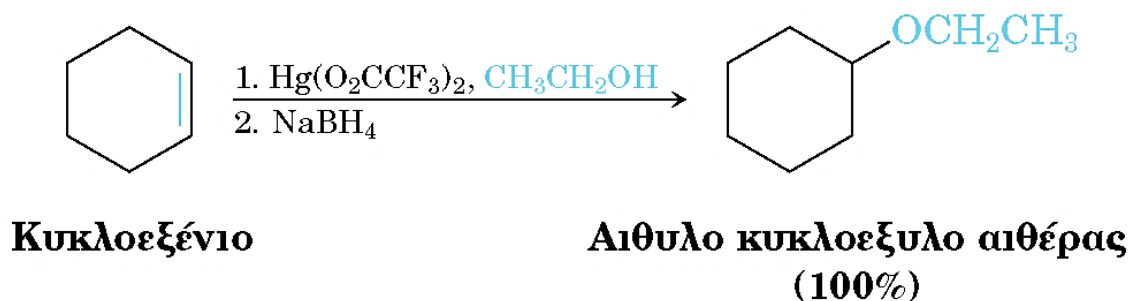
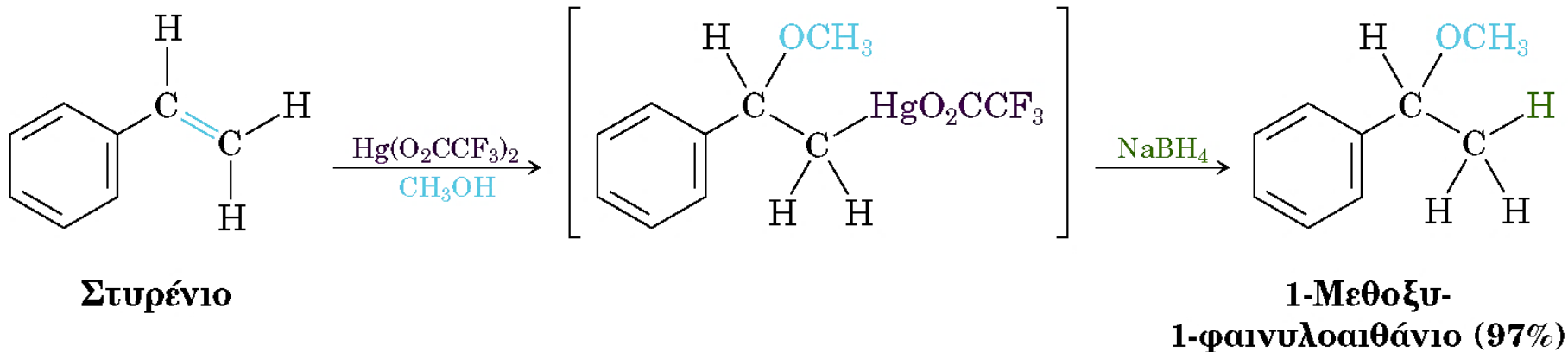
(β) Ανισόλη (μεθυλο φαινυλο αιθέρας)

(γ) Βενζυλο ισοπροπυλο αιθέρας

(δ) Αιθυλο 2,2-διμεθυλοπροπυλο αιθέρας

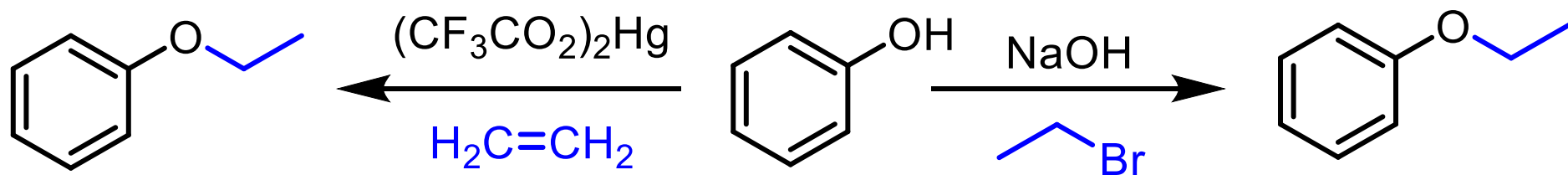
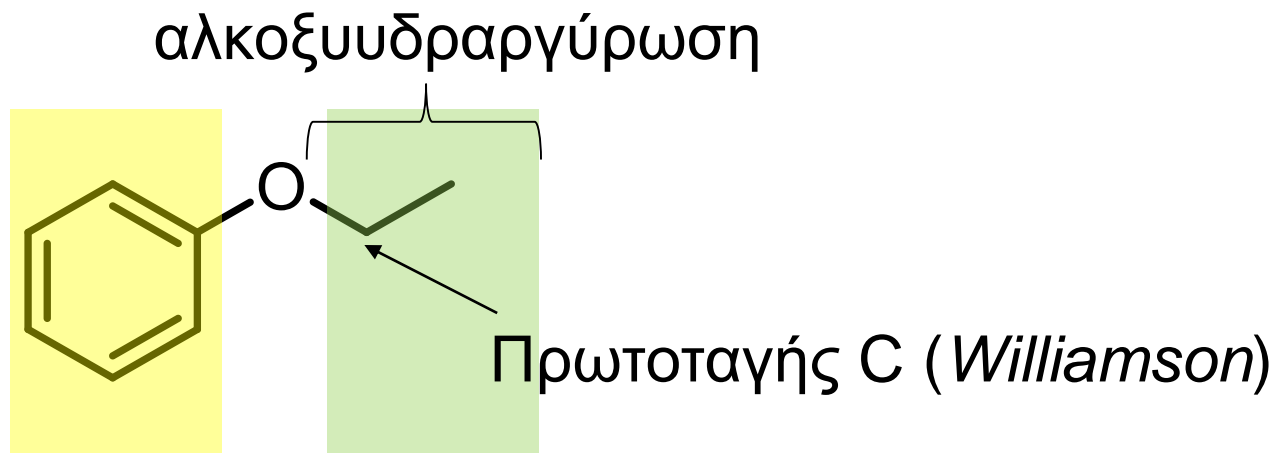


Σύνθεση μέσω αλκοξυυδραργύρωσης αλκενίων

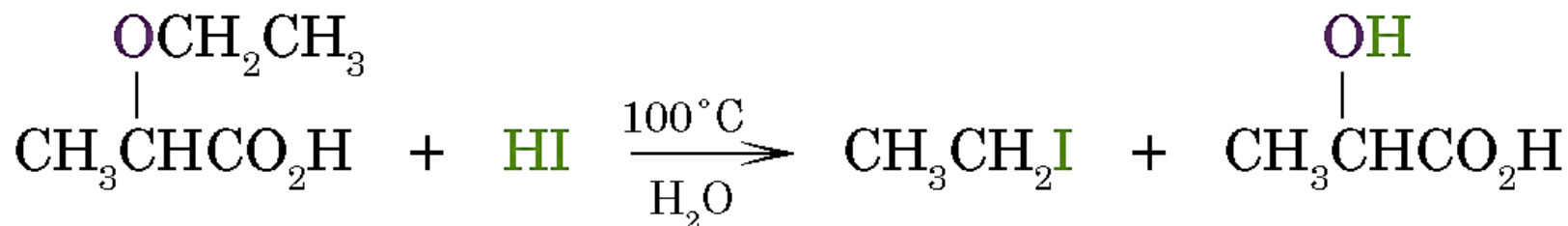


- ✓ μεγάλη ποικιλία από πρωτοταγείς, δευτεροταγείς και τριτοταγείς αλκοόλες
- ✓ Αιθέρες με 2 τριτοταγείς ομάδες είναι αδύνατον να παρασκευαστούν

Πώς θα παρασκευάσετε τον παρακάτω αιθέρα;



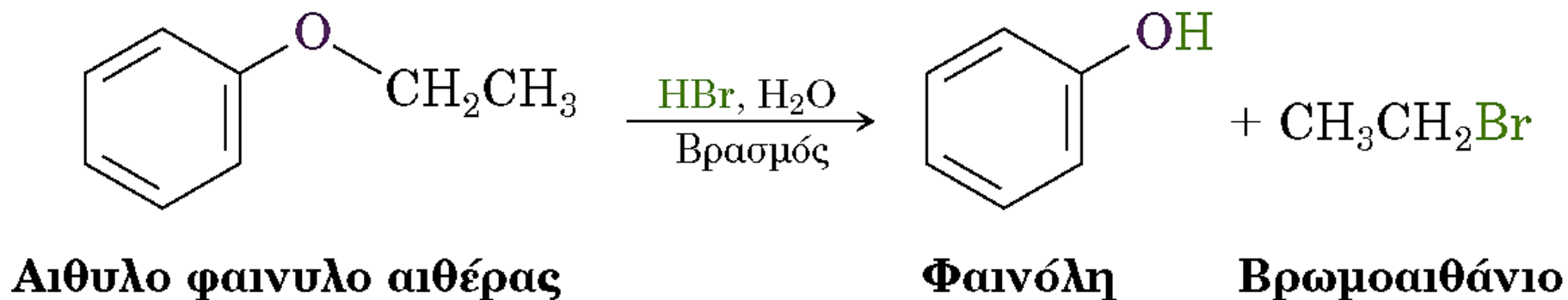
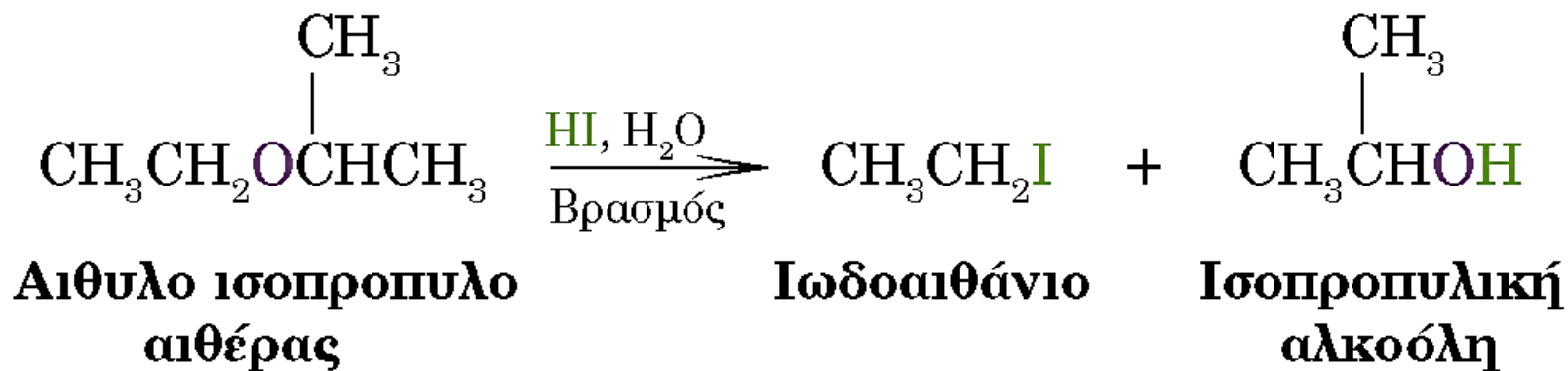
18.3

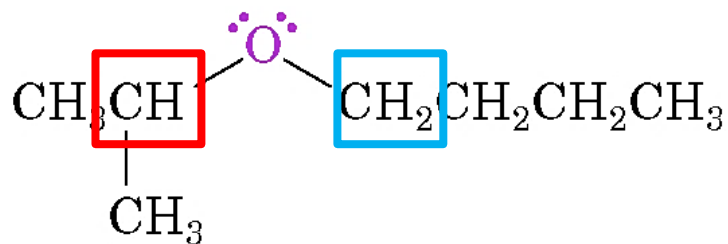


2-Αιθοξυπροπανοϊκό
οξύ

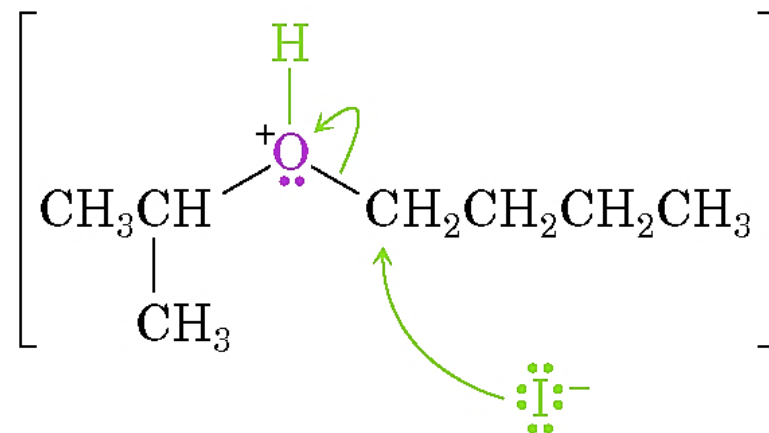
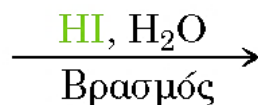
Ιωδοαιθάνιο

Γαλακτικό οξύ

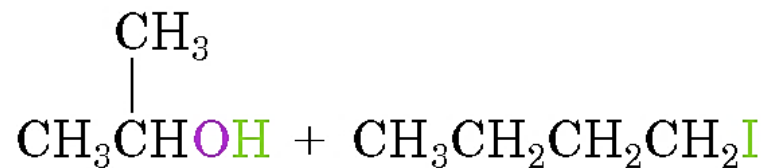




Βουτυλο ισοπροπυλο αιθέρας

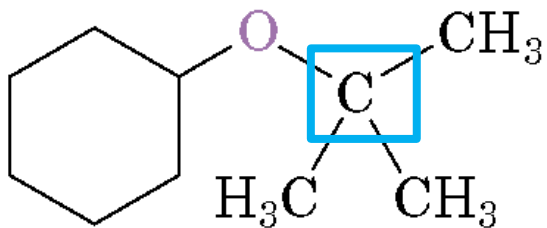


Αντίδραση S_N2

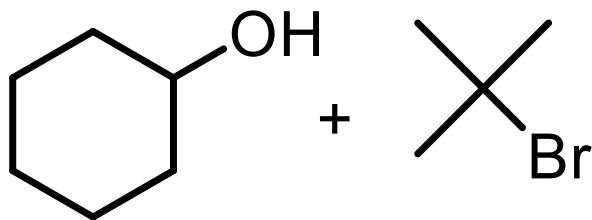
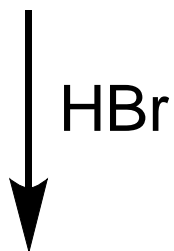


**Ισοπροπυλική
αλκοόλη**

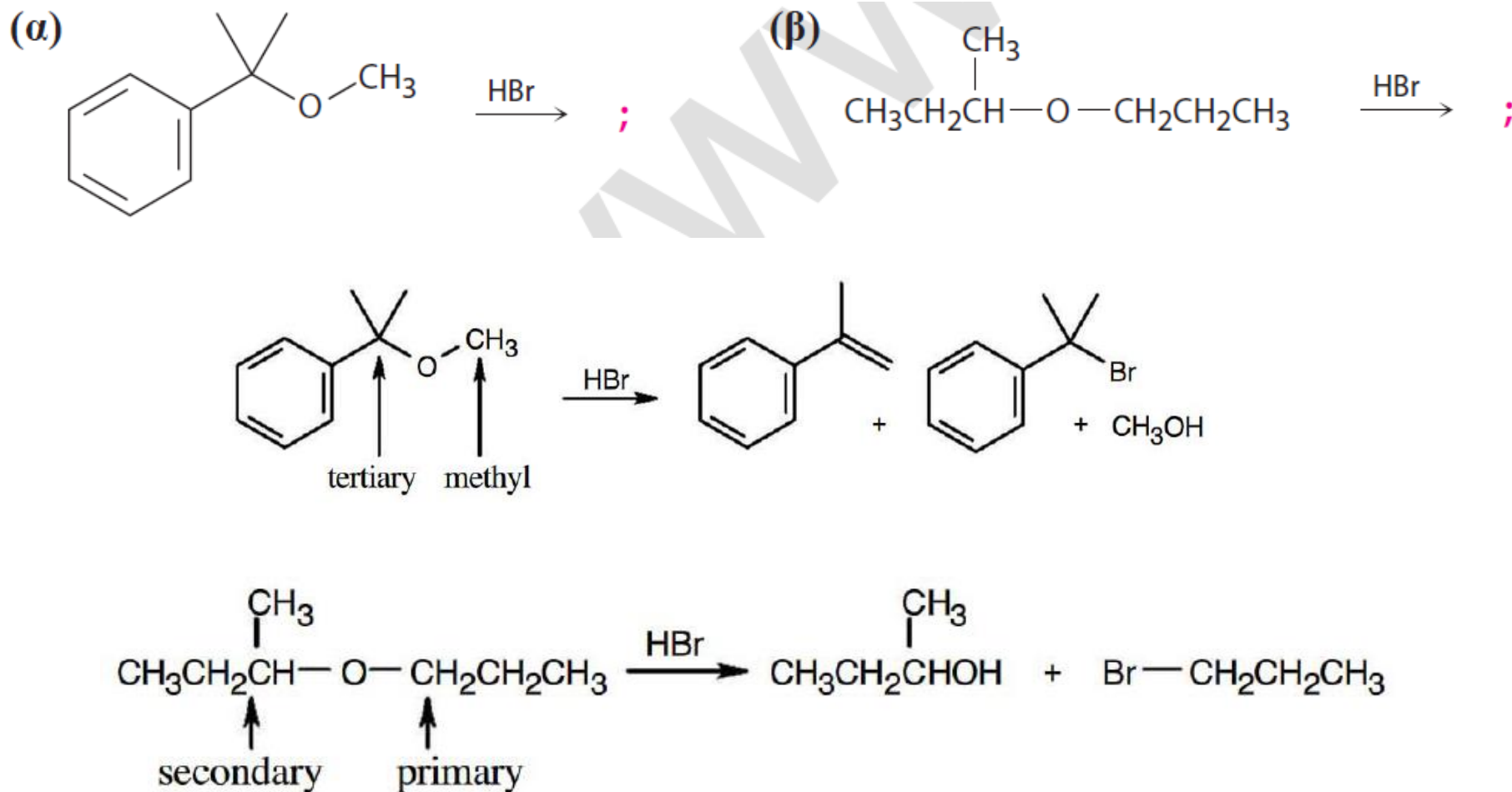
1-Ιωδοβουτάνιο



***tert*-Βουτυλο κυκλοεξυλο
αιθέρας**

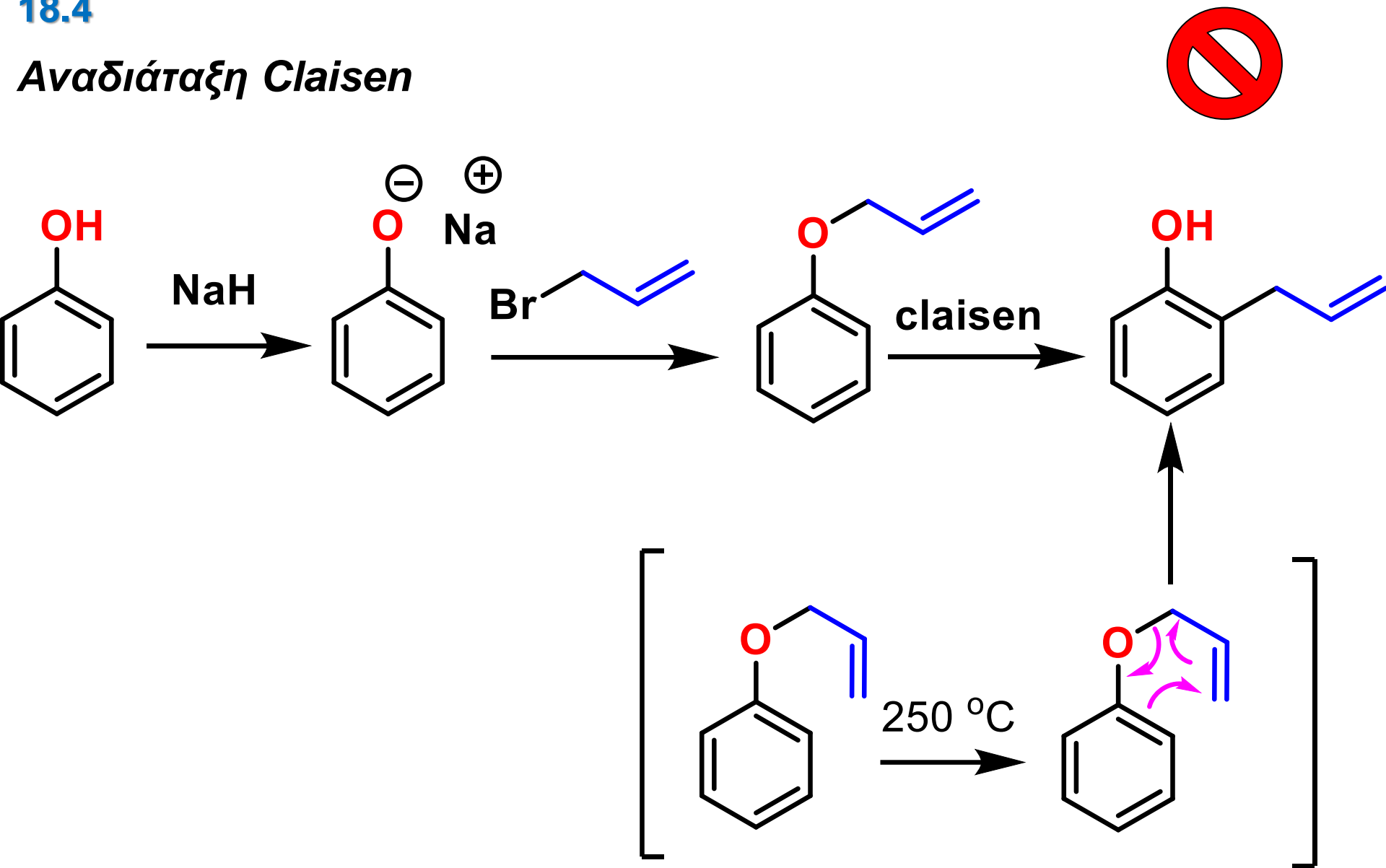


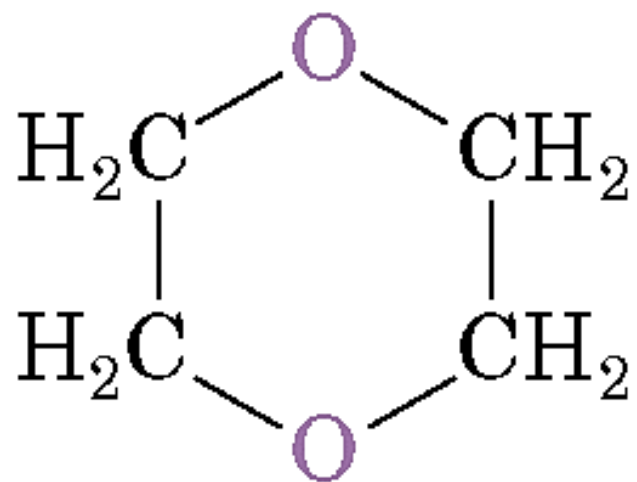
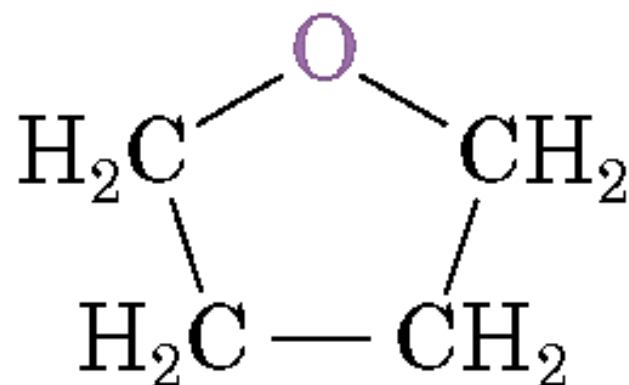
18-7 Προβλέψτε τα προϊόντα των ακόλουθων αντιδράσεων:

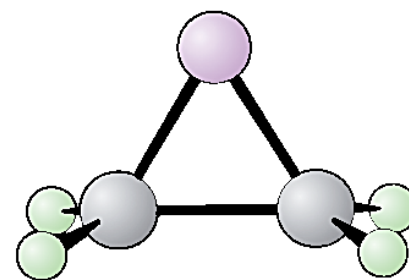
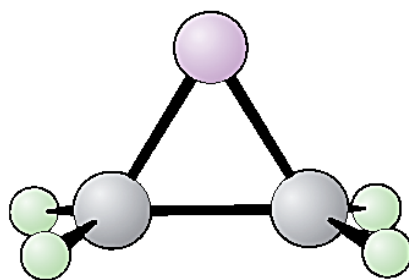
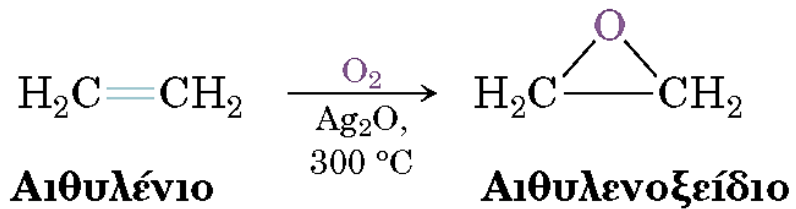


18.4

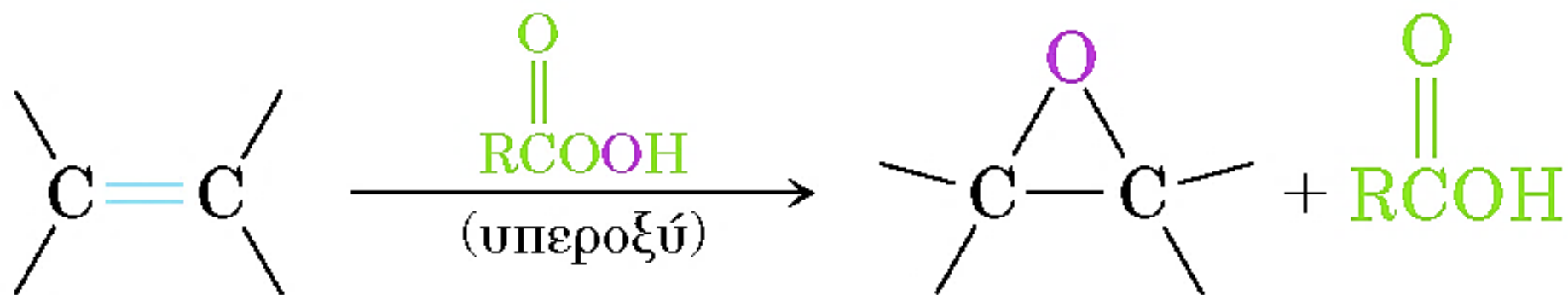
Αναδιάταξη Claisen



**1,4-Διοξάνιο****Τετραϋδροφουράνιο**

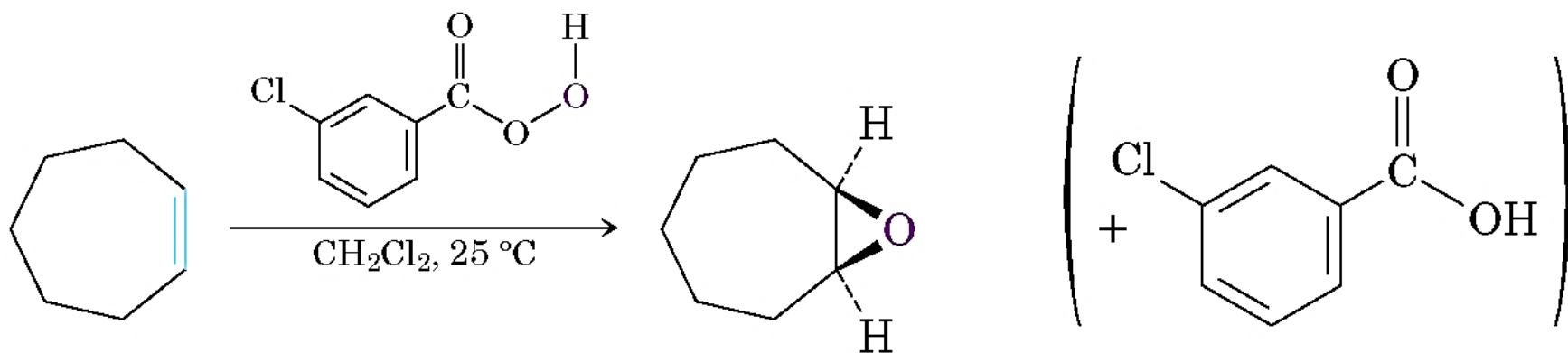


Στερεοσκοπική άποψη



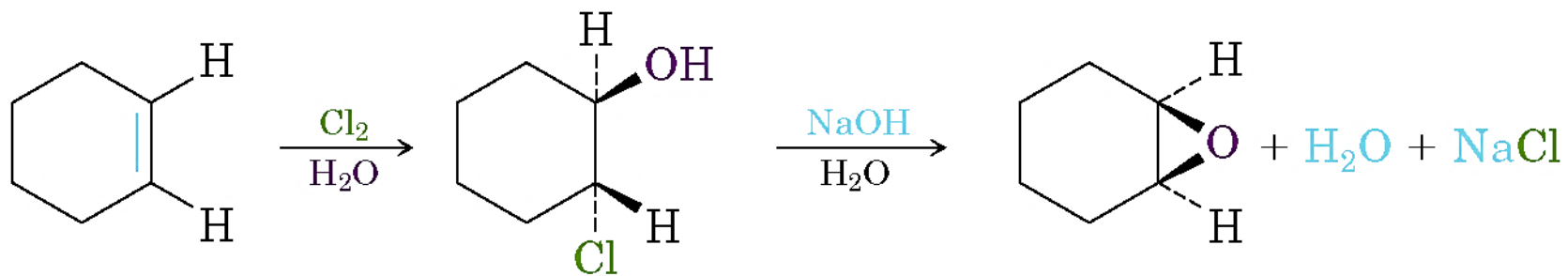
Αλκένιο

Εποξειδίο



Κυκλοεπένιο

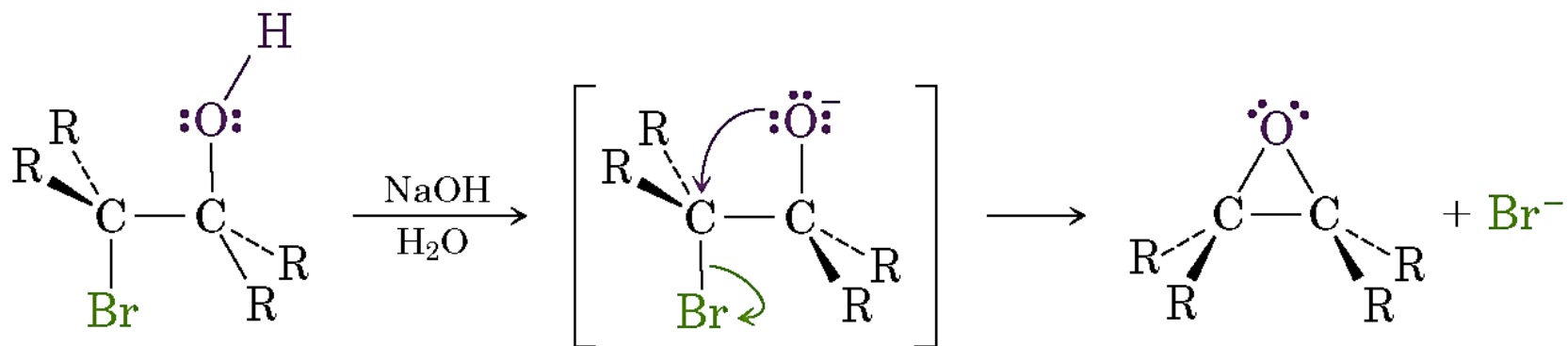
1,2-Εποξικυκλοεπάνιο
(78%)



Κυκλοεξένιο

***trans*-2-Χλωρο-
κυκλοεξανόλη**

**1,2-Εποξυκυκλοεξάνιο
(73%)**



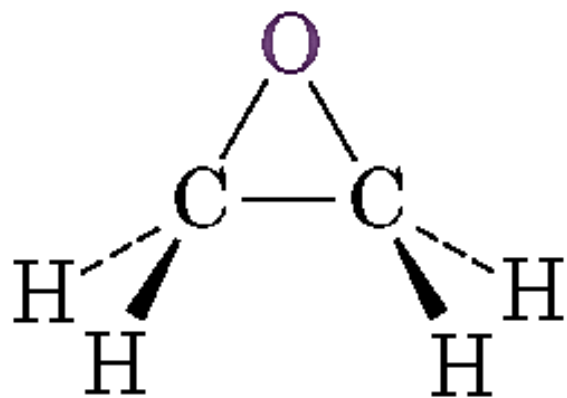
Βρωμοϋδρίνη

**Ενδομοριακή υποκατάσταση
(μέσα στο ίδιο το μόριο)**

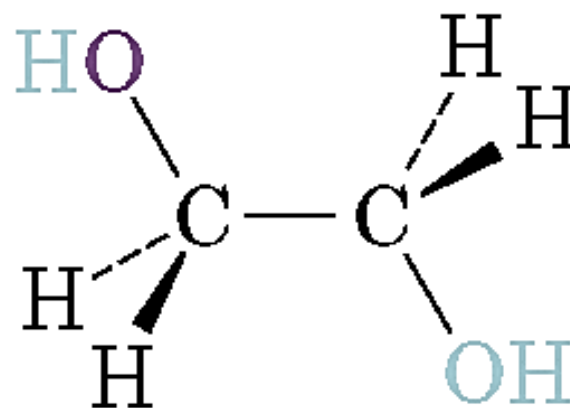
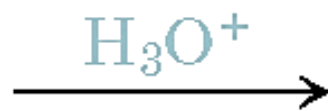
Εποξειδίο

18.6

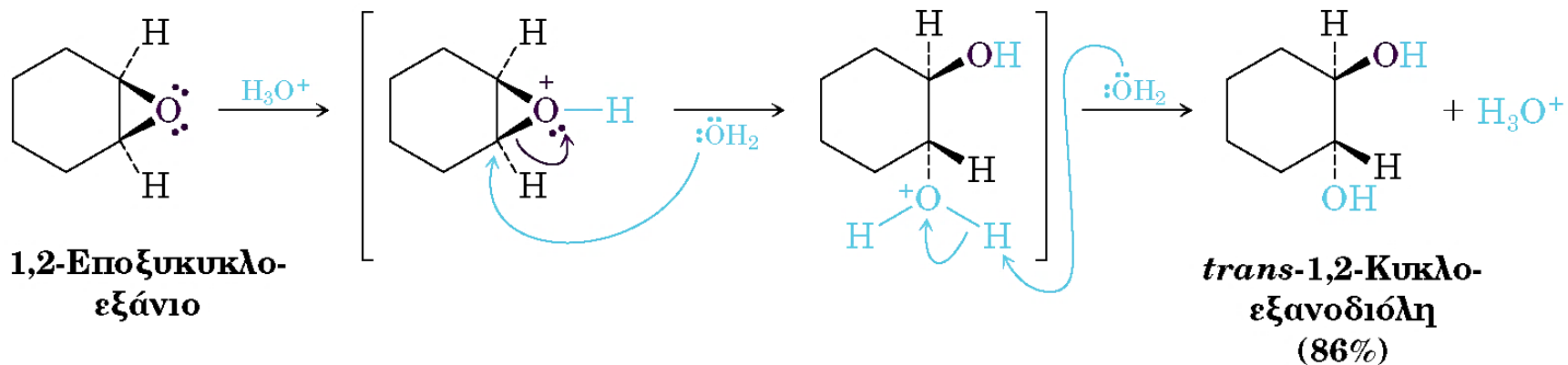
Διάνοιξη με οξέα



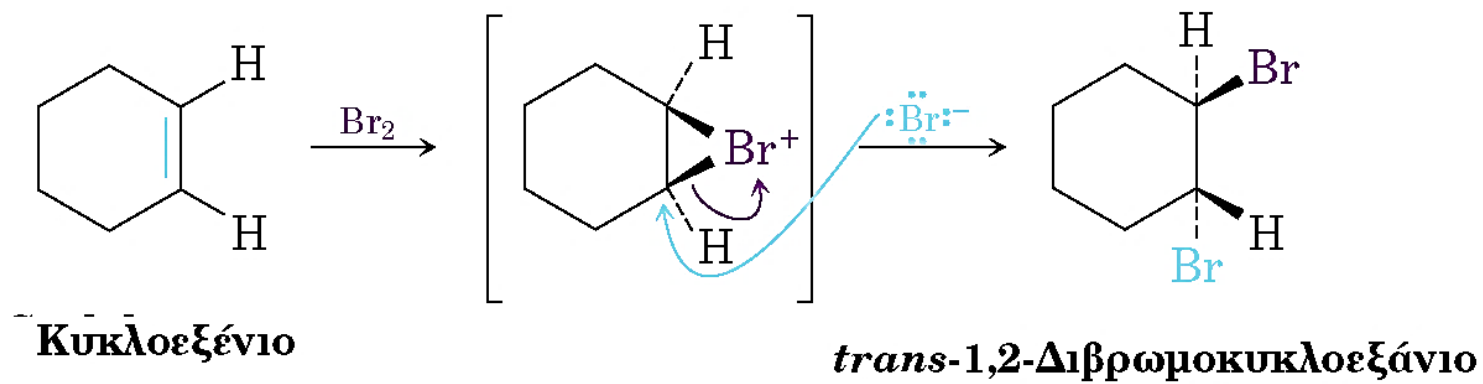
Αιθυλενοξείδιο

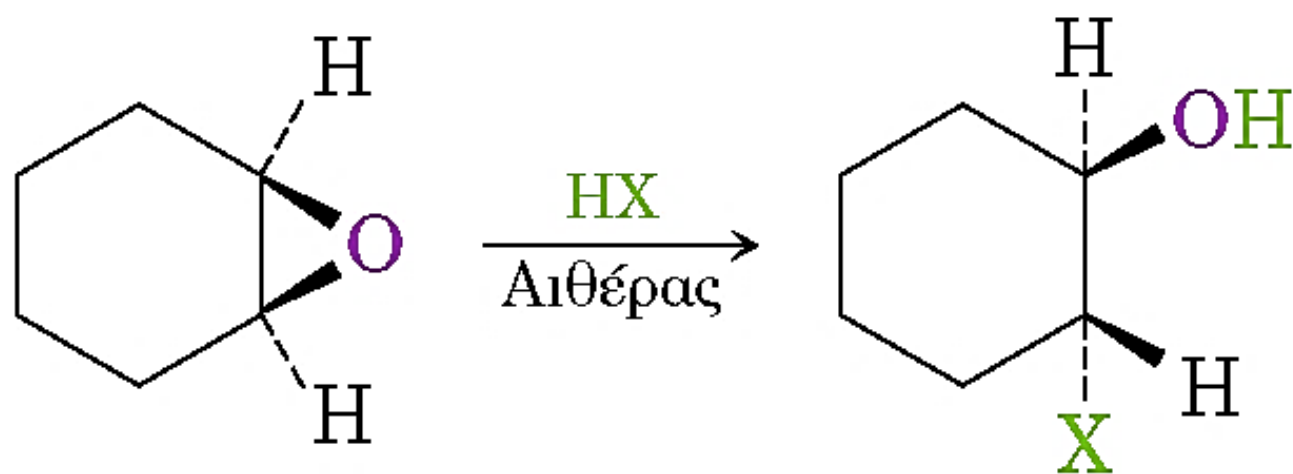


**Αιθυλενογλυκόλη
(1,2-Αιθανοδιόλη)**



Θυμηθείτε τα ακόλουθα:





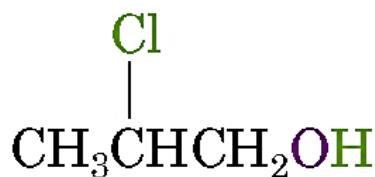
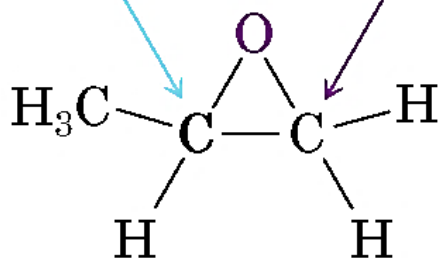
trans 2-Αλογονοκυκλοεξανόλη

όπου $X = F, Br, Cl$ ή I

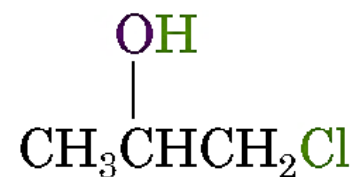
S_N2

Δευτεροταγής

Πρωτοταγής



+

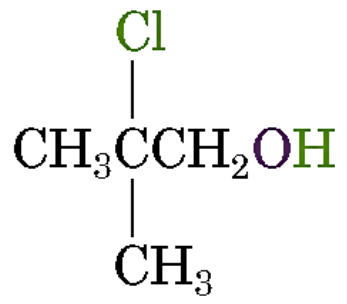
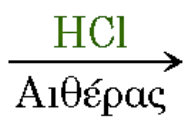
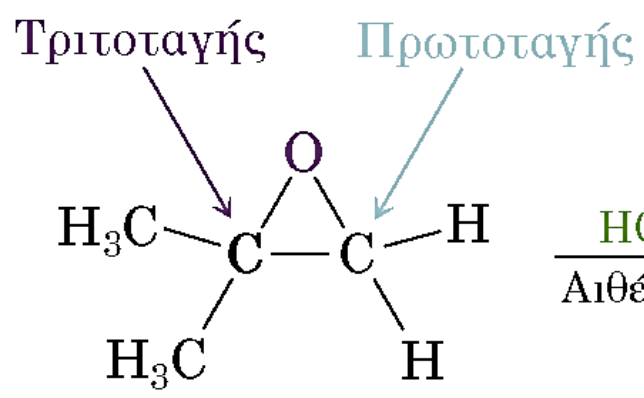


1,2-Εποξυπροπάνιο

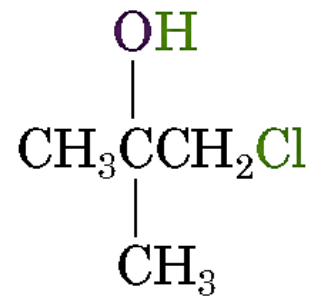
**2-Χλωρο-1-προπανόλη
(10%)**

**1-Χλωρο-2-προπανόλη
(90%)**

S_N1



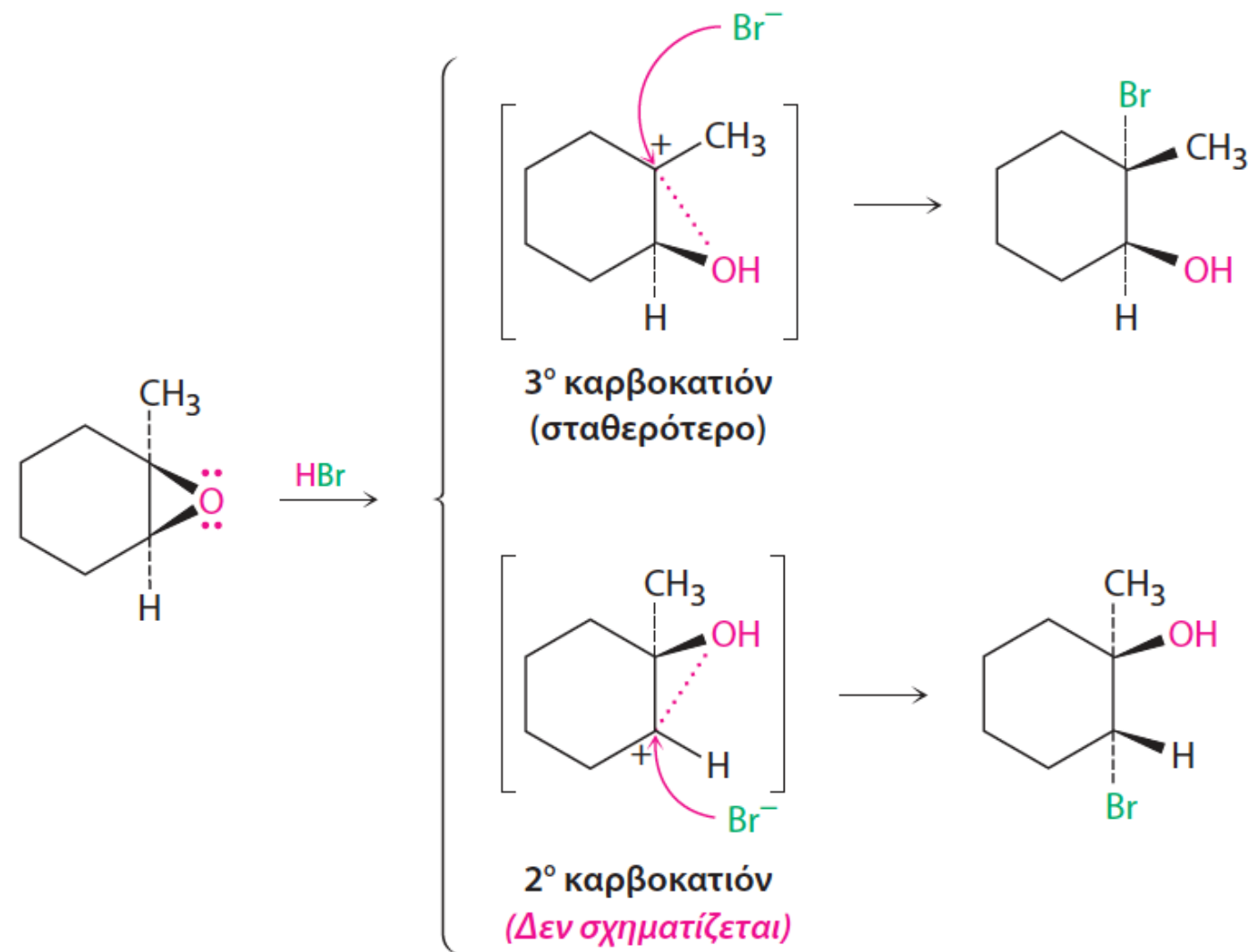
+



2-Μεθυλο-1,2-εποξυπροπάνιο

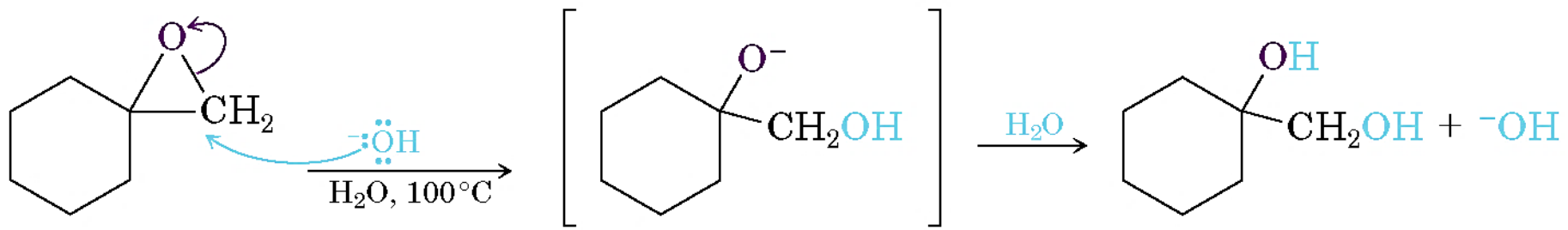
2-Μεθυλο-2-χλωρο-1-προπανόλη (60%)

2-Μεθυλο-1-χλωρο-2-προπανόλη (40%)



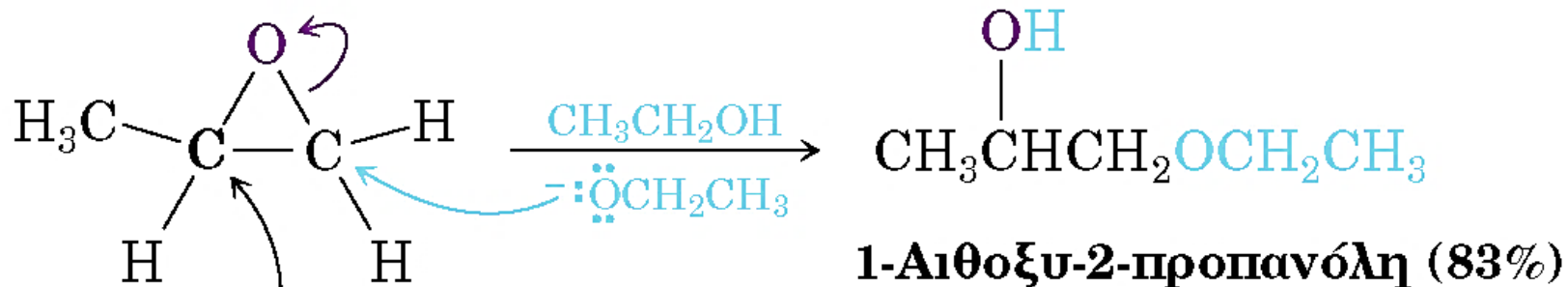
ΕΙΚΟΝΑ 18-2 Διάνοιξη δακτυλίου του 1,2-εποξυ-1-μεθυλοκυκλοεξανίου με επίδραση HBr. Στη μεταβατική κατάσταση υπάρχει μεγάλος βαθμός καρβοκατιοντικού χαρακτήρα τύπου S_N1, γεγονός που οδηγεί στην προσβολή του πυρηνόφιλου Br⁻ στο τριτοταγές άτομο άνθρακα, με αναστροφή στερεοχημείας, και στον σχηματισμό ενός ισομερούς προϊόντος που φέρει τις ομάδες —Br και —OH σε θέση trans.

Διάνοιξη με βάσεις

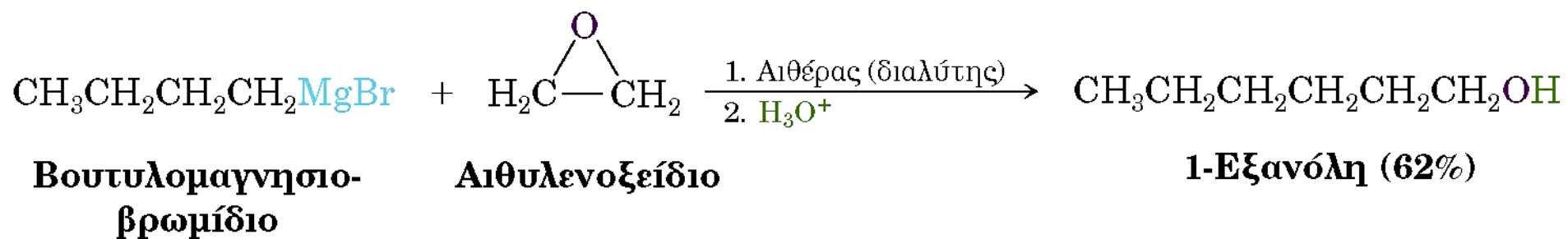


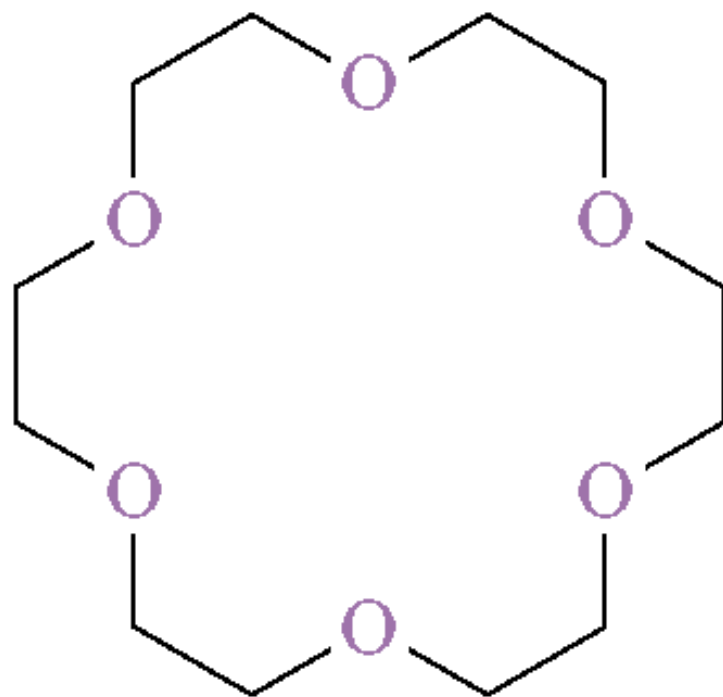
Εποξυμεθυλενοκυκλοεξάνιο

**1-Υδροξυμεθυλο-
κυκλοεξανόλη (70%)**

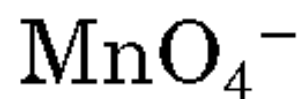
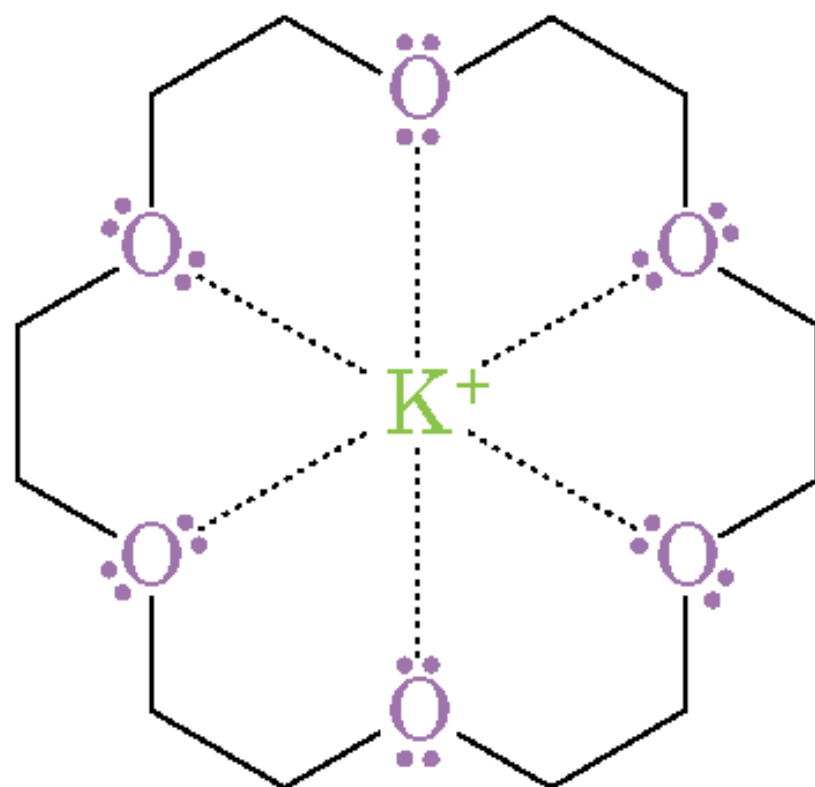


Δε λαμβάνει χώρα
 προσβολή εδώ (2°)



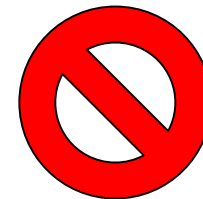


Αιθέρας 18-στέμμα-6

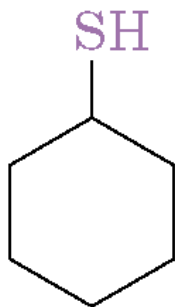


KMnO_4 επιδιαλυτωμένο από τον αιθέρα 18-στέμμα-6
(το σύμπλοκο είναι διαλυτό στο βενζόλιο)

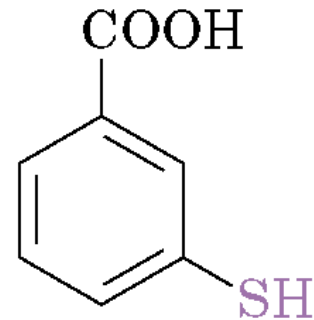
18.8



Αιθανοθειόλη



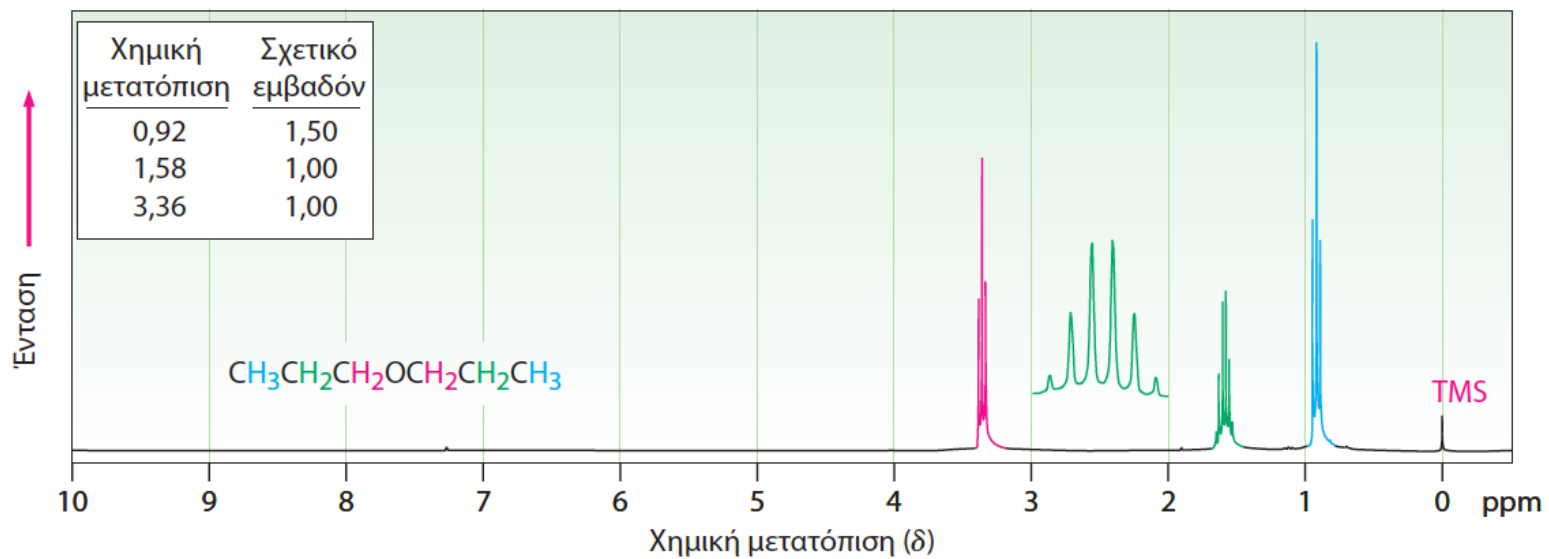
Κυκλοεξανοθειόλη



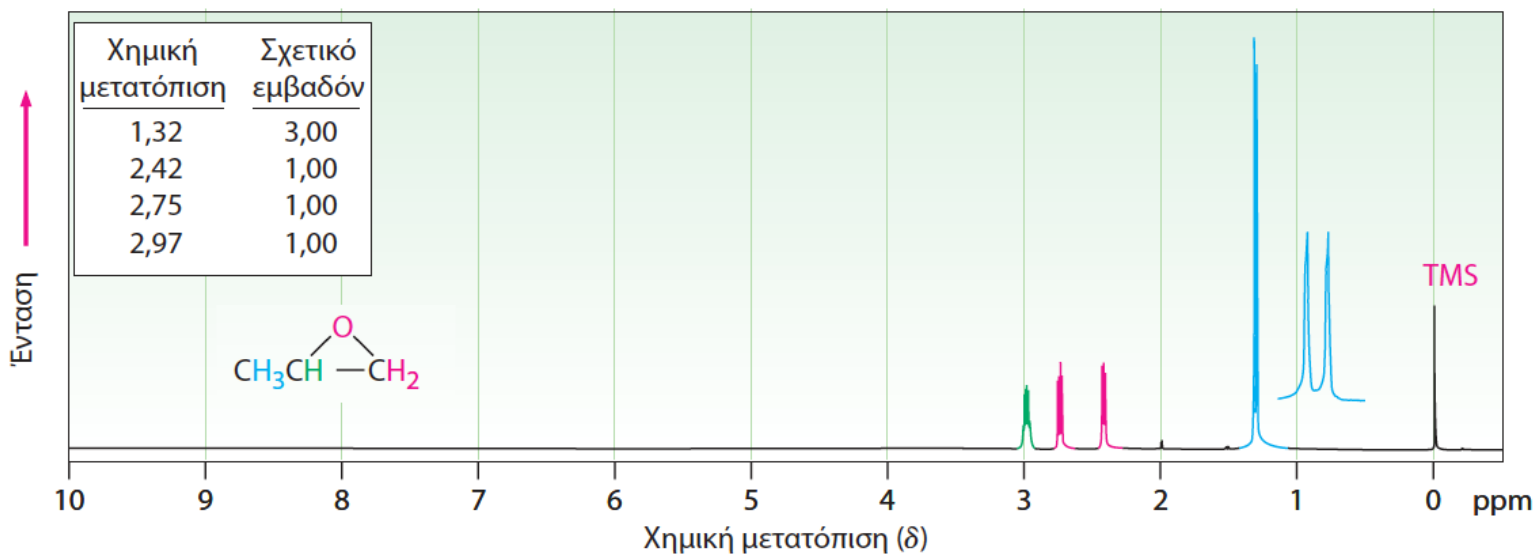
m-Μερκαπτοβενζοϊκό οξύ



ΕΙΚΟΝΑ 18-5 Το φάσμα ^1H NMR του διπροπυλο αιθέρα. Τα πρωτόνια που ανήκουν στο άτομο άνθρακα δίπλα στο αιθερικό οξυγόνο απορροφούν σε χαμηλότερα πεδία, στα 3,4 δ .

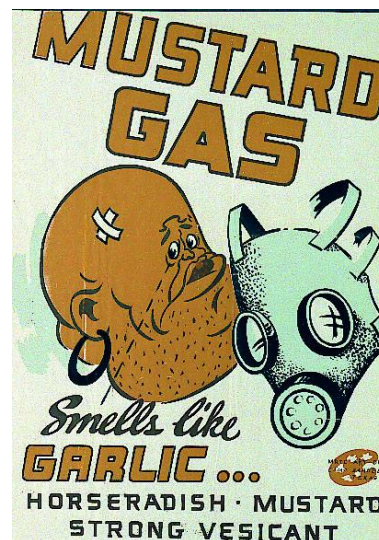
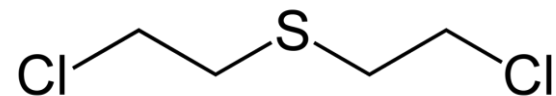


ΕΙΚΟΝΑ 18-6 Το φάσμα ^1H NMR του 1,2-εποξυπροπανίου.



● Αέριο της μουστάρδας $\{(\text{CH}_3\text{CH}_2)_2\text{S}\}$

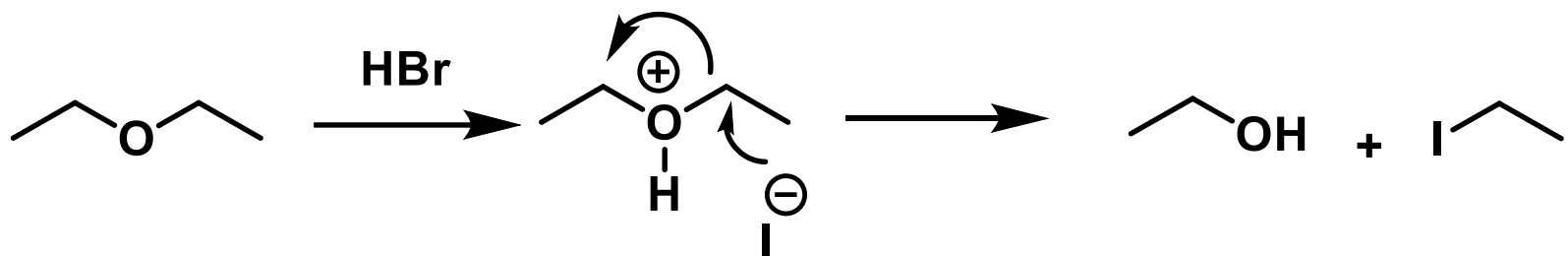
- Ονομάζεται και Υπερίτης
- Άχρωμο, οσμή μουστάρδας-σκόρδου
- Τύφλωση, φλεγμονές στο δέρμα



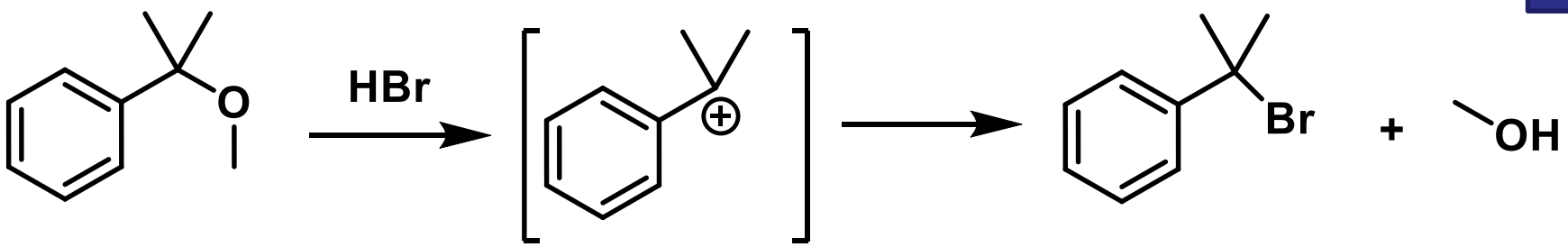
ΚΕΦ.18. ΑΙΘΕΡΕΣ ΚΑΙ ΕΠΟΞΕΙΔΙΑ, ΘΕΙΟΛΕΣ ΚΑΙ ΣΟΥΛΦΙΔΙΑ

επανάληψη

Όξινη υδρόλυση αιθέρων



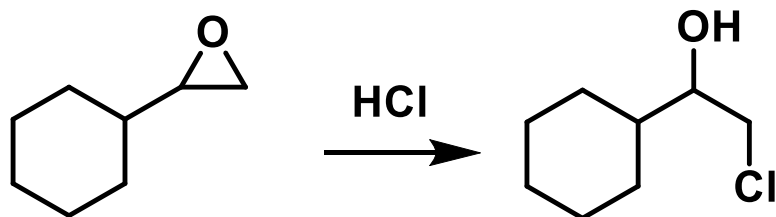
S_N2



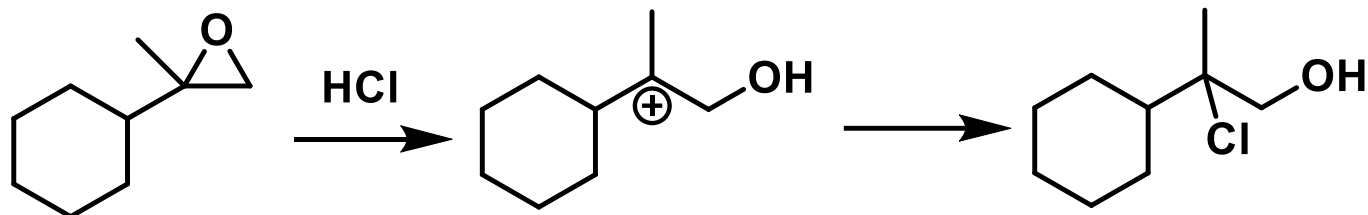
S_N1

E1

Όξινη διάνοιξη εποξειδίων

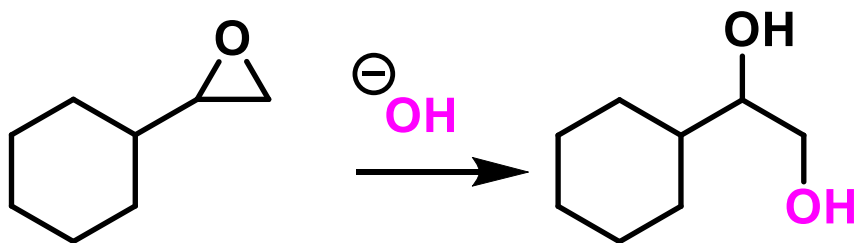


S_N2



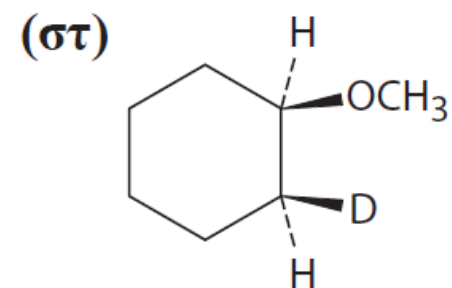
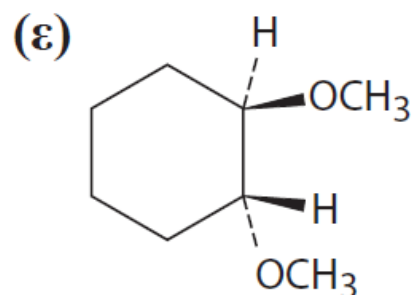
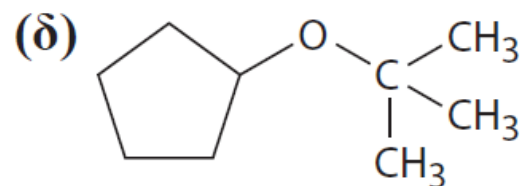
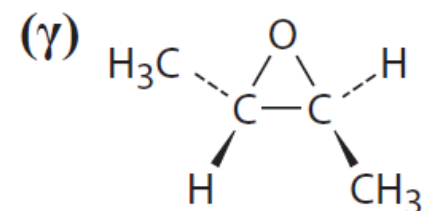
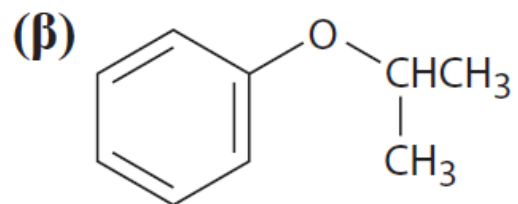
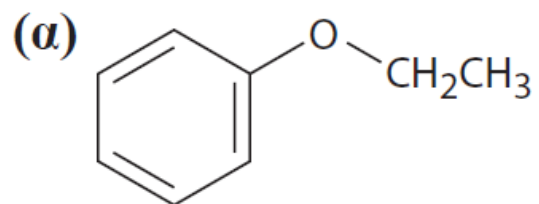
S_N1

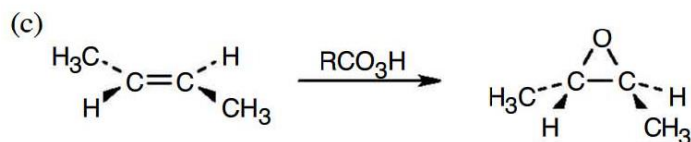
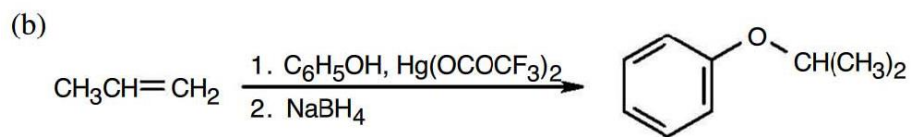
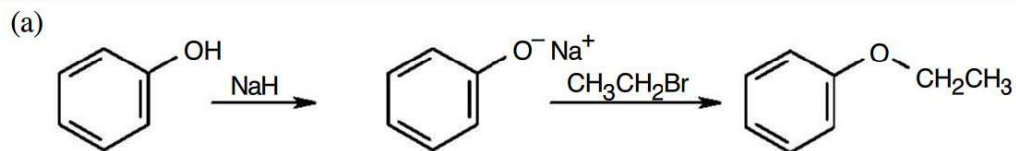
Βασική διάνοιξη εποξειδίων



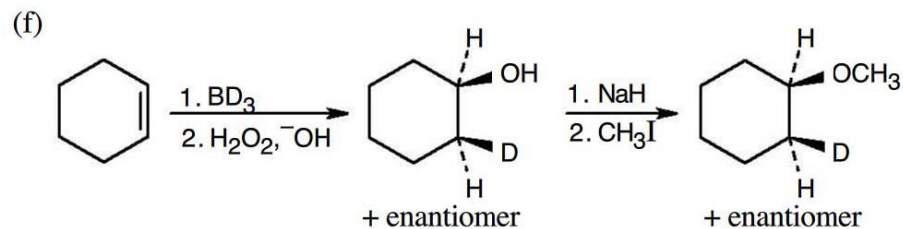
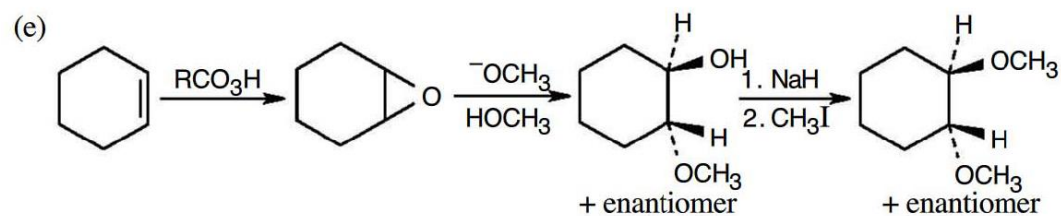
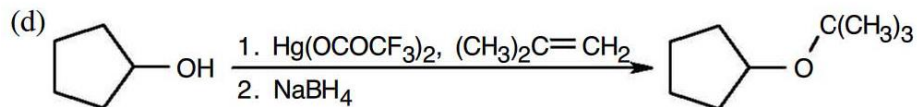
S_N2

18-40* Πώς θα παρασκευάσετε τους παρακάτω αιθέρες





[RCO_3H = *meta*-Chloroperoxybenzoic acid]

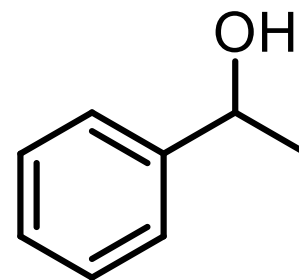


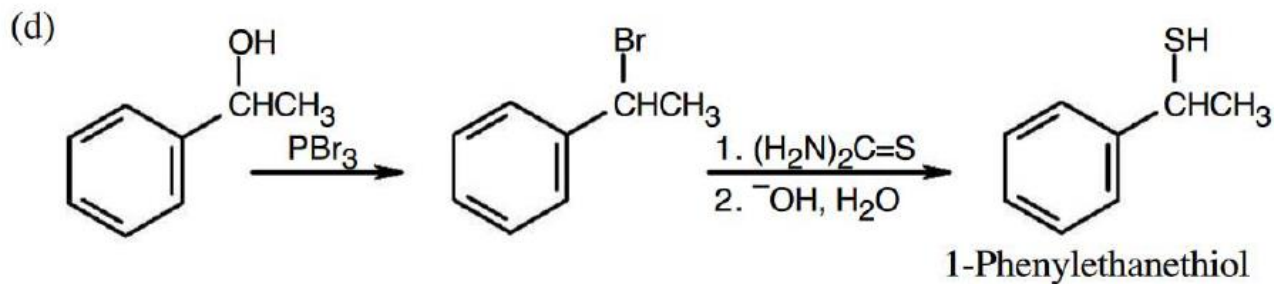
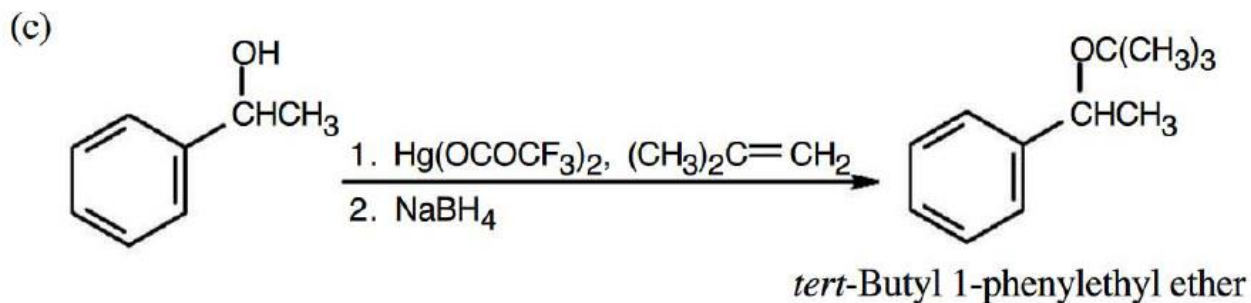
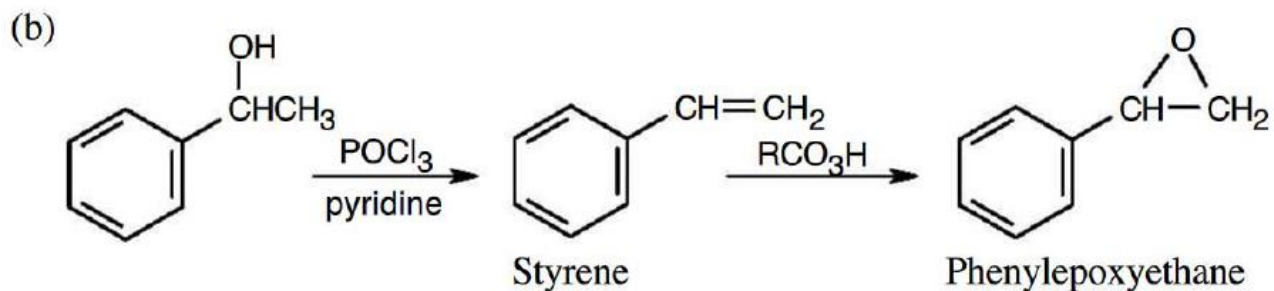
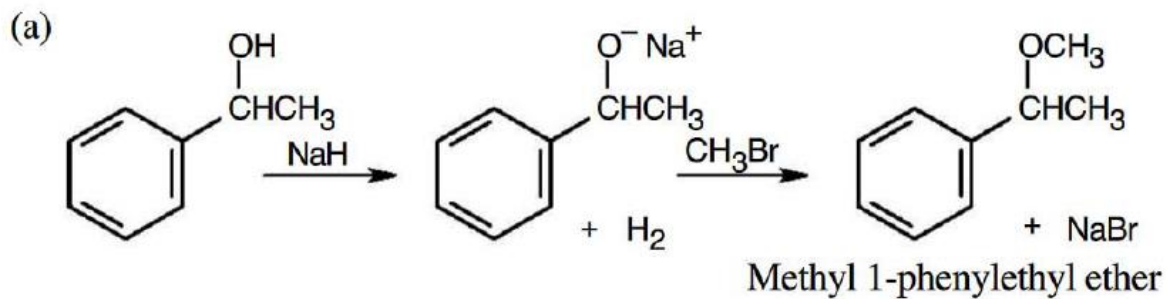
18-41* Πώς θα παρασκευάσετε τις ακόλουθες ενώσεις από 1-φαινυλοαιθανόλη

(α) Μεθυλο 1-φαινυλοαιθυλο αιθέρας

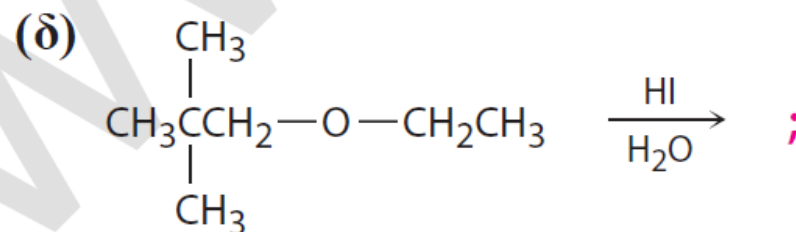
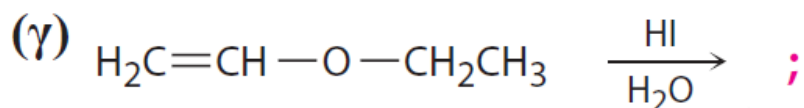
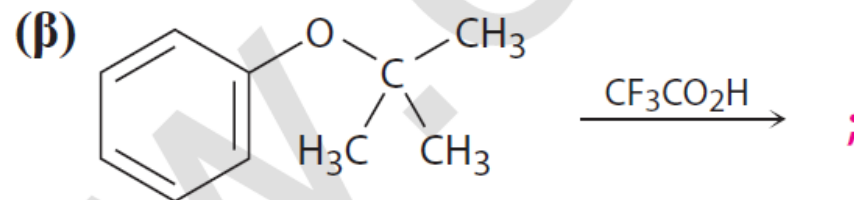
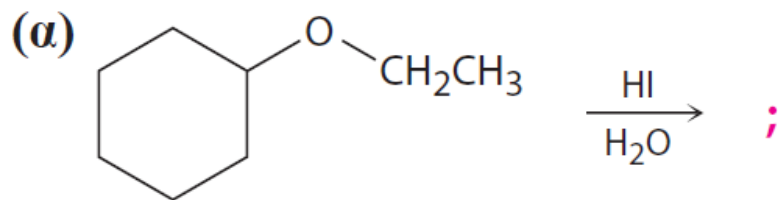
(β) Φαινυλοεποξυαιθάνιο

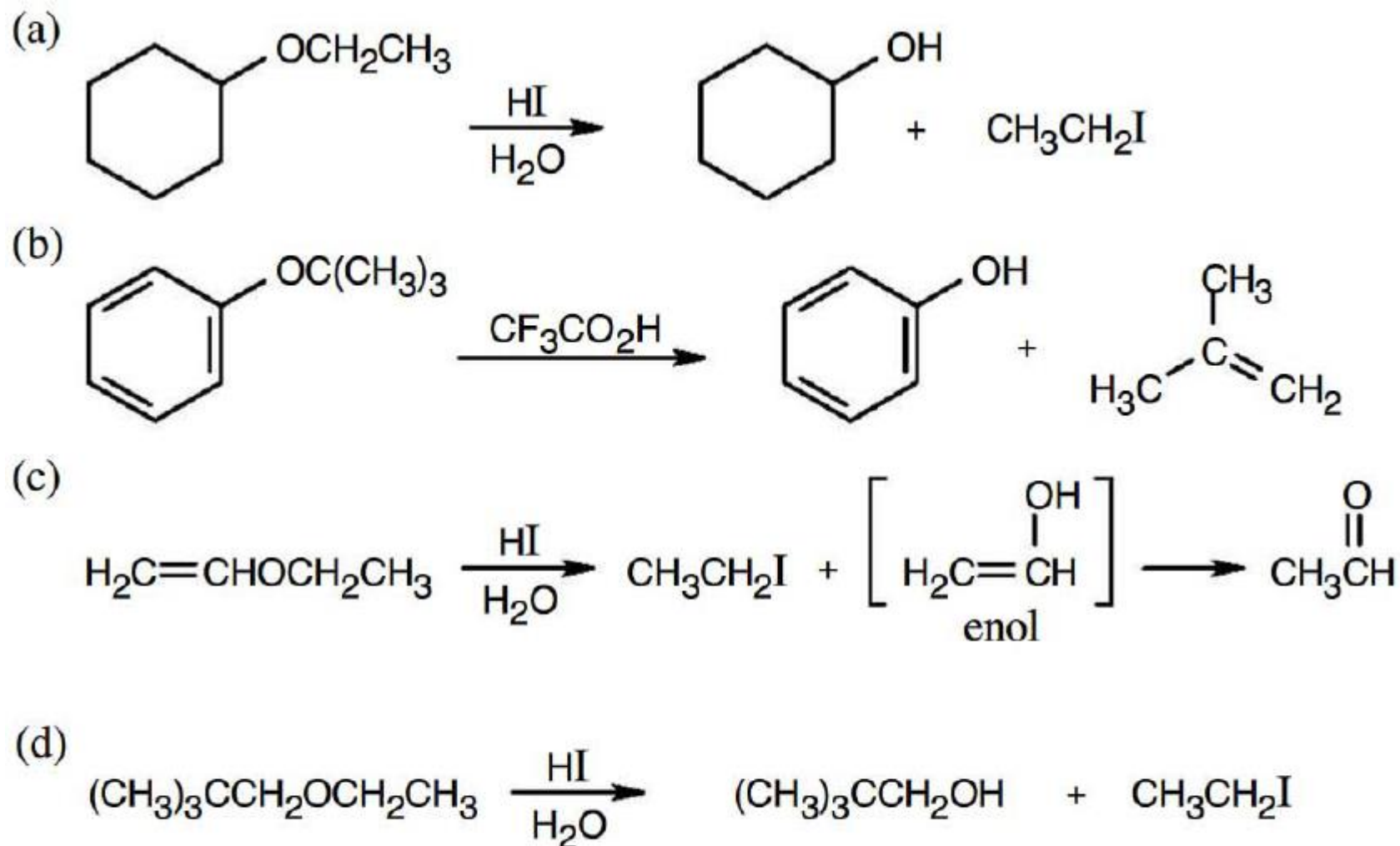
(γ) *tert*-Βουτυλο 1-φαινυλοαιθυλο αιθέρας



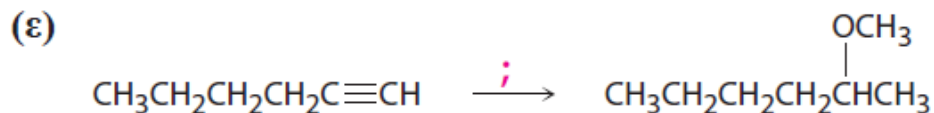
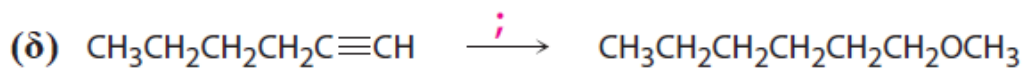
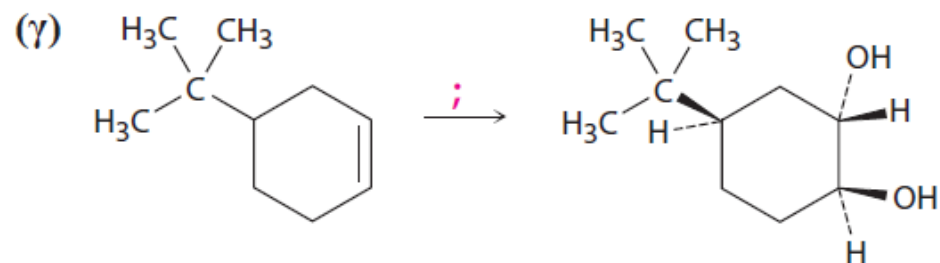
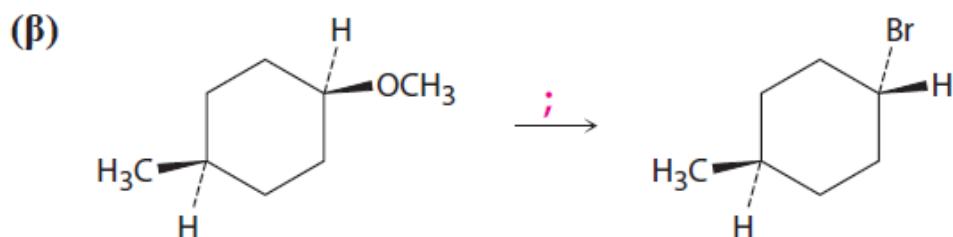
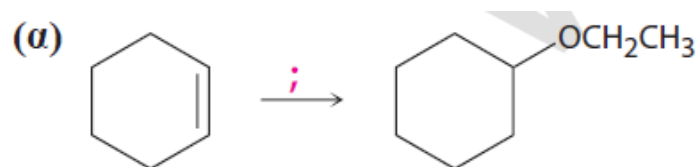


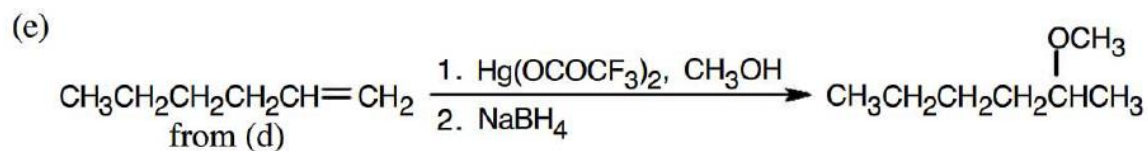
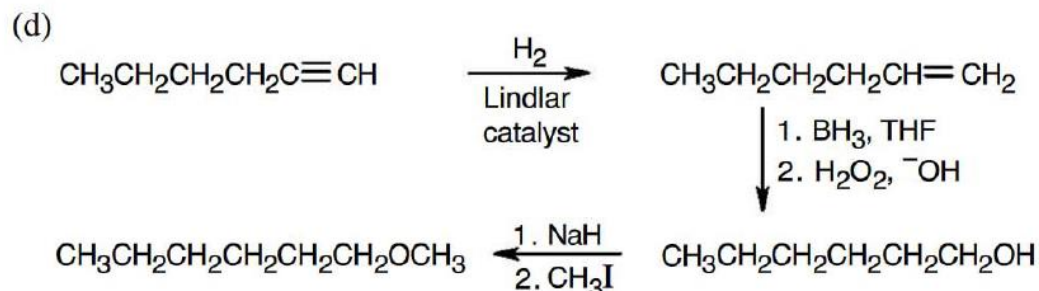
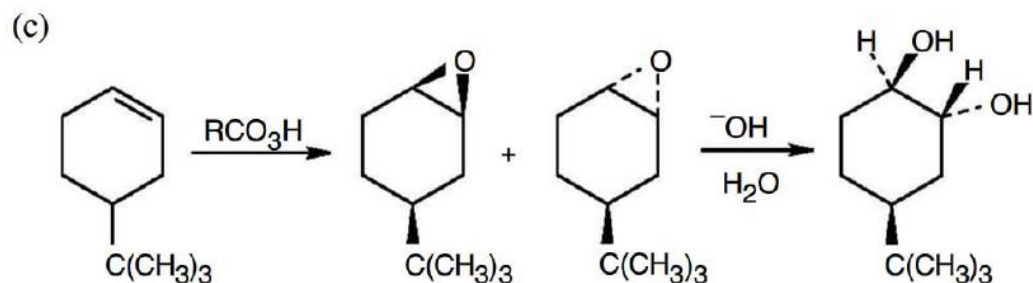
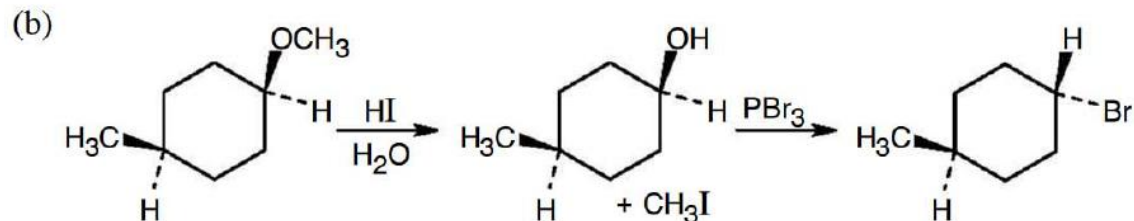
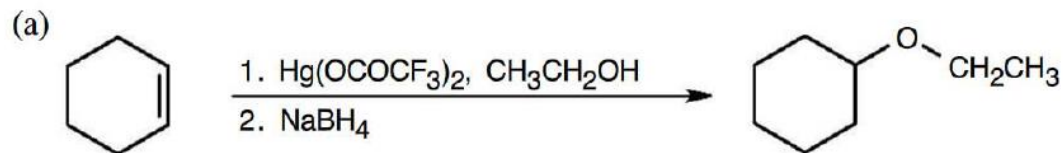
18-44* Προβλέψτε τα προϊόντα των παρακάτω αντιδράσεων διάσπασης αιθέρων:



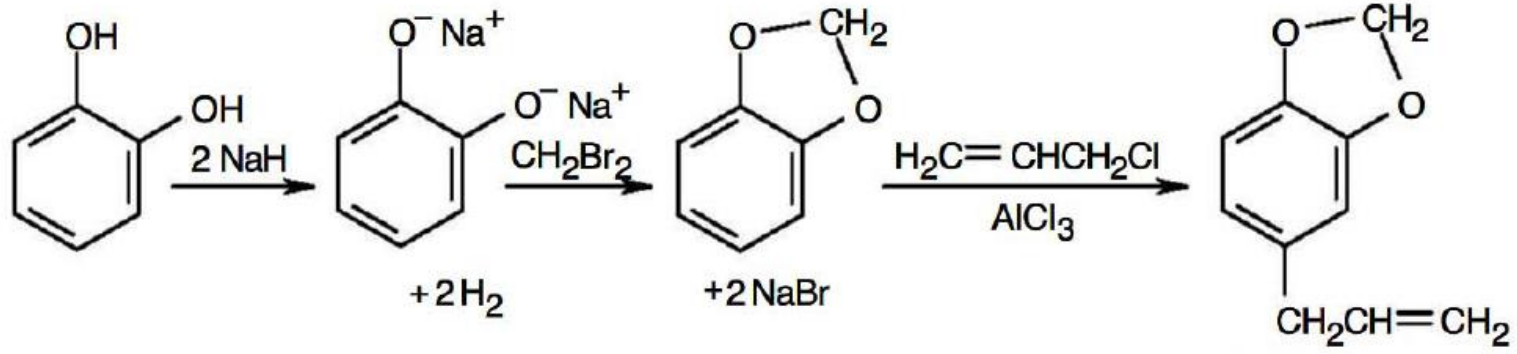
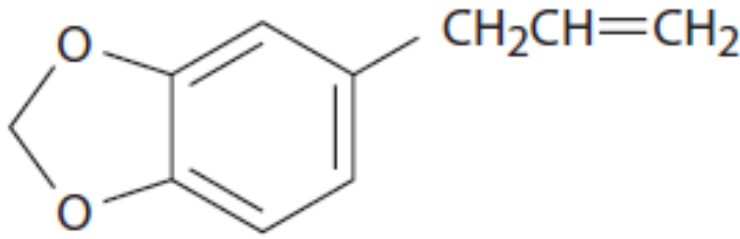


18-45* Πώς θα πραγματοποιήσετε τους παρακάτω μετασχηματισμούς; Μπορεί να απαιτηθούν περισσότερα από ένα στάδια.

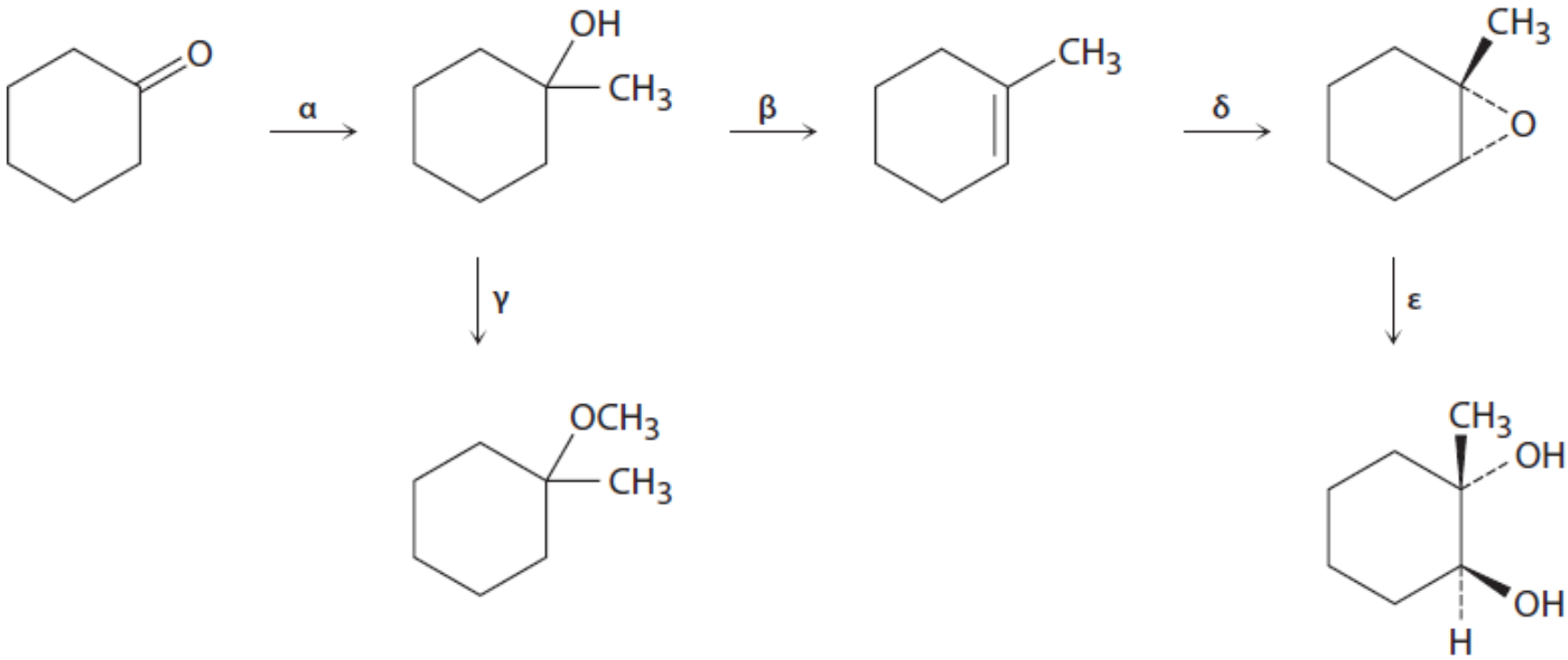




18-60* Η σαφρόλη, μια ένωση που απομονώνεται από το αιθέριο έλαιο του φυτού σασσαφρά, χρησιμοποιείται στην αρωματοποίηση. Προτείνετε μια σύνθεση της σαφρόλης από την κατεχόλη (1,2-βενζολοδιόλη).



18-66 Προσδιορίστε τα αντιδραστήρια (α) έως (ε) στο ακόλουθο συνθετικό σχήμα:



<https://forms.gle/3epYRc5wzX1YUDJ99>

Ερωτήσεις κατανόησης
ανασκόπηση σε κεφάλαια 13, 15-18