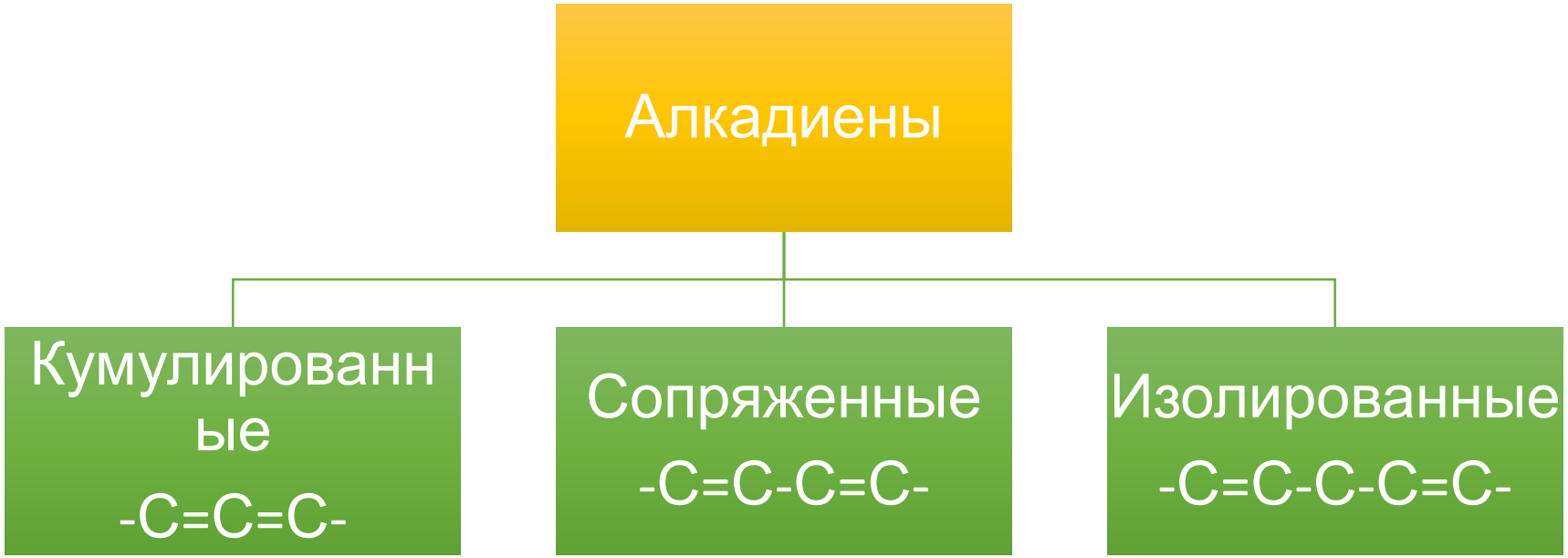
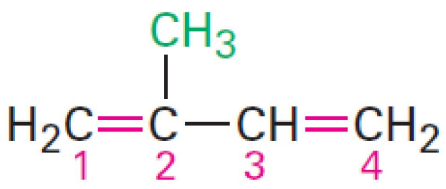
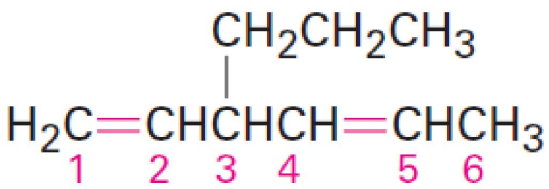
АЛКАДИЕНЫ


Алкадиены
Кумулированн
ые
-C=C=C-
Сопряженные
-C=C-C=C-
Изолированные
-C=C-C-C=C-

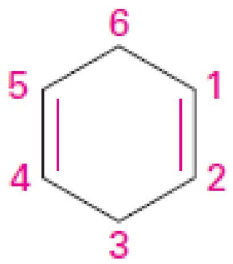


2-Methyl-1,3-butadiene



3-Propyl-1,4-hexadiene

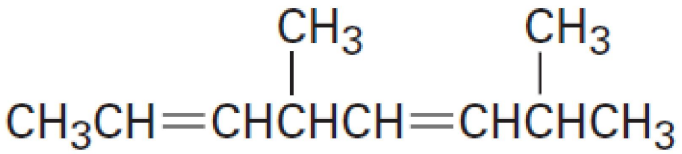
3-Propylhexa-1,4-diene)

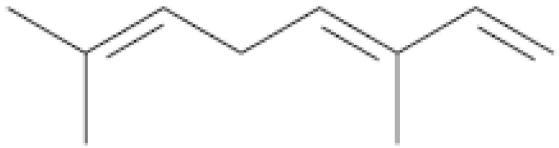


1,4-Cyclohexadiene

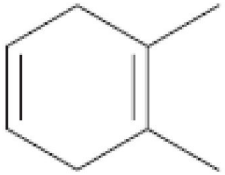
(New: Cyclohexa-1,4-diene)

(c)

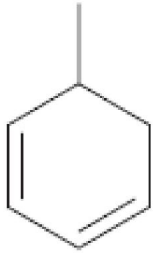




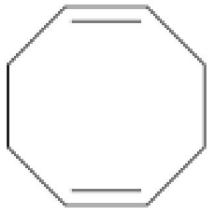
(d)

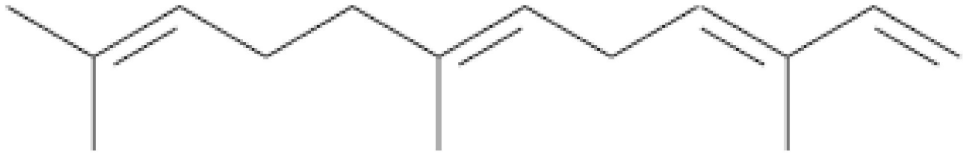


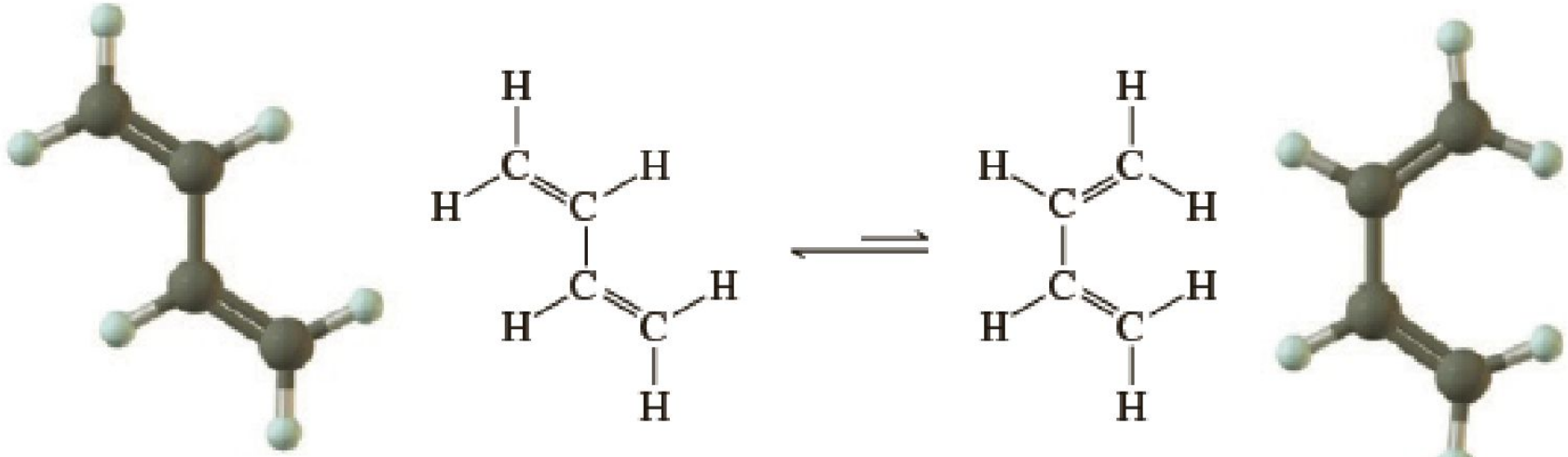
(e)



(f)

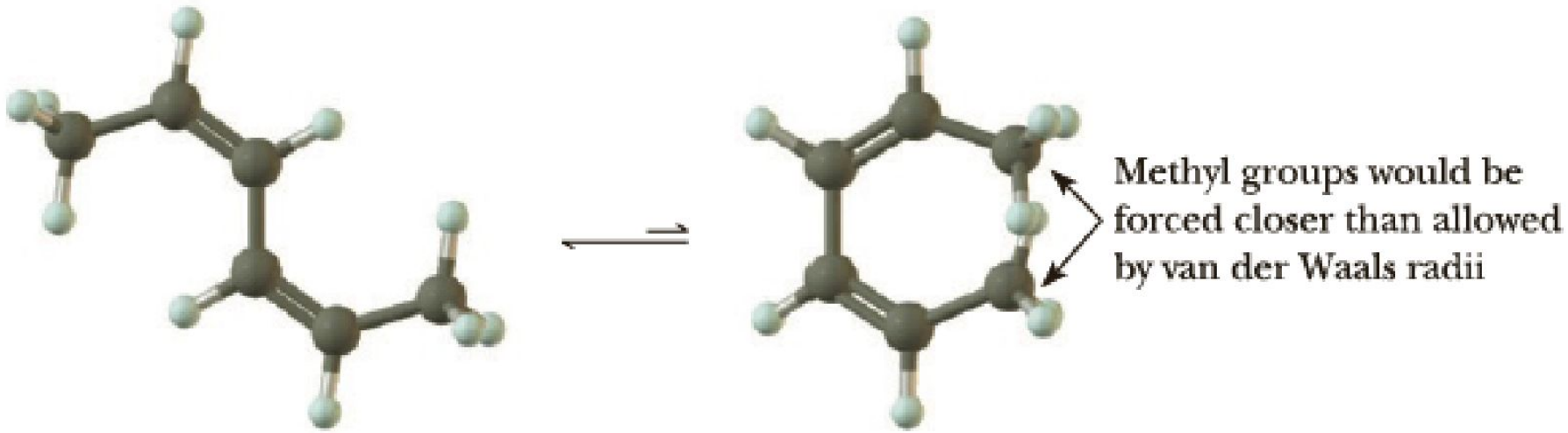






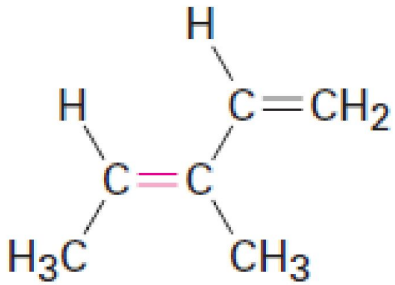
s-trans conformation
(Lower in energy)

s-cis conformation
(Higher in energy)

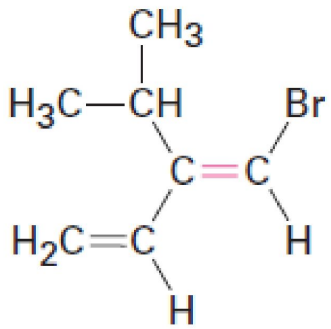


s-trans conformation
(Lower in energy)

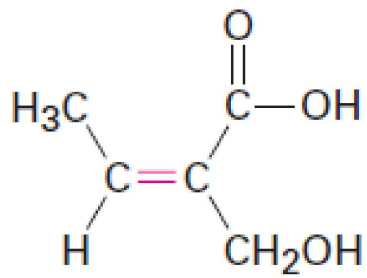
s-cis conformation
(Higher in energy)



(*E*)-3-Methyl-1,3-pentadiene

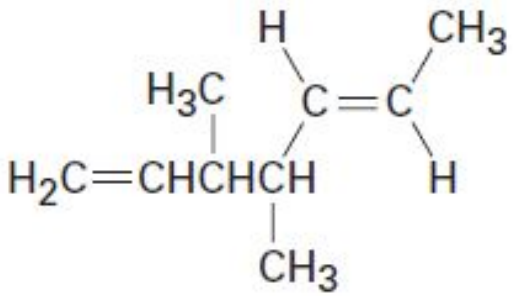


(*E*)-1-Bromo-2-isopropyl-1,3-butadiene

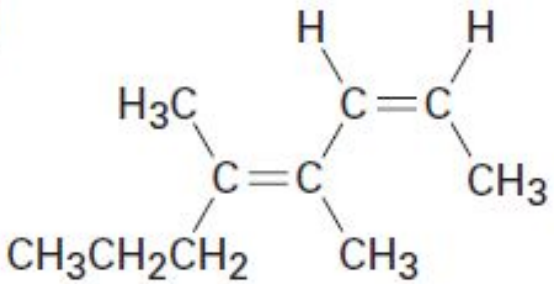


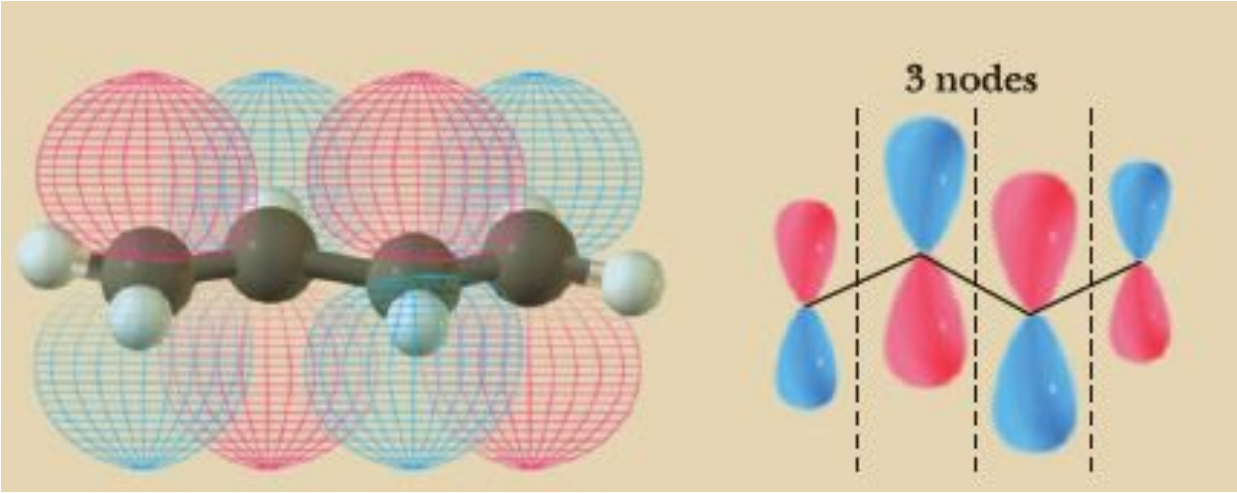
(*Z*)-2-Hydroxymethyl-2-butenoic acid

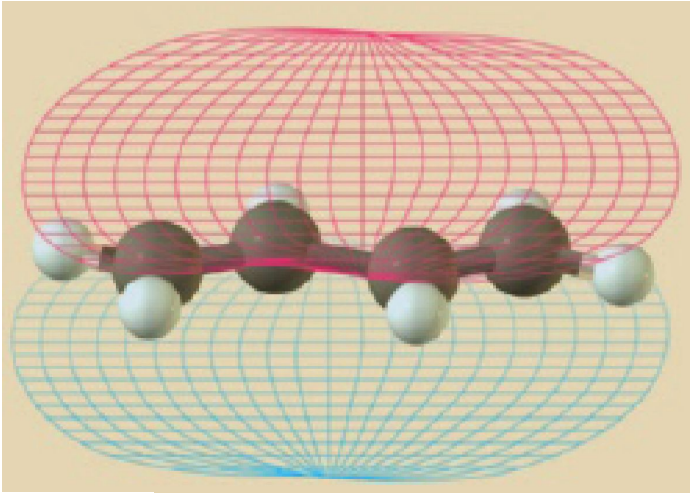
(d)



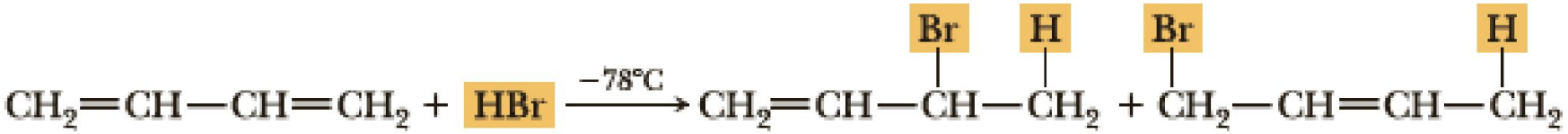
(e)







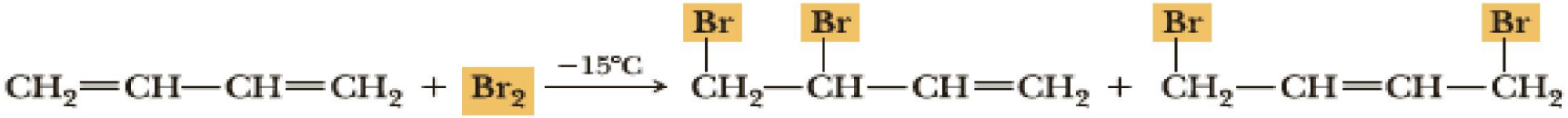
1,2-Addition and 1,4-Addition



1,3-Butadiene

3-Bromo-1-butene (90%) (1,2-addition)

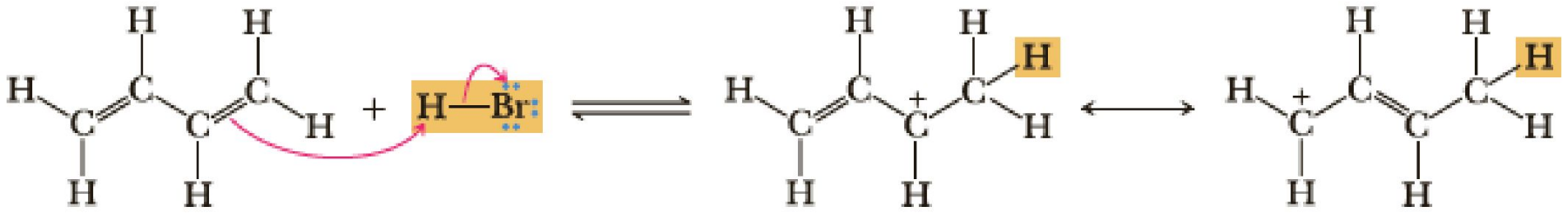
1-Bromo-2-butene (10%) (1,4-addition)



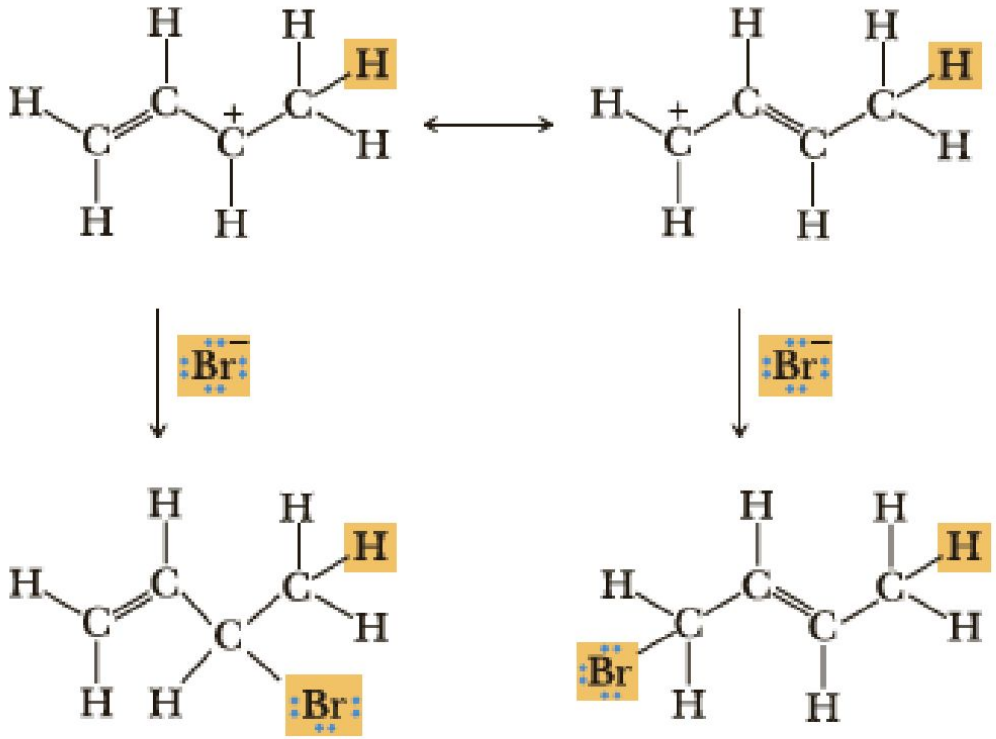
1,3-Butadiene

3,4-Dibromo-1-butene (54%, racemic) (1,2-addition)

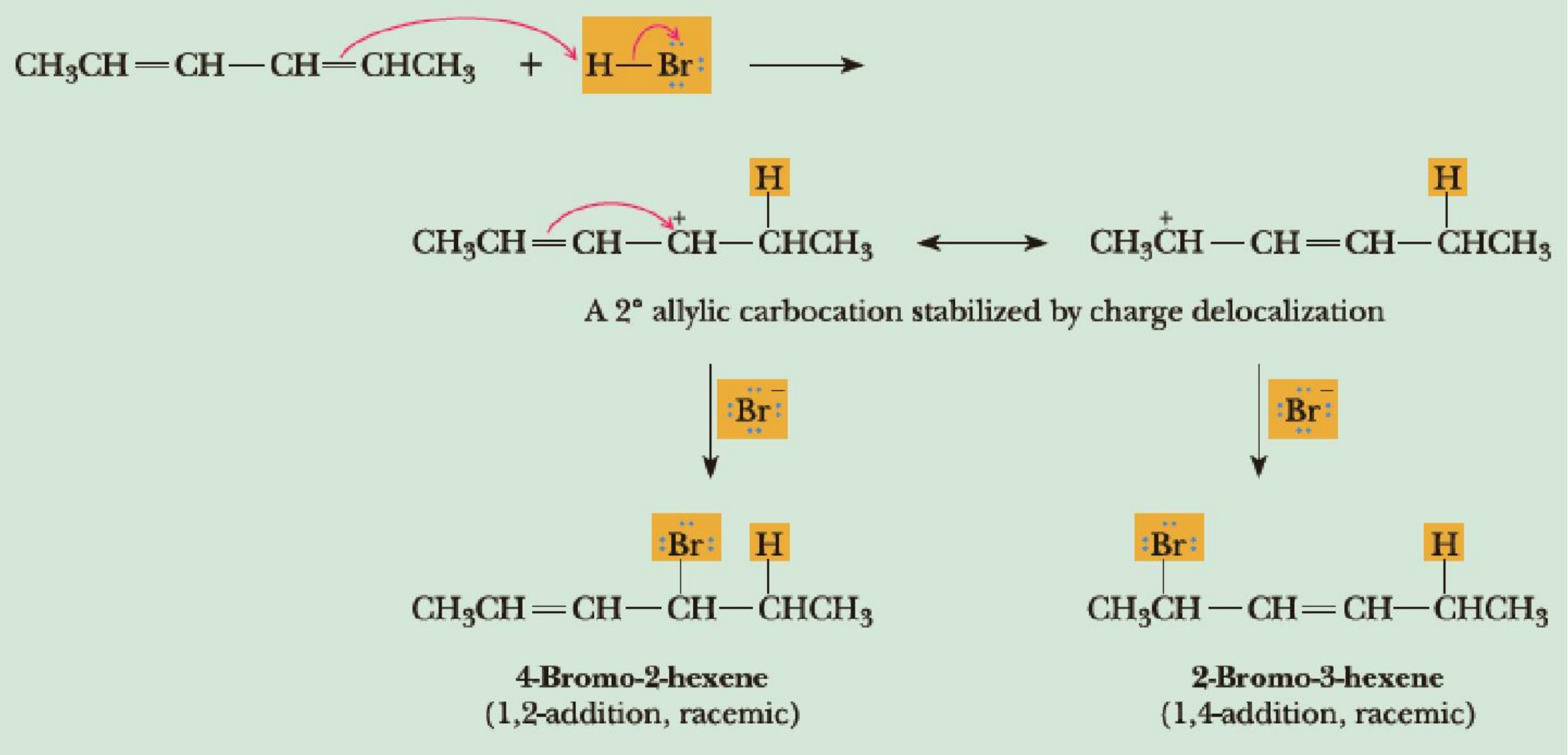
1,4-Dibromo-2-butene (46%) (1,4-addition)

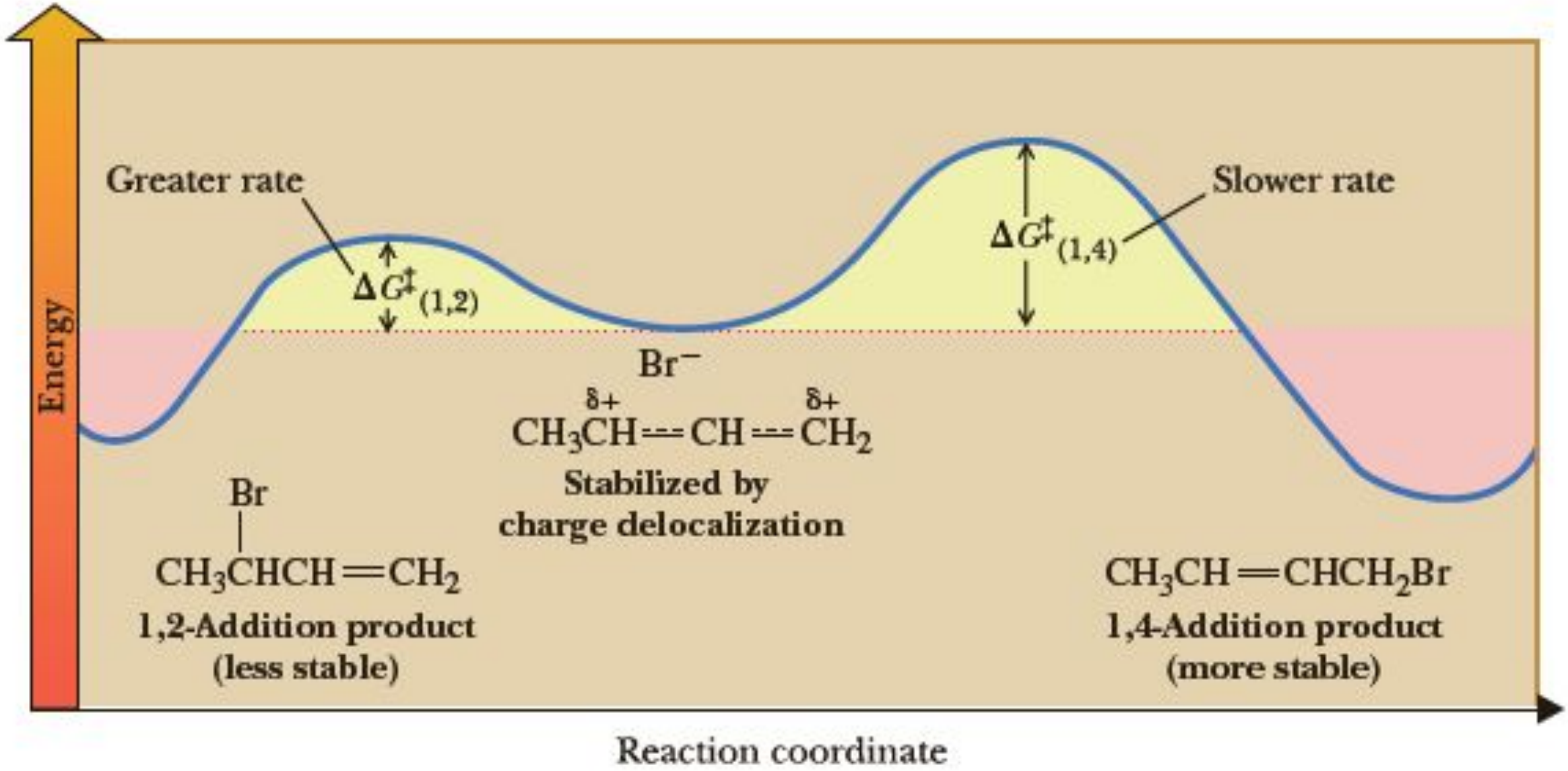


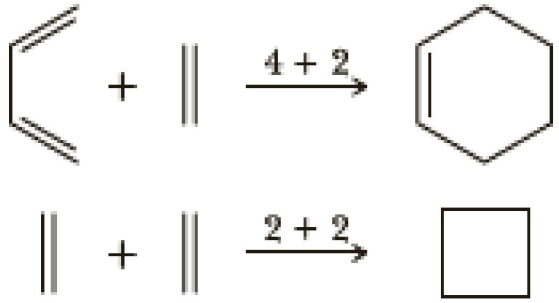
Allylic carbocation stabilized by resonance

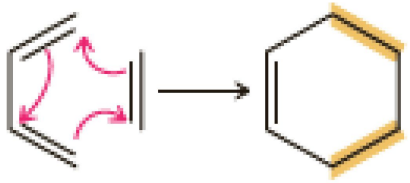


(1,2-addition, racemic) (1,4-addition)

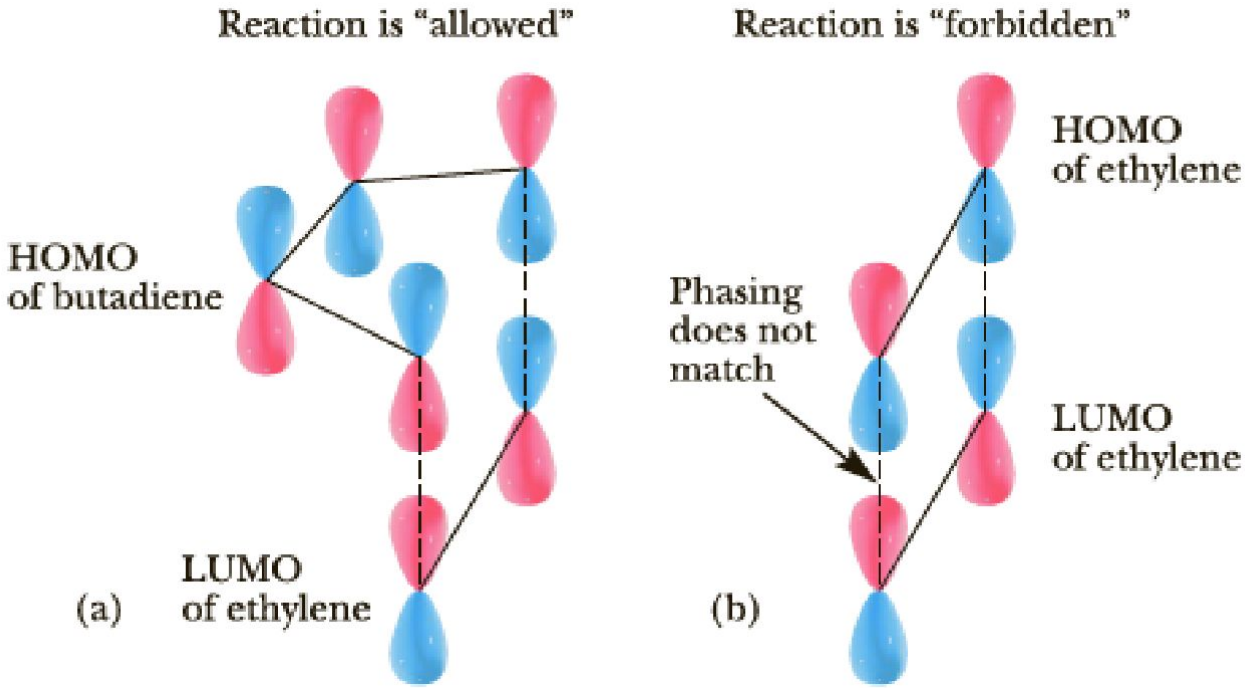

CH3CH=CH—CH=CHCH3 + H—Br
H
CH3CH=CH—CH—CHCH3
CH3CH—CH=CH—CHCH3
A 2° allylic carbocation stabilized by charge delocalization
Br
Br
H
CH3CH=CH—CH—CHCH3
4-Bromo-2-hexene
(1,2-addition, racemic)
Br
H
CH3CH—CH=CH—CHCH3
2-Bromo-3-hexene
(1,4-addition, racemic)

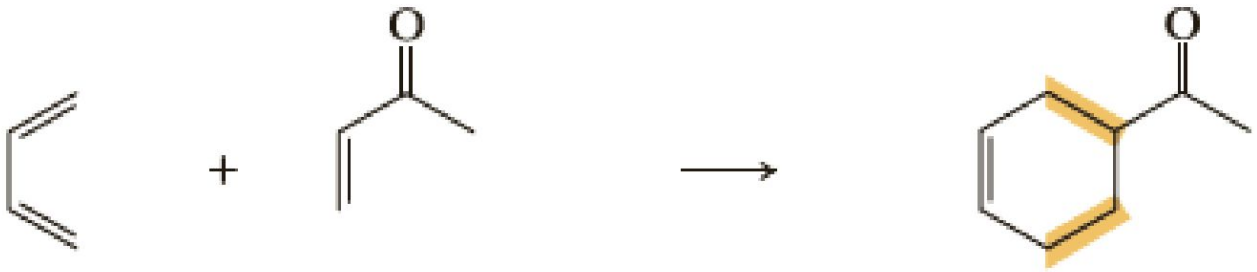

Greater rate
Slower rate
$\Delta G^{\ddagger}_{(1,2)}$
$\Delta G^{\ddagger}_{(1,4)}$
Energy
Br^-
$CH_3\overset{\delta+}{C}H{-}{-}CH{-}{-}\overset{\delta+}{C}H_2$
Stabilized by
charge delocalization
Br
$CH_3CHCH{=}CH_2$
1,2-Addition product
(less stable)
$CH_3CH{=}CHCH_2Br$
1,4-Addition product
(more stable)
Reaction coordinate





Diels-Alder reaction

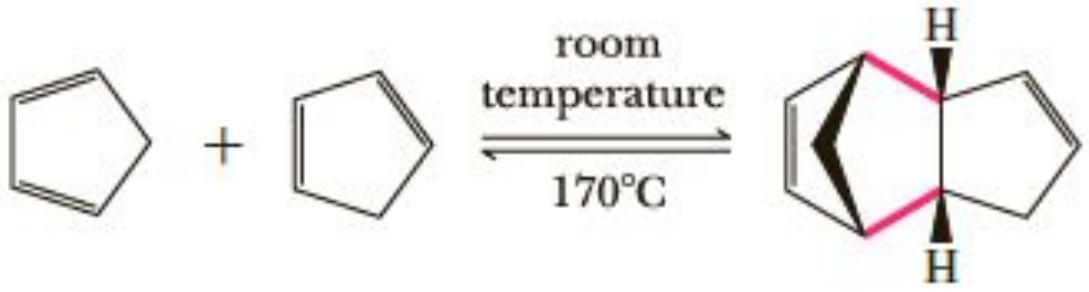


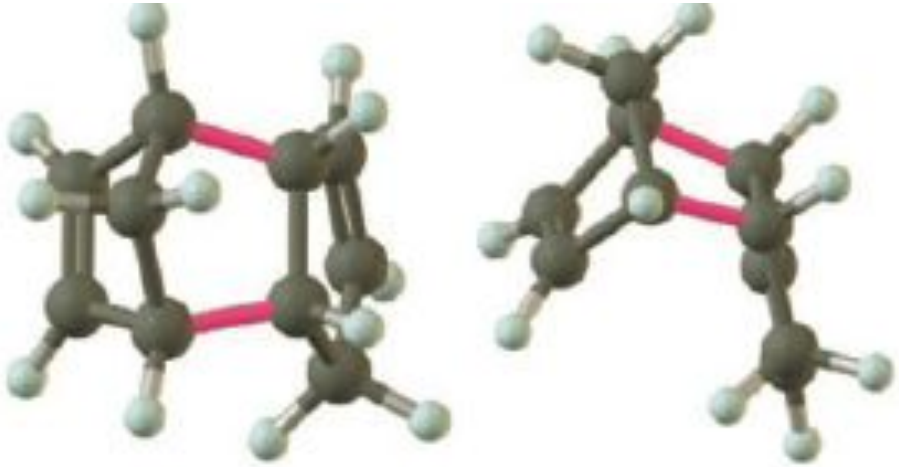


1,3-Butadiene
(a diene)

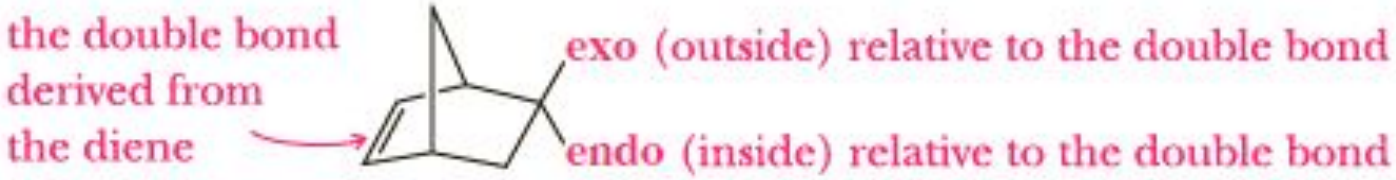
3-Buten-2-one
(a dienophile)

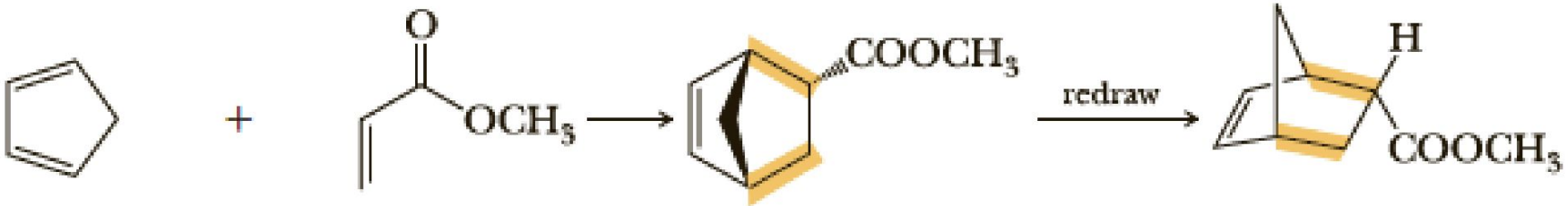
3-Cyclohexenyl methyl ketone
(a Diels-Alder adduct)
(racemic mixture)



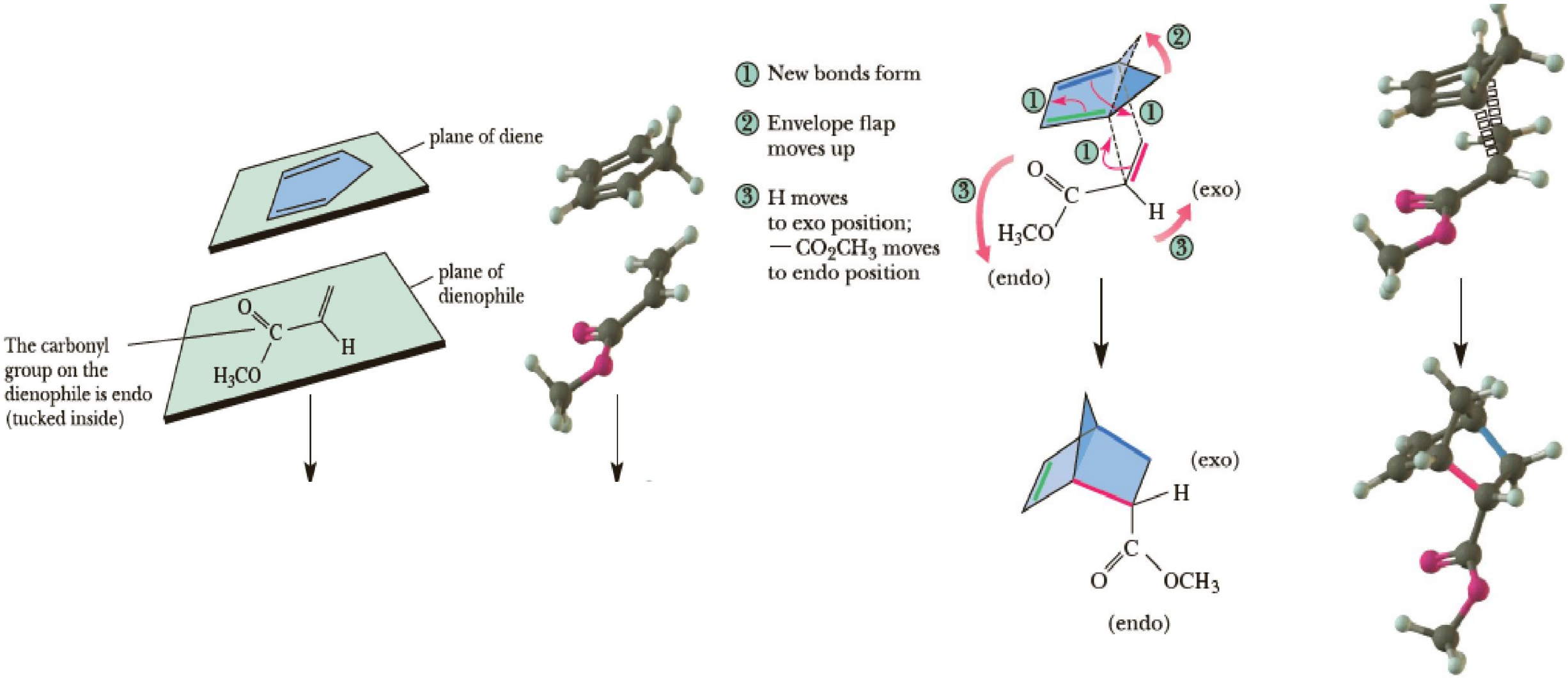


Diene Dienophile Dicyclopentadiene (endo form) From top From side





Cyclopentadiene Methyl propenoate The endo adduct(racemic)

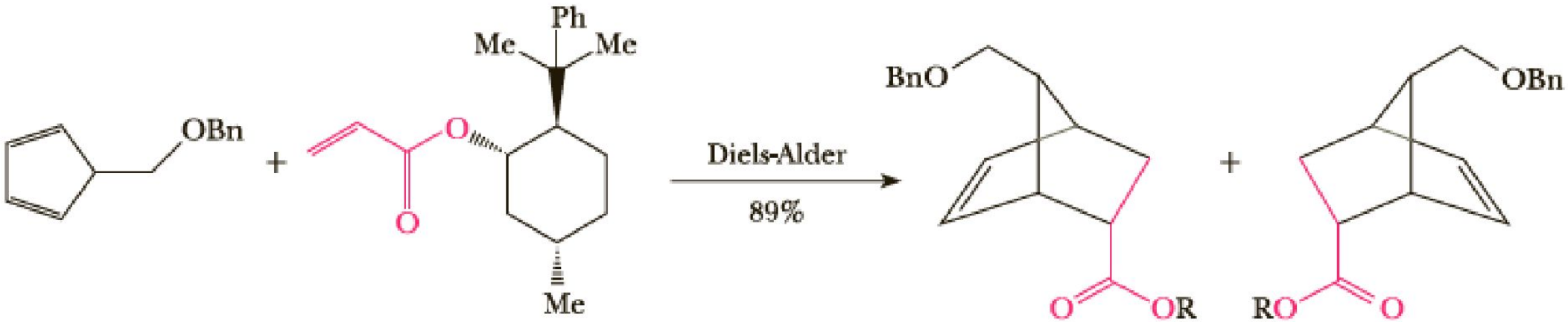

plane of diene
plane of dienophile
The carbonyl group on the dienophile is endo (tucked inside)
O
C
H
H_3CO
① New bonds form
② Envelope flap moves up
③ H moves to exo position; — CO_2CH_3 moves to endo position
(exo)
(endo)
OCH_3

Dimethyl *cis*-2-butenedioate
(a *cis* dienophile)

Dimethyl *cis*-4-cyclohexene-1,2-dicarboxylate

Dimethyl *trans*-2-butenedioate
(a *trans* dienophile)

Dimethyl *trans*-4-cyclohexene-1,2-dicarboxylate (racemic)

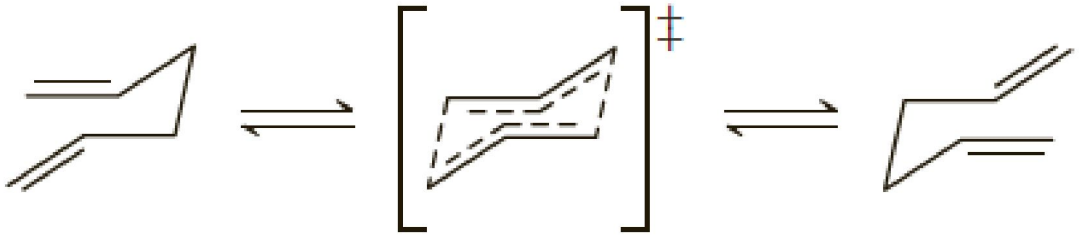


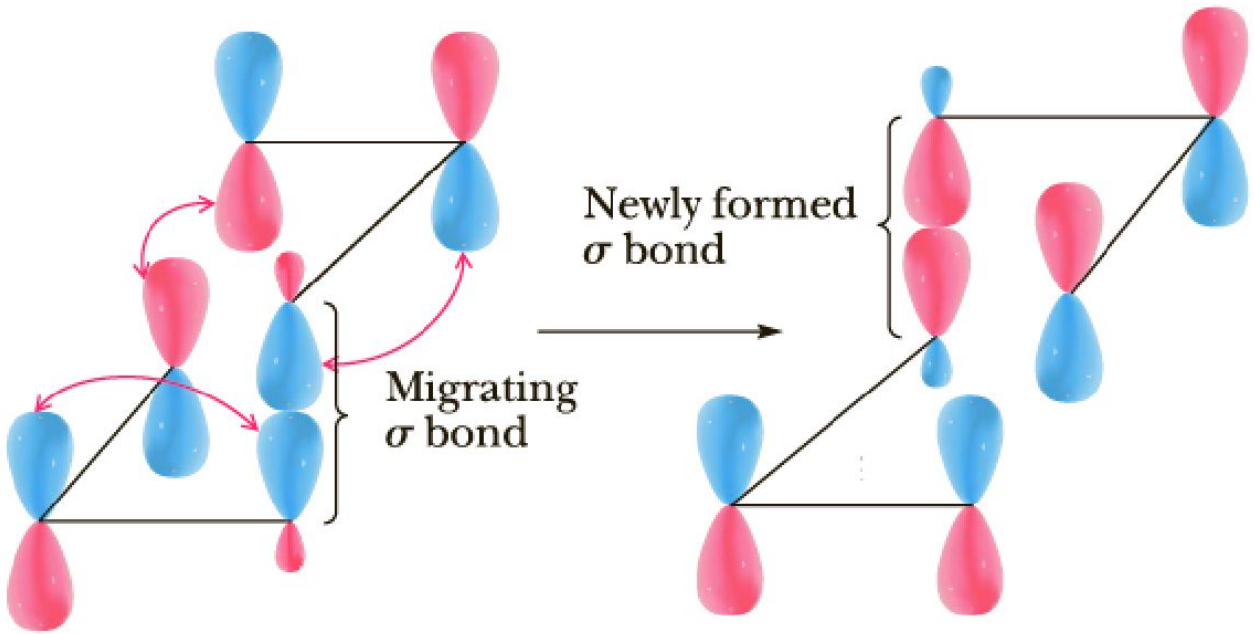
Achiral

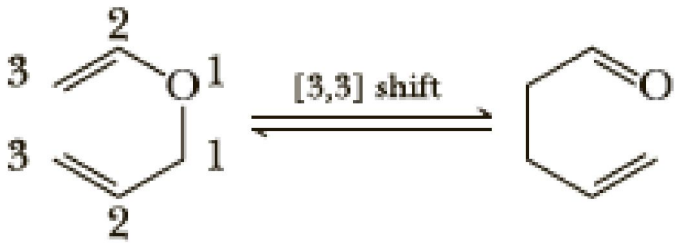
Enantiomerically pure

97%

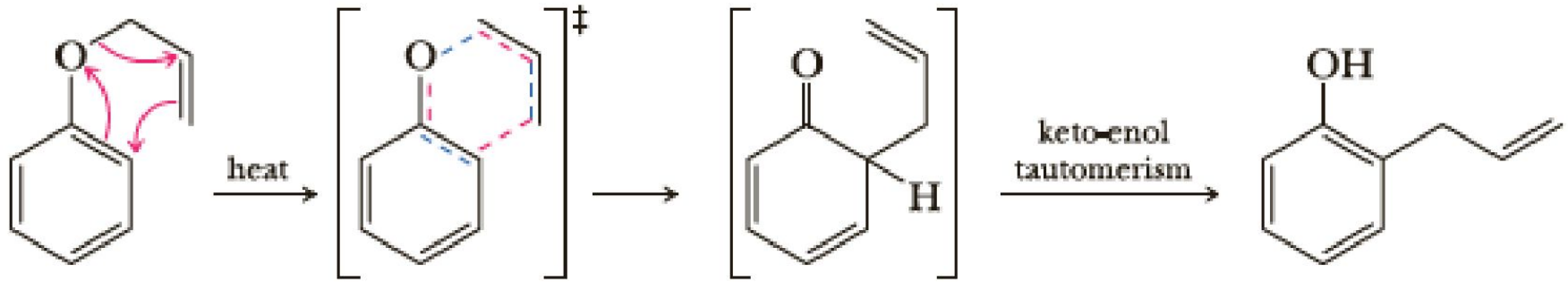
3%



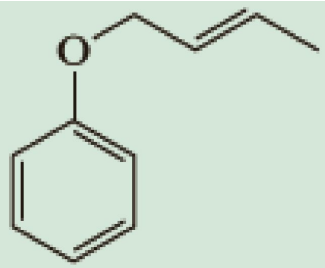

Newly formed
σ bond
Migrating
σ bond



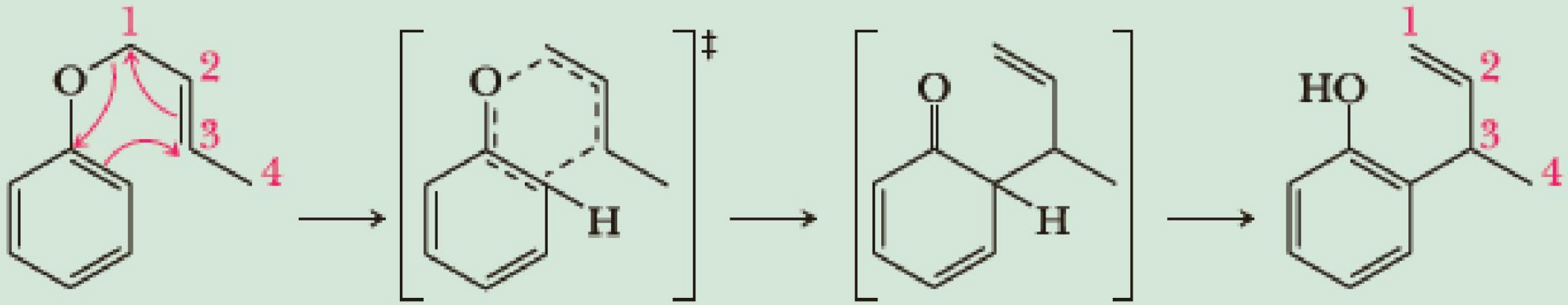
The Claisen rearrangement



Allyl phenyl ether | Transition state | A cyclohexadienone intermediate | **2-Allylphenol**



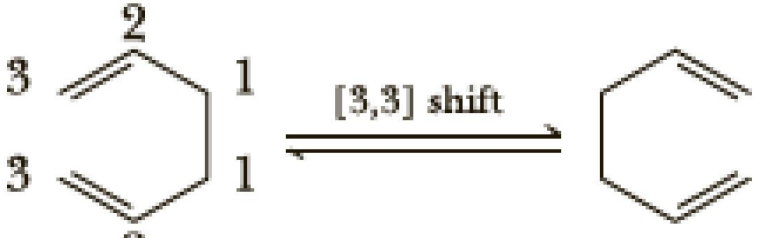
trans-2-Butenyl phenyl ether



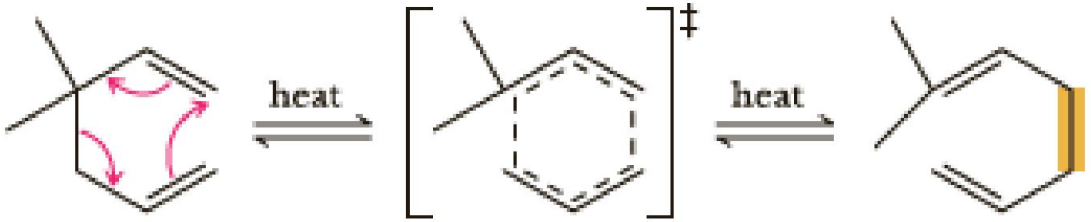
Transition state

A cyclohexadienone intermediate

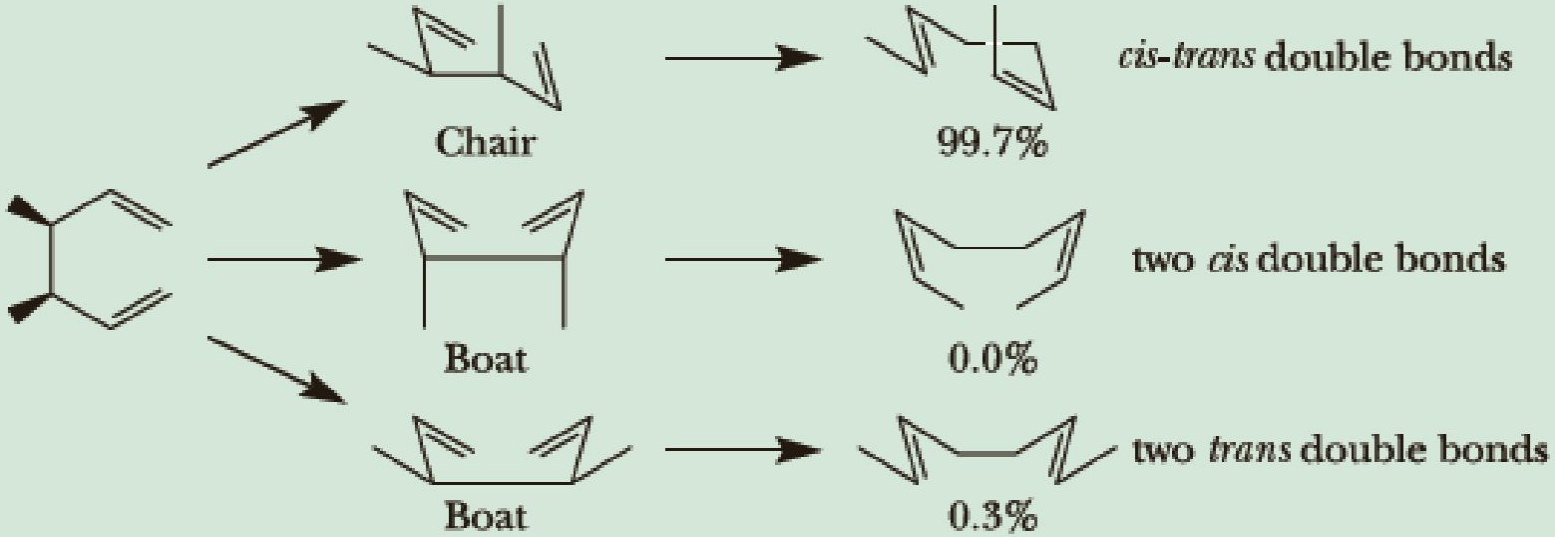
(racemic)

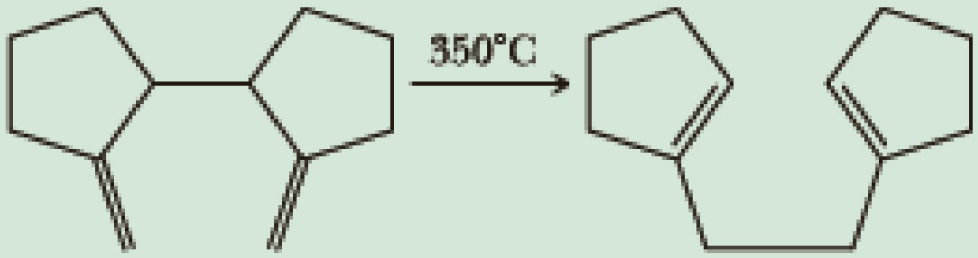


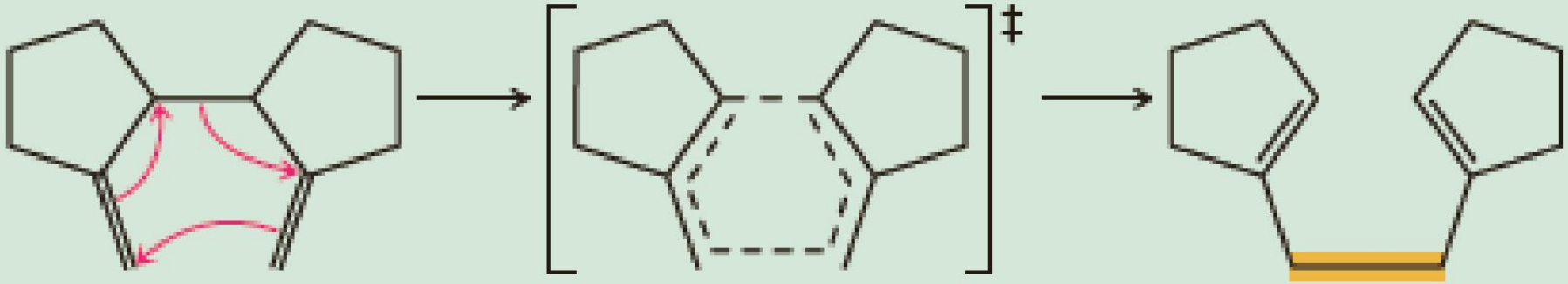
The Cope rearrangement



3,3-Dimethyl-1,5-hexadiene | **Transition state** | **6-Methyl-1,5-heptadiene**



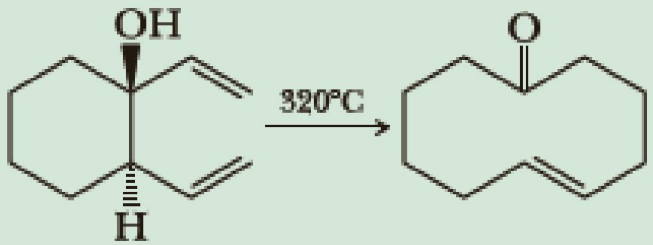




Transition state

Problem 20.11

Propose a mechanism for the following Cope rearrangement.



20.16 Predict the structure of the major product formed by 1,2-addition of HCl to 2-methyl-1,3-butadiene (isoprene).

20.17 Predict the major product formed by 1,4-addition of HCl to isoprene.

20.18 Predict the structure of the major 1,2-addition product formed by reaction of one mole of Br_2 with isoprene. Also predict the structure of the major 1,4-addition product formed under these conditions.

20.30 Draw structural formulas for the products of reaction of cyclopentadiene with each dienophile.

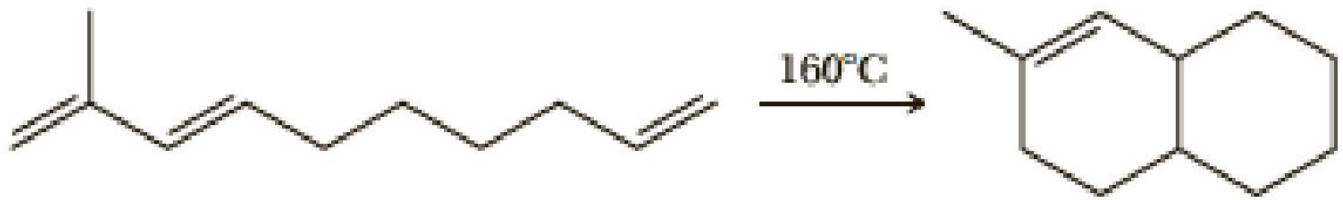
(a) $CH_2{=}CHCl$ (b) $CH_2{=}CHC(=O)OCH_3$ (c) $HC{\equiv}CH$ (d) $CH_3OC(=O)C{\equiv}CC(=O)OCH_3$

20.31 Propose structural formulas for compounds A and B and specify the configuration of compound B.

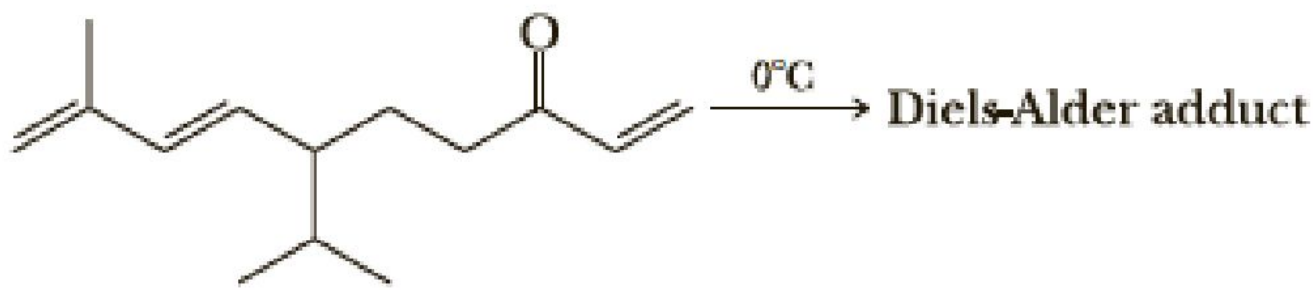
$$+\ CH_2{=}CH_2 \xrightarrow{200^\circ C} C_7H_{10} \xrightarrow[2.\ (CH_3)_2S]{1.\ O_3} C_7H_{10}O_2$$

(A) (B)

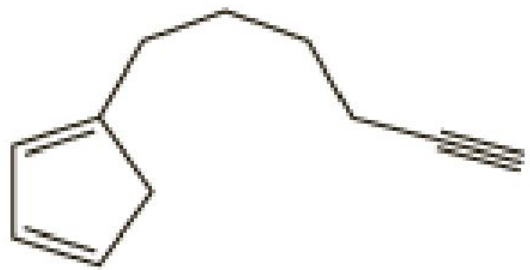
20.34 The following triene undergoes an intramolecular Diels-Alder reaction to give the product shown. Show how the carbon skeleton of the triene must be coiled to give this product and show by curved arrows the redistribution of electron pairs that takes place to give the product.



20.35 The following triene undergoes an intramolecular Diels-Alder reaction to give a bicyclic product. Propose a structural formula for the product. Account for the observation that the Diels-Alder reaction given in this problem takes place under milder conditions (at lower temperature) than the analogous Diels-Alder reaction shown in Problem 20.34.

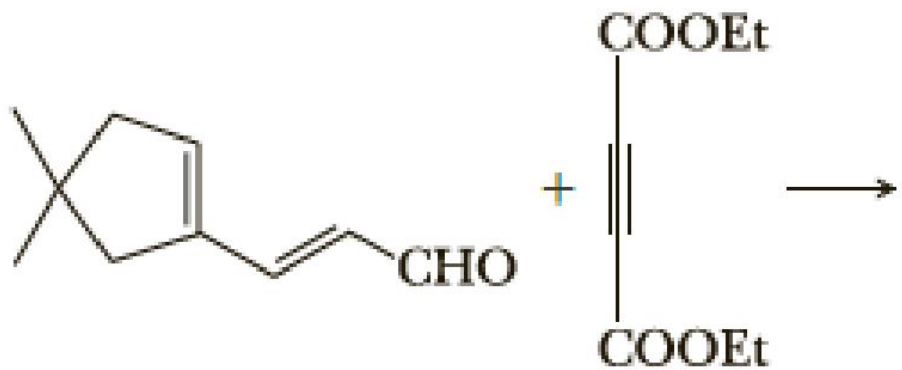


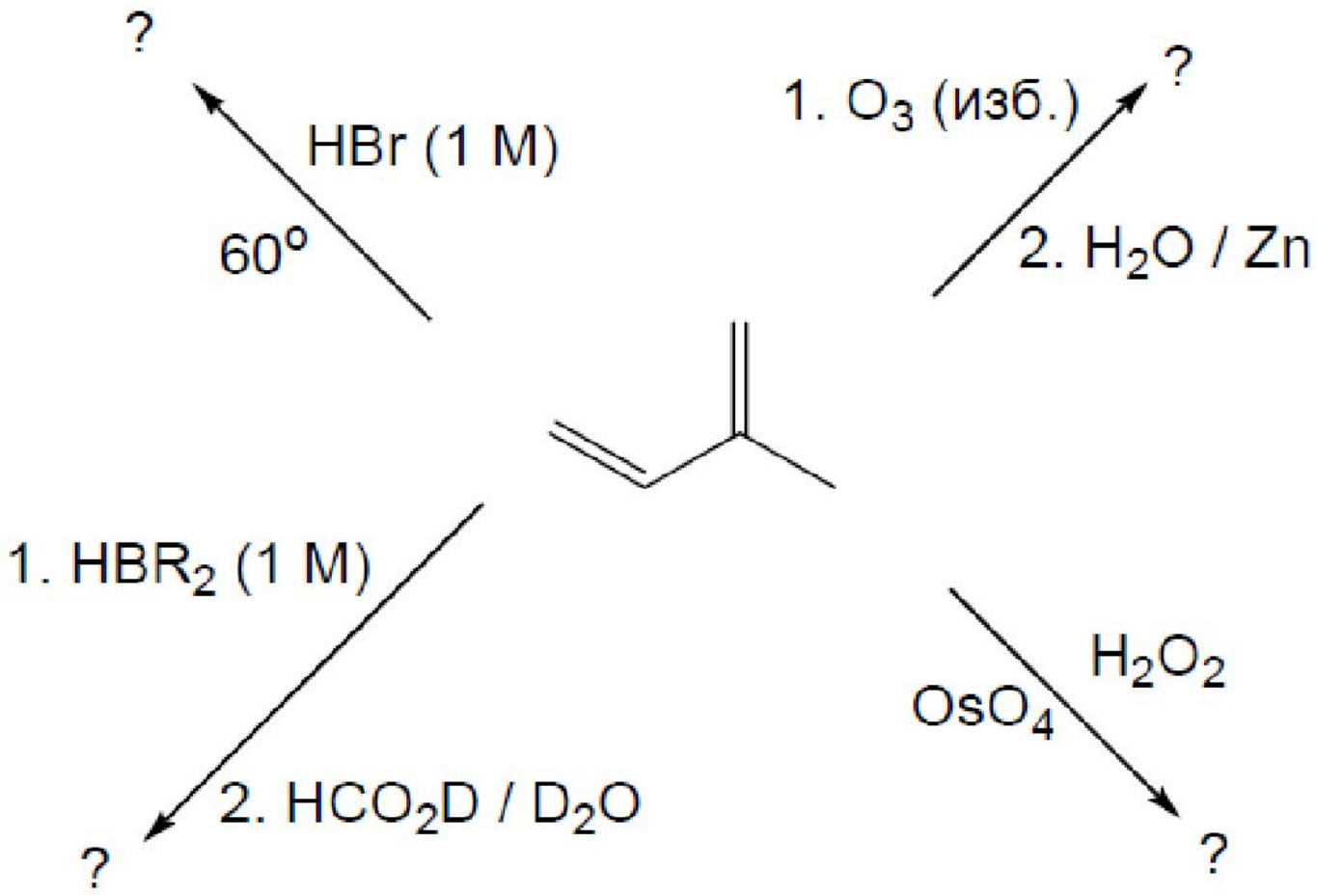
20.36 The following compound undergoes an intramolecular Diels-Alder reaction to give a tricyclic product. Propose a structural formula for the product.



heat → An intramolecular Diels-Alder adduct

20.37 Draw a structural formula for the product of this Diels-Alder reaction, including the stereochemistry of the product.

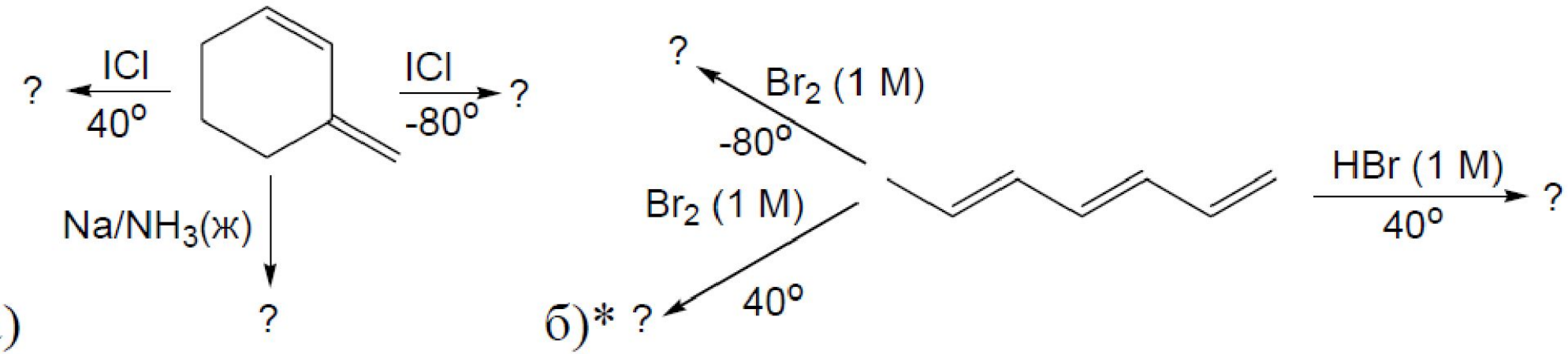



?
HBr (1 M)
60°
1. O3 (изб.)
?
2. H2O / Zn
1. HBR2 (1 M)
2. HCO2D / D2O
?
H2O2
OsO4
?

пропен $\xrightarrow[500^o]{Cl_2\ (1\ M)}$? $\xrightarrow{Na}$? $\xrightarrow{H_3O^+}$? $\xrightarrow[300^o]{Al_2O_3}$? $\xrightarrow[40^o]{Br_2\ (1\ M)}$?

б)

2-метилбутан $\xrightarrow[h\nu]{Br_2\ (1\ M)}$? $\xrightarrow[EtOH]{KOH}$? $\xrightarrow[HCO_2H]{H_2O_2}$? $\xrightarrow[300^o]{Al_2O_3}$? $\xrightarrow[ROOH]{HBr}$?

в)

2-метилбутен-1 $\xrightarrow{HCl}$? $\xrightarrow[EtOH]{KOH}$? $\xrightarrow[HO^-]{KMnO_4}$? $\xrightarrow[300^o]{Al_2O_3}$? $\xrightarrow[NH_3\ (жидк.)]{Na}$?