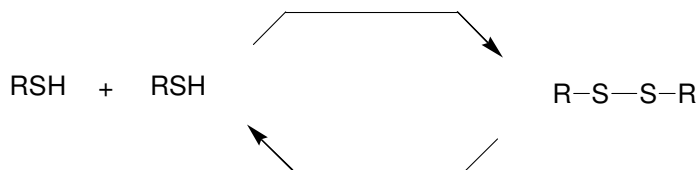
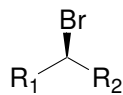
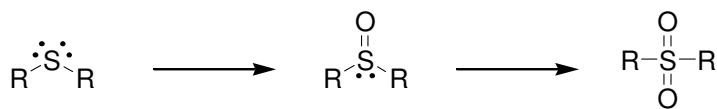
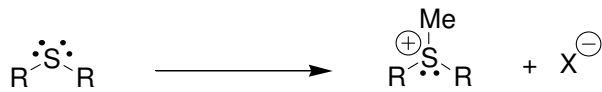
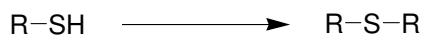
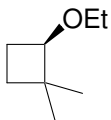
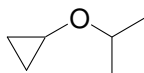


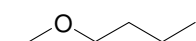
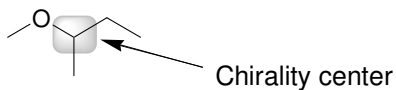
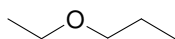
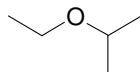
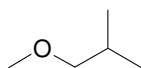
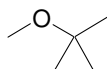
Thiols and Sulfides*Thiols**Sulfides***Solutions****14.1.**

- 2-ethoxypropane
- (*S*)-2-chloro-1-ethoxypropane
- 2,4-dichloro-1-ethoxybenzene
- (*1R,2R*)-2-ethoxycyclohexanol
- 1-ethoxycyclohexene

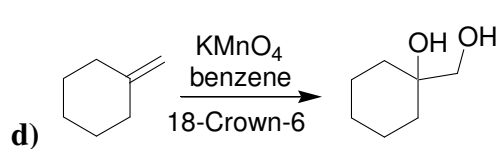
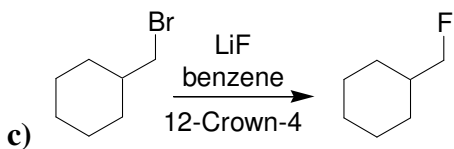
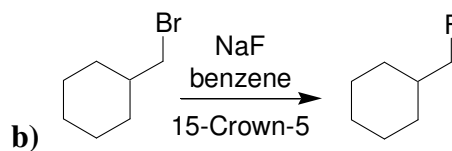
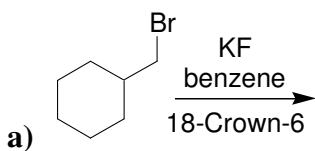
14.2.**a)****b)**

14.3.

Common names in parentheses:

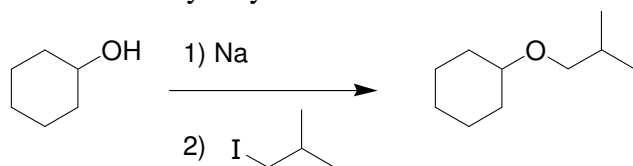
1-methoxybutane
(butyl methyl ether)2-methoxybutane
(*sec*-butyl methyl ether)1-ethoxypropane
(ethyl propyl ether)2-ethoxypropane
(ethyl isopropyl ether)1-methoxy-2-methylpropane
(isobutyl methyl ether)2-methoxy-2-methylpropane
(*tert*-butyl methyl ether)

14.4.

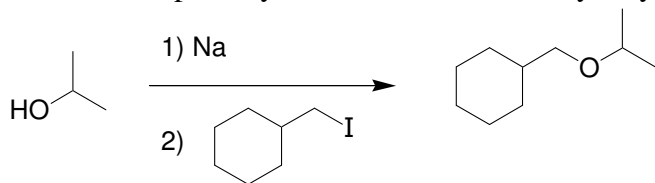


14.5.

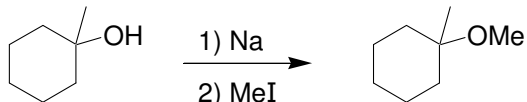
a) A Williamson ether synthesis will be more efficient with a less sterically hindered substrate, since the process involves an S_N2 reaction. Therefore, in this case, it is better to start with a secondary alcohol and a primary alkyl halide, rather than a primary alcohol and a secondary alkyl halide:



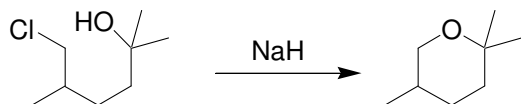
b) In this case, it is better to start with a secondary alcohol and a primary alkyl halide, rather than a primary alcohol and a secondary alkyl halide:



c) In this case, it is better to start with a tertiary alcohol and a methyl halide, rather than methanol and a tertiary alkyl halide:

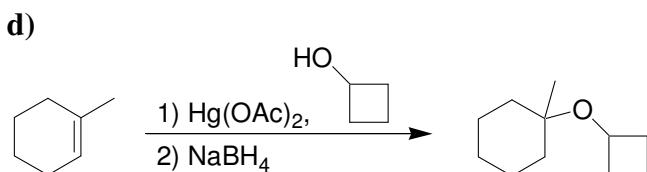
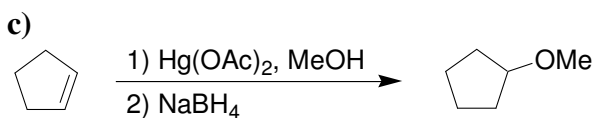
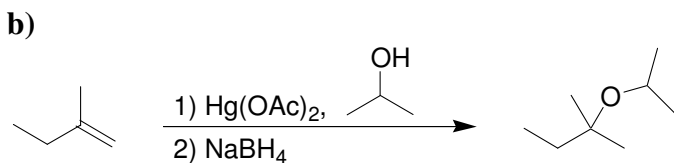
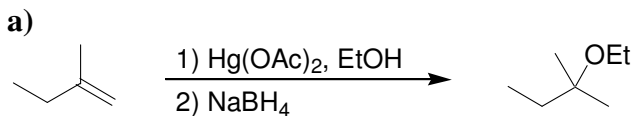


14.6.

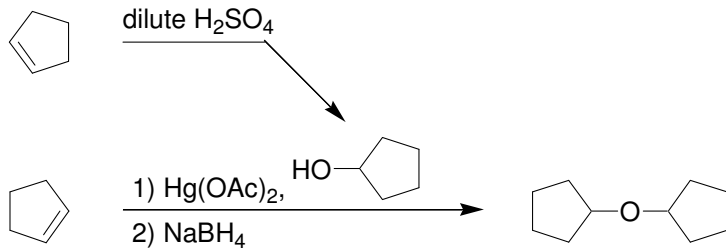


14.7. No. The Williamson ether synthesis employs an $\text{S}_{\text{N}}2$ process, which cannot occur readily at tertiary or vinylic positions. Making this ether would require at least one of these two processes, neither of which can be used.

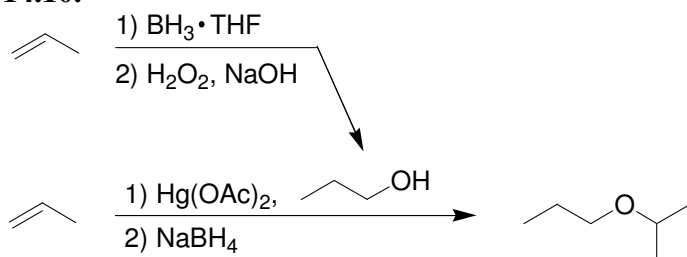
14.8.



14.9.

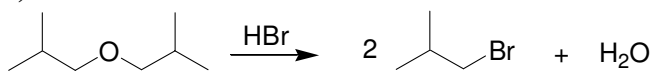


14.10.

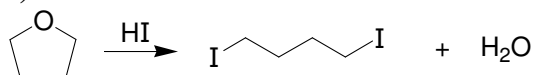


14.11.

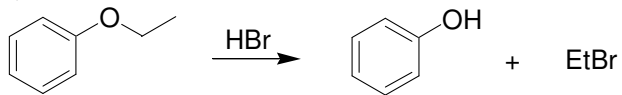
a)



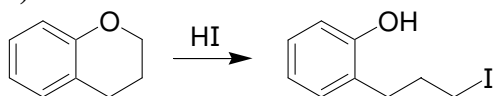
b)

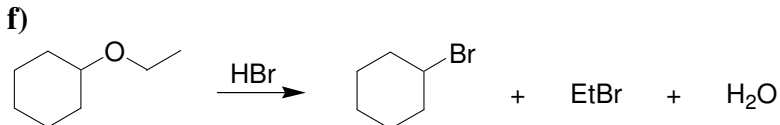
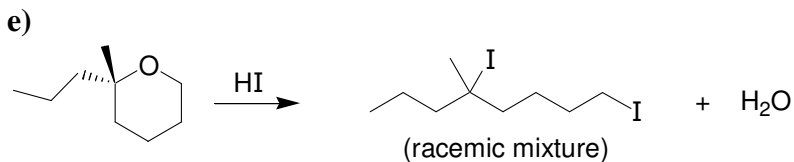


c)



d)

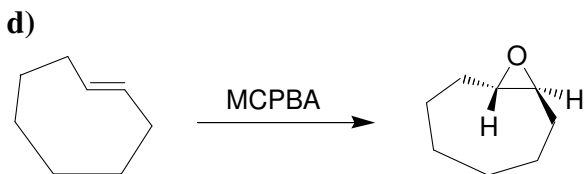
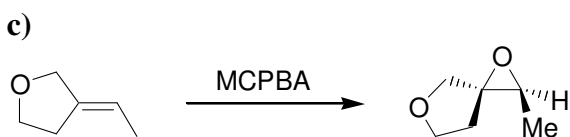
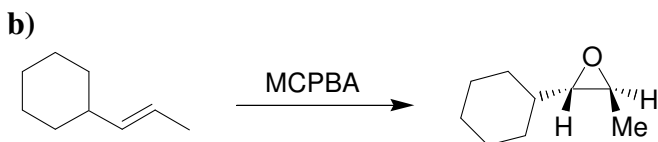
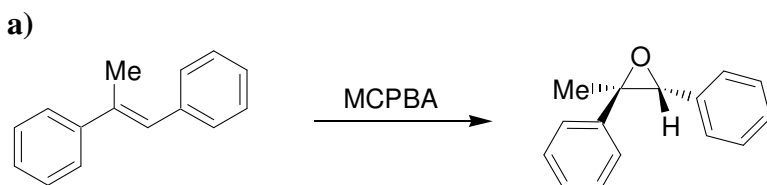


**14.12.**

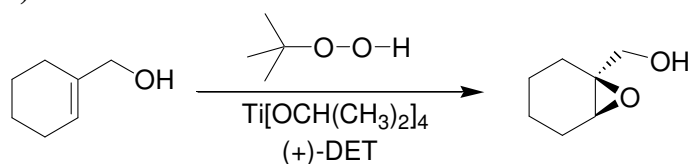
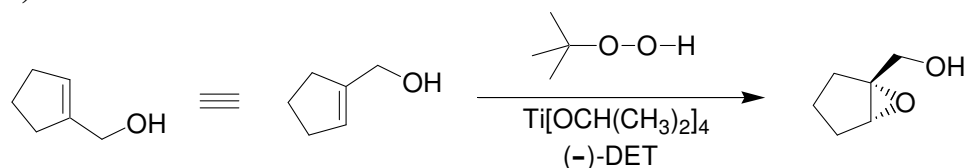
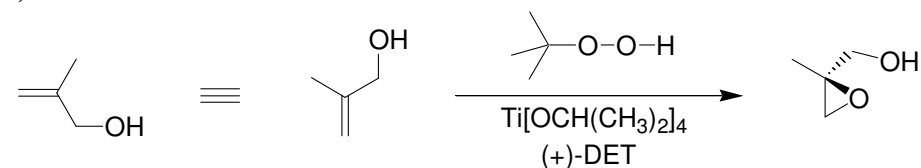
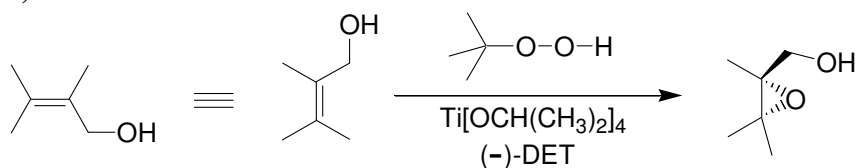
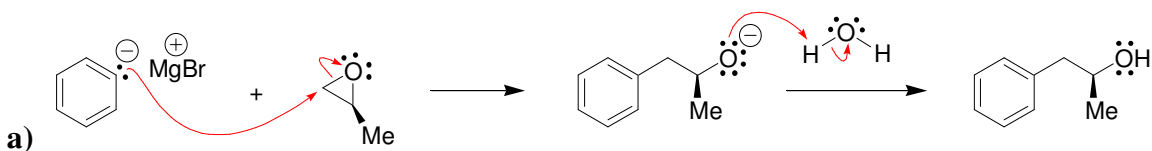
- a) 2-methyl-1,2-epoxypropane or 1,1-dimethyloxirane
 b) 1,1-diphenyl-1,2-epoxyethane or 1,1-diphenyloxirane
 c) 1,2-epoxycyclohexane

14.13.

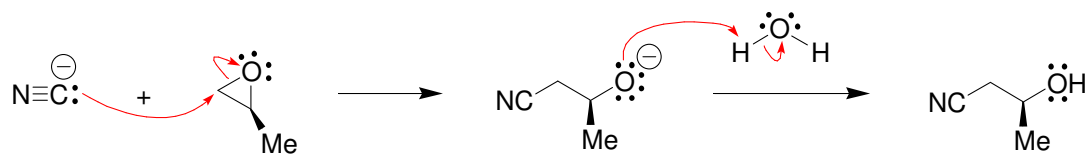
- a) (*S*)-2-phenyl-1,2-epoxypropane or (*S*)-1-methyl-1-phenyloxirane
 b) (*3R,4R*)-3,4-epoxyheptane or (*1R,2R*)-1-ethyl-2-propyloxirane
 c) (*2R,3S*)-4-methyl-2,3-epoxypentane or (*1S,2R*)-1-isopropyl-2-methyloxirane

14.14.

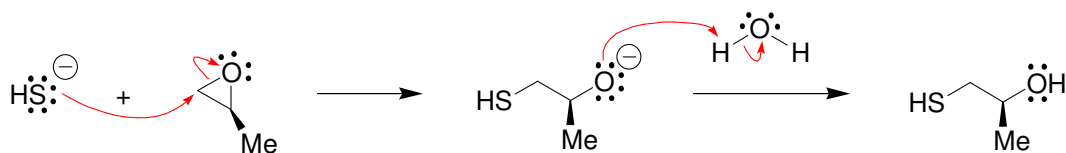
14.15. This process for epoxide formation involves deprotonation of the hydroxyl group, followed by an intramolecular S_N2 attack. The S_N2 step requires back-side attack, which can only be achieved when both the hydroxyl group and the bromine occupy axial positions. Due to the steric bulk of a tert-butyl group, Compound A spends most of time in a chair conformation that has the tert-butyl group in an equatorial position. In this conformation, the OH and Br are indeed in axial positions, so the reaction can occur quite rapidly. In contrast, Compound B spends most of its time in a chair conformation in which the OH and Br occupy equatorial positions. The S_N2 process cannot occur from this conformation.

14.16.**a)****b)****c)****d)****14.17.**

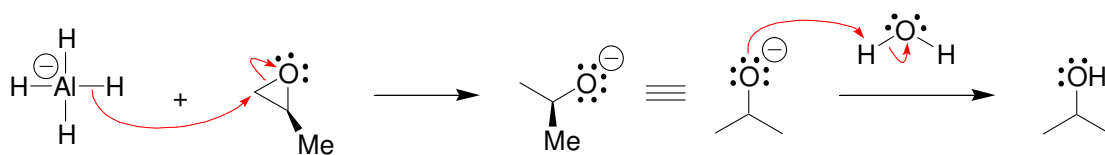
b)



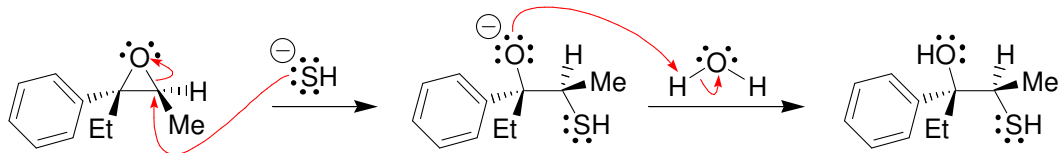
c)



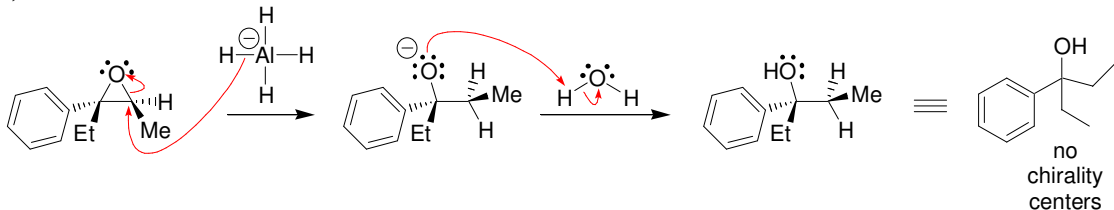
d)



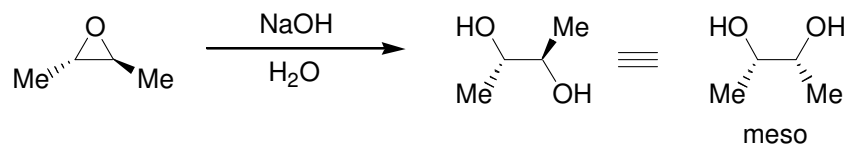
e)



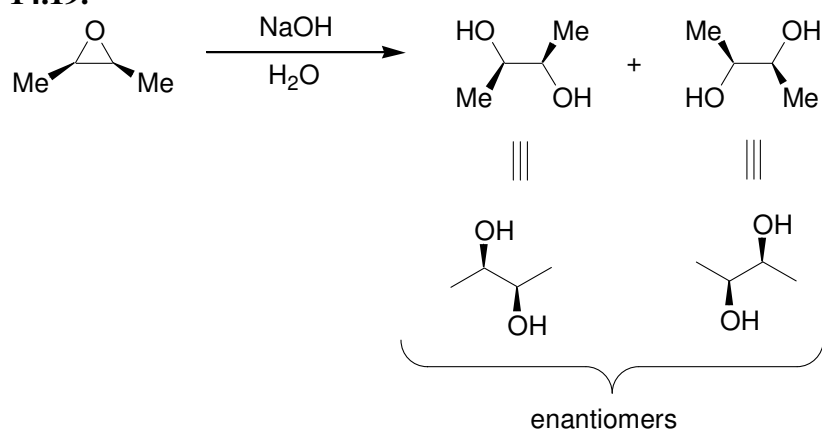
f)



14.18. The reaction yields a meso compound, regardless of which electrophilic position is attacked by hydroxide.

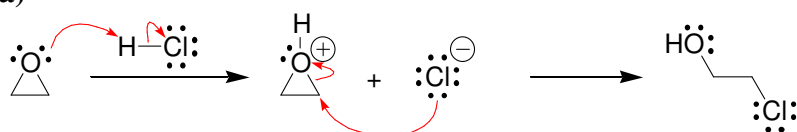


14.19.

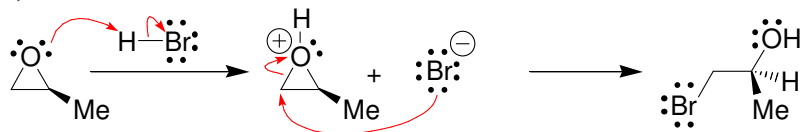


14.20.

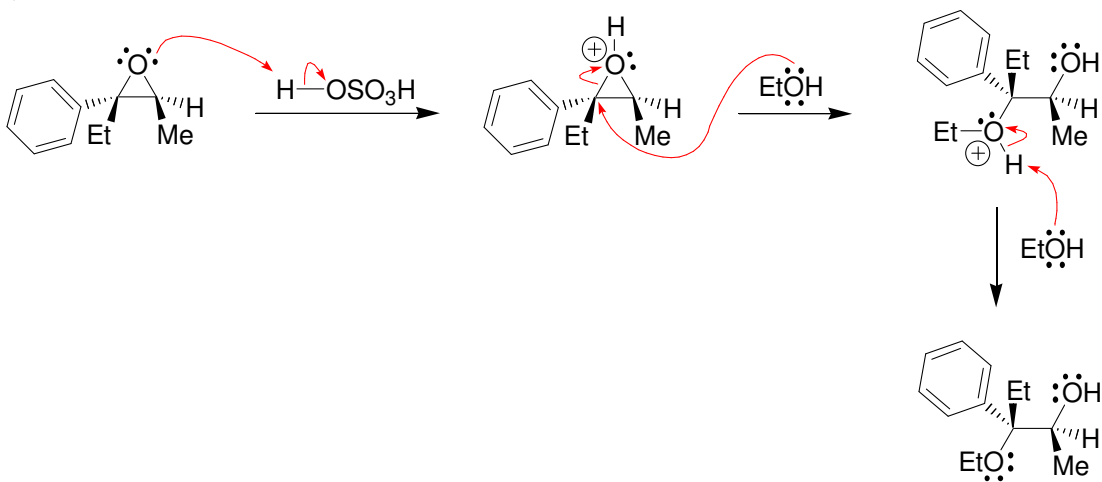
a)



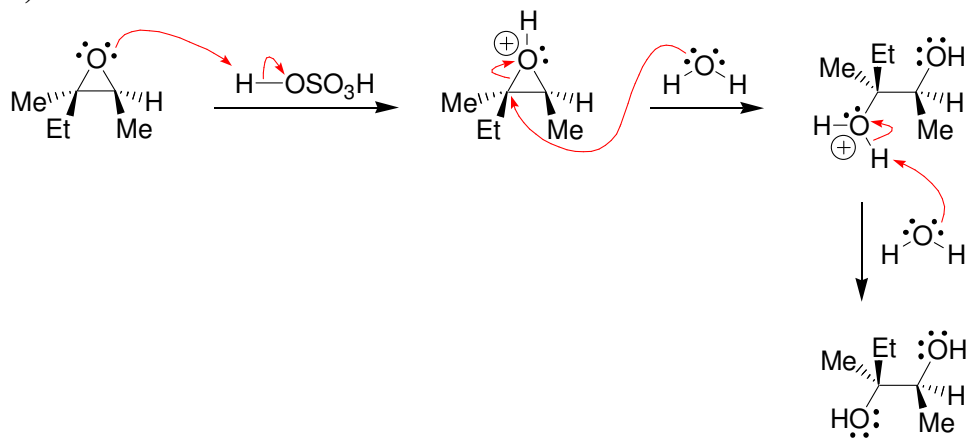
b)



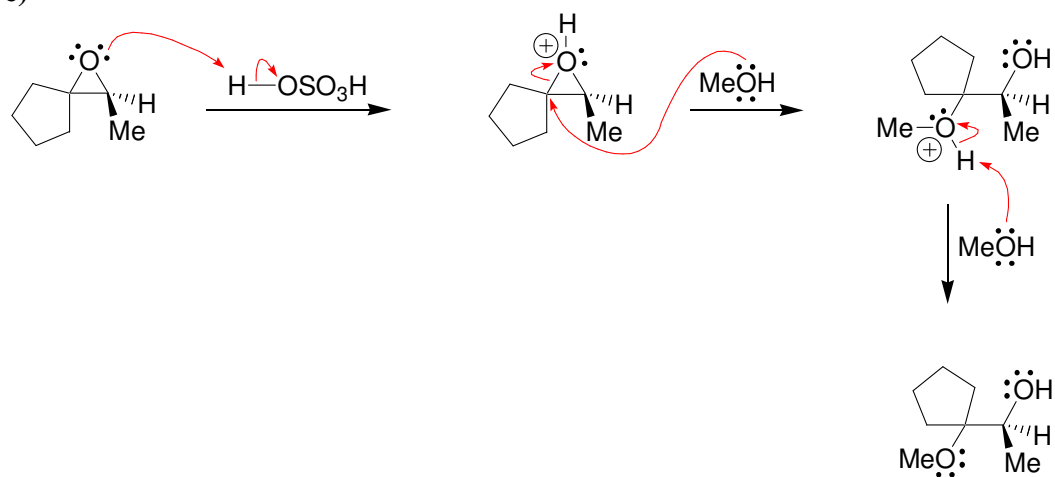
c)



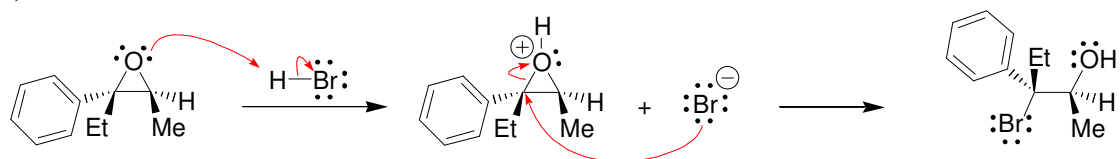
d)



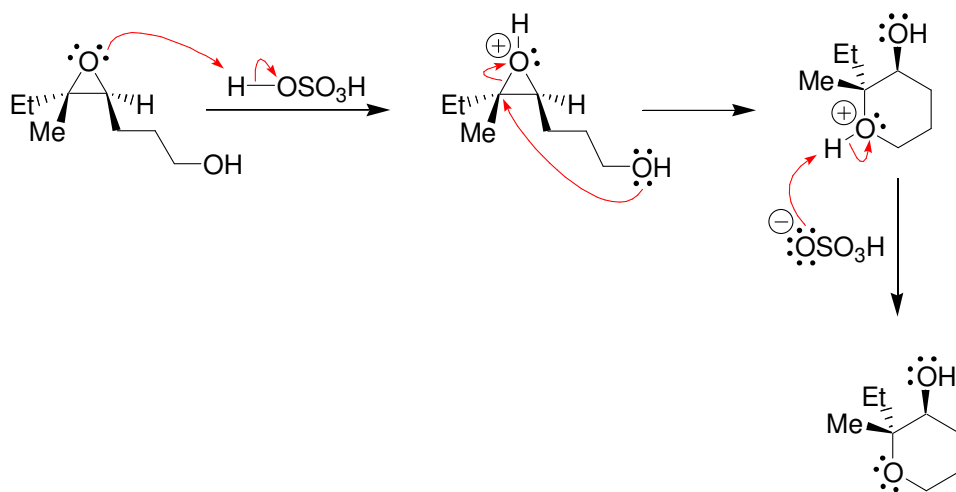
e)



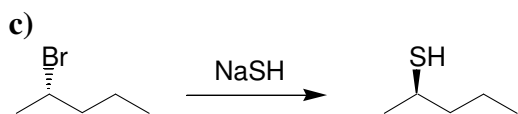
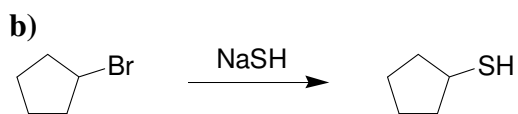
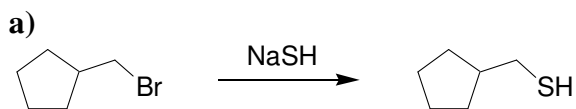
f)



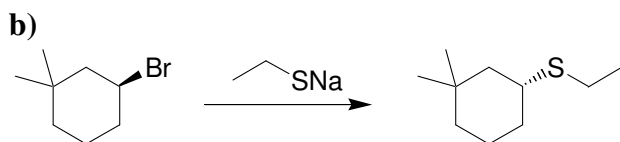
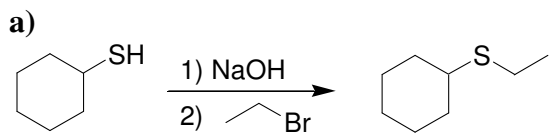
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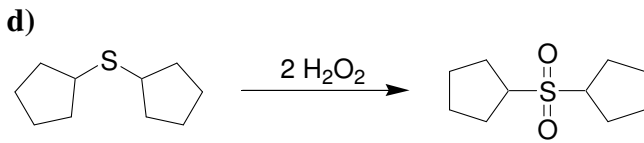
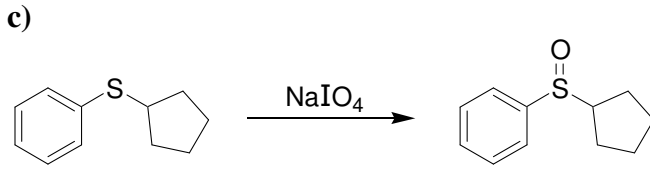


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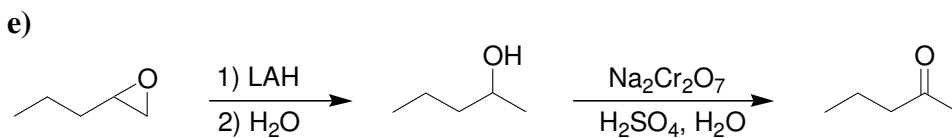
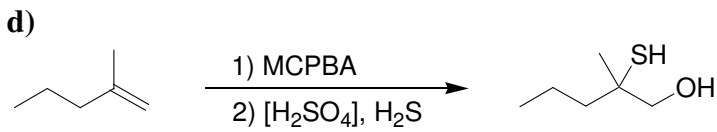
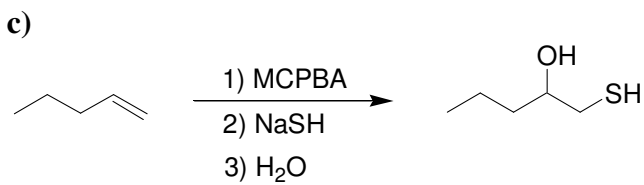
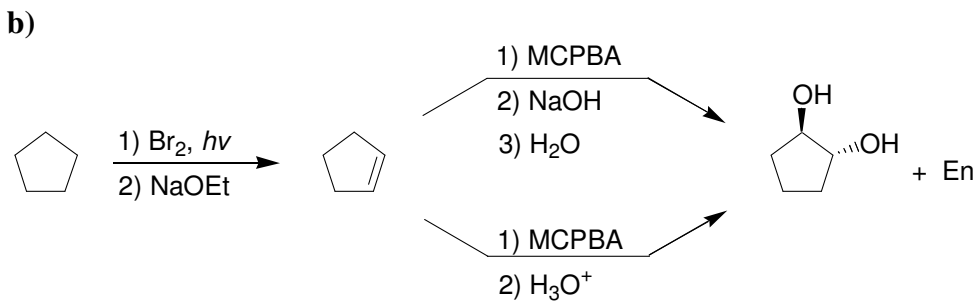
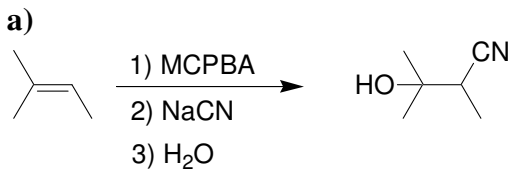


14.23.

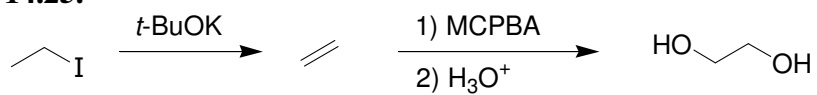




14.24.

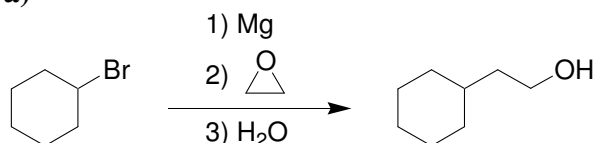


14.25.

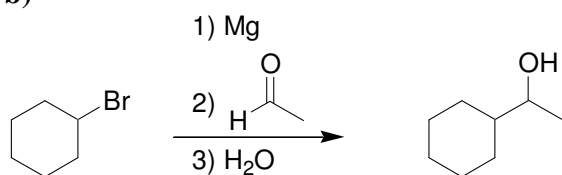


14.26.

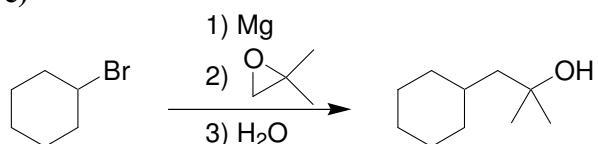
a)



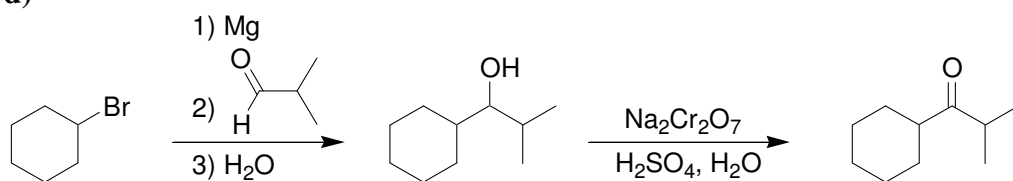
b)



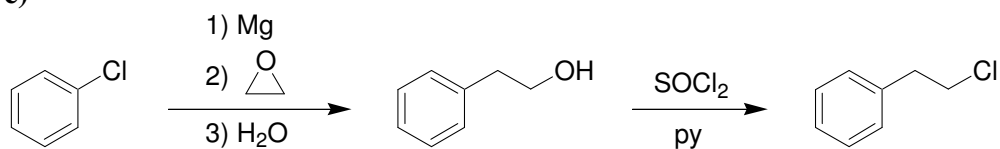
c)



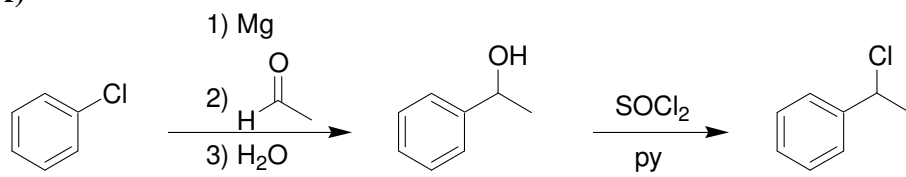
d)



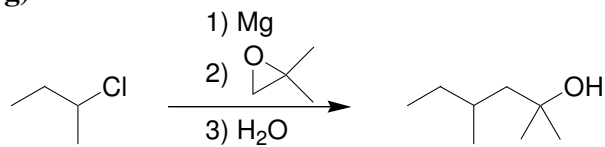
e)



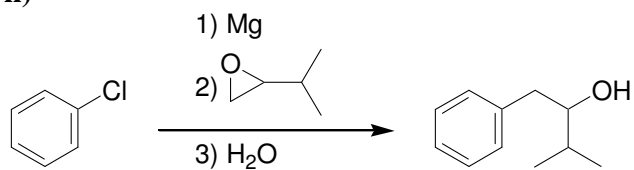
f)



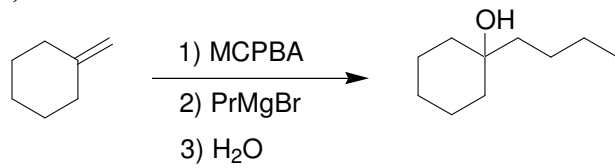
g)



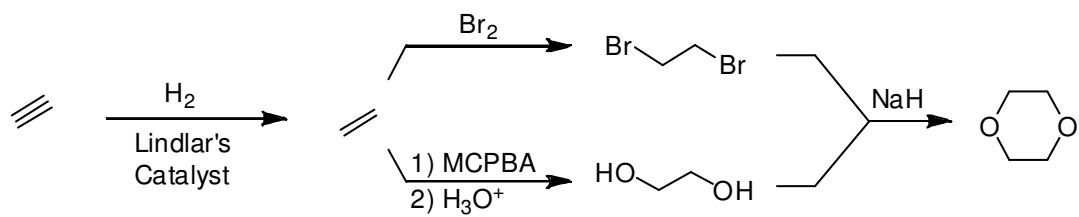
h)



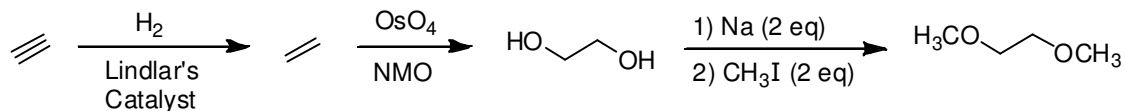
i)



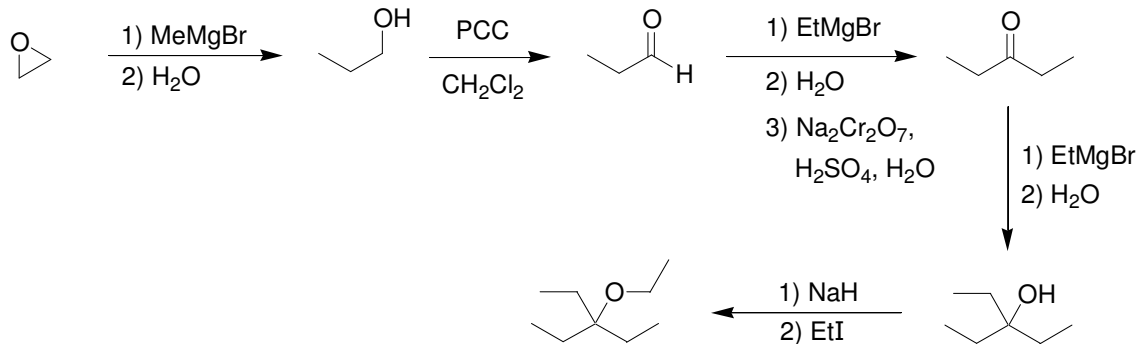
14.27.



14.28.



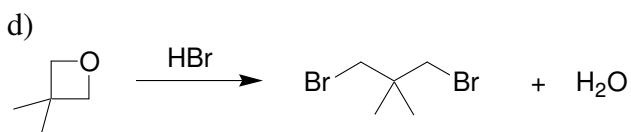
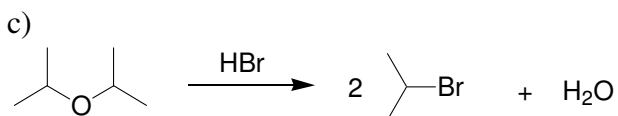
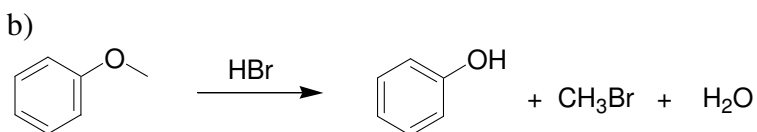
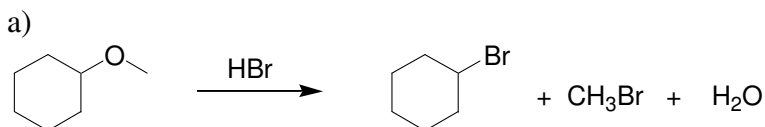
14.29.



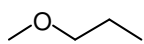
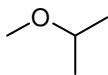
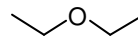
14.30

- (1*S*, 2*S*)-1-ethoxy-2-methylcyclohexane
- (*R*)-2-ethoxybutane
- (*S*)-3-hexanethiol
- ethyl propyl sulfoxide
- (*E*)-2-ethoxy-3-methyl-2-pentene
- 1,2-dimethoxybenzene
- ethyl propyl sulfide

14.31

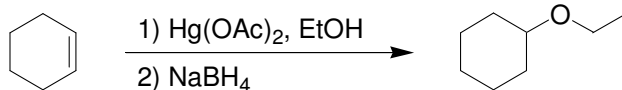


14.32

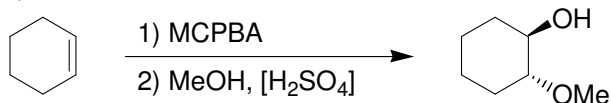
1-methoxypropane
(methyl propyl ether)2-methoxypropane
(isopropyl methyl ether)ethoxyethane
(diethyl ether)

14.33

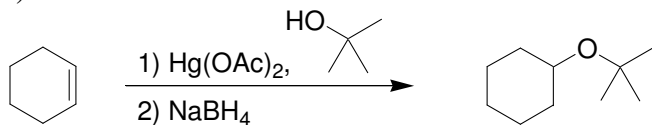
a)



b)



c)



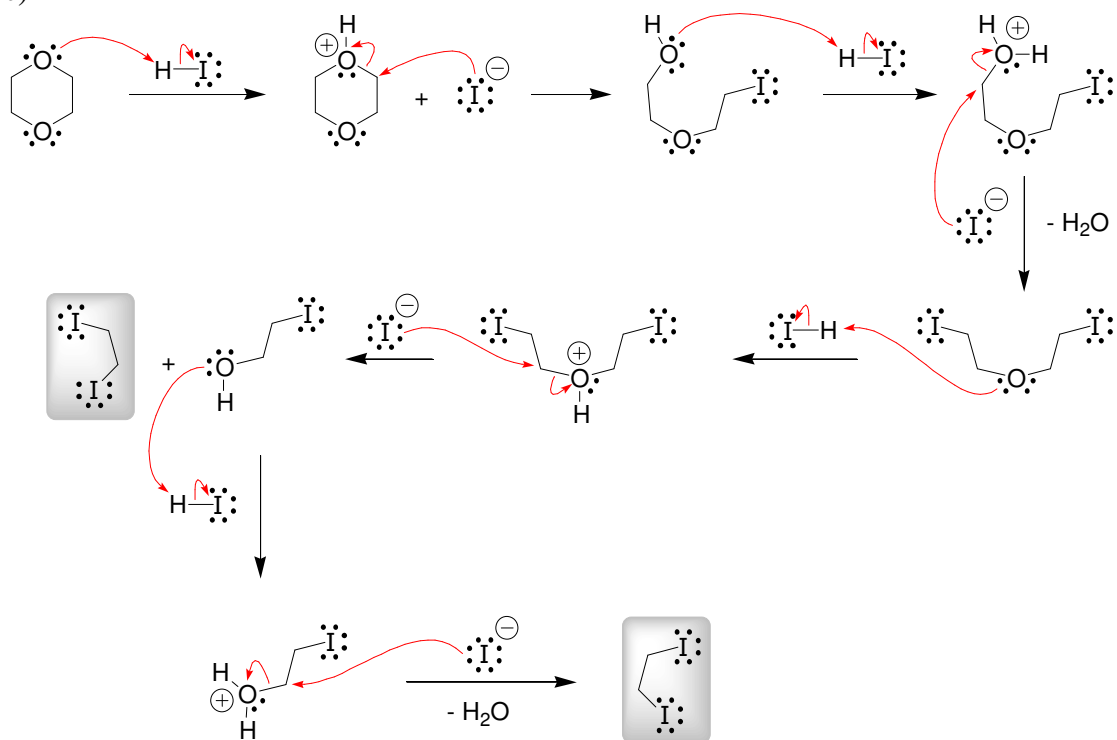
14.34

a)

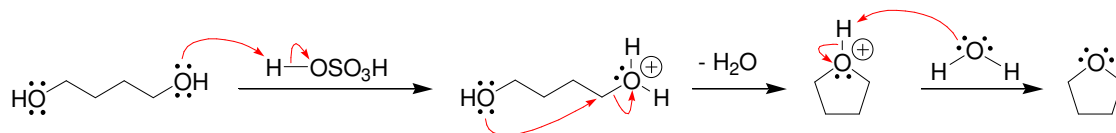
**Compound A**

b) Two moles of Compound A are produced for every one mole of 1,4-dioxane.

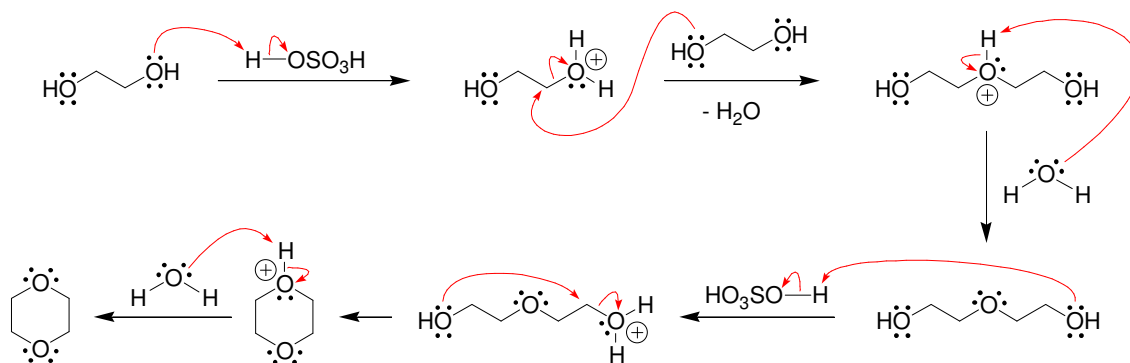
c)



14.35



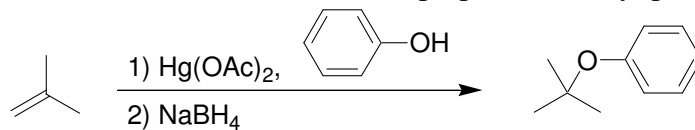
14.36



14.37

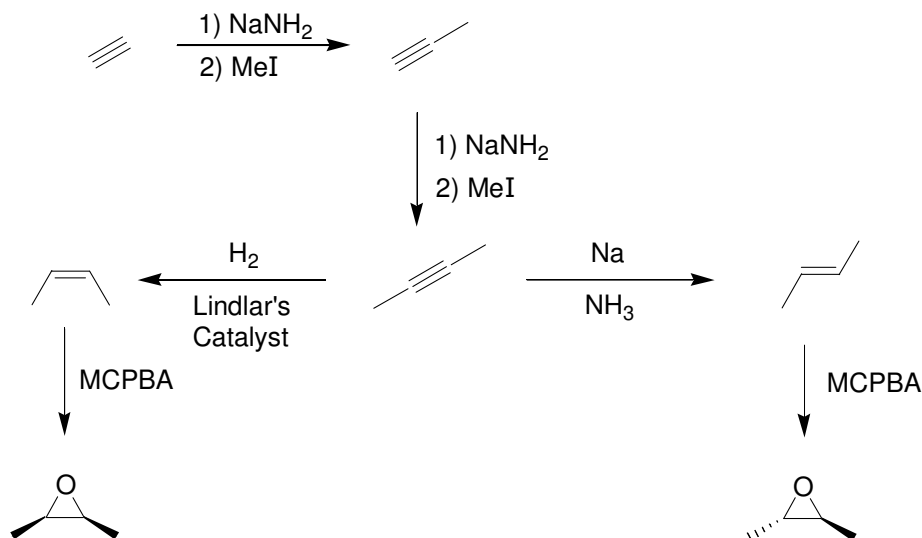
a) Neither alkyl group (on either side of the oxygen atom) can be installed via a Williamson ether synthesis. Installation of the *tert*-butyl group would require a tertiary alkyl halide, which is too sterically hindered to serve as an electrophile for an $\text{S}_{\text{N}}2$ process. Installation of the phenyl group would require an $\text{S}_{\text{N}}2$ reaction taking place at an sp^2 hybridized center, which does not readily occur.

b) Oxymercuration-demercuration can be used to prepare *tert*-butyl phenyl ether:

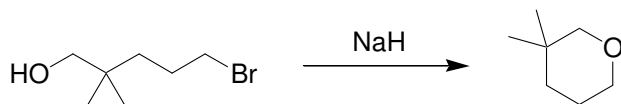


14.38 Ethylene oxide has a high degree of ring strain, and readily functions as an electrophile in an S_N2 reaction. The reaction opens the ring and alleviates the ring strain. Oxetane has less ring strain and is, therefore, less reactive as an electrophile towards S_N2 . The reaction can still occur, albeit at a slower rate, to alleviate the ring strain associated with the four membered ring. THF has almost no ring strain (very little) and does not function as an electrophile in an S_N2 reaction.

14.39

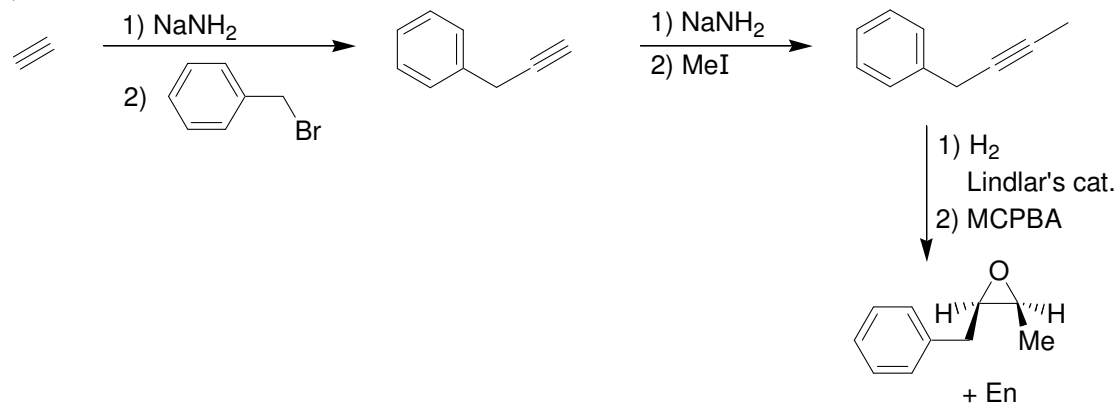


14.40

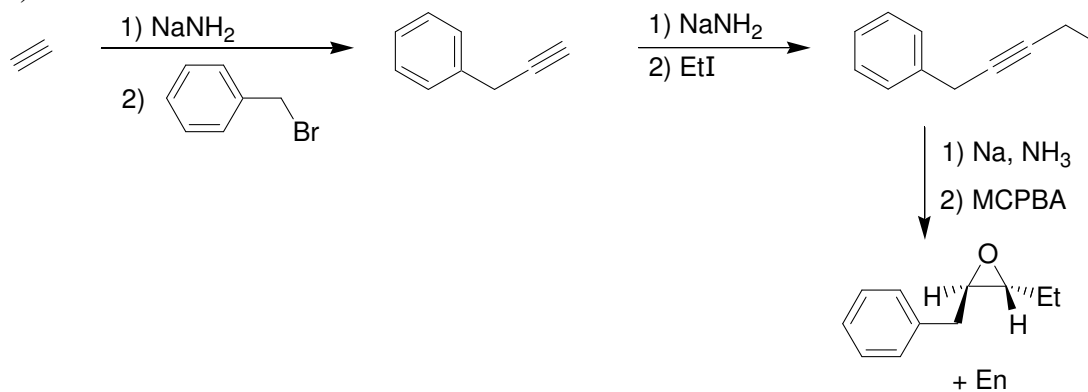


14.41

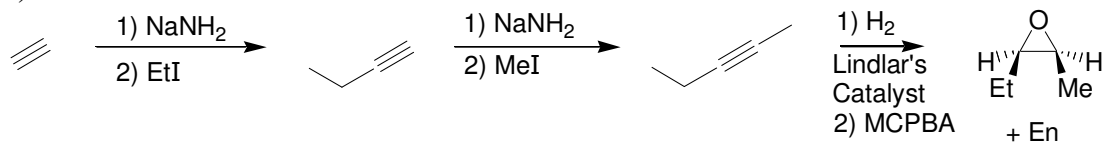
a)



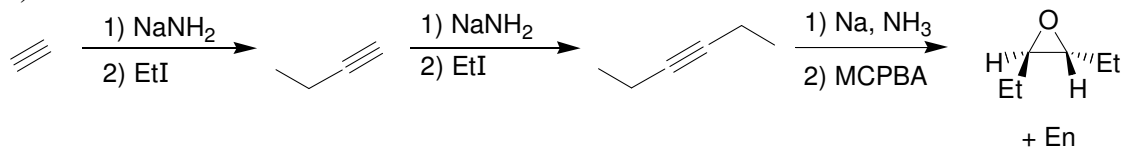
b)



c)

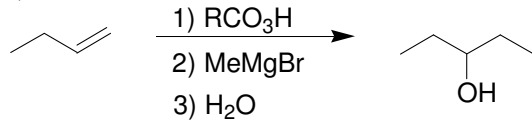


d)

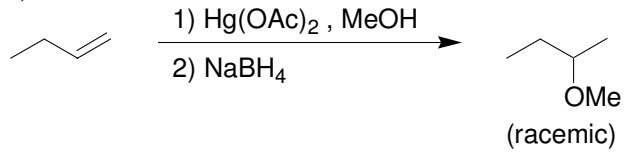


14.42

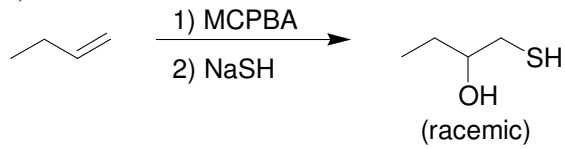
a)



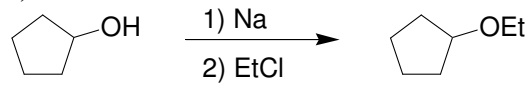
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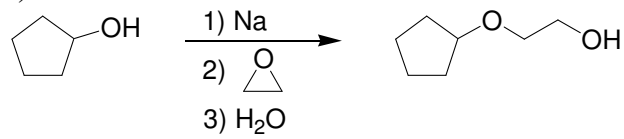
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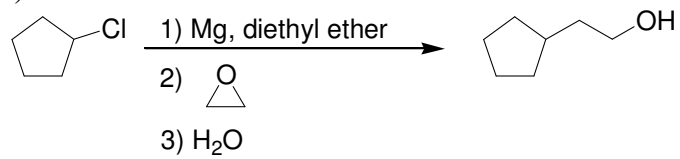
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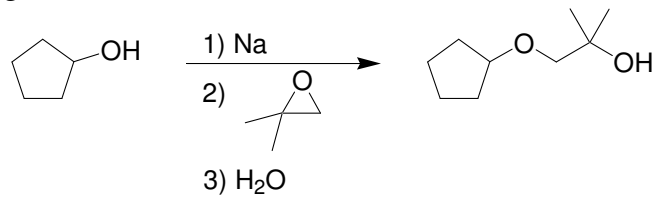
e)



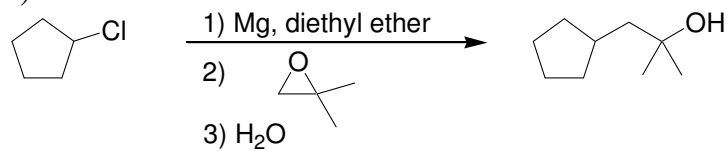
f)



g)

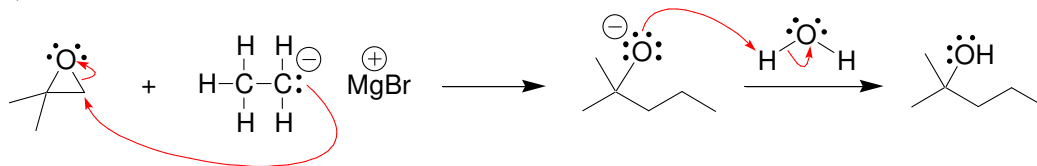


h)

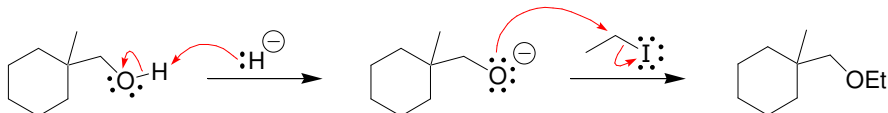


14.43

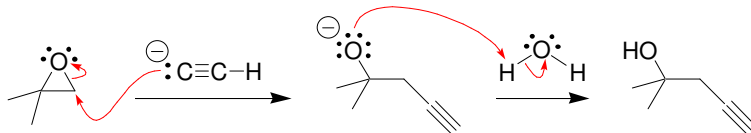
a)



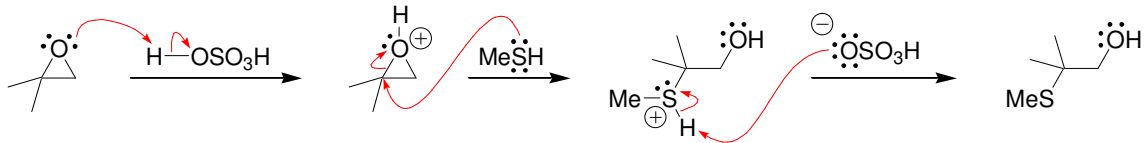
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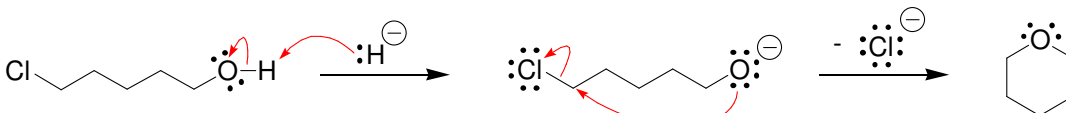
c)



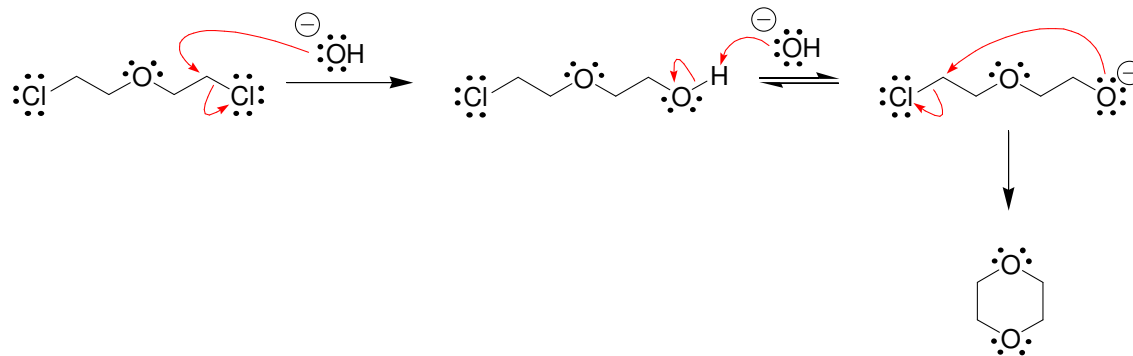
d)



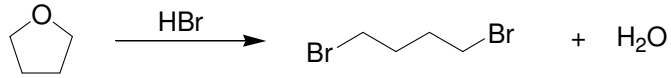
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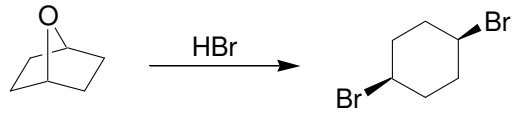
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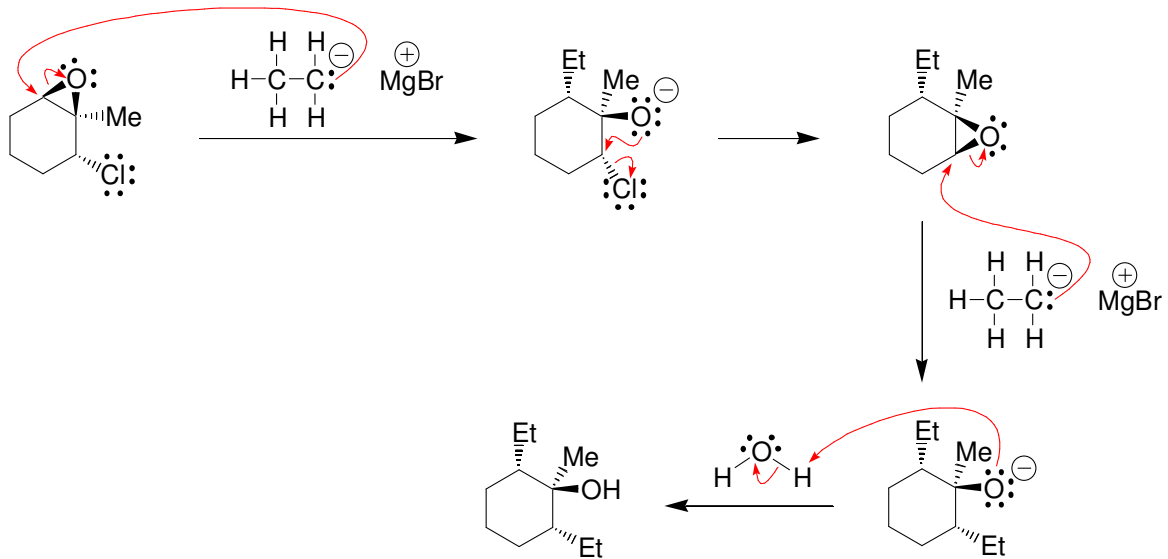
14.44



14.45

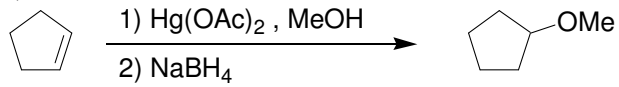


14.46

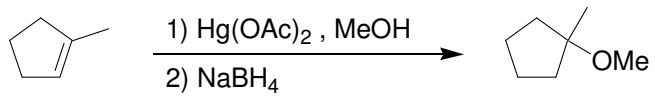


14.47

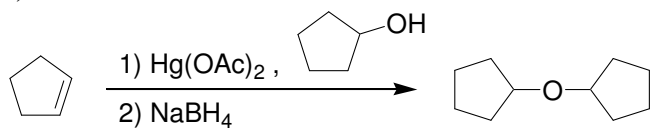
a)



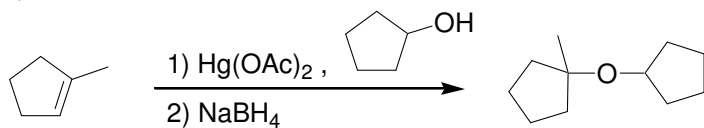
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c)

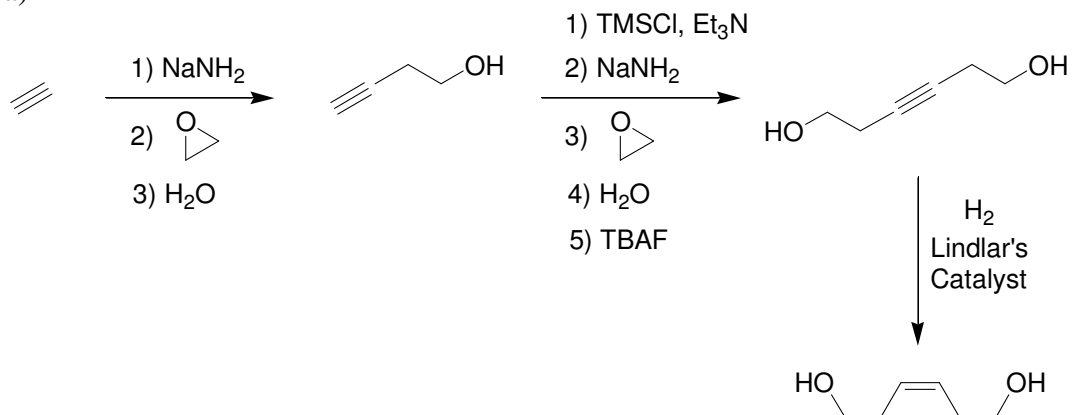


d)

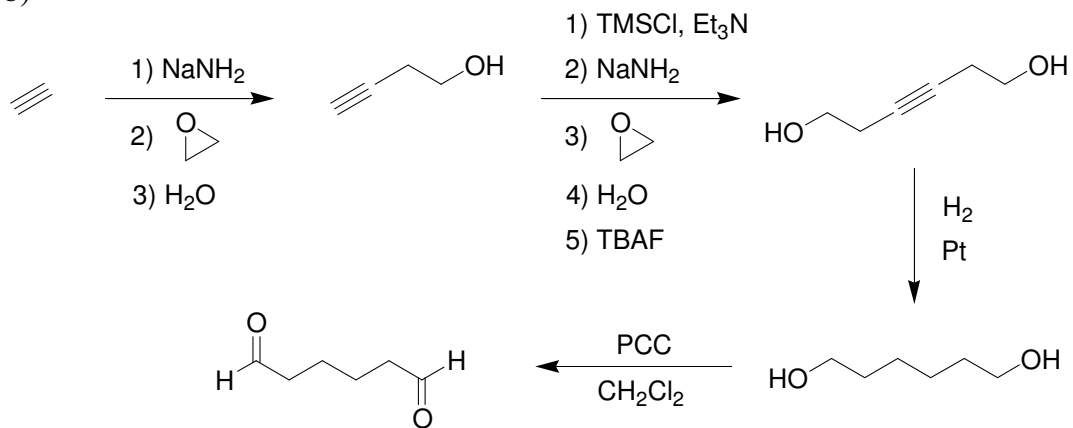


14.48

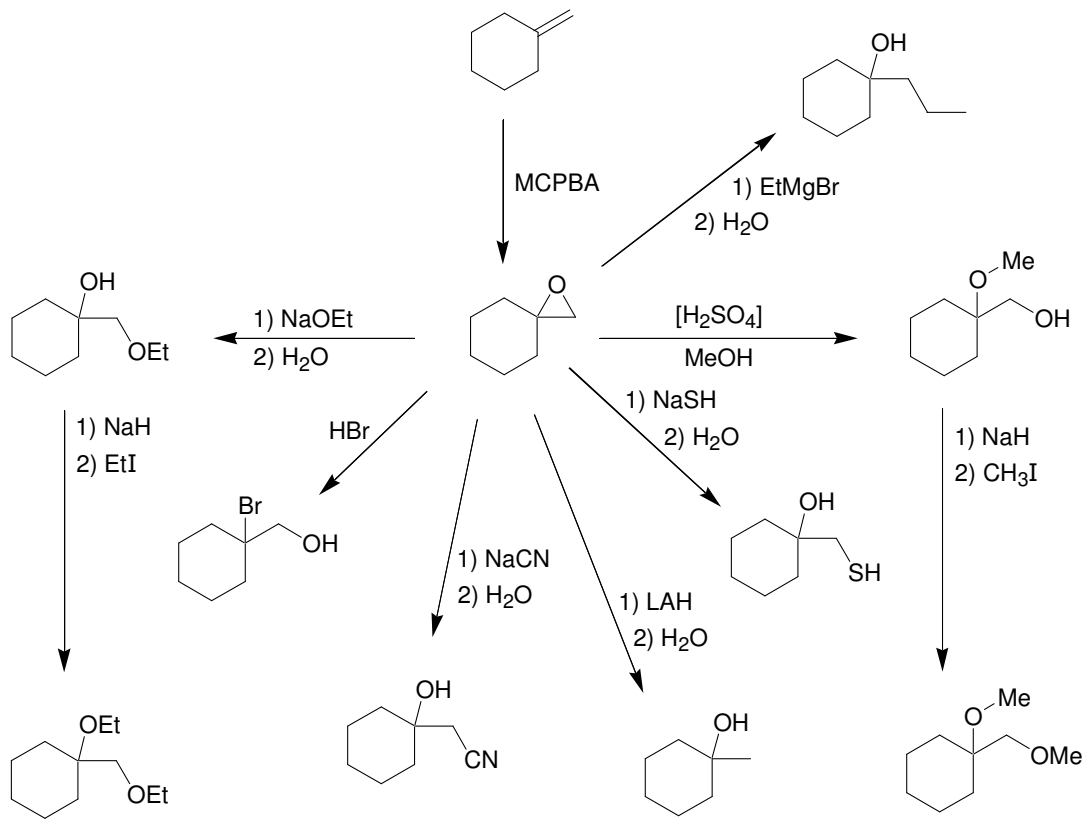
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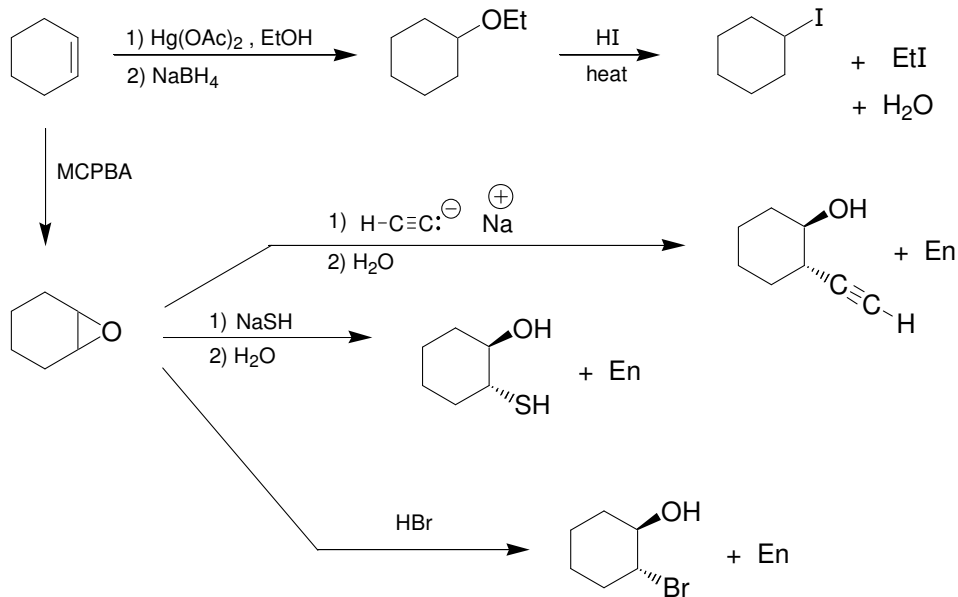
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14.49

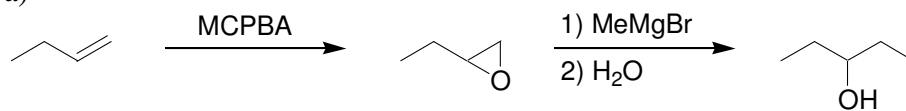


14.50

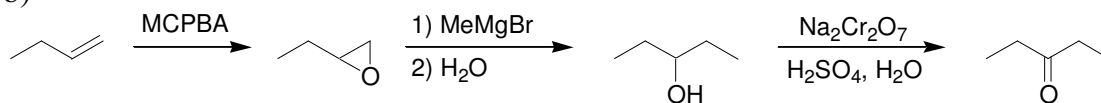


14.51

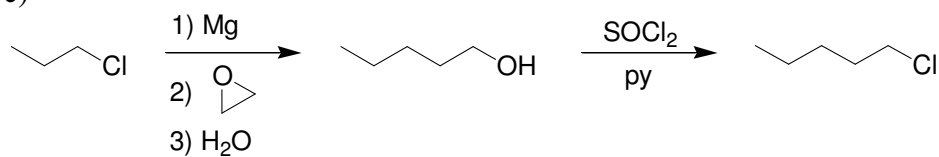
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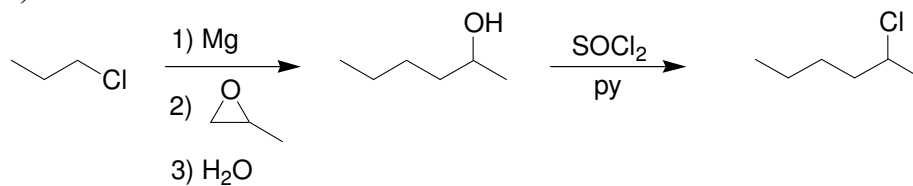
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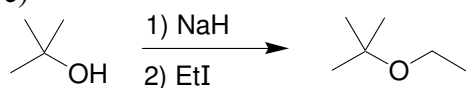
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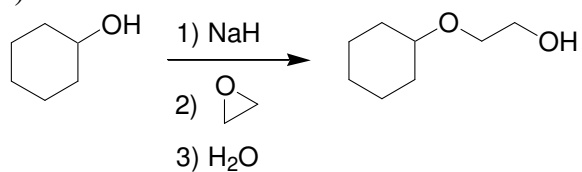
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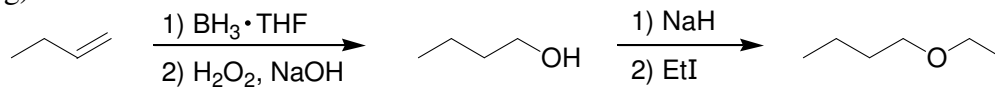
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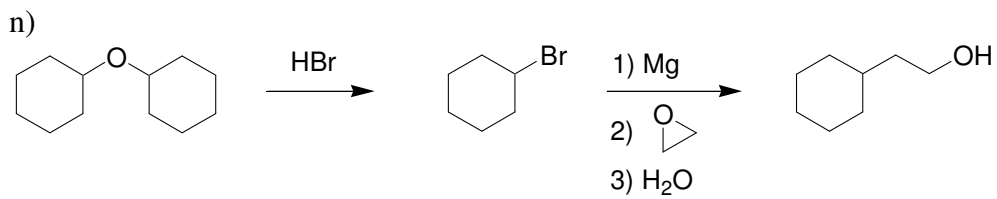
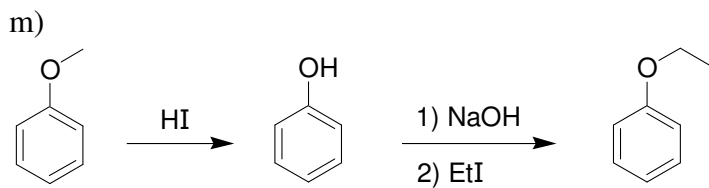
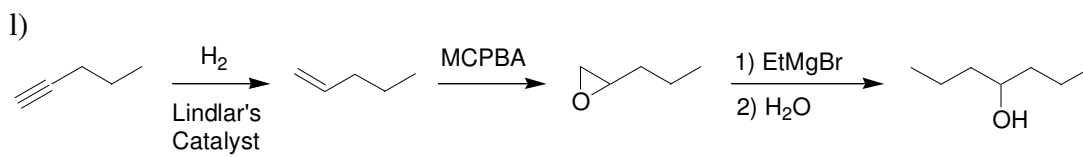
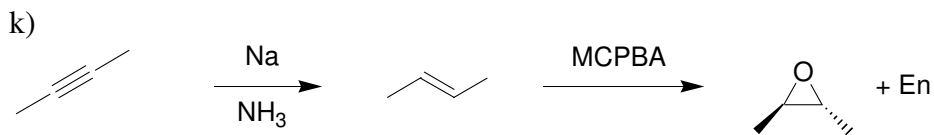
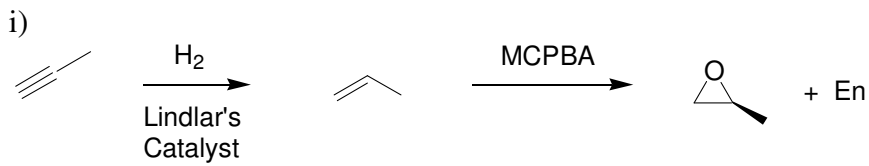
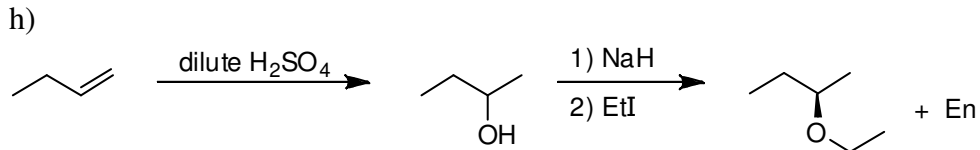


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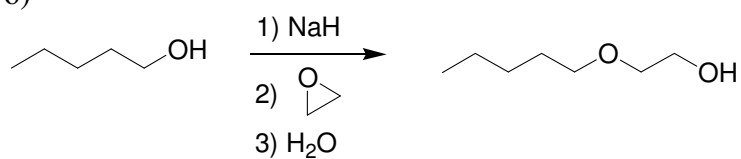


g)

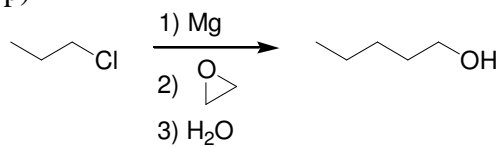




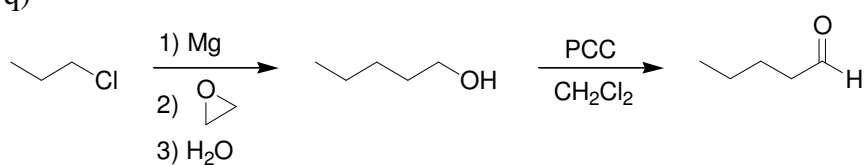
o)



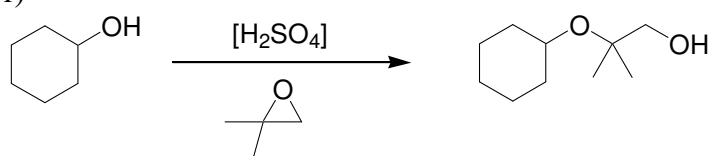
p)



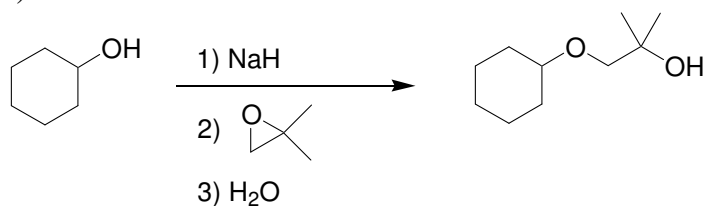
q)



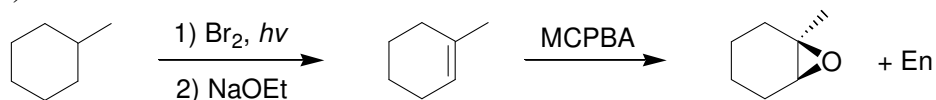
r)



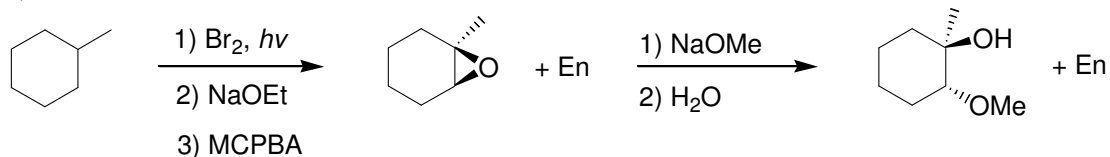
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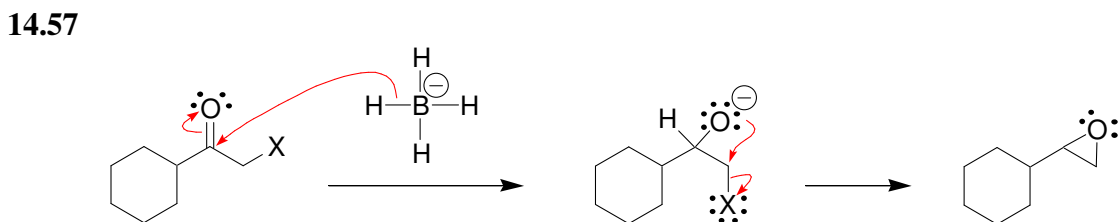
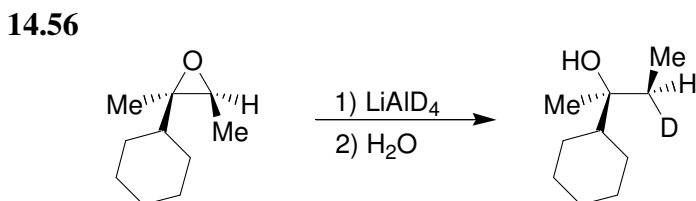
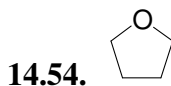
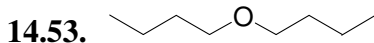
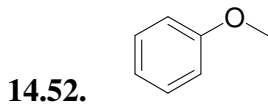


t)



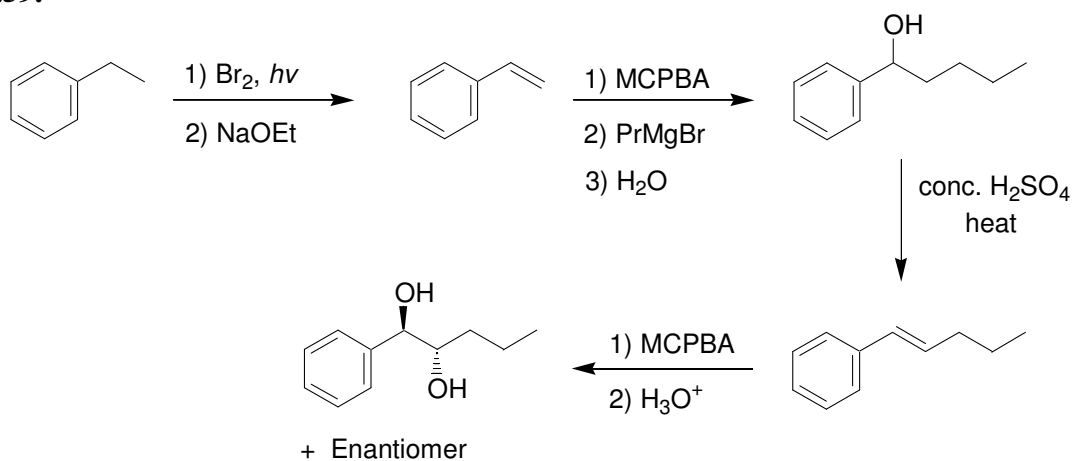
u)



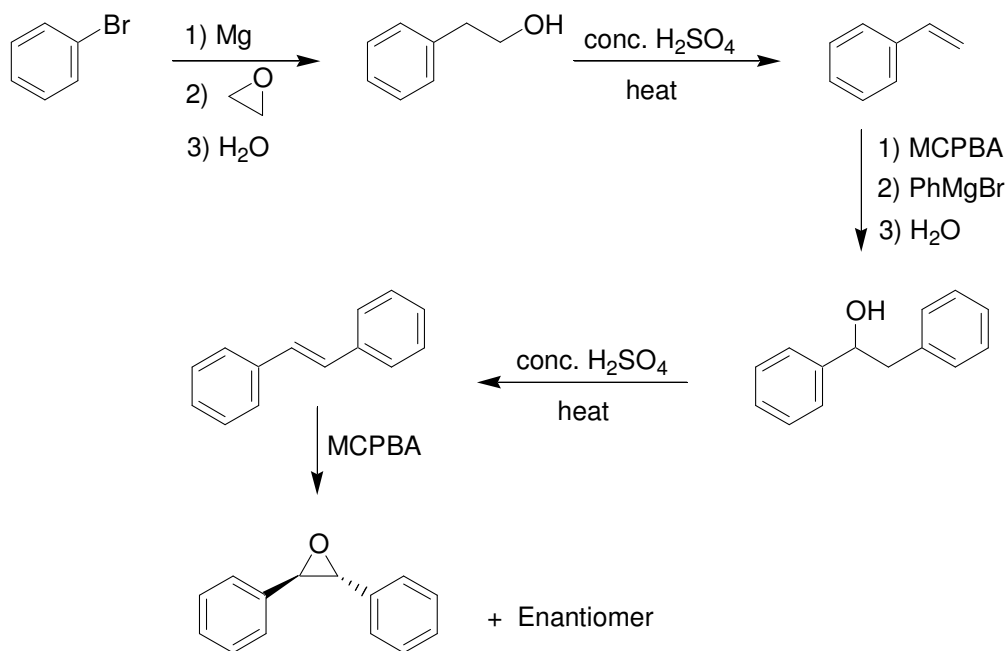


14.58 When methyloxirane is treated with HBr, the regiochemical outcome is determined by a competition between steric and electronic factors, with steric factors prevailing – the Br is positioned at the less substituted position. However, when phenyloxirane is treated with HBr, electronic factors prevail in controlling the regiochemical outcome. Specifically, the position next to the phenyl group is a benzylic position and can stabilize a large partial positive charge. In such a case, electronic factors are more powerful than steric factors, and the Br is positioned at the more substituted position.

14.59.



14.60



14.61 Since the Grignard reagent is both a strong base and a strong nucleophile, substitution and elimination can both occur. Indeed, they compete with each other. As we discussed in Chapter 8, elimination will be favored when the substrate is secondary. Both electrophilic positions in this epoxide are secondary, and so, elimination predominates:

