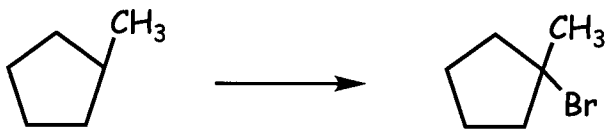
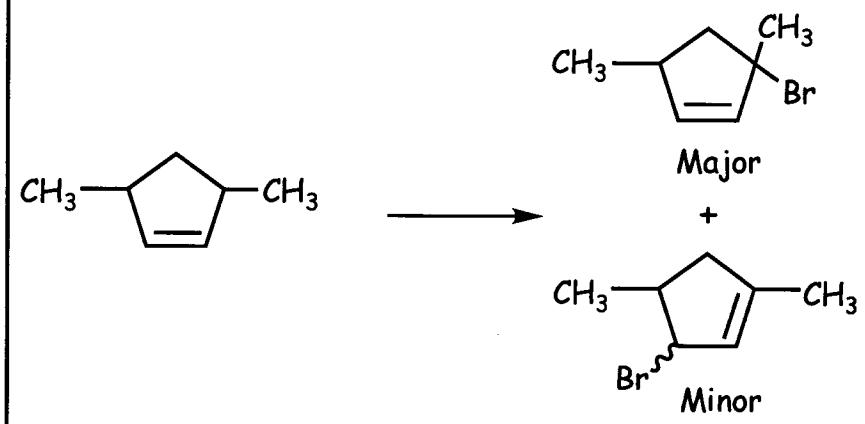
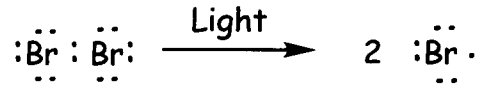
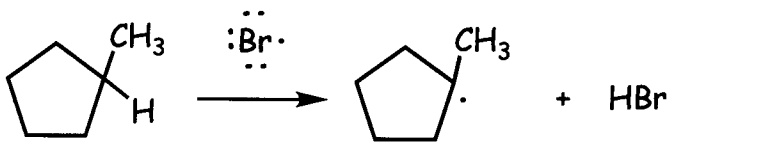




Answer: Br_2, Light





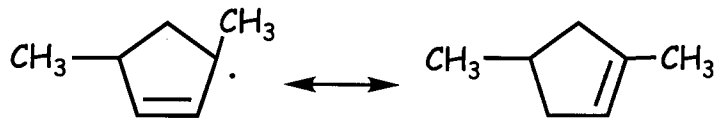
Br_2

Product

3° radical more stable

Answer: NBS (*N*-bromosuccinimide)

via

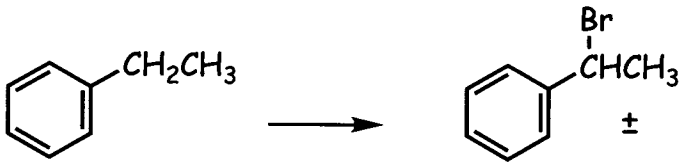


3°, allylic

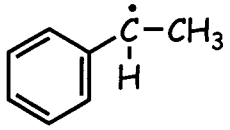
2°, allylic

Note: NBS is preferable to Br_2, light since it produces Br_2 in low concentration as the reaction progresses:

NBS + HBr ⟶ Br_2 + Succinimide

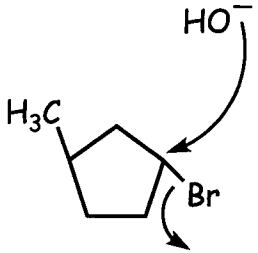


Answer: Br_2, Light

via 

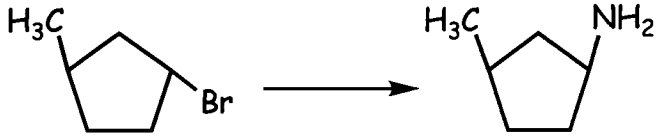
resonance stabilized benzylic radical

Answer: NaOH

via 

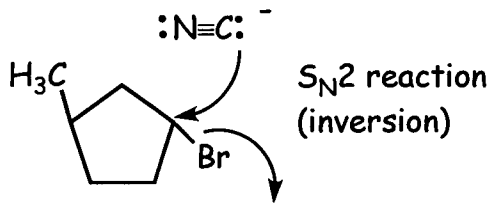
S_N2 reaction (inversion)

Note: An alcohol such as CH_3OH is frequently used as the solvent but water can be used if the starting material is soluble.



Answer: NaCN, acetone

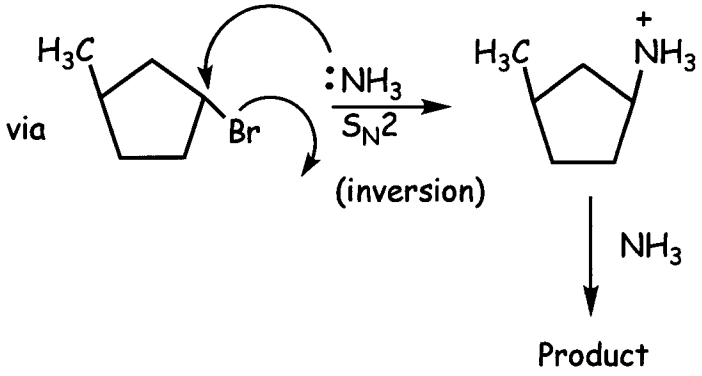
via

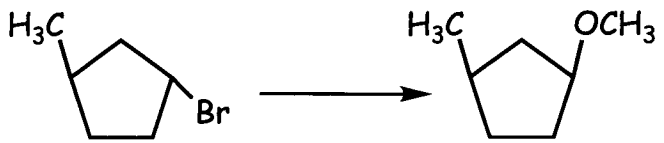


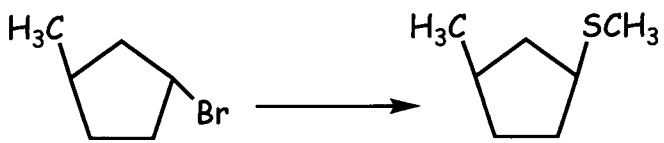
S_N2 reaction (inversion)

Note: Acetone ($CH_3\overset{O}{\overset{\|}{C}}CH_3$) is frequently used as a solvent in S_N2 reactions.

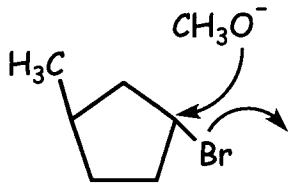
Answer: NH_3 (excess)







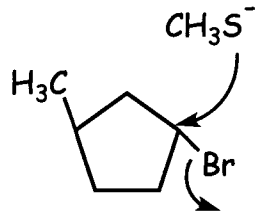
Answer: $NaOCH_3$, CH_3OH (Williamson ether synthesis)

via 

S_N2 reaction (inversion)

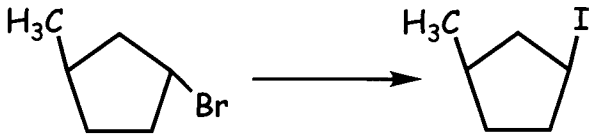
Note: Elimination occurs to a significant extent with 2° halides.

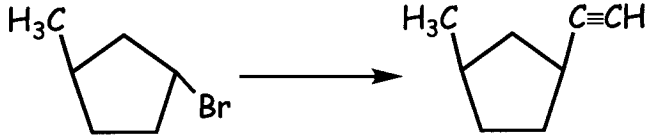
Answer: $NaSCH_3$, CH_3OH
(Williamson thioether synthesis)

via 

S_N2 reaction (inversion)

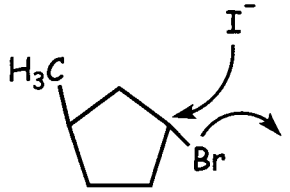
Note: An alcohol such as CH_3OH is frequently used as the solvent.





Answer: NaI, acetone

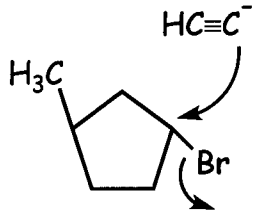
via



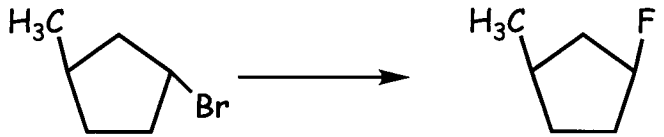
S_N2 reaction
(inversion)

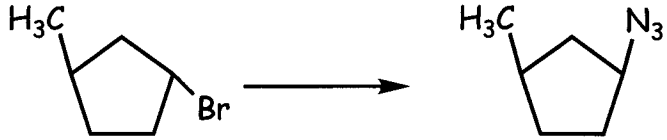
Answer: $HC\equiv C^-Li^+$

via



S_N2 reaction
(inversion)

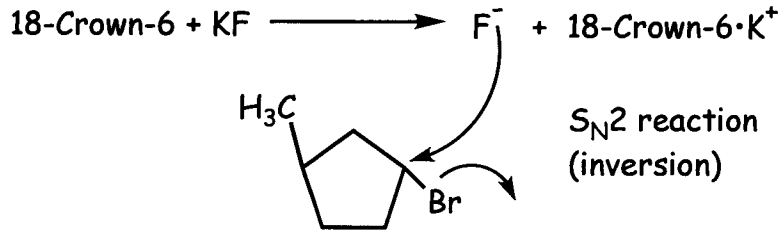




an alkyl azide

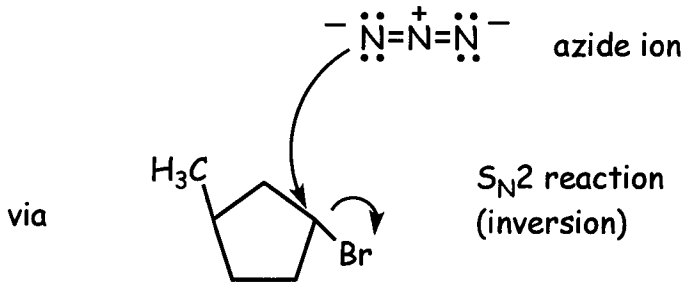
Answer: KF, 18-Crown-6, CH_3CN

via

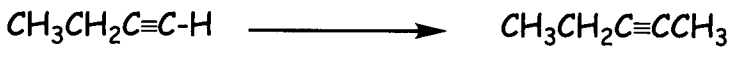


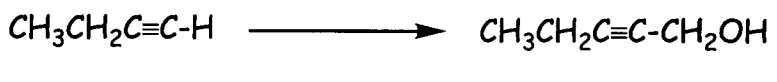
Note: CH_3CN is used as the solvent.

Answer: NaN_3, acetone

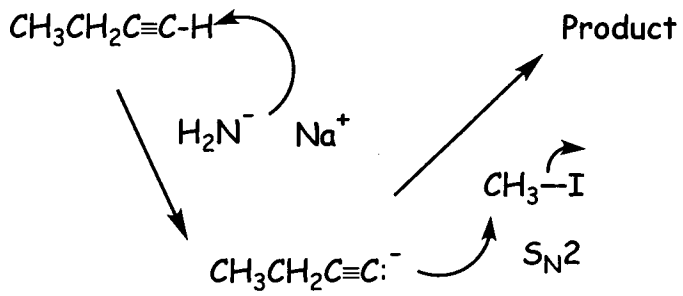


Note: Acetone is used as the solvent.



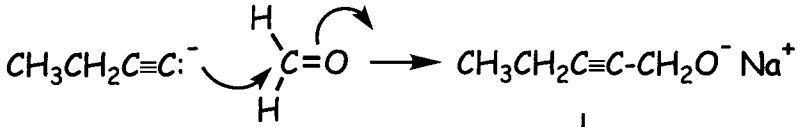


Answer: 1. $NaNH_2$, 2. CH_3I



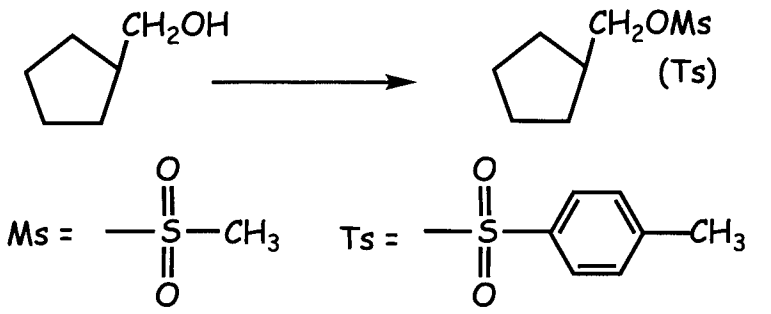
Answer: 1. $NaNH_2$, 2. $H_2C{=}O$, 3. Acidify

via

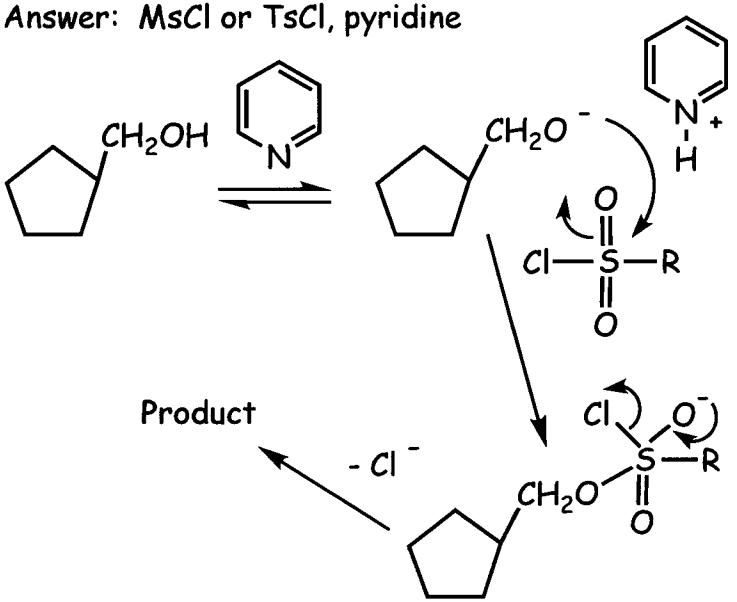


Acidify

Product

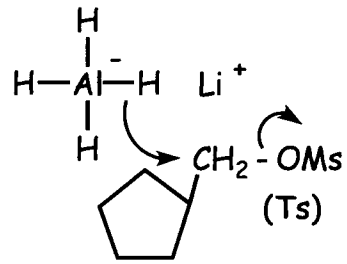


Answer: MsCl or TsCl, pyridine



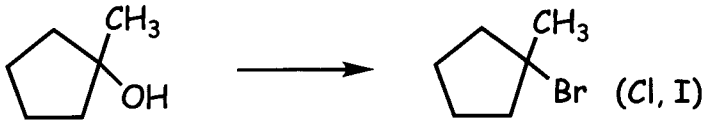
Answer: 1. $LiAlH_4$, 2. Acidify

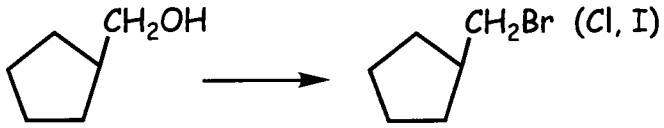
via



S_N2 reaction

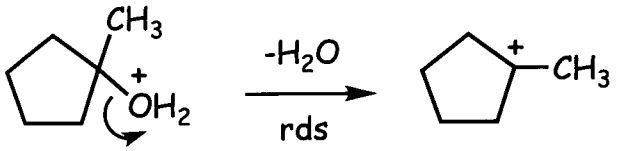
Note: Tosyl and mesyl esters are good leaving groups in other S_N2 reactions.





Answer: HBr or HCl or HI

via

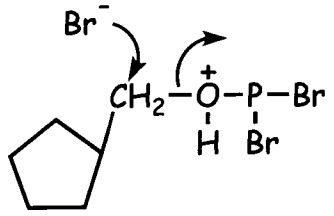


Br^- or Cl^- or I^-

Product

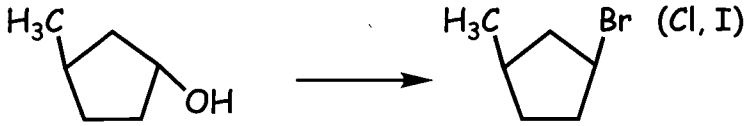
Answer: PBr_3 or PCl_3 or P/I_2

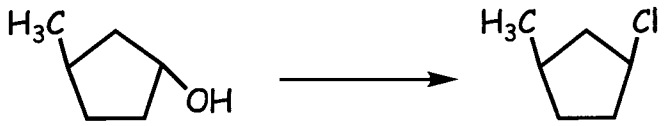
via



S_N2 reaction

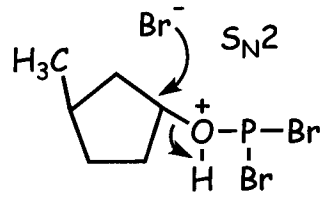
Note: P/I_2 generates PI_3 (unstable) *in situ*





Answer: PBr_3 or PCl_3 or P/I_2

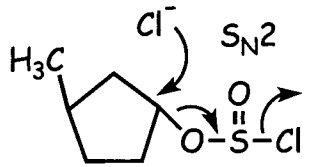
via



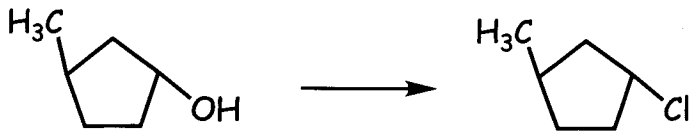
Note: S_N2 reaction; P/I_2 generates PI_3 *in situ*

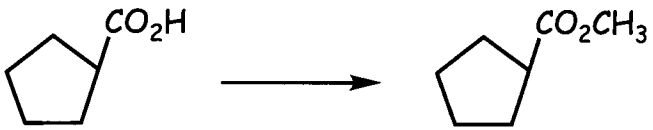
Answer: $SOCl_2$ (neat, no solvent)

via

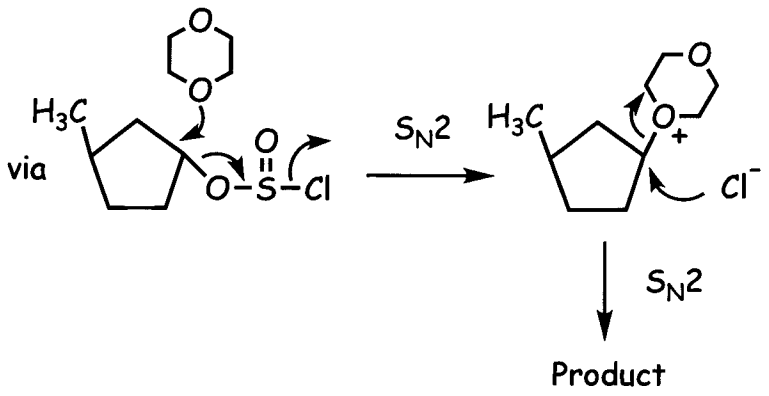


Note: S_N2 reaction; non-nucleophilic solvents (e.g. benzene) can also be used.



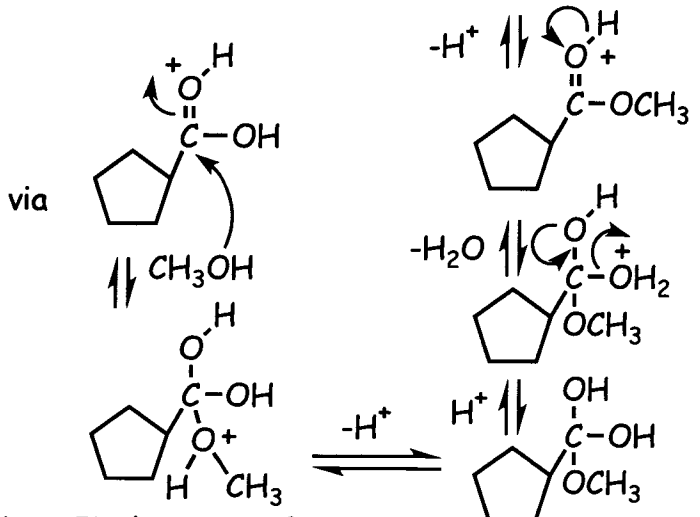


Answer: $SOCl_2$, dioxane

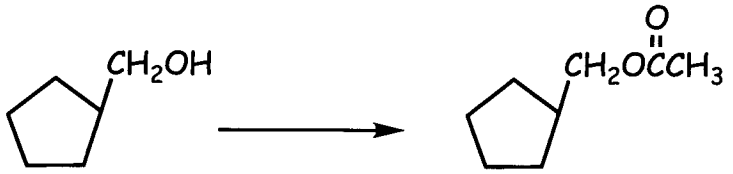


Note: Double inversion gives overall retention.

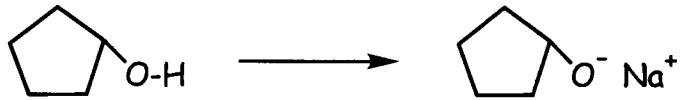
Answer: CH_3OH, H_2SO_4



Note: Fischer esterification

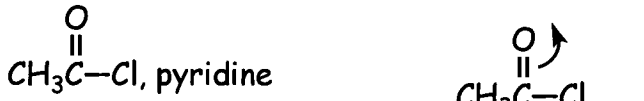


 R23

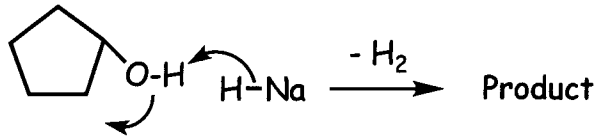


 R24

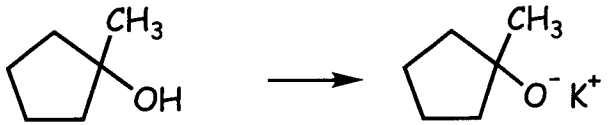
Answer:

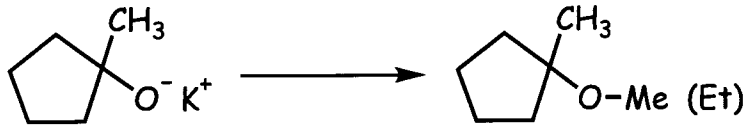


Answer: Na or NaH

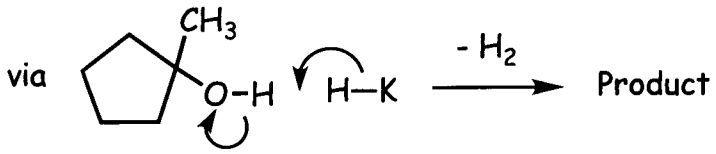


Note: Sodium metal and NaH deprotonate 1° or 2° alcohols but 3° alcohols react very slowly. Potassium metal is used for 3° alcohols.



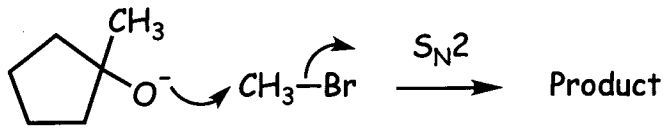


Answer: K or KH



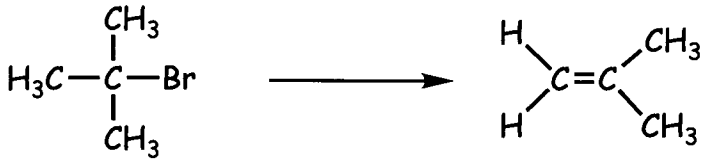
Note: Potassium metal or KH used to deprotonate 3° alcohols

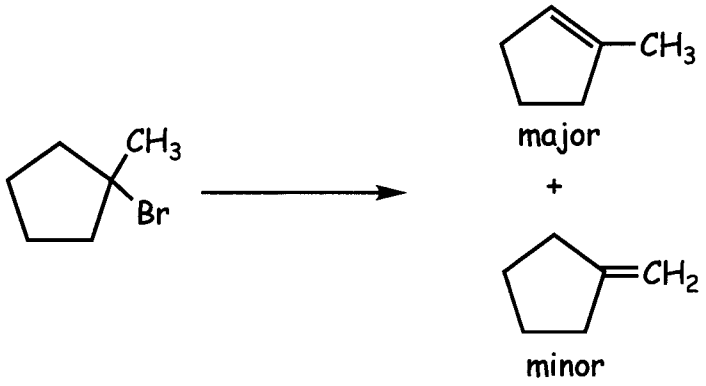
Answer: CH_3Br or CH_3CH_2Br



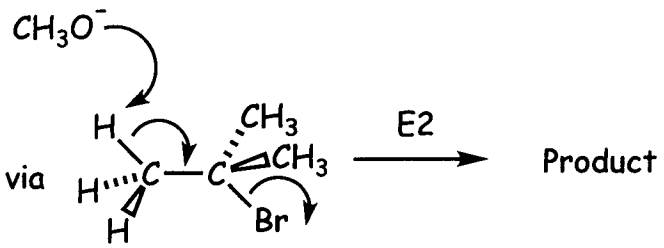
Williamson ether synthesis

Note: Methyl or 1° alkyl halides or tosylates (mesylates) must be used as the electrophile, otherwise elimination (E2) usually occurs.





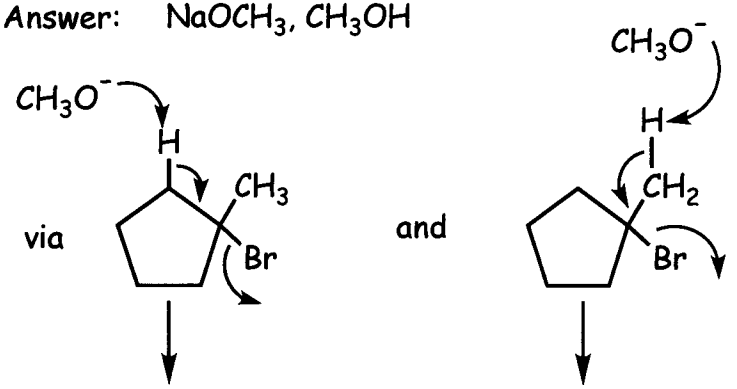
Answer: $NaOCH_3$, CH_3OH



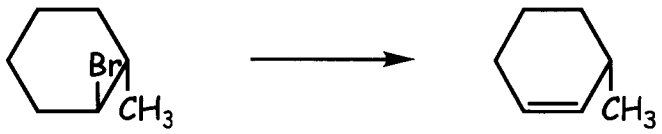
Product

Note: E2 reaction; 3° halide does not undergo S_N2 reaction.

Answer: $NaOCH_3$, CH_3OH

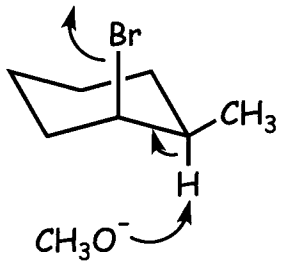


Note: E2 reaction; 3° halide does not undergo S_N2 reaction.



Answer: $NaOCH_3$, CH_3OH

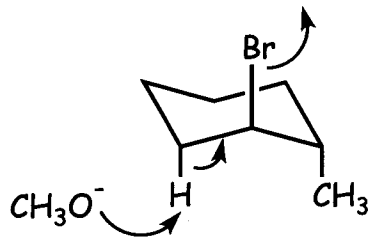
via



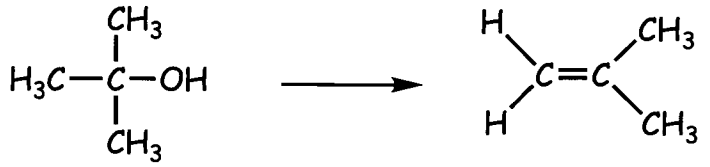
Note: E2 reaction; H and Br must be anticoplanar in the transition state. The most highly substituted alkene is the major product.

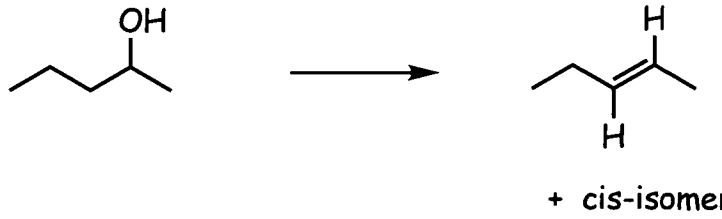
Answer: $NaOCH_3$, CH_3OH

via



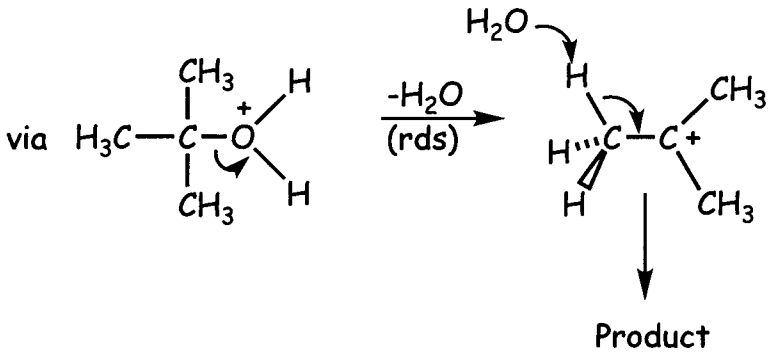
Note: Anticoplanar transition state. The most highly substituted alkene (see product in R29) cannot be formed.





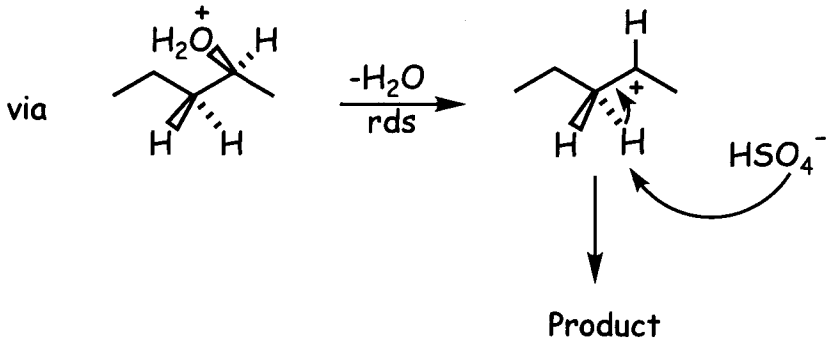
+ cis-isomer

Answer: H_2SO_4 or H_3PO_4 , heat

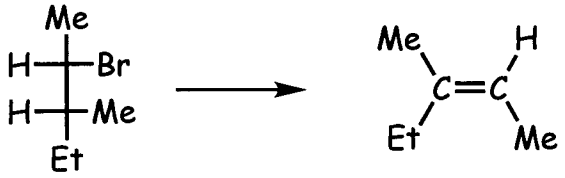


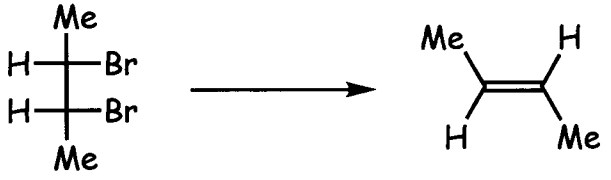
Note: A strong acid is required to protonate the alcohol.

Answer: H_2SO_4 or H_3PO_4 , heat

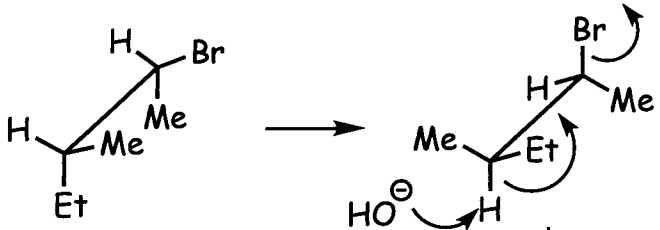


Note: E1 reaction; Saytzeff product predominates. The trans alkene is more stable.



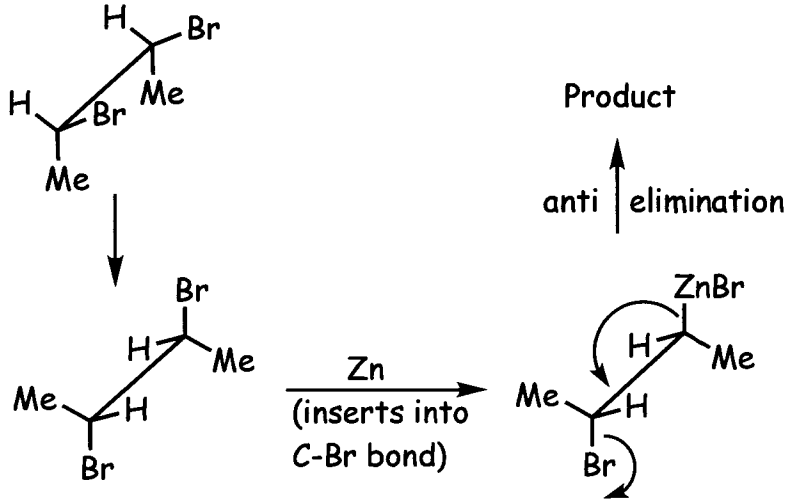


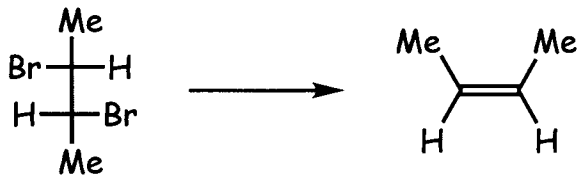
Answer: KOH, heat

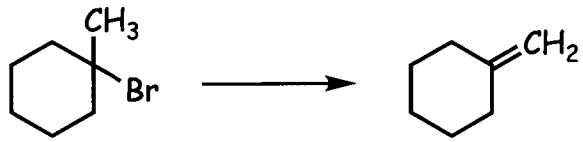


Note: Anticoplanar T.S. for E2 Rxn; β branching favors elimination over substitution.

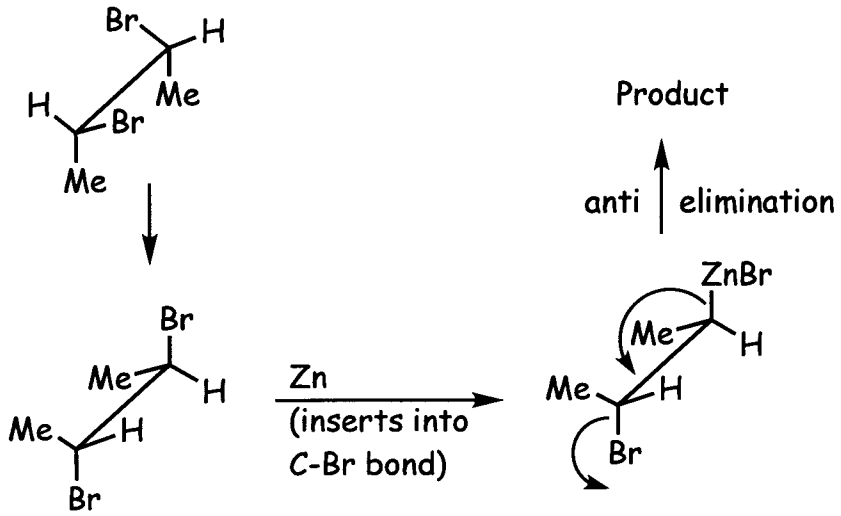
Answer: Zn, CH_3CO_2H or NaI in acetone





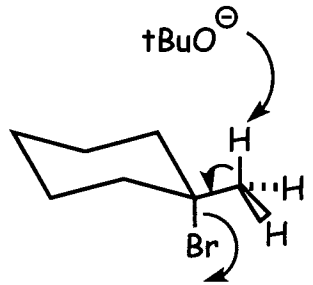


Answer: Zn, CH_3CO_2H or NaI in acetone

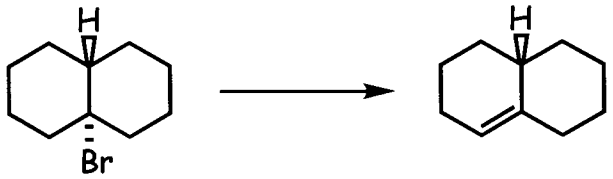


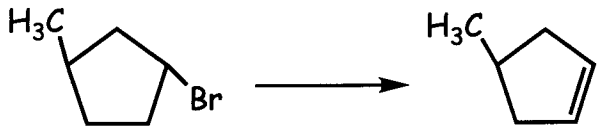
Answer: tBuOK in tBuOH

via

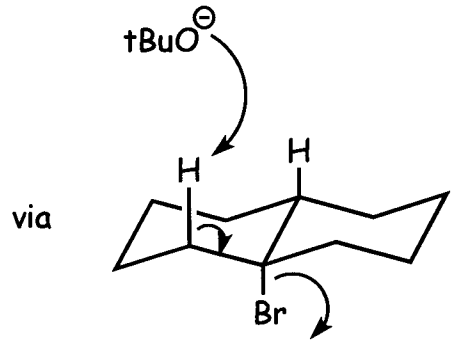


Note: Hindered base favors Hofmann product (E2 reaction).



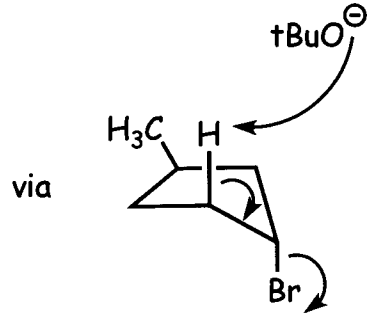


Answer: tBuOK in tBuOH

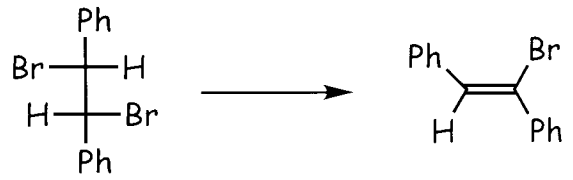


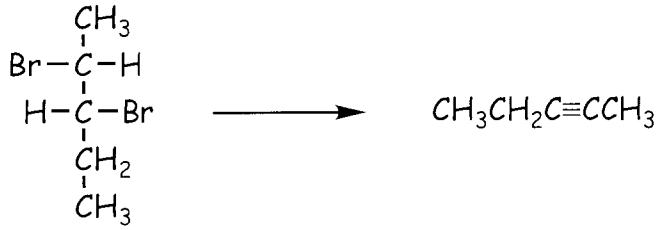
Note: Hindered base favors Hofmann product.

Answer: tBuOK in tBuOH

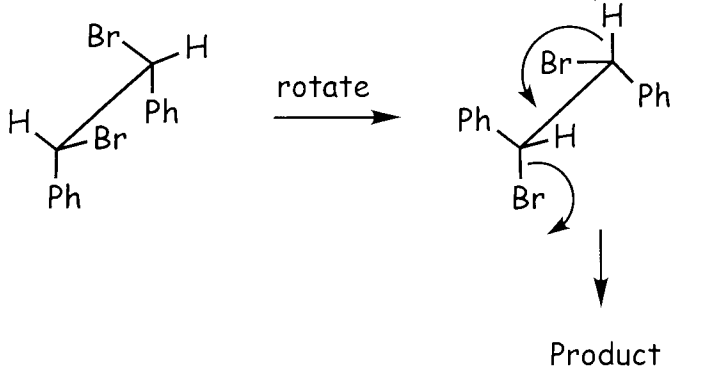


Note: Hindered base gives E2 product rather than S_N2 product (see S7); abstraction of H farthest from methyl group favored.



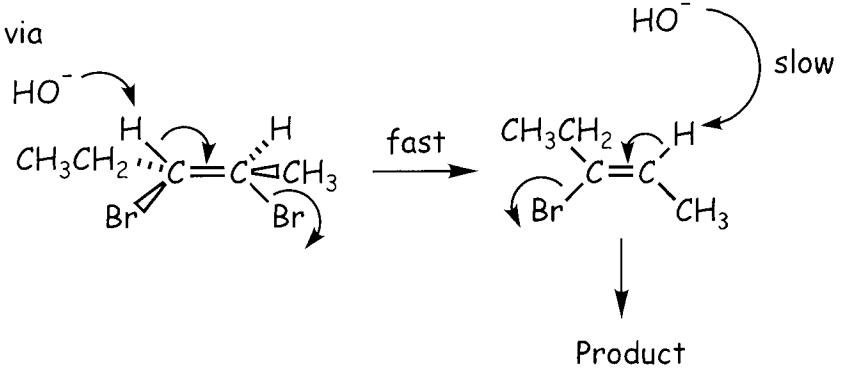


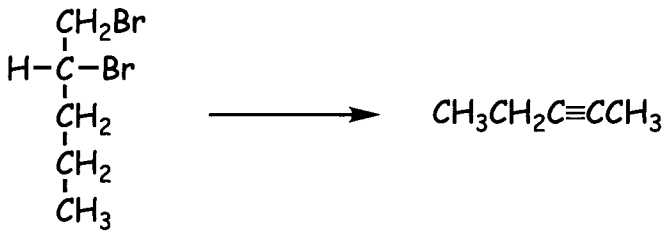
Answer: Et_3N, heat



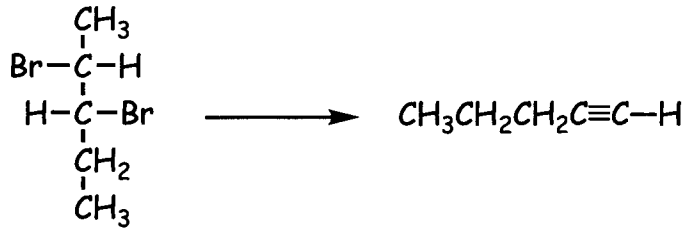
Note: The vicinal dibromide undergoes E2 *dehydrohalogenation* when treated with a hindered base.

Answer: KOH (fused), 200 °C



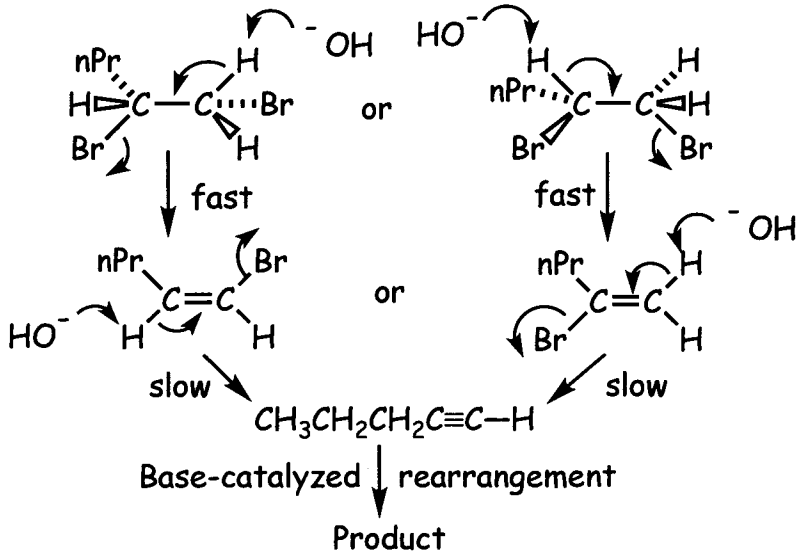


$CH_3CH_2C{\equiv}CCH_3$

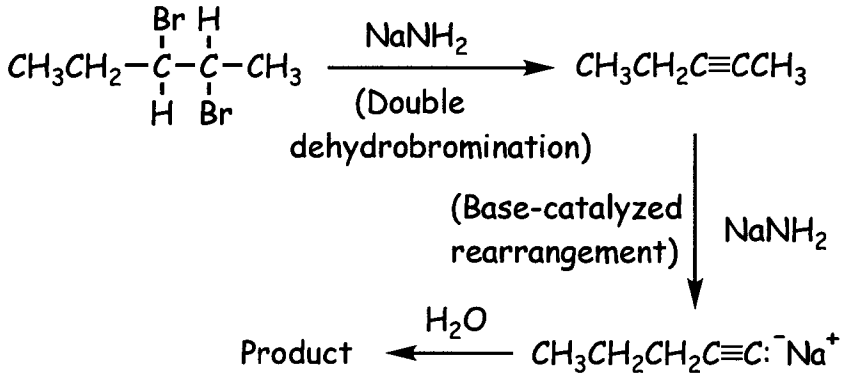


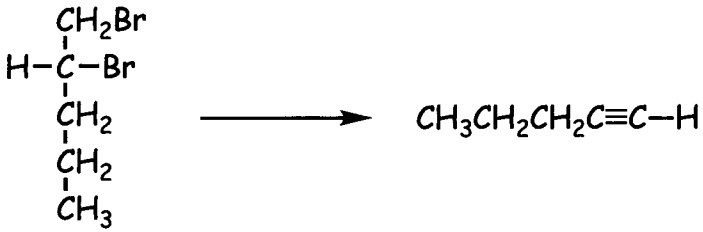
$CH_3CH_2CH_2C{\equiv}C{-}H$

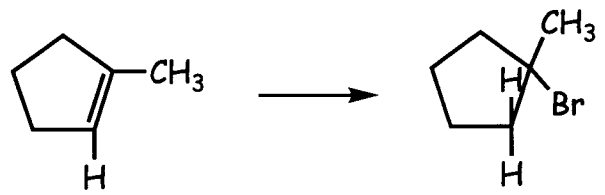
Answer: KOH (fused), 200 °C



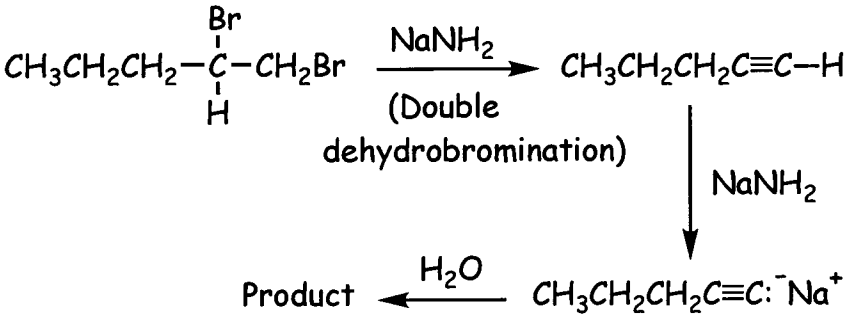
Answer: 1. $NaNH_2$, heat 2. H_2O



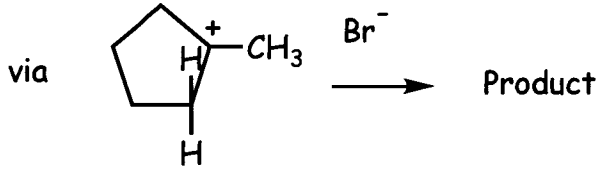




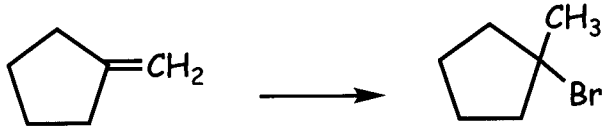
Answer: 1. $NaNH_2$, heat 2. H_2O

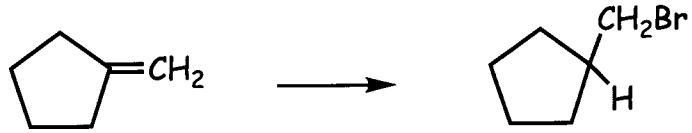


Answer: HBr

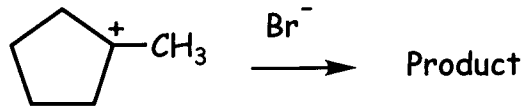


Note: Markovnikov addition



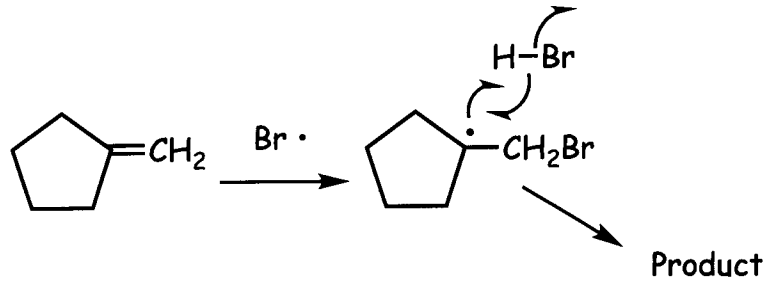


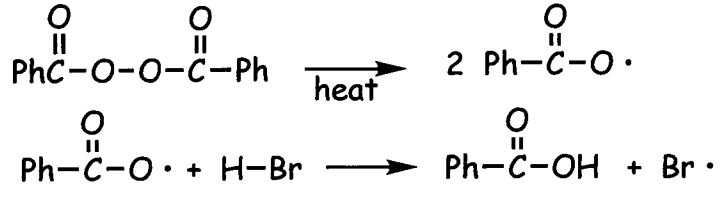
Answer: HBr

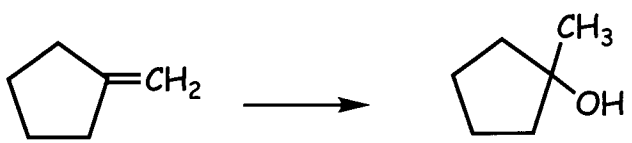
via 

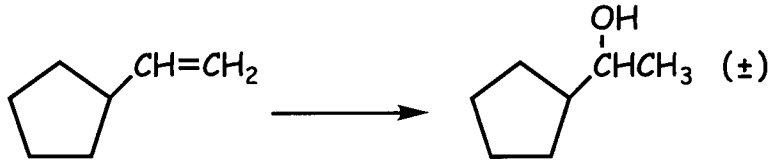
Note: Markovnikov addition

Answer: HBr, -78° + $(PhCO_2)_2$ or $(MeCO_2)_2$

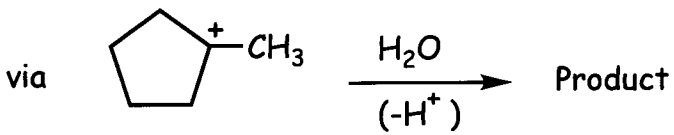






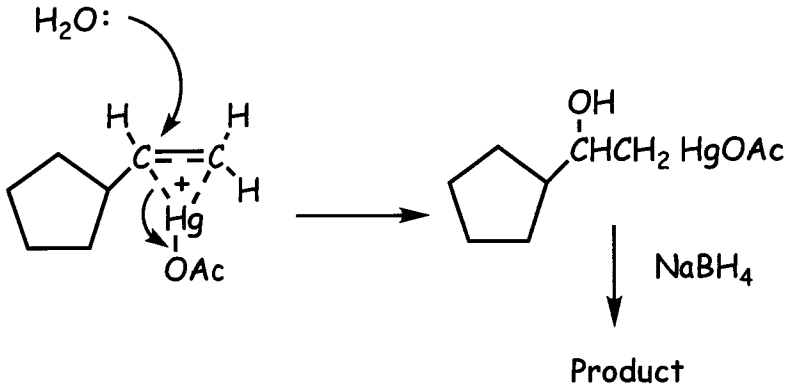


Answer: H_2O, H_2SO_4

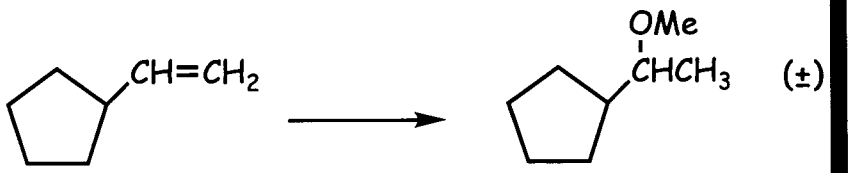


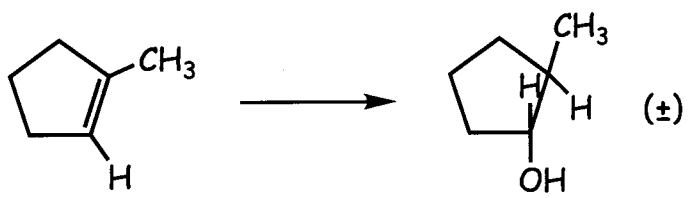
Note: Markovnikov addition

Answer: 1. $Hg(OAc)_2$, H_2O 2. $NaBH_4$

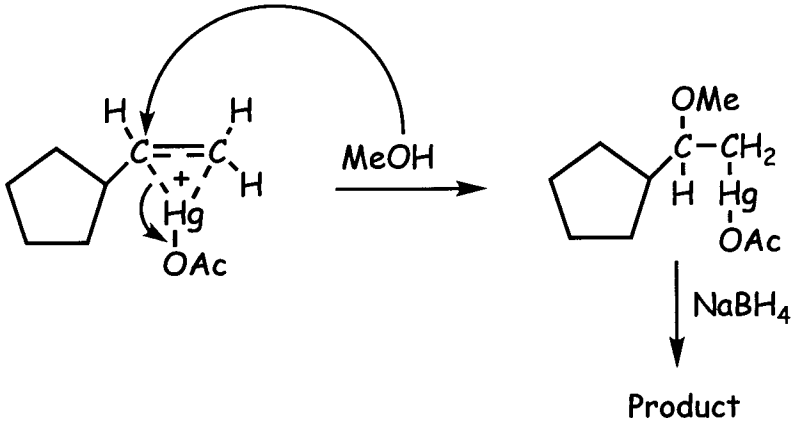


Note: Hydroxymercuration/demercuration



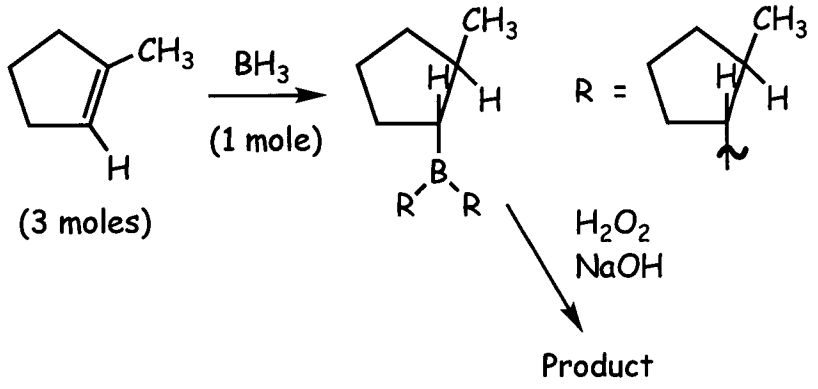


Answer: 1. $Hg(OAc)_2$, MeOH 2. $NaBH_4$

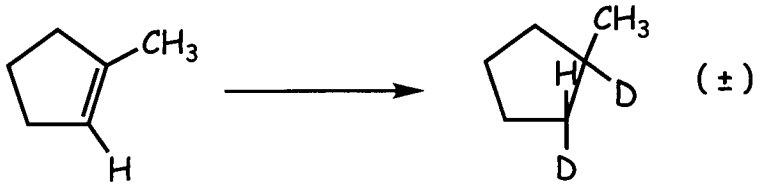


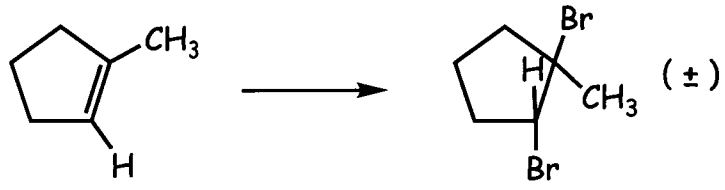
Note: Alkoxymercuration/demercuration

Answer: 1. B_2H_6 or $THF{\cdot}BH_3$ 2. H_2O_2, NaOH



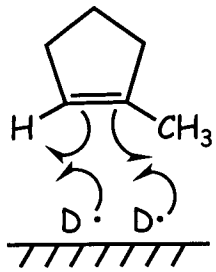
Note: Hydroboration/oxidation - syn addition





Answer: D_2, Pt or Pd/C or Raney Ni

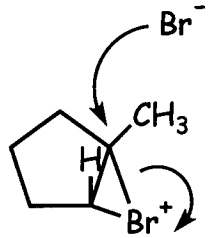
via



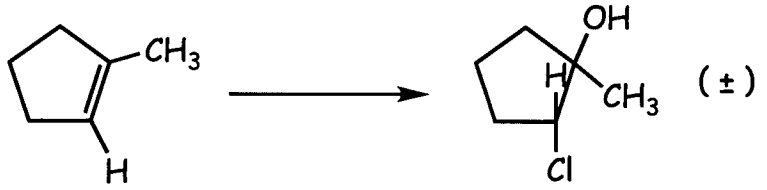
Note: Catalytic hydrogenation - syn addition

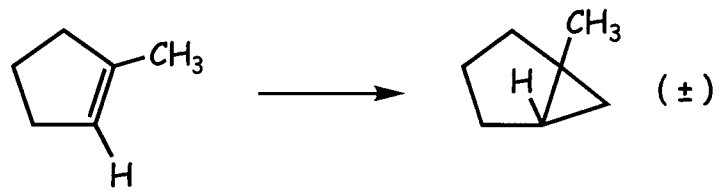
Answer: Br_2 in CCl_4

via

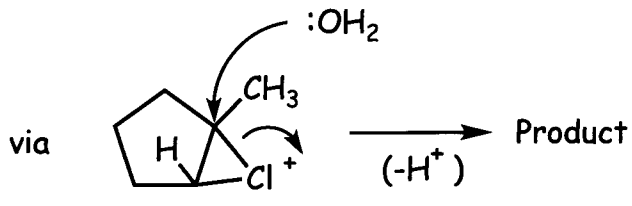


Note: Bromination - anti addition



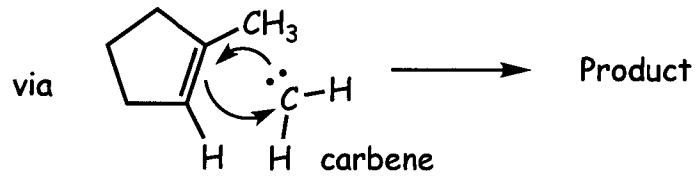


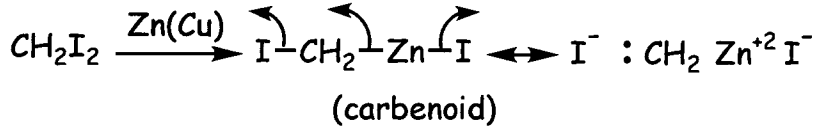
Answer: $NaOCl, HCl, H_2O$ (HOCl)

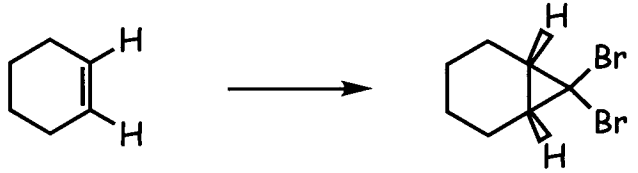


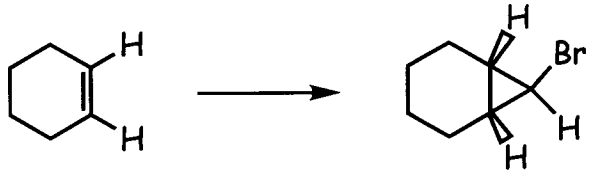
Note: Hydrochlorination - anti addition (Markovnikov)

Answer: CH_2I_2, Zn(Cu)

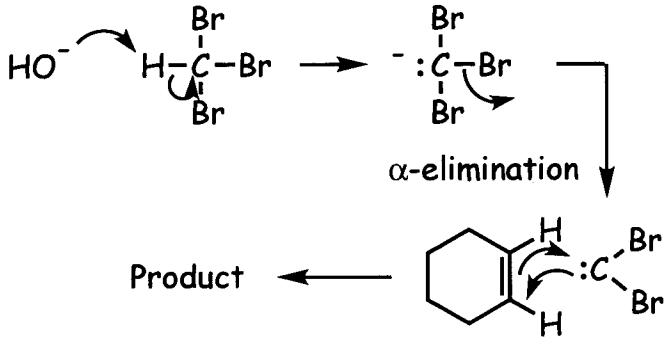






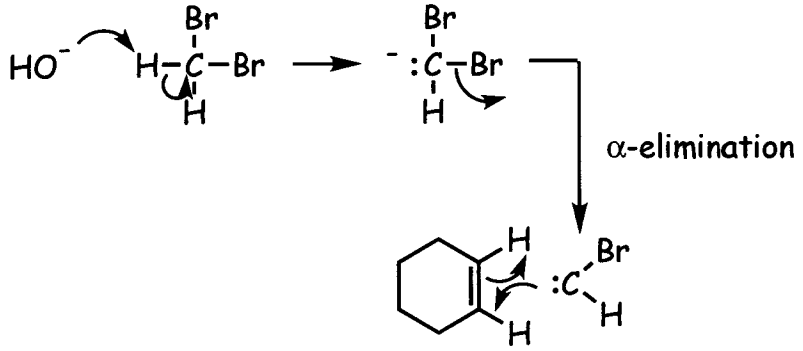


Answer: $CHBr_3$, KOH

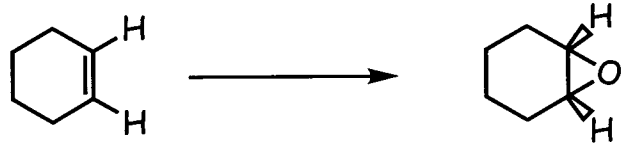


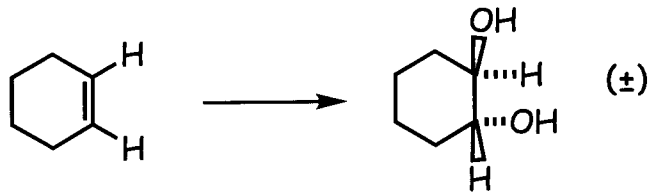
Note: Dibromocarbene is the electrophile

Answer: CH_2Br_2, NaOH

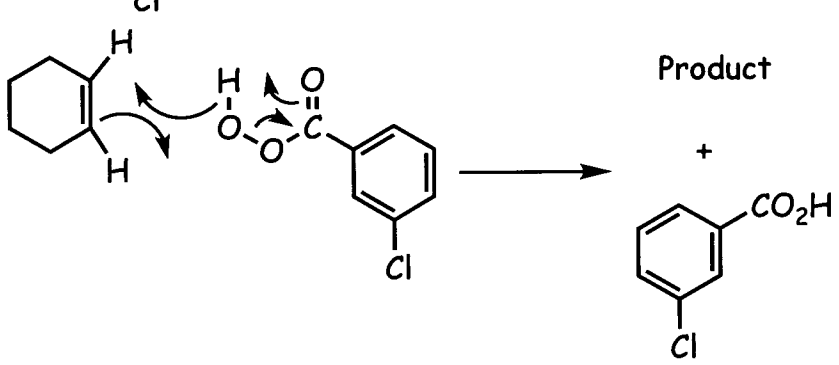


Note: Bromocarbene is the electrophile



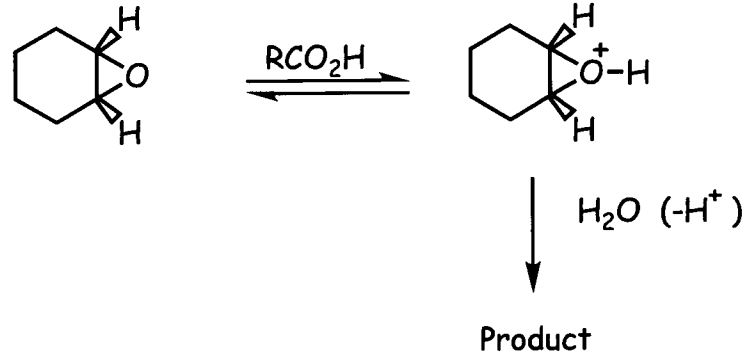


Answer: CO_3H (MCPBA) in dioxane

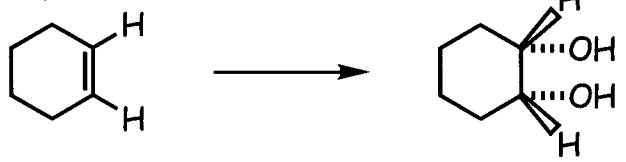


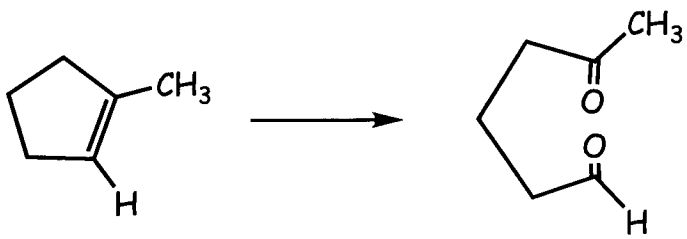
Note: Epoxidation reaction

Answer: RCO_3H (R = H, CH_3), H_2O

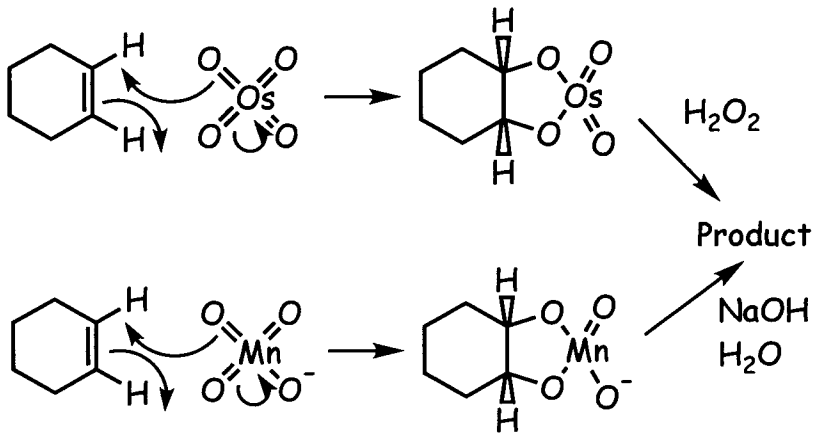


Note: Epoxidation followed by hydrolysis of the oxirane (anti-hydroxylation)



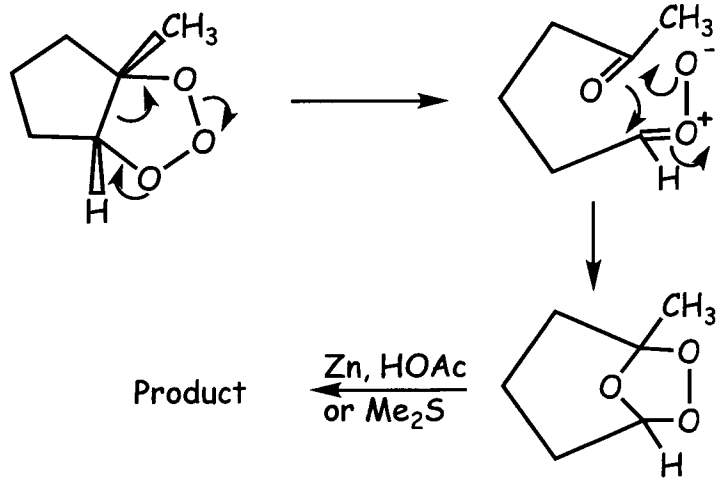


Answer: cat. OsO_4 , H_2O_2 or dil. $KMnO_4$, NaOH, H_2O

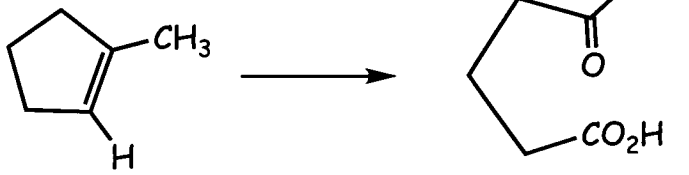


Note: syn-hydroxylation

Answer: 1. O_3 2. Zn, HOAc or Me_2S

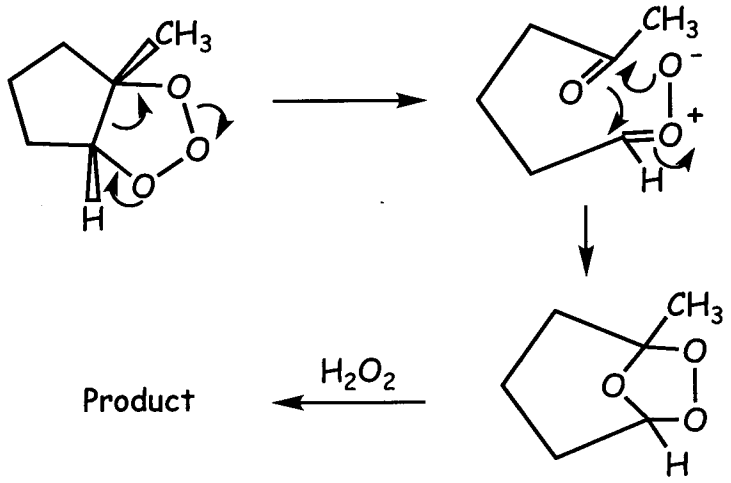


Note: Reductive Ozonolysis



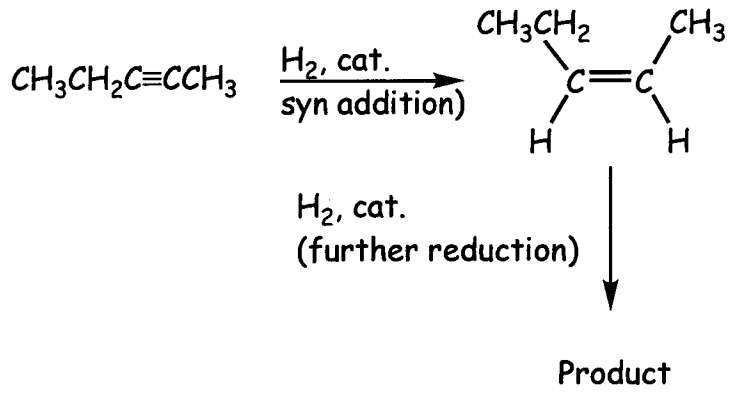
$CH_3CH_2C{\equiv}CCH_3 \longrightarrow CH_3CH_2CH_2CH_2CH_3$

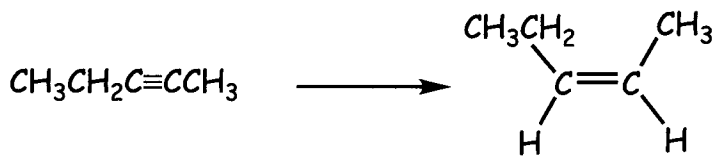
Answer: 1. O_3 2. H_2O_2

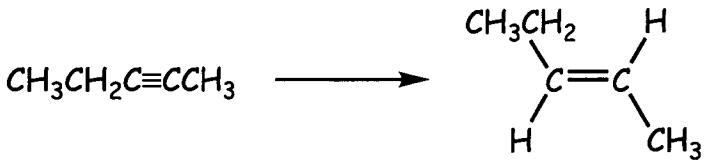


Note: Oxidative ozonolysis

Answer: H_2 , Pt or Pd or Ni







Answer: H_2 , $Pd/BaSO_4$, Quinoline

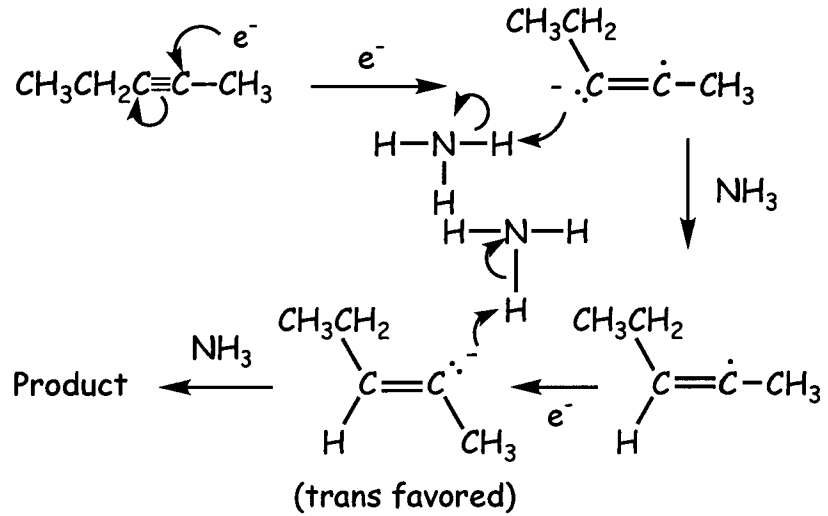
$CH_3CH_2C{\equiv}CCH_3$

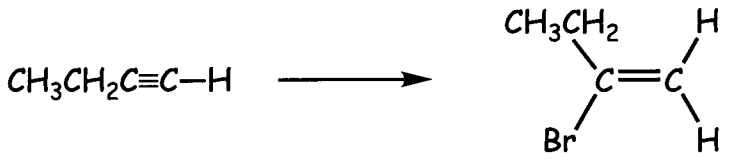
H_2, Lindlar's catalyst
(syn-addition)

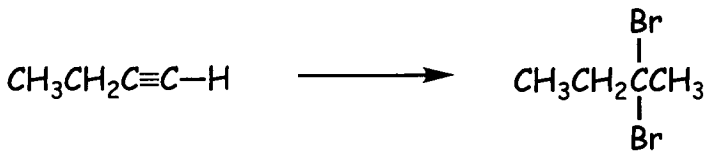
Product

Note: Lindlar's catalyst can reduce alkynes to alkenes but can not reduce alkenes (poisoned catalyst).

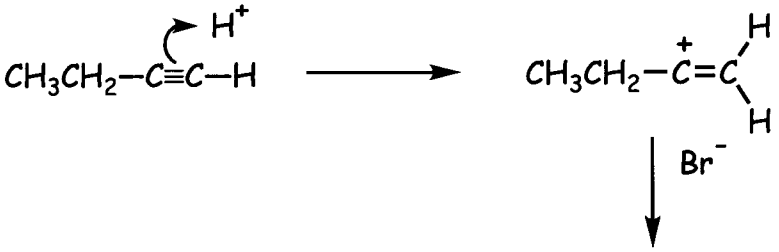
Answer: Na , NH_3 (liq) , very cold





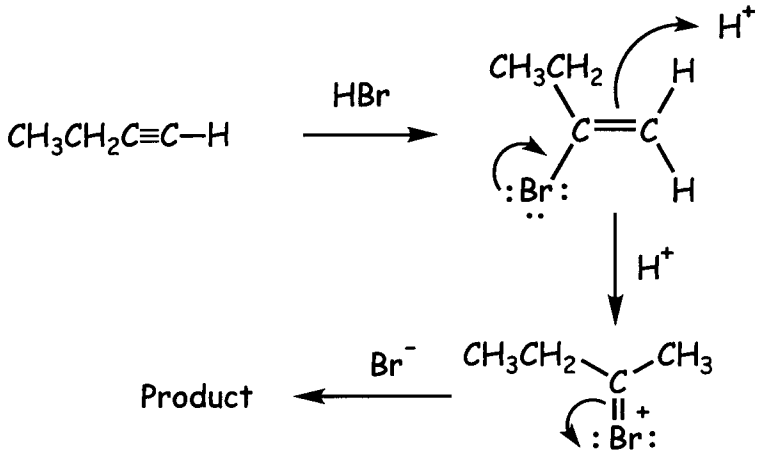


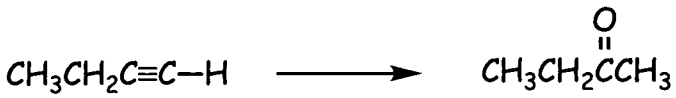
Answer: HBr, low temperature

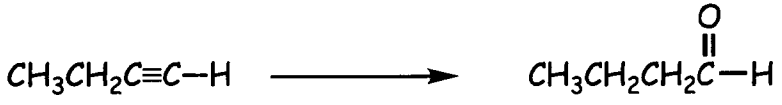


Note: Markovnikov addition

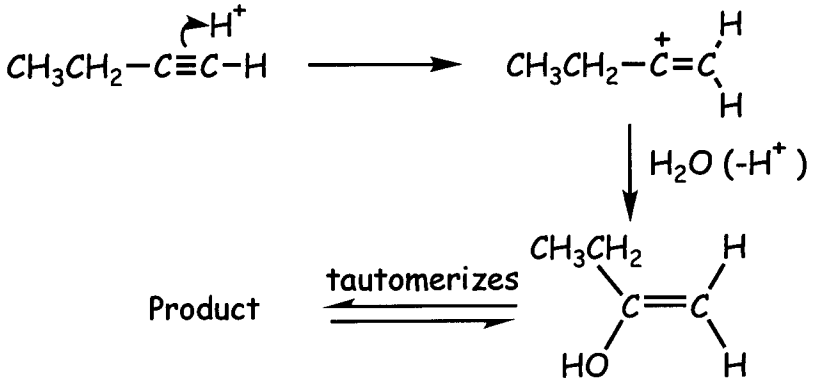
Answer: HBr, high temperature





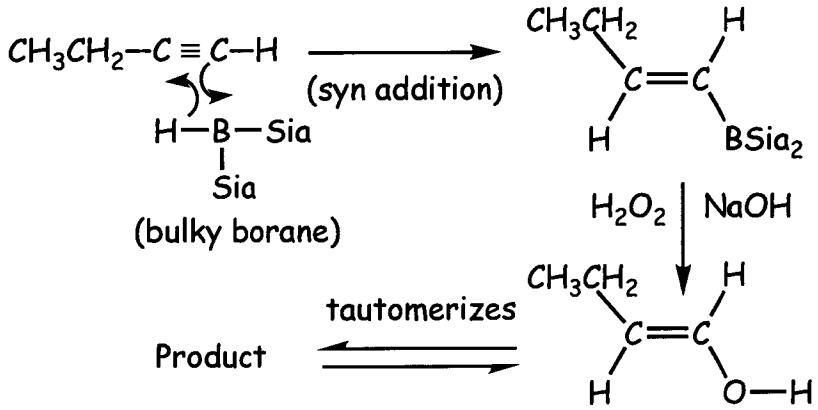


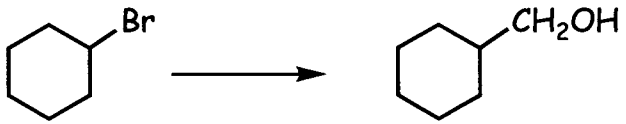
Answer: H_2O, H_2SO_4, $HgSO_4$



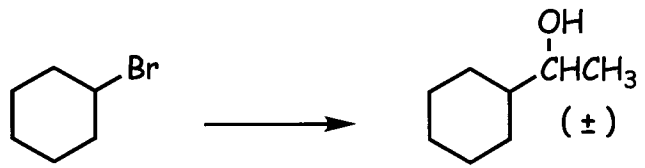
Note: Hg^{+2} catalyzes reaction; see text.

Answer: 1. Sia_2BH 2. H_2O_2, NaOH



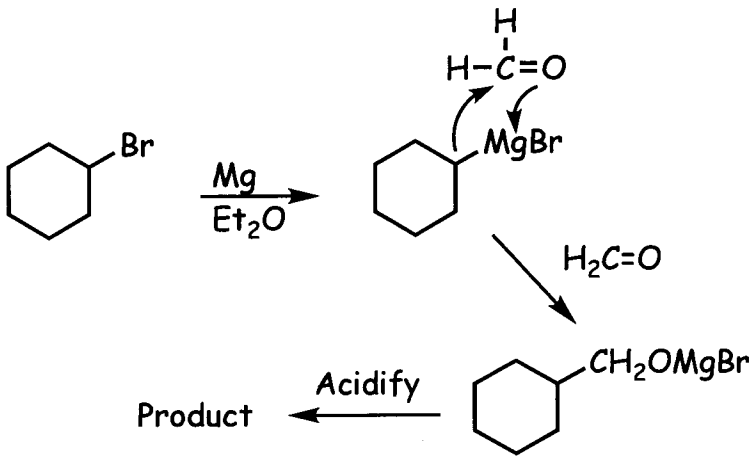


 R69

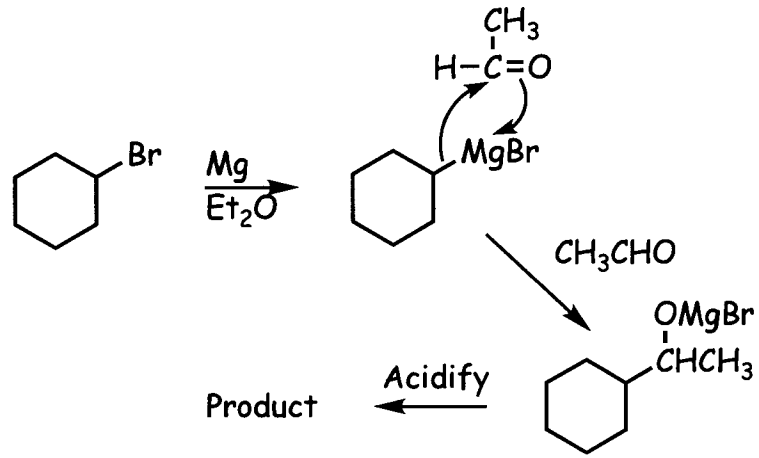


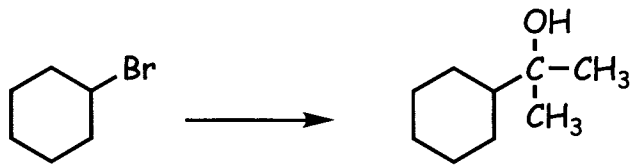
 R70

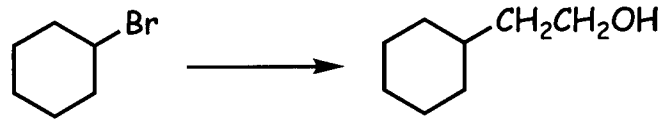
Answer: 1. Mg, Et_2O 2. $H_2C{=}O$ 3. Acidify



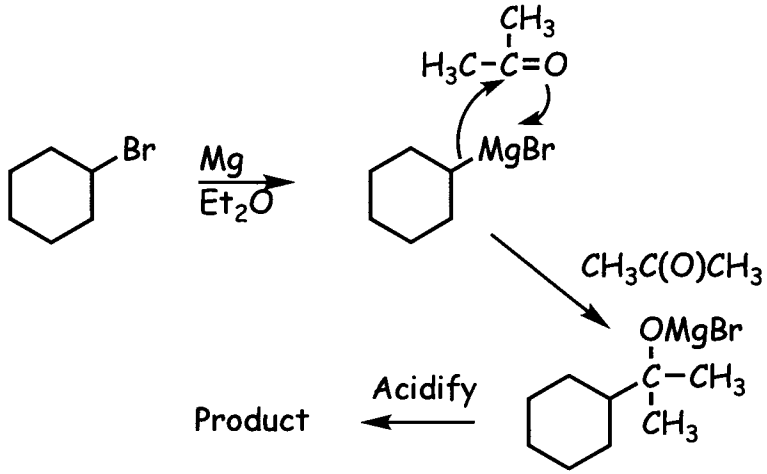
Answer: 1. Mg, Et_2O 2. CH_3CHO 3. Acidify



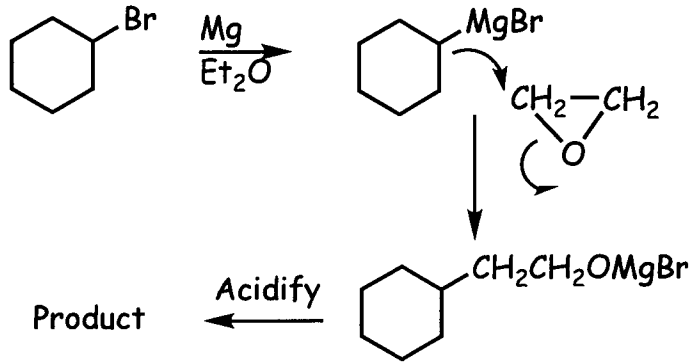


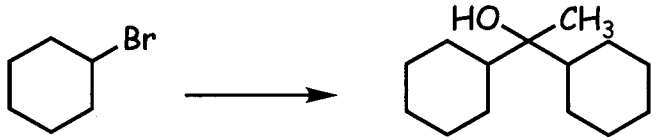


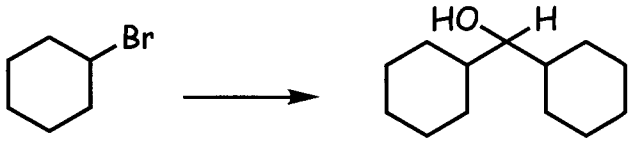
Answer: 1. Mg, Et_2O 2. $CH_3C(O)CH_3$ 3. Acidify



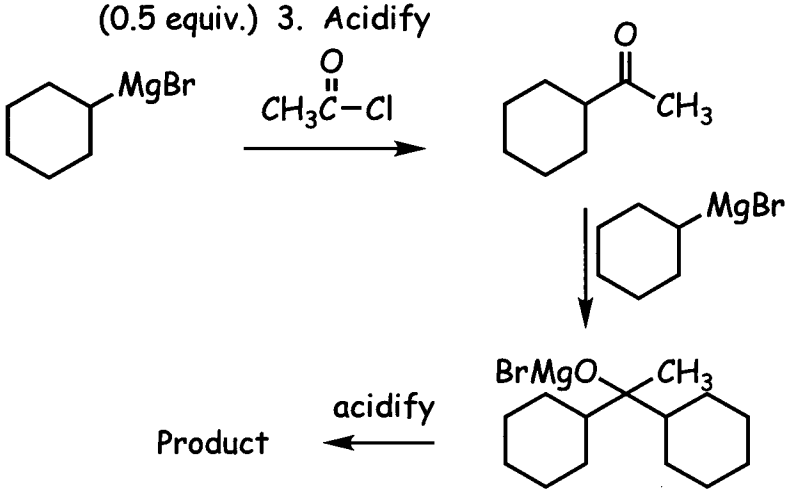
Answer: 1. Mg, Et_2O 2. $H_2C(O)CH_2$ 3. Acidify





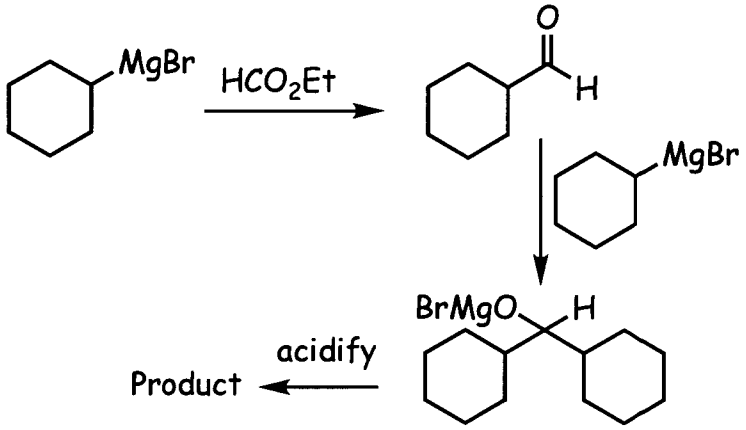


Answer: 1. Mg, Et_2O 2. CH_3COCl or CH_3CO_2Et (0.5 equiv.) 3. Acidify

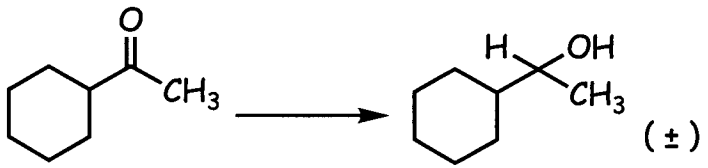


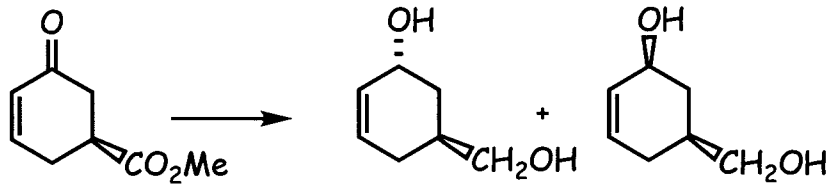
Note: See text for complete mechanism.

Answer: 1. Mg, Et_2O 2. HCO_2Et (0.5 equiv.) 3. Acidify

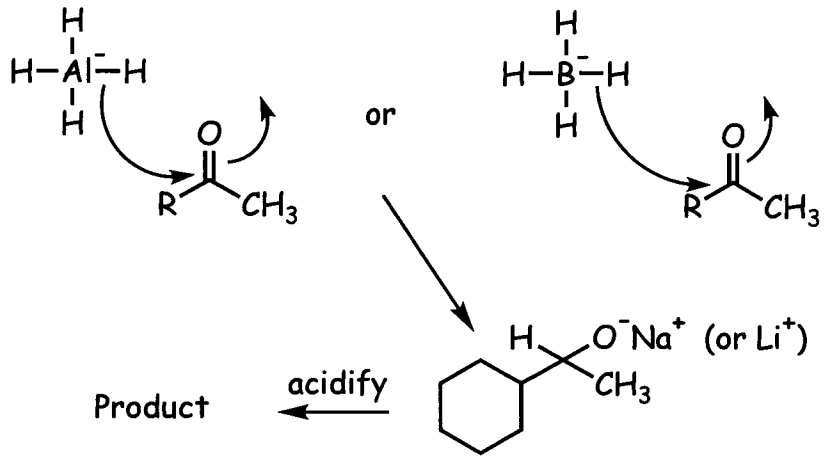


Note: See text for complete mechanism. Formyl chloride is unstable.



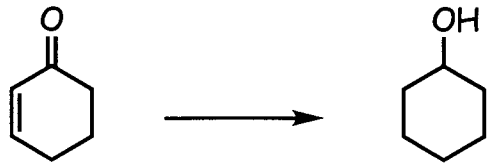


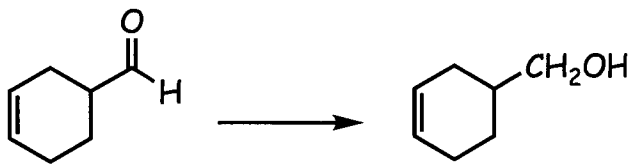
Answer: 1. $NaBH_4$ or $LiAlH_4$ 2. Acidify



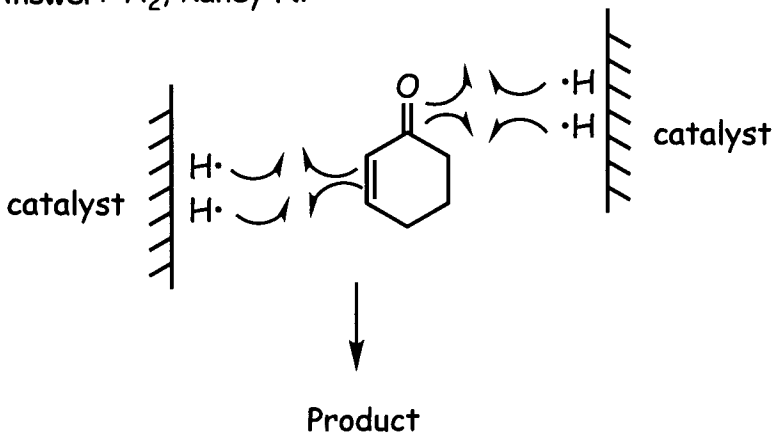
Answer: 1. $LiAlH_4$ 2. Acidify

Note: $LiAlH_4$ reduces aldehydes, ketones, and esters but not alkenes. See A 35 for complete mechanism.



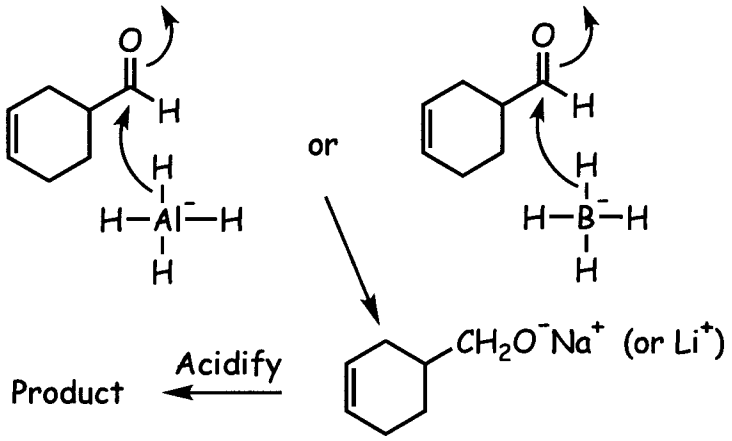


Answer: H_2, Raney Ni

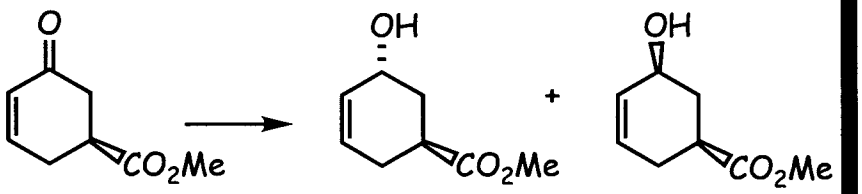


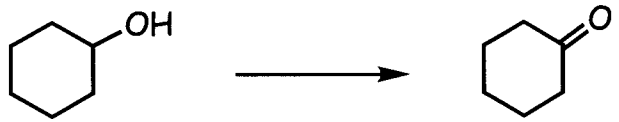
Note: Raney Ni and H_2 also reduces alkynes to alkanes.

Answer: 1. $NaBH_4$ or $LiAlH_4$ 2. Acidify

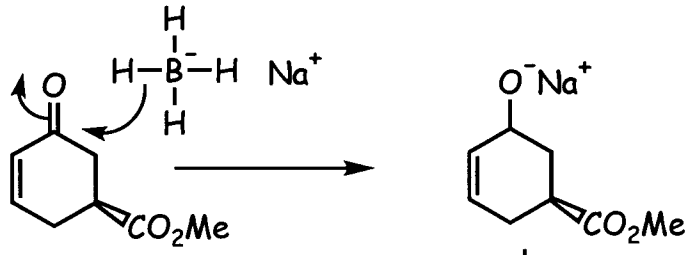


Note: Alkenes are not reduced.





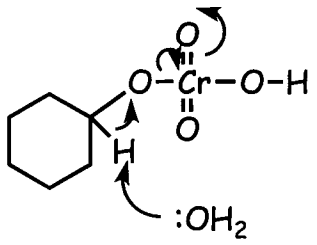
Answer: 1. $NaBH_4$ 2. Acidify



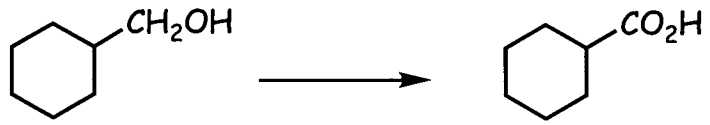
Note: $NaBH_4$ reduces aldehydes and ketones but does not reduce esters or alkenes.

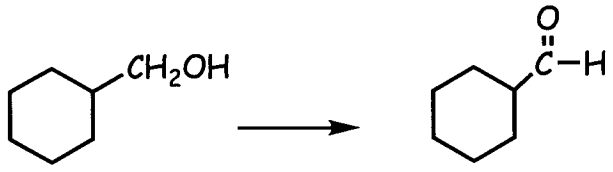
Answer: H_2CrO_4 or $Na_2Cr_2O_7$, H_2SO_4, H_2O

via

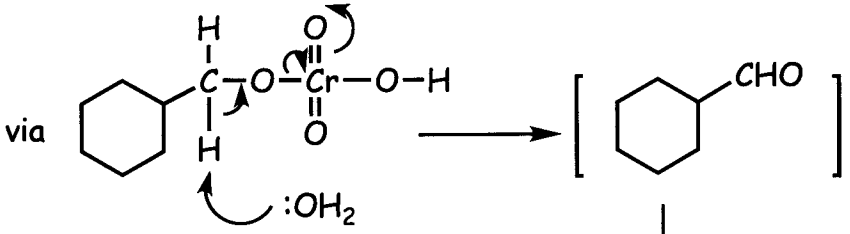


Note: Chromic acid oxidation



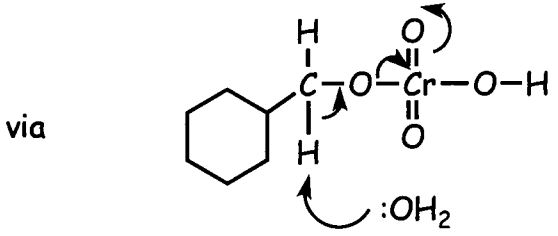


Answer: H_2CrO_4 or $Na_2Cr_2O_7$, H_2SO_4 , H_2O



Note: Chromic acid oxidation

Answer: dil. $Na_2Cr_2O_7$, H_2SO_4 , H_2O, acetone (Jones Reagent) or CrO_3·Pyr or pyridinium chlorochromate (PCC)



Note: CrO_3·pyridine = Collins reagent;
CrO_3·pyridine · HCl = pyridinium chlorochromate