Organic Ch 9 Homework KEY

1. (6S)-~~6~~3-isopropyl-2,6-dimethyloct-4-yne

6-cyclopropyl-5-(1,2-dimethylpropyl)oct-(5E)-en-1-yne

3-benzyl-4-(2-butynyl)cyclohexene

2. $C_{16}H_{22}O_2 \xrightarrow[Pt]{H_2} C_{16}H_{30}O_2$ + $AgNO_3$ = terminal alkyne

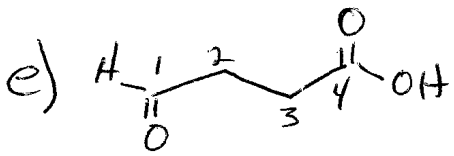
a) $C_{16}H_{22}O_2$ rewrite as $C_{16}H_{22}$
compare to $C_{16}H_{34}$ $\frac{}{12/2}$ = (6)

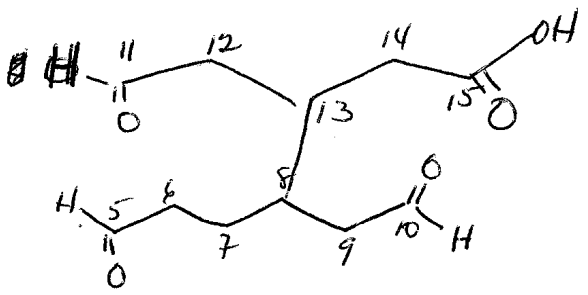
b) fragments show 4 aldehydes so (2) C=C

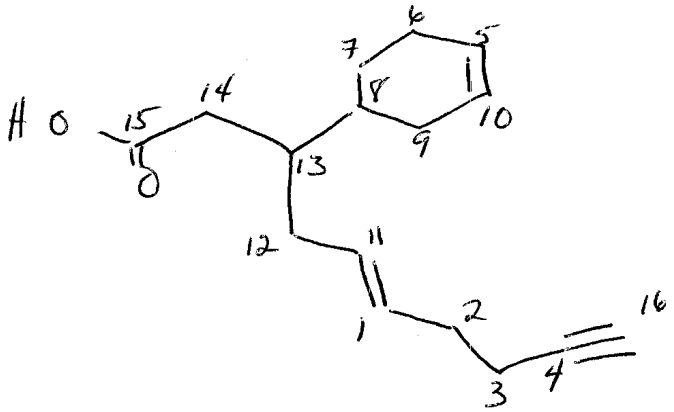
c) fragments show 2 acids - however total # C in fragments is 15 & have terminal alkyne so 1C lost as CO_2 - this means one of the acid groups was present before ozonolysis! & it accounts for 1 IHD so (1 C≡C)

d) 6 IHD total − 2 C=C ⇒ 4 − 1 C≡C ⇒ 2 − acid in original molecule

e) so (1 Ring) →  see next page

e) 





3. $C_{18}H_{26}O_2$ acid so has 1 IHD due to $-\overset{O}{\overset{\|}{C}}OH$ group

$C_{18}H_{38}$

$12/2 = 6$ IHD $- 1$ for acid $= (5)$

absorbs 5 moles H_2 so no Rings

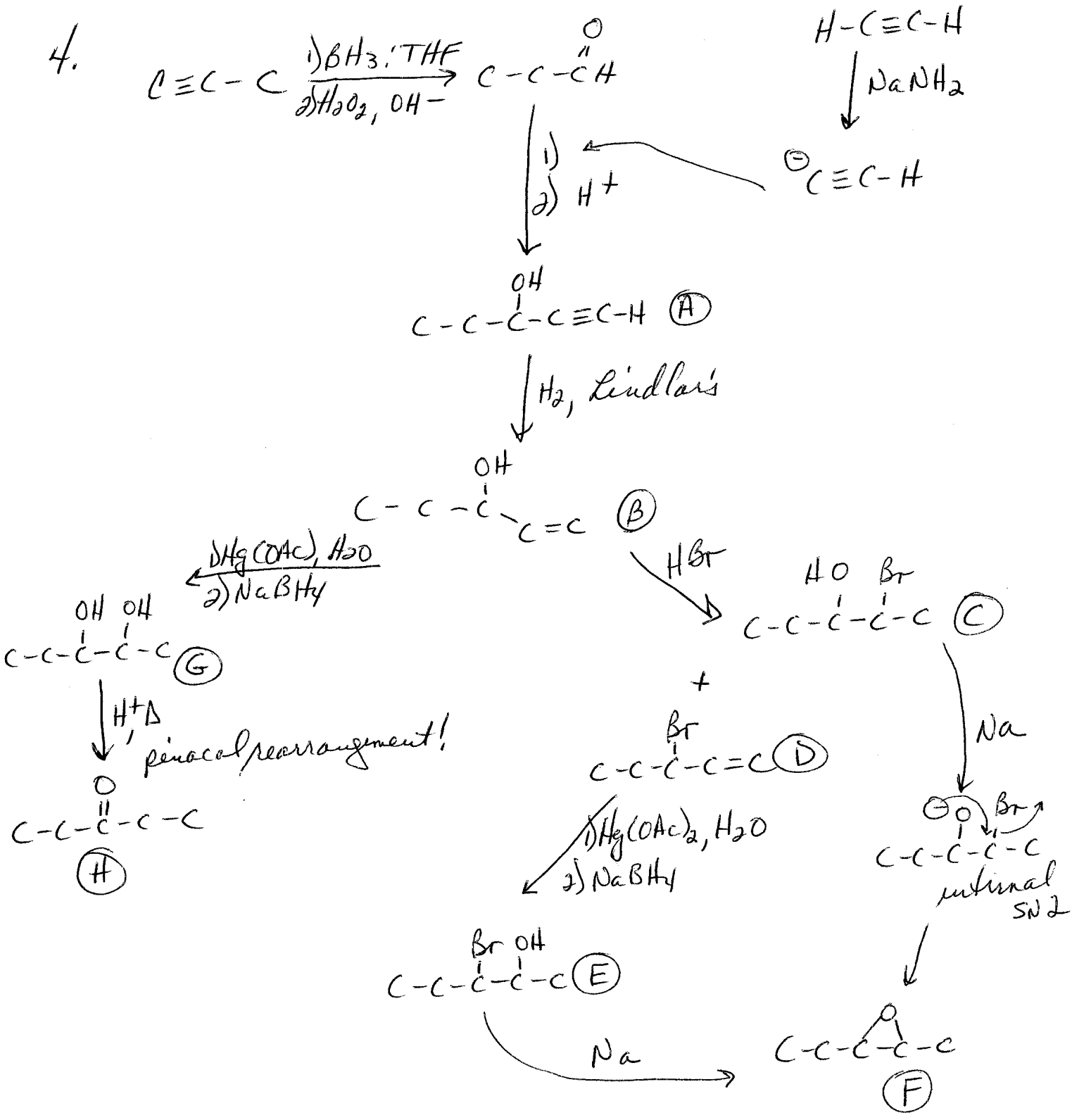
fragments show 1) 5 acids groups $- 1$ already present

$= 4 = 2\ C\equiv C$

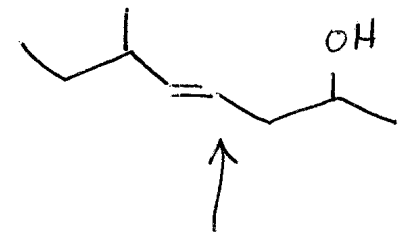
2) 2 ald $= 1\ C=C$

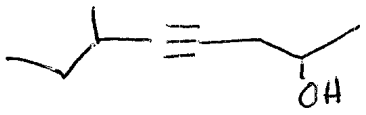
$$C=C-(CH_2)_4-C\equiv C-C\equiv C-(CH_2)_7-\overset{O}{\overset{\|}{C}}OH$$

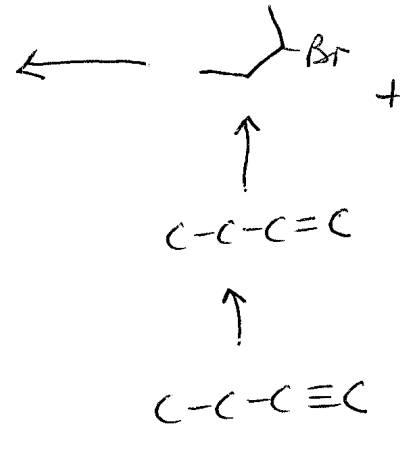
4.

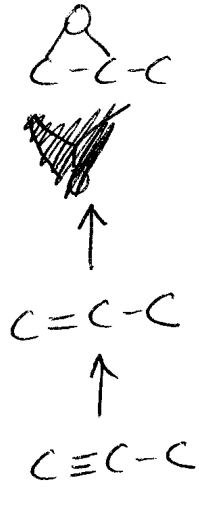

1) BH3 : THF
2) H2O2, OH−
1)
2) H+
H−C≡C−H
NaNH2
⊖C≡C−H
A
H2, Lindlar's
B
1) Hg(OAc)2, H2O
2) NaBH4
HBr
G
H+ Δ
pinacol rearrangement!
H
C
+
D
1) Hg(OAc)2, H2O
2) NaBH4
Na
intramol SN2
E
Na
F

5. working backwards



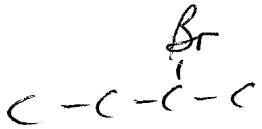


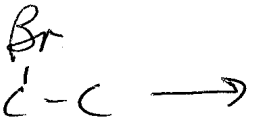


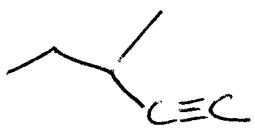
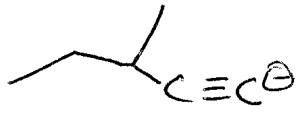


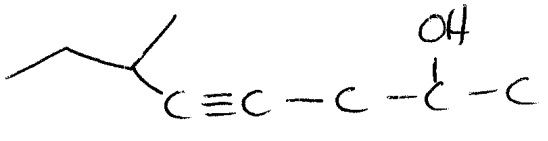
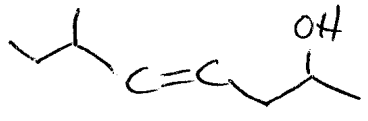
SO.....

1) $C\equiv C-C \xrightarrow[\text{Lindlars catalyst}]{H_2} C=C-C \xrightarrow{MCPBA}$ 

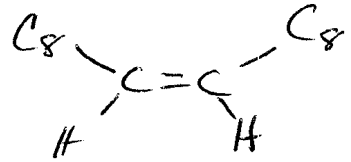
2) $C-C-C\equiv C \xrightarrow[\text{Lindlars cat}]{H_2} C-C-C=C \xrightarrow{HBr}$ 

3) $C\equiv C \xrightarrow{NaNH_2} C\equiv C^{\ominus} +$  $\longrightarrow$

 $\xrightarrow{NaNH_2}$  + 

$\xrightarrow{H^+}$  $\xrightarrow[NH_3]{Na}$ 

work backwards

6.  ← $C_8-C\equiv C-C_8$ ← $C\equiv C^-$ + C_7-C-Br

$C_4-C=C \longrightarrow C_6Br + C\equiv C^{\ominus} \longrightarrow C_6-C=C$

$C_3-C-Br + C\equiv C^{\ominus}$

$C-C-C\equiv C$ Br

so .....

$C-C-C\equiv C \xrightarrow[Lindlars]{H_2} C-C-C=C \xrightarrow[ROOR]{HBr} C-C-C-C(Br)$

$C\equiv C \xrightarrow{NaNH_2} C\equiv C^{\ominus} \longrightarrow C-C-C-C-C\equiv C$

$\xrightarrow[Lindlars]{H_2} C-C-C-C-C=C \xrightarrow[ROOR]{HBr} C-C-C-C-C-C-Br$

$C\equiv C \xrightarrow{NaNH_2} C\equiv C^{\ominus} \longrightarrow C_6-C\equiv C \xrightarrow[Lindlars]{H_2} C_6-C=C$

$\xrightarrow[ROOR]{HBr} C_6-C-C-Br$

$C\equiv C \xrightarrow{NaNH_2} C\equiv C^{\ominus} \longrightarrow C\equiv C-C_8 \xrightarrow[2)]{1)\ NaNH_2}$

$C_8-C\equiv C-C_8 \xrightarrow[Lindlars]{H_2}$ muscalure