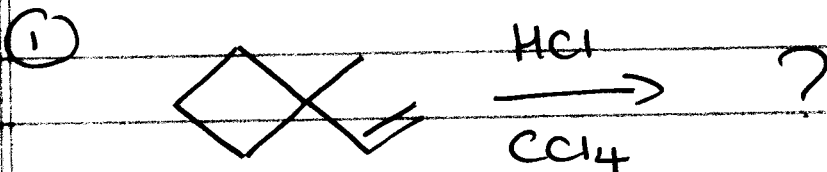


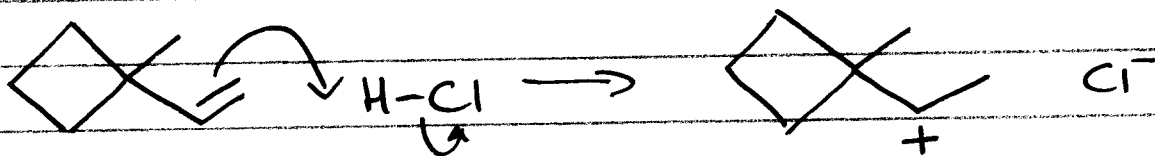
# QUIZ #2

## "HOW-TO" GUIDE

(1)

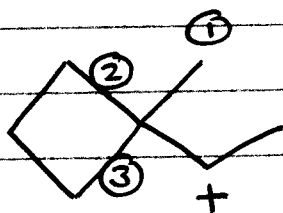


So, the first step of this reaction is the nucleophilic attack of the alkene on H-Cl:



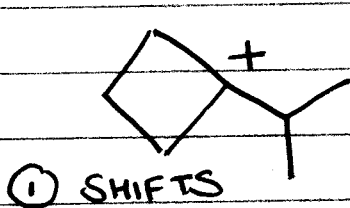
The H adds to the alkene C atom that already has the most H atoms on it, resulting in the formation of the more stable secondary carbocation.

What happens next?

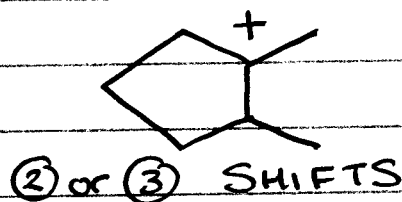


ANY ONE OF THREE ALKYL GROUPS COULD NOW UNDERGO A 1,2-SHIFT TO FORM A MORE STABLE 3° CARBOCATION

So you get



OR

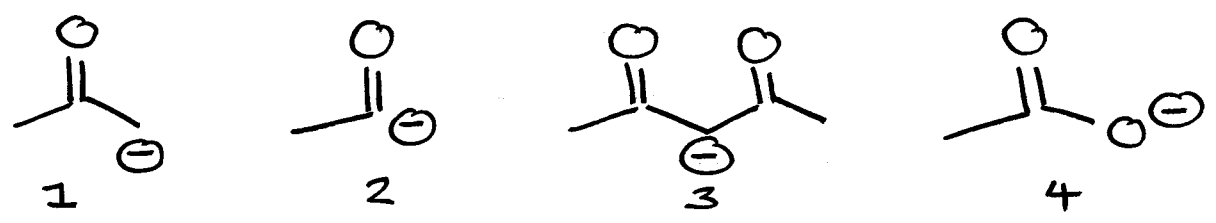


2

So, which is more likely? Well, you should recall that four-membered rings are quite strained, whereas five membered rings are MUCH more stable. So, the carbocation will rearrange to form the more stable 3° CARBOCATION WITH A LESS STRAINED 5-MEMBERED RING.

\* THIS QUESTION IS VERY SIMILAR TO 6.36 IN BROWN & FOOTE (WHICH WAS ASSIGNED AS A HOMEWORK PROBLEM)

2 So, lowest pKa value to highest, means most acidic → least acid. So, if we compare the structures in Q2, let's consider the stability of each CONJUGATE BASE i.e.,

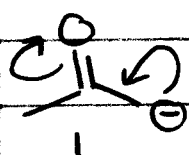


In structures 1-3, the -ve charge is on carbon, but in 4, it is on the oxygen atom, so by comparing EN values, it's a pretty good guess that #4 is the most acidic...

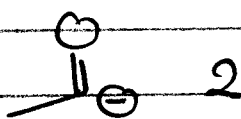
③

Just as an aside, compound #1 is a ketone, #2 is an aldehyde, #3 is a diketone, and #4 is a CARBOXYLIC ACID!! So, based on that, we can rule out any answer that does not begin 4,...

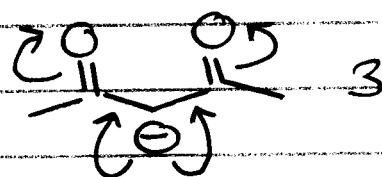
Anyway, let's compare 1, 2 and 3



RESONANCE  
STABILIZED



NOT REASONABLE  
RESONANCE  
FORMS



CAN DRAW TWO  
RESONANCE FORMS

So, it is our conclusion that 2 is the least acidic, followed by 1, and of the three conjugate bases above, #3 is the most stable, and so is more acidic than the other two, so the ordering is 4, 3, 1, 2.

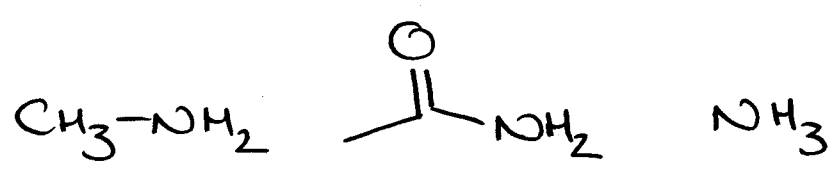
③ The stronger acid (lower  $pK_a$ ) is on the left, and the weaker acid is on the right, so the equilibrium will lie to the right, i.e., the  $K_{eq}$  will be greater than 1.

So,  $pK_{eq} = 19 - 21$   
 $= -2$

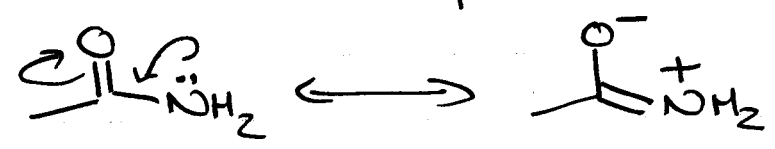
$\therefore K_{eq} = 10^{-(-2)}$   
 $= 100$

④ Strongest base?

Consider  $NH_4^+$   $\Leftarrow$  not basic at all, wants to DONATE  $H^+$ , not ACCEPT ONE.



These compounds are all neutral nitrogen-containing species, and can accept protons.  $CH_3NH_2$  and  $NH_3$  are relatively basic, the lone pair can be donated to  $H^+$  to form an ammonium ion — the middle compound is an amide, and the lone pair on the N atom is not as available for donation as in the other cases, because you can draw a resonance form in which the lone pair is not there i.e.,

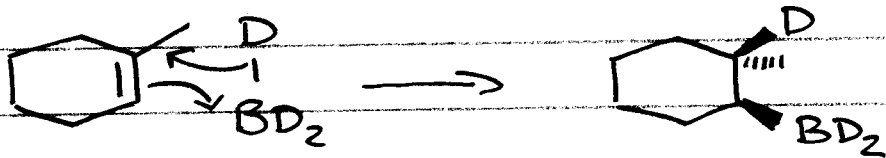


⑤

$\text{NaNH}_2$  however, or  $\text{Na}^+ \text{NH}_2^-$  is a VERY STRONG BASE

$:\ddot{\text{N}}\text{H}_2^-$  really would like to grab a proton ( $\text{H}^+$ ) from wherever it can, to form  $\text{NH}_3$  — i.e.,  $\text{NH}_2^-$  is not really very stable

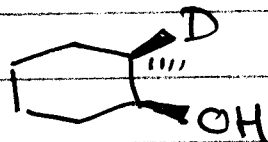
⑤



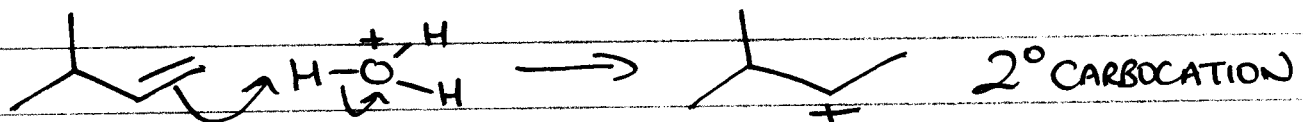
REGIOSPECIFIC  $\rightarrow$  B ATOM adds to least substituted C atom of the alkene

STEREOSPECIFIC  $\rightarrow$  The  $\text{BD}_2$  and  $\text{D}$  add to the same face of the alkene

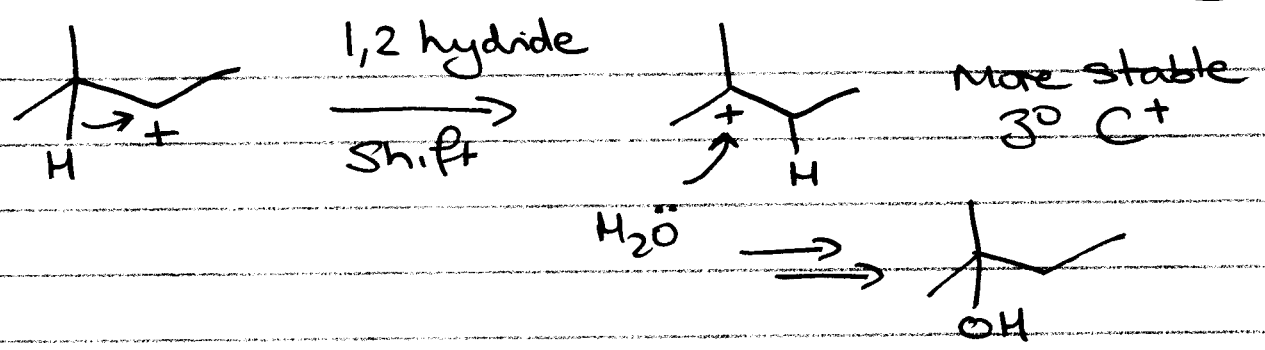
After WORK-UP of reaction, the B turns into an OH, so the final product is:



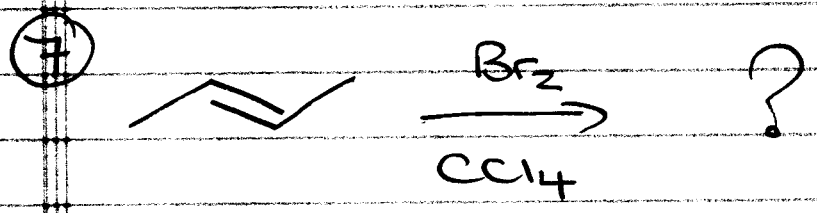
⑥ First step is formation of the carbocation



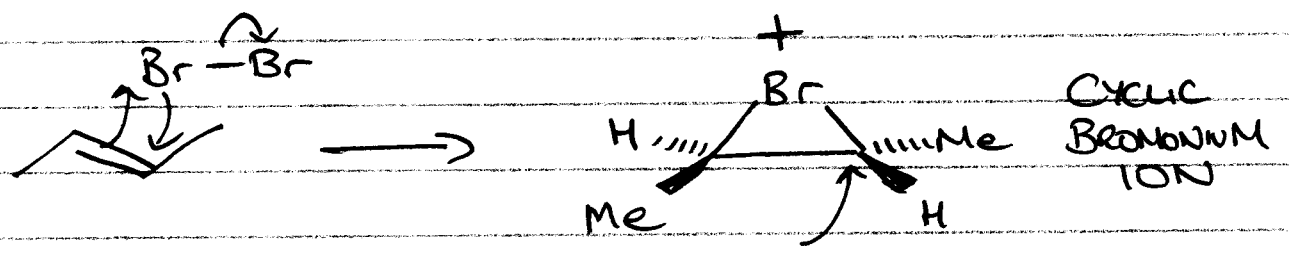
6



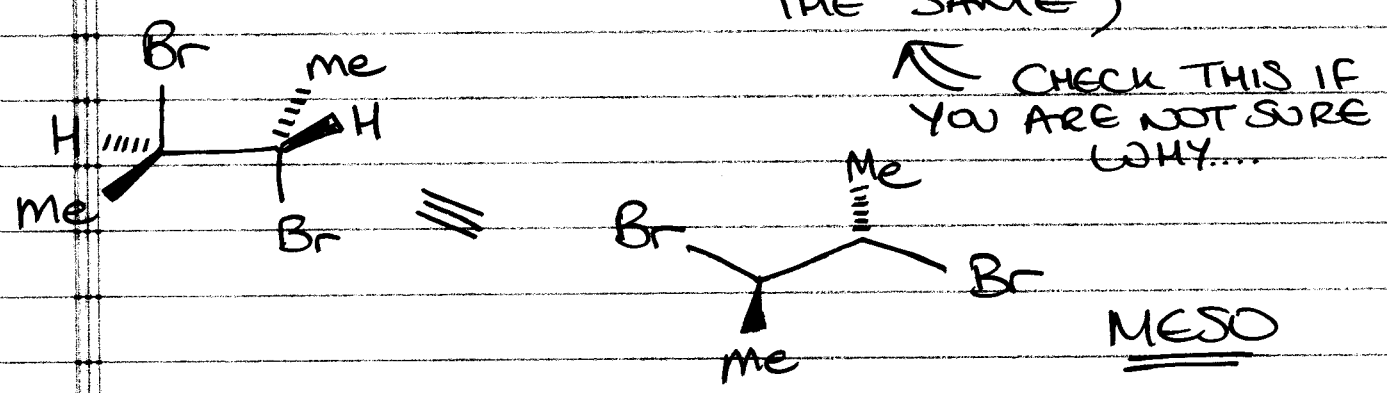
... and the name of this compound is:  
2-METHYL-BUTAN-2-OL



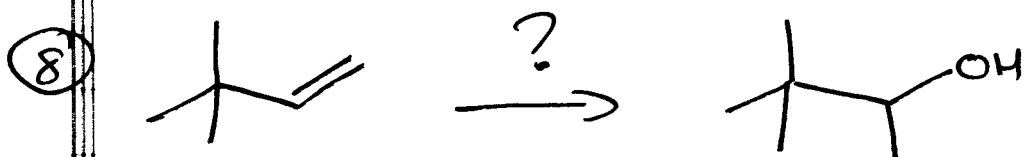
So, consider the BROMONIUM ION that is formed:



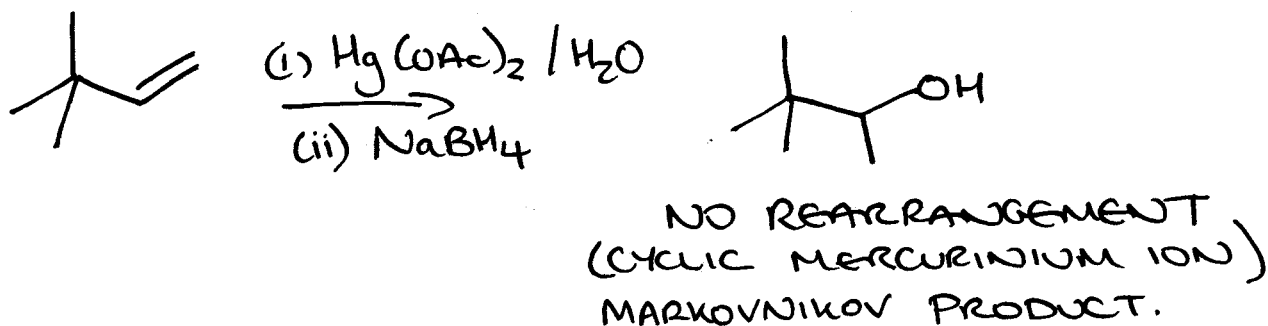
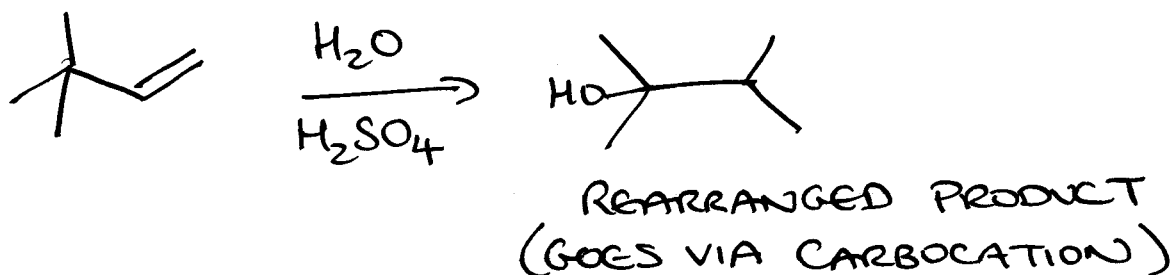
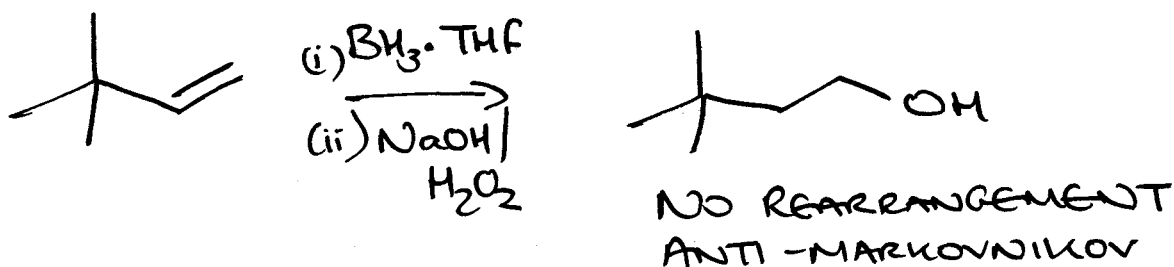
$\text{Br}^-$   
 (can attack either C atom, product is THE SAME)



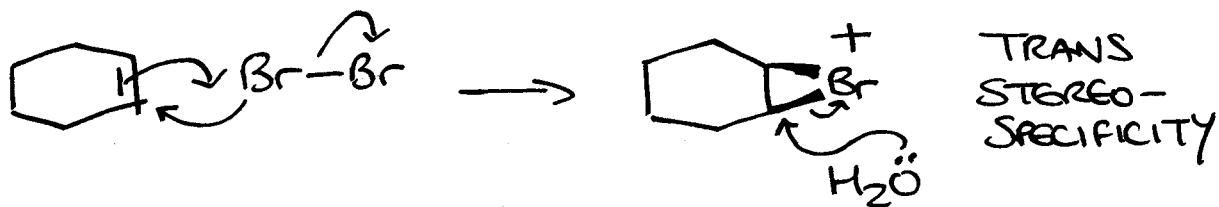
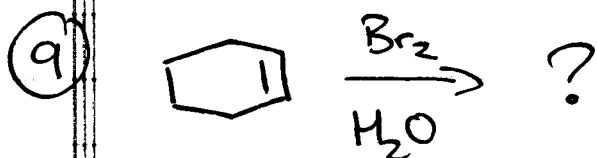
7 ~~8~~



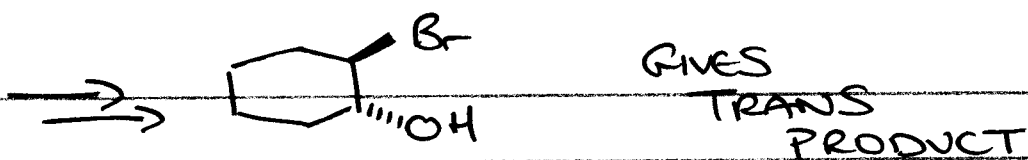
What reagent (reagents) do this reaction?



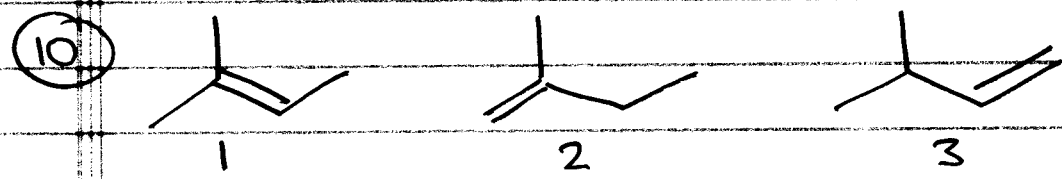
So, ONLY #2 WILL WORK.



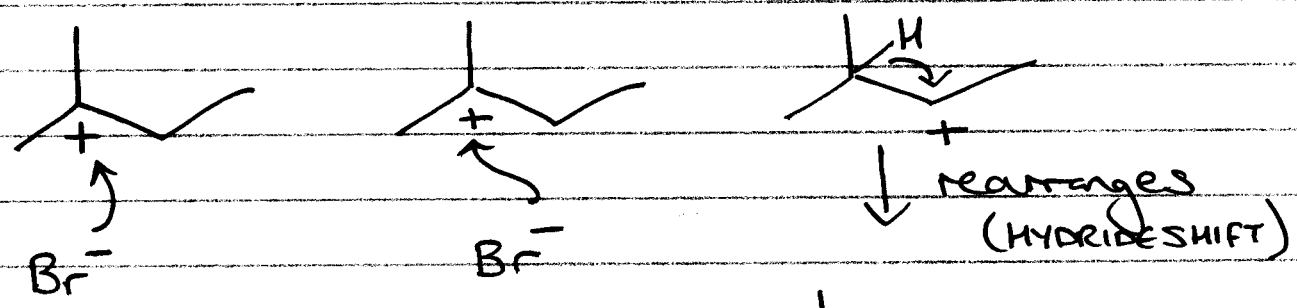
8) ~~9)~~



ONE Br, ONE OH group, as nucleophile in second step is  $\text{H}_2\text{O}$ , not  $\text{Br}^-$

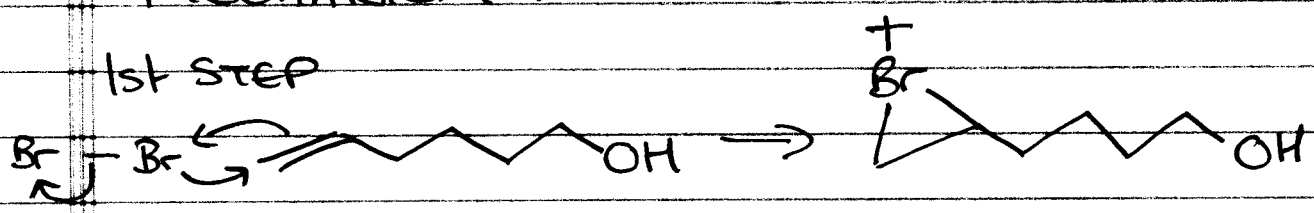


consider the carbocation that would be formed when each of the above reacts with  $\text{H-Br}$



SO, THEY ALL GIVE THE SAME PRODUCT (2-BROMO 2-METHYL BUTANE)

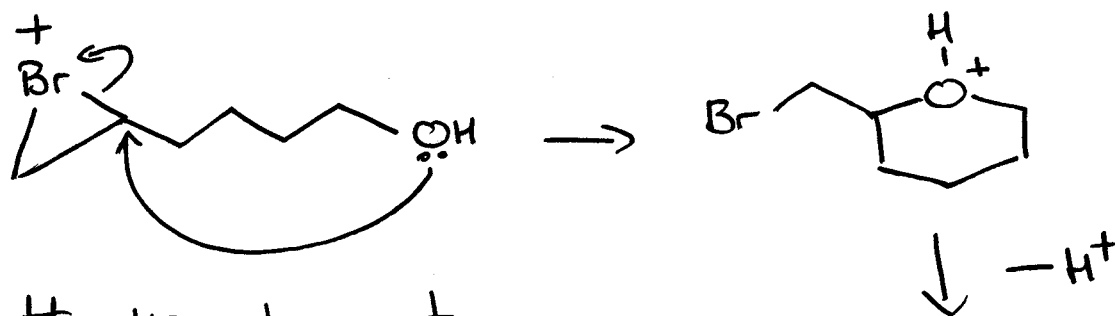
BONUS I'm just going to do one of them, they all go via the same MECHANISM:



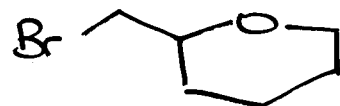


9 ~~10~~

Nucleophile in the second step is not  $\text{Br}^\ominus$ , but the OH group in the compound  $\rightarrow$  this is an INTRAMOLECULAR reaction, which is MUCH FASTER than an INTERMOLECULAR one, so:



attacks at most substituted position, more stabilization of  $\delta^+$ , as with BROMOHYDRIN formation



THIS QUESTION WAS VERY SIMILAR TO 6.34 FROM BROWN & FOOTE, WHICH WAS ASSIGNED FOR HOMEWORK.

This is also a GREAT example of people NOT READING the QUESTION. You were told the formula of the product was  $\text{C}_6\text{H}_{11}\text{BrO}$  - so WHY ON EARTH DID MOST OF YOU FEEL THE NEED TO INCLUDE TWO BROMINE ATOMS IN YOUR PRODUCT!! (THAT'S JUST STUPID) - SORRY, BUT IT IS.