Which are the best reagents/conditions to perform the following reaction?

\[
\begin{array}{cc}
\text{Br} & \text{K}^+ \cdot \text{O-t-Bu} \\
\text{A} & \text{K}^+ \cdot \text{OMe} \\
\text{B} & \text{Na}^+ \cdot \text{OH} \\
\text{C} & \text{MeOH/heat} \\
\end{array}
\]

\[
\begin{array}{cc}
\text{Br} & \text{K}^+ \cdot \text{O-t-Bu} \\
\text{D} & \text{DMF or acetone or acetonitrile etc.} \\
\end{array}
\]

This reaction converts a 3° halide into the less substituted of two possible elimination alkene products.

In order to ensure that the least substituted product is formed we need to use a bulky base, such as t-BuO⁻.

Use of a non-bulky base, such as MeO⁻, would lead to formation of the most substituted (and more stable) Sayetzeff product.

E₂ eliminations are fastest in polar aprotic solvents such as DMF, acetone or acetonitrile. However, use of an aprotic solvent is not REQUIRED, and in fact we will see that many of the standard bases such as t-BuO⁻ are most readily prepared in polar protic solvents. For this reason we will soon start to put less emphasis the solvent in E₂ and SN₂ reactions.
QUESTION 2
MC26c

Give the major product of the following reaction

\[ \text{t-BuO}^- \text{+ K} \rightarrow \text{DMF} \]

A  B  C  D

Blue reaction would give the more stable alkene, but it is slower for steric reasons, the red reaction "wins"

t-BuO- is a strong and bulky base, also we have a 3° halide, MUST be E2

A bulky base with a 3° halide tends to give the LEAST substituted alkene for steric reasons, it abstracts the least hindered proton, and does not give the Sayetzeff alkene, gives the Hofmann alkene instead
QUESTION 3
MC27aa
Give the best reaction sequence to accomplish the following transformation

A  1. Br\textsubscript{2}/hv  2. Na\textsuperscript{+}–OH  3. NBS/hv
B  1. Br\textsubscript{2}/hv  2. Na\textsuperscript{+}–O-t-Bu  3. Br\textsubscript{2}/hv
C  1. NBS/hv  2. Na\textsuperscript{+}–O-t-Bu  3. Br\textsubscript{2}
D  1. NBS/hv  2. Na\textsuperscript{+}–OH  3. Br\textsubscript{2}
QUESTION 4
MC26d

Which is the product of the following reaction sequence?

1. Br₂, hv
2. t-BuO⁻ + K / DMF
3. BH₃·THF
4. −OH/H₂O₂

A  B  C  D

Br₂, hv  t-BuO⁻ + K  DMF  BH₃·THF
(remember, Br₂/hv works as well as NBS/hv for simple alkanes)
E2 conditions, but remember, bulky base and 3Y halide does NOT give Sayetzeff product

remember, three alkenes add and the alkaline hydroperoxide really is a separate step in the Anti-Markovnikov synthesis of alcohols from alkenes
QUESTION 5
MC27k
Which correctly describes the reagents/conditions/reaction sequence to synthesize the provided alcohol from methylcyclohexane (ignore stereochemistry)?

B  1. Br₂/hv, 2. K⁺ −O−t-Bu, 3. BH₃·THF, 4. −OH/H₂O₂
D  1. NBS/hv, 2. Na+ −OH, 3. BH₃·THF, 4. −OH/H₂O₂

\[
\text{NBS/hv} \quad \text{Br} \quad \text{Na⁺ −OH} \quad \text{1. Hg(OAc)₂/H₂O} \quad \text{2. NaBH₄}
\]

\[
\text{Br}_2/hv \quad \text{K⁺ −O−t-Bu} \quad \text{1. BH₃·THF} \quad \text{2. −OH/H₂O₂}
\]

\[
\text{Br}_2/hv \quad \text{K⁺ −O−t-Bu} \quad \text{1. Hg(OAc)₂/H₂O} \quad \text{2. NaBH₄}
\]
QUESTION 6
MC27z
Give the best reaction sequence to accomplish the following transformation

C  1. NBS/hv  2. Na\(^+\) –O-t-Bu  3. BH\(_3\).THF  4. –OH/H\(_2\)O\(_2\)
D  1. NBS/hv  2. Na\(^+\) –OH  3. BH\(_3\).THF  4. –OH/H\(_2\)O\(_2\)
QUESTION 7
MC27o

Which describes the best synthesis of those shown below (stereochemistry is ignored in this problem)?

A

1. HBr
2. Na⁺ -OCH₃/DMF
3. BH₃·THF
4. H₂O₂/-OH

B

1. HBr
2. K⁺ -O-t-Bu/DMF
3. Hg(OAc)₂/H₂O
4. NaBH₄/EtOH

C

1. HBr
2. Na⁺ -OCH₃/DMF
3. Hg(OAc)₂/H₂O
4. NaBH₄/EtOH

D

1. HBr
2. K⁺ -O-t-Bu/DMF
3. BH₃·THF
4. H₂O₂/-OH
QUESTION 8

MC27x

Which are the best reagents/conditions to perform the following conversion?

A  1. NBS/h \( \nu \) 2. Na\(^+\)–OH
B  1. NBS/h \( \nu \) 2. Na\(^+\)–O-tBu
C  1. Br\(_2\)/h \( \nu \) 2. Na\(^+\)–OH
D  1. Br\(_2\)/h \( \nu \) 2. Na\(^+\)–O-tBu

we need to add Br in the allylic position and AVOID addition of Br\(_2\) to the C=C bond, which means that we must use NBS/h \( \nu \) instead of Br\(_2\)/h \( \nu \). NBS/h \( \nu \) is useful for ALL radical brominations, including simple alkanes.

we next need to make sure that we get elimination and not substitution, so we need a bulky base, not Na\(^+\)–OH.