Massachusetts Institute of Technology
Problem Set 6, Due 4pm April 7

1. Consider the following reaction.

$$
\mathrm{CH}_{3} \mathrm{Br} \quad \mathrm{OH}^{-} \xrightarrow{\text { acetone }} \mathrm{CH}_{3} \mathrm{OH} \mathrm{Br}^{-}
$$

a. If $\left[\mathrm{CH}_{3} \mathrm{Br}\right]$ is doubled, the rate of the reaction is:
quartered halved same doubled quadrupled
b. If $\left[\mathrm{OH}^{-}\right]$is doubled, the rate of the reaction is:
quartered halved same doubled quadrupled
c. If both $\left[\mathrm{CH}_{3} \mathrm{Br}\right]$ and $\left[\mathrm{OH}^{-}\right]$are doubled, the rate of the reaction is:
quartered halved same doubled quadrupled
2. Consider the following reaction.

a. If $\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}\right]$ is doubled, the rate of the reaction is: quartered halved same doubled quadrupled b. If $\left[\mathrm{H}_{2} \mathrm{O}\right]$ is doubled, the rate of the reaction is:
quartered halved same doubled quadrupled
c. If both $\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}\right]$ and $\left[\mathrm{H}_{2} \mathrm{O}\right]$ are doubled, the rate of the reaction is:
quartered halved same doubled quadrupled
3. Draw the mechanism of the following reactions and the resulting products. Use curved arrows to indicate the direction of electron flow and show any reaction intermediates.
a

b


C


Show your answer for $c$ in the lowest energy chair conformation.
4. Draw the products of the following reactions. Indicate the sterochemistry of the products.


5. Some molecules have more than one nucleophilic center. Draw the possible products of the following reactions.
i $\quad{ }^{-} \mathrm{C} \equiv \mathrm{N}: \quad \mathrm{CH}_{3} \mathrm{I} \quad$ polar aprotic solvent
ii $\quad \mathrm{O}=\ddot{\mathrm{N}}-\mathrm{O}^{-} \quad \mathrm{CH}_{3} \mathrm{I} \quad$ polar aprotic solvent
6. Explain, in one sentence plus a chemical structure, why the following reaction will not occur

7. The following reaction does not occur. Explain why in 1-2 sentences.


8a. Rank the following series of nucleophiles in methanol. 1 is the best.

$$
\begin{array}{lllll}
\mathrm{Cl}^{-} & \mathrm{OH}^{-} & \mathrm{F}^{-} & \mathrm{SH}^{-} & \mathrm{H}_{2} \mathrm{O}
\end{array}
$$

$\qquad$
b. Rank the following series of leaving groups. 1 is the best

$$
\mathrm{CH}_{3} \mathrm{O}^{-} \quad \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{SO}_{3}^{-} \quad \mathrm{H}_{2} \mathrm{~N}^{-} \quad \mathrm{H}_{2} \mathrm{O}
$$

9a. Which reacts faster by the $S_{N} 2$ mechanism, compound A or B? Why?

A

B
b. Which reacts faster by the $\mathrm{S}_{\mathrm{N}} 1$ mechanism, compound C or D ? Why?


C


D
10. For the following pairs of reactions predict which is faster and explain why.
a. $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}+\mathrm{N}_{3} \xrightarrow{\mathrm{MeOH}}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{~N}_{3}+\mathrm{Cl}^{-}$ $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{I}+\mathrm{N}_{3}{ }^{\mathrm{MeOH}}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{~N}_{3}+\mathrm{I}^{-}$
b. $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr} \xrightarrow{\mathrm{H}_{2} \mathrm{O}}\left(\mathrm{CH}_{3}\right)_{3} \mathrm{COH}+\mathrm{HBr}$
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHBr} \xrightarrow{\mathrm{H}_{2} \mathrm{O}}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{HBr}$

$$
\text { c. } \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}+\mathrm{CN}^{-} \xrightarrow{\mathrm{MeOH}} \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CN}+\mathrm{Br}^{-} \mathrm{CH} \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CN}+\mathrm{Br}^{-} .
$$

$$
\begin{aligned}
\text { d. } \mathrm{CH}_{3} \mathrm{Br}+\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N} \longrightarrow\left(\mathrm{CH}_{3}\right)_{4} \mathrm{~N}^{+} \mathrm{Br}^{-} \\
\mathrm{CH}_{3} \mathrm{Br}+\left(\mathrm{CH}_{3}\right)_{3} \mathrm{P} \longrightarrow\left(\mathrm{CH}_{3}\right)_{4} \mathrm{P}^{+} \mathrm{Br}
\end{aligned}
$$

e. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}+\mathrm{SCN}^{-} \xrightarrow{\mathrm{EtOH}} \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{SCN}+\mathrm{Br}^{-}$ $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}+\mathrm{SCN}^{-} \xrightarrow{\mathrm{EtOH}} \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NCS}+\mathrm{Br}^{-}$ $\mathrm{SCN}^{-}=-\mathrm{S}-\mathrm{C} \equiv \mathrm{N}$ :
f. $\mathrm{CH}_{3} \mathrm{I}+\mathrm{OH}^{-} \longrightarrow \mathrm{CH}_{3} \mathrm{OH}+\mathrm{I}^{-}$

g. $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Br}+\mathrm{N}_{3}^{-} \xrightarrow{\mathrm{EtOH}}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{~N}_{3}+\mathrm{Br}$ $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Br}+\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~S}^{\mathrm{EtOH}}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{SC}_{6} \mathrm{H}_{5}+\mathrm{Br}$ pKa $\left(\mathrm{HN}_{3}\right) \approx \mathrm{pKa}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{SH}\right)$
11. Design a synthesis of the following compound from acetylene and a ketone. (Hint- use your answer from problem set 5 \# 4 to help)


