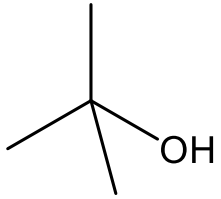
1. The solvolysis reaction of 2-bromo-2-methylpropane is carried out in different solvents as shown below with the relative rates. What kind of nucleophilic substitution is occurring ? What will be the products in each solvent mixture?

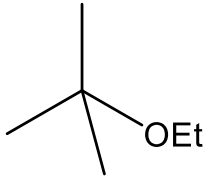
Solvent	Relative rate
100% water	1200
80% water/20% ethanol	400
50% water/50% ethanol	60
20% water/80% ethanol	10
100% EtOH	1

Ans. S_N1

For 100% water:



For EtOH:



For solvent mixtures, mixture of products

2. The rate law for the substitution reaction of 2-bromobutane in 75:25 ethanol-water at 30°C is the following:

$$\text{Rate} = 3.20 \times 10^{-5}\,[\text{2-bromobutane}][\text{HO-}] + 1.5 \times 10^{-6}\,[\text{2-bromobutane}]$$

What percentage of the reaction takes place by an S_N2 pathway when [OH-] = 1 M and 0.01 M?

Ans. The proportion of S_N2 reaction:

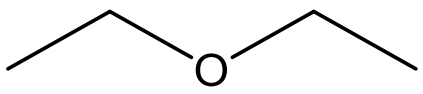
$$\frac{3.20 \times 10^{-5}\,[\text{2-bromobutane}][\text{HO}^-]}{3.20 \times 10^{-5}\,[\text{2-bromobutane}][\text{HO}^-] + 1.5 \times 10^{-6}\,[\text{2-bromobutane}]} \times 100\ \%$$

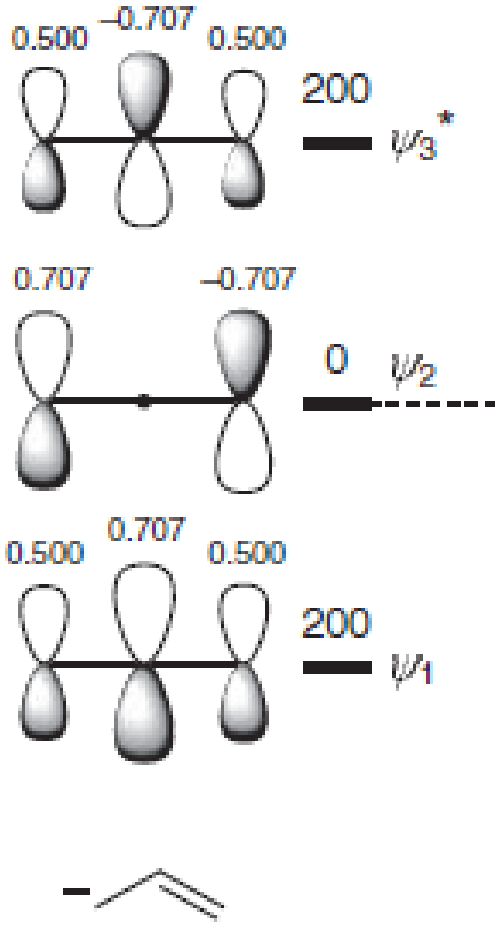
[OH-] = 1 M; S_N2 = 96%

[OH-] = 0.01 M; S_N2 = 17.6 %

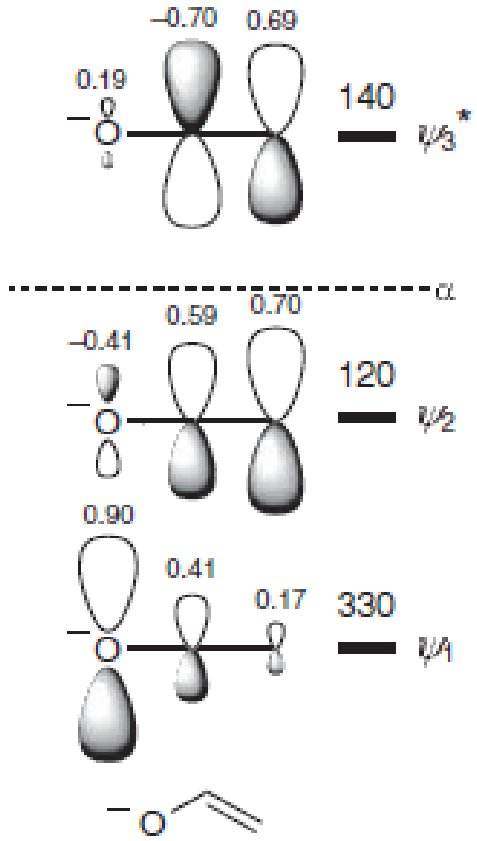
3. You are given a supply of ethyl iodide, tert-butyl iodide, sodium ethoxide, and sodium tert-butoxide. Your task is to use the S_N2 reaction to make as many different ethers as you can. In practice, how many can you make? Explain.

Ans. Only one:



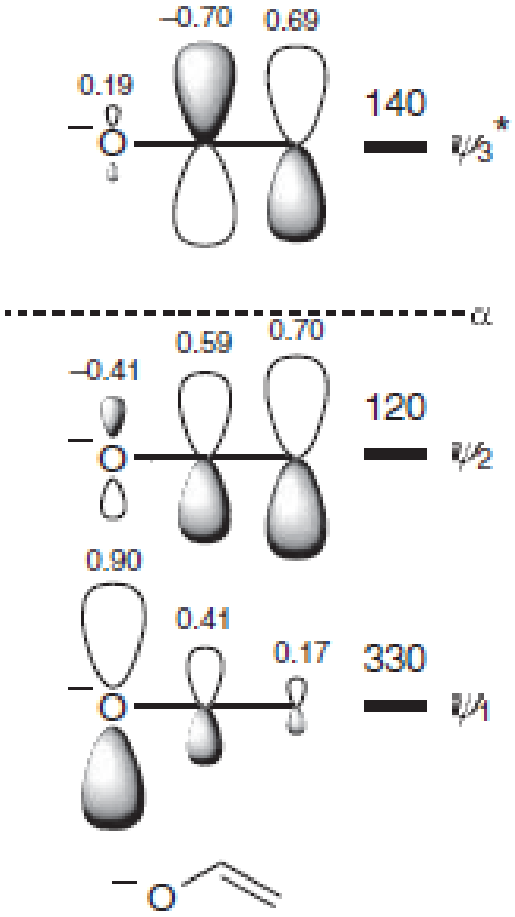


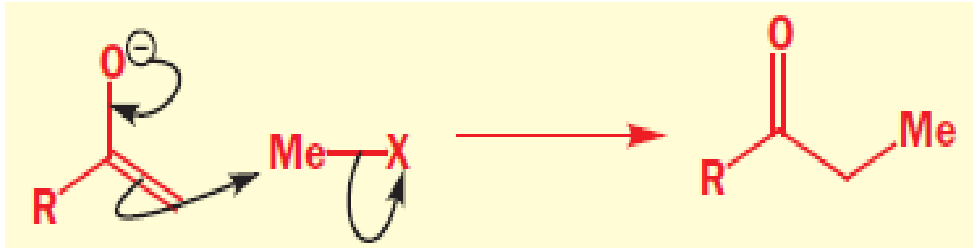
Allyl anion



Enolate ion

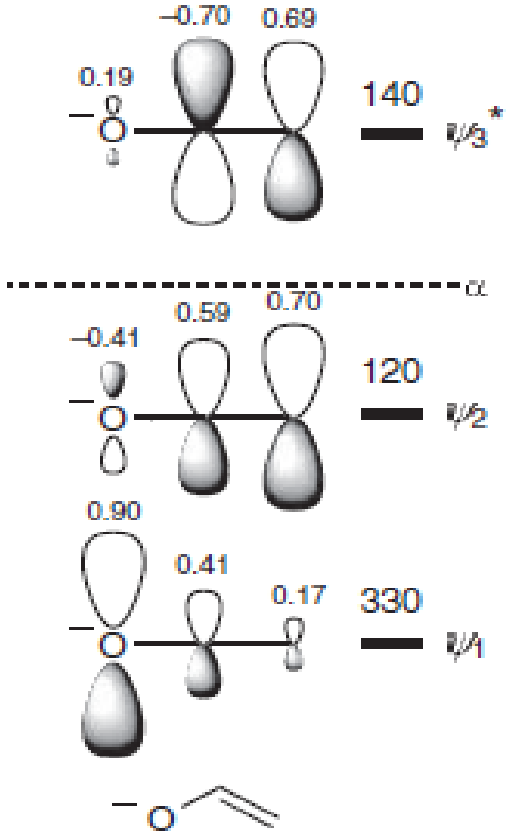
- Oxygen being the more electronegative atom, is supposed to have a higher share of π-electrons in the enolate
- How do we show it from the molecular orbitals?

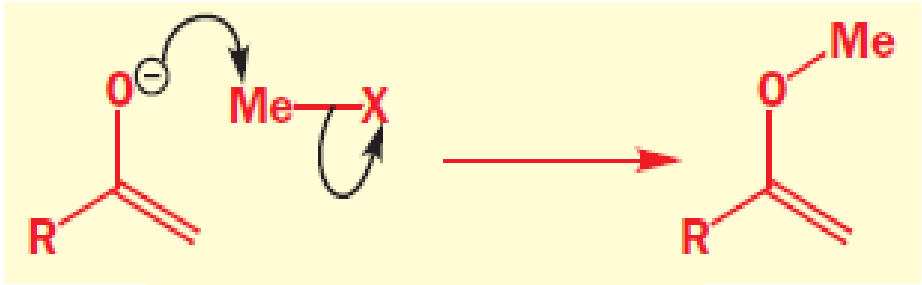




X = I, Br, Cl

❑The electron probability distribution in HOMO tells you that it would react with electrophiles through C_α





X = OMs, OSO_2OMe, $^+OMe_2$

❑ But how to explain the reaction with hard electrophiles?

✓ *Hard-hard* interactions are promoted by *charge interactions*, molecular orbitals play lesser roles

✓ *Soft-soft* interactions are dominated by *molecular orbital interactions*, charge interactions are less important