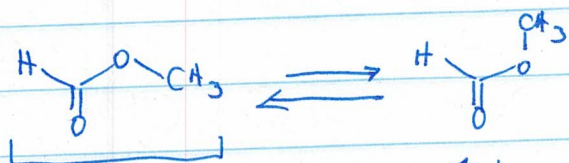
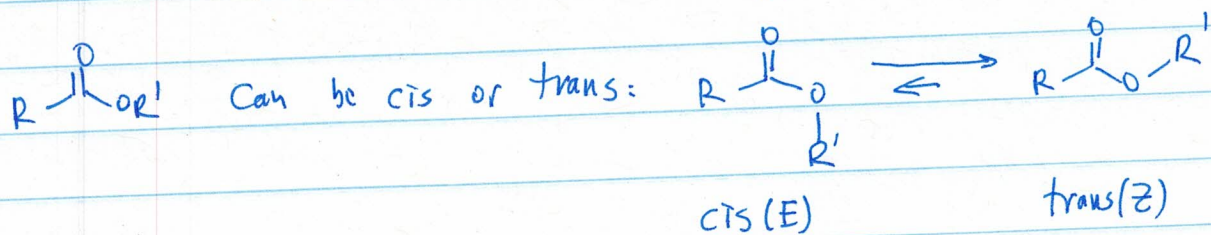
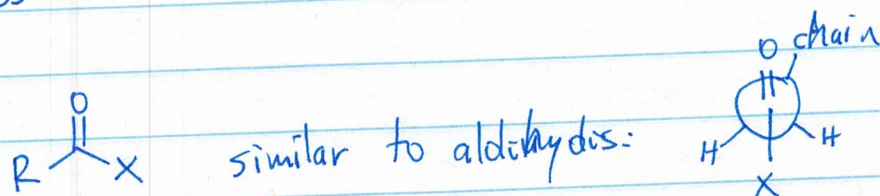


Lecture XVIII: Conformations of Acyclic Molecules, cont'd

02-25-2020

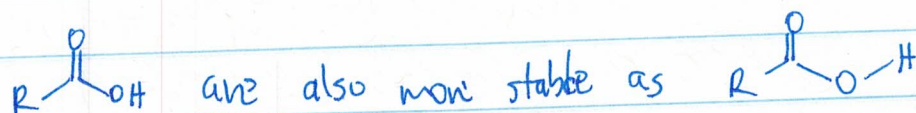
What about molecules in which some degree of conjugation is possible?



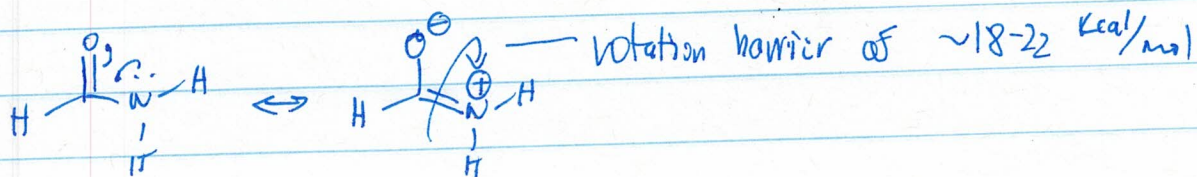
more favorable even with small R'

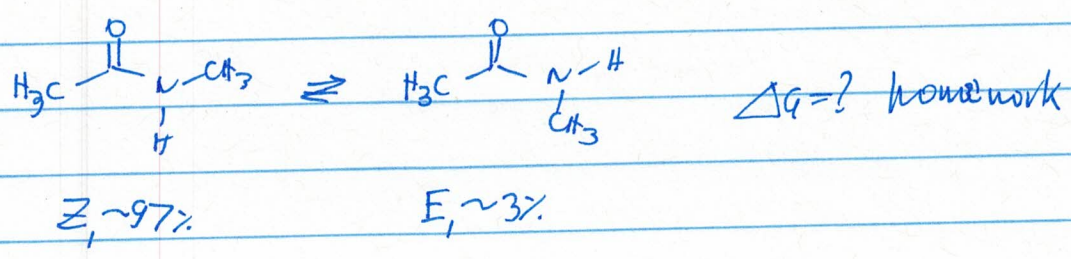
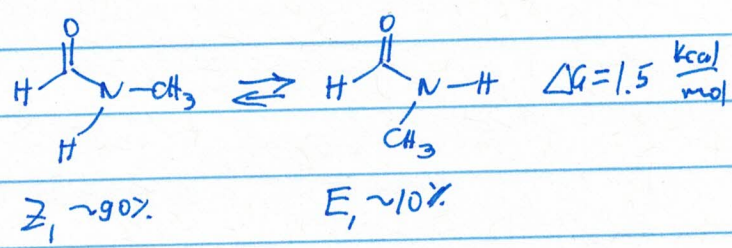
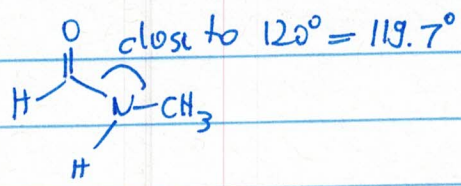
very favored, so this \uparrow basically doesn't exist

The energy difference could still be determined to be 4.75 kcal/mol using matrix isolation techniques. A hot beam of ester molecules is rapidly frozen in an argon matrix and then analyzed by low temperature IR spectroscopy.

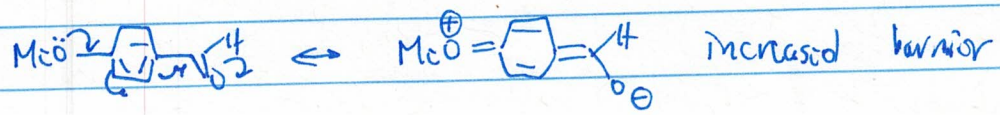
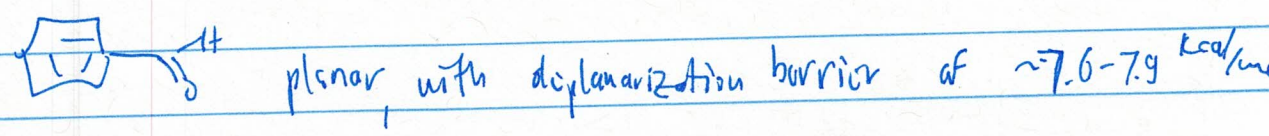
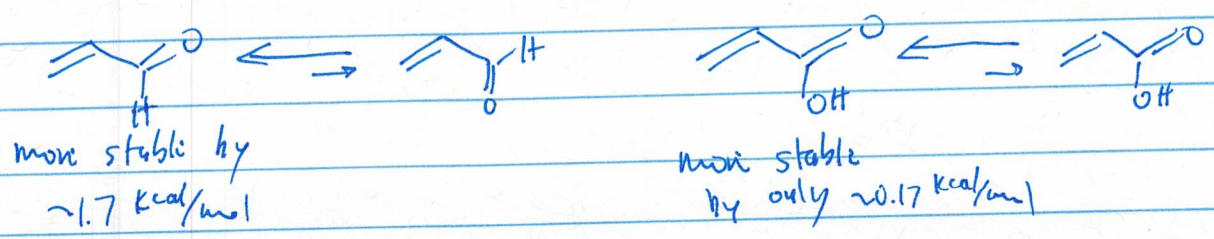
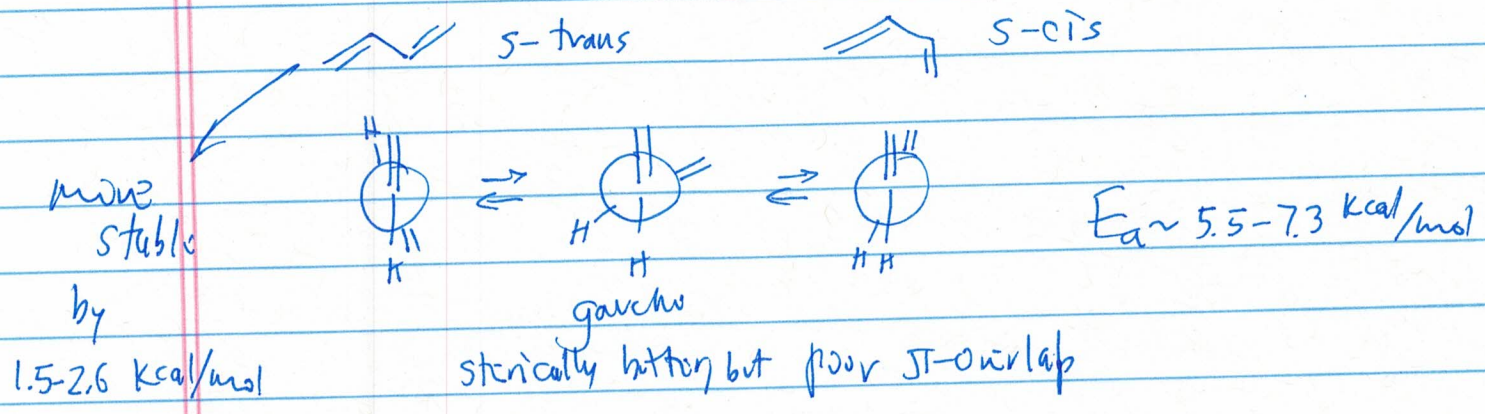


Amides are probably the most extensively studied, because of their relevance to peptide chemistry. Small ones are mostly planar, because

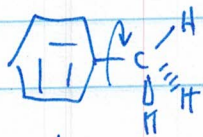




What about conjugated double bonds?

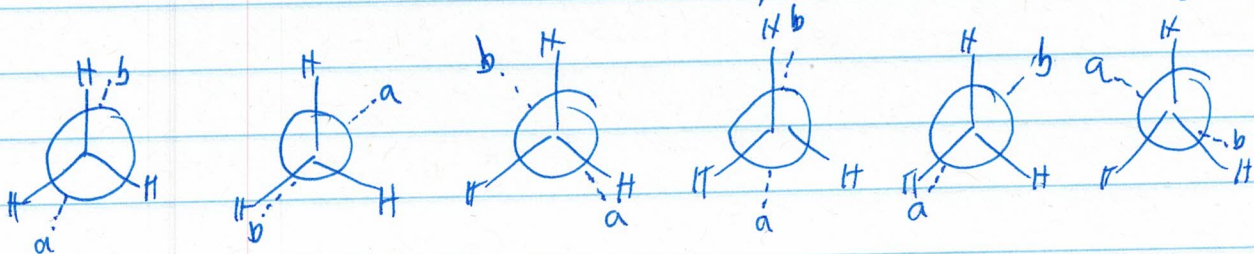


Alkylbenzenes



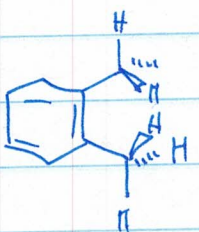
barrier to this rotation is very small: 4 cal mol⁻¹

↳ this is a sixfold rotation barrier, and those tend to be quite small

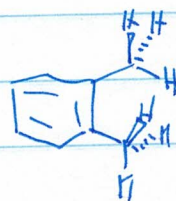


In higher alkylbenzenes, this symmetry is broken and the barriers

increase:

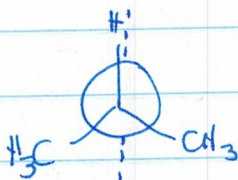


Opposed, more stable

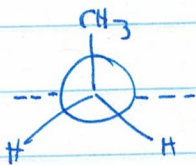


gearing

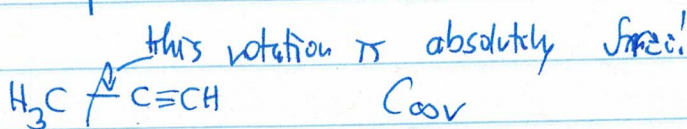
Isopropylbenzene:



Ethylbenzene



Triply bonded species have zero barrier:

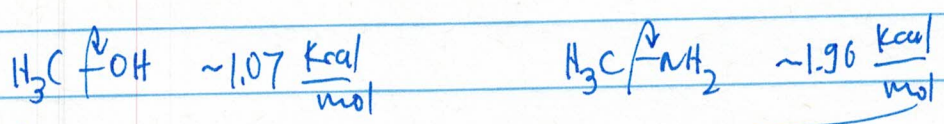


Coov

But in

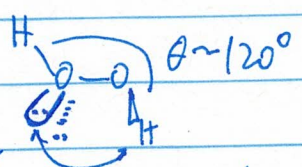
$\text{H}_3\text{C}-\text{C} \equiv \text{C}-\text{CH}_3$ the two methyl groups influence each other. Still, they are far and the barrier is only ~30 cal mol⁻¹!

Other compounds

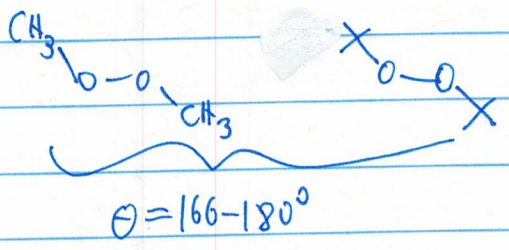
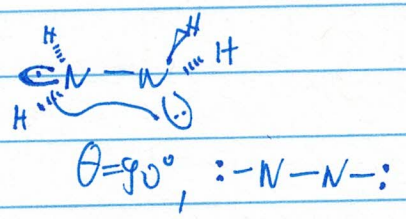


only one or two eclipsing H-H interactions

Simple inorganics:



but there may be some attraction, but this is poorly explained!



There are several important lessons to be learned here. For compound which has multiple conformers close in energy, total E is going to be:

$$H_{\text{TOTAL}} = n_A \times H_A + n_B \times H_B + n_C \times H_C \dots$$

↳ mole fractions of individual conformers

Entropy (~statistical likelihood) of individual conformers also needs to be considered.

Observations of individual conformers will depend on the time scale of their conversion and the observation technique:

$$E = h\nu \Rightarrow \nu = \frac{c}{\lambda}$$

↳ timescale of experiment

μm wave spectroscopy:	$\lambda \sim 0.3 \text{ mm} \Rightarrow \nu = 10^{12} \text{ s}^{-1}$	} extremely fast
IR	" : $\lambda \sim 3 \mu\text{m} \Rightarrow \nu = 10^{14} \text{ s}^{-1}$	
UV/Vis	" : $\lambda \sim 300 \text{ nm} \Rightarrow \nu = 10^{15} \text{ s}^{-1}$	

NMR " : $\Delta\nu = 100 \text{ Hz} \Rightarrow \nu = 10^2 \text{ s}^{-1} \rightarrow$ much smaller

Rate of interconversion:

$$k = 2.084 \times 10^{10} \times T \times e^{-\Delta G^\ddagger / 1.987T} \quad (\text{for } \Delta G^\ddagger \text{ in kcal/mol})$$

10 kcal/mol $\rightarrow k = 2.9 \times 10^5 \text{ s}^{-1}$ @ 25°C — way too fast for NMR
 0.86 s⁻¹ @ -100°C — can be observed by NMR

3 kcal/mol $\rightarrow k = 3.9 \times 10^{10} \text{ s}^{-1}$ @ 25°C } too fast for NMR
 $k = 5.9 \times 10^8 \text{ s}^{-1}$ @ -100°C }