CH 335

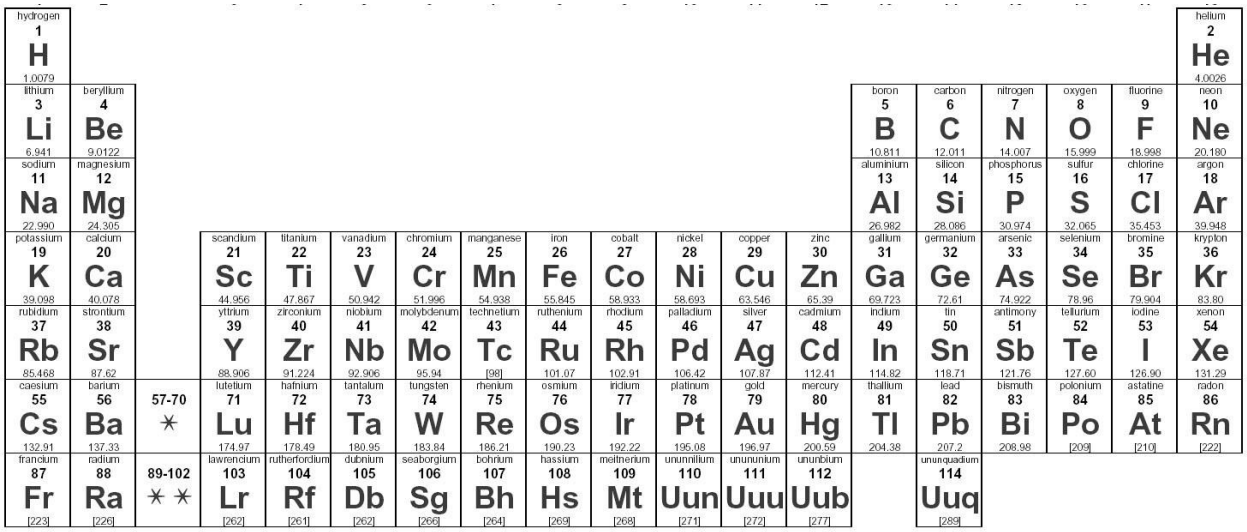
Second Midterm Exam Monday, February 21, 2022

Form A

Name_____

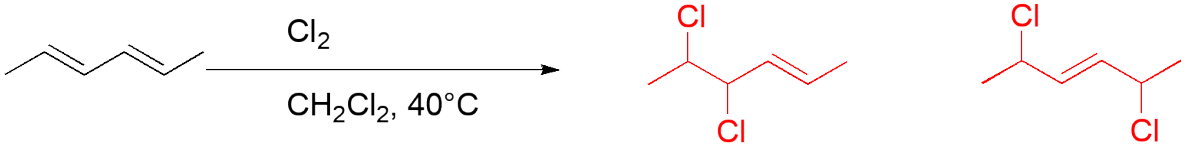
You may use model kits but no other material with chemical information without instructor approval.

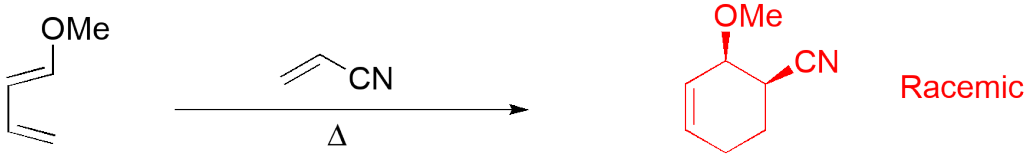
Please do not use ipods or other music players.



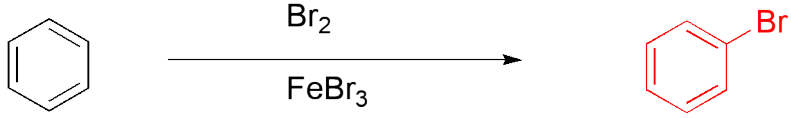
1. (30 points) Write the expected product(s) for each of the following reactions. Specify stereochemistry where appropriate, and include all expected organic products.

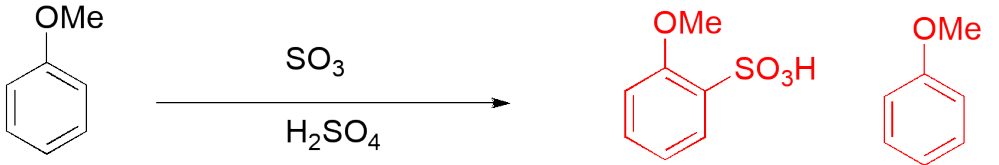
A. 

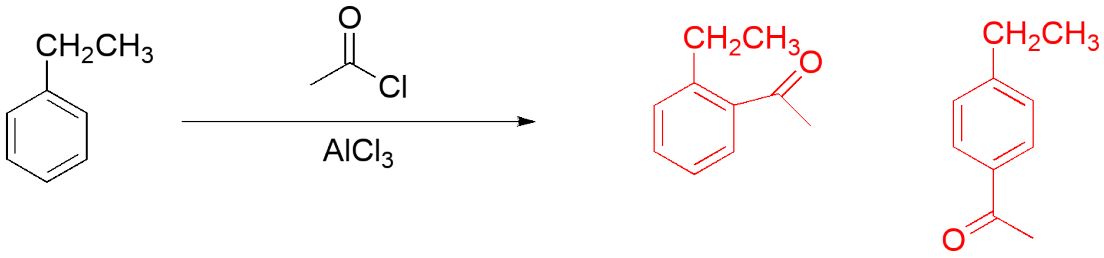
B. 

C. 

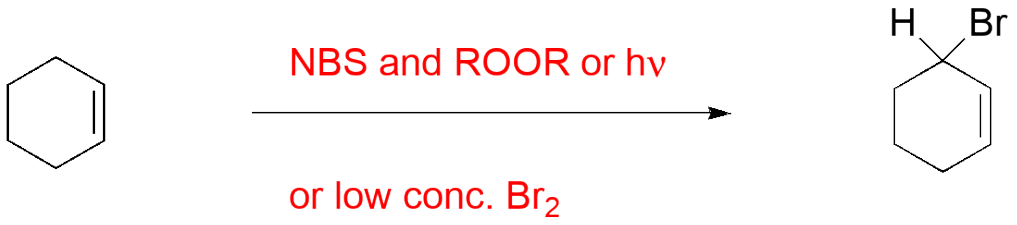
Racemic

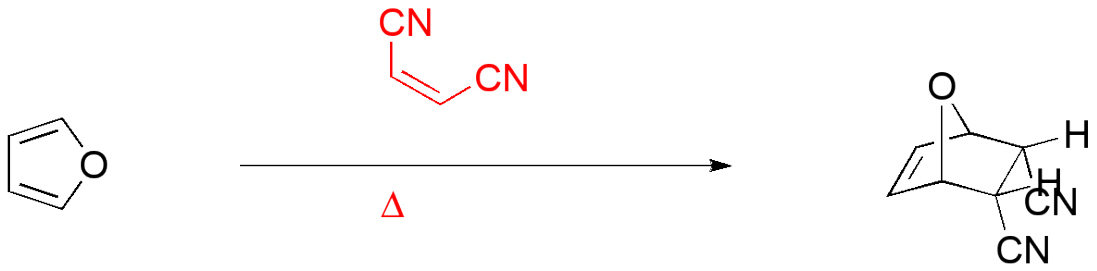
D. 

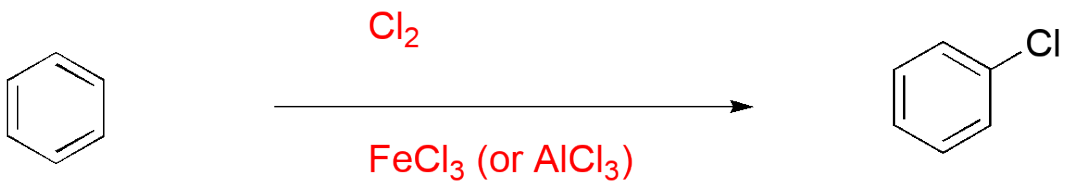
E. 

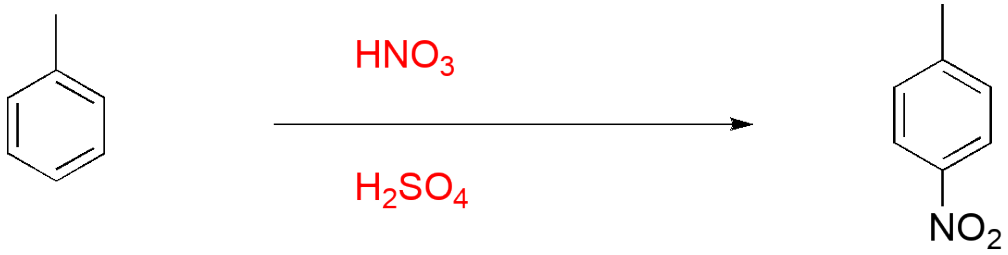
F. 

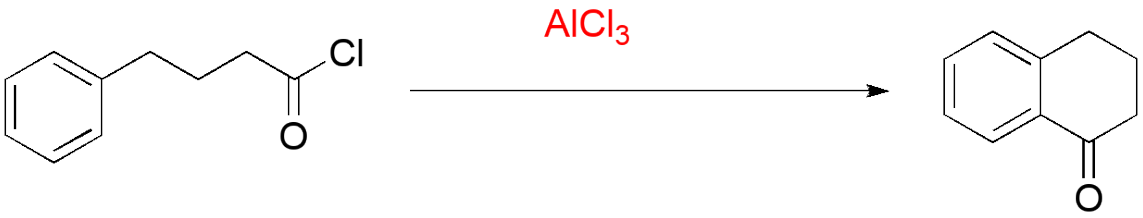
2. (25 points) Write (over the arrow) the reagents and/or conditions needed to accomplish the following transformations.

A. 

B. 

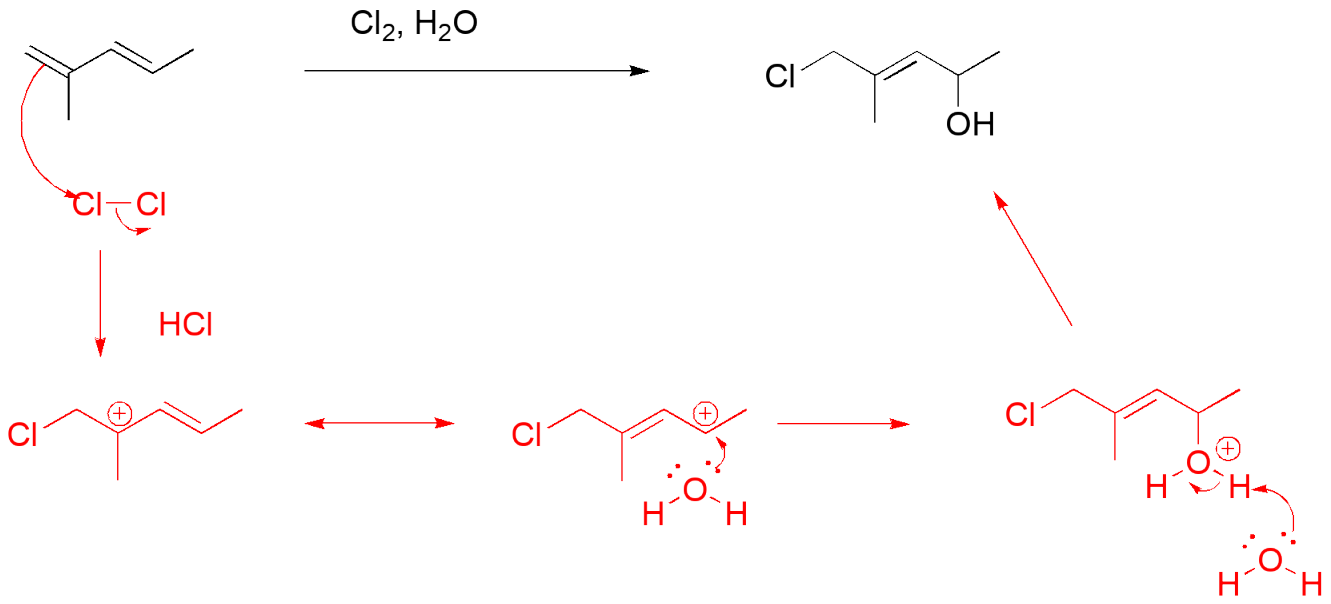
C. 

D. 

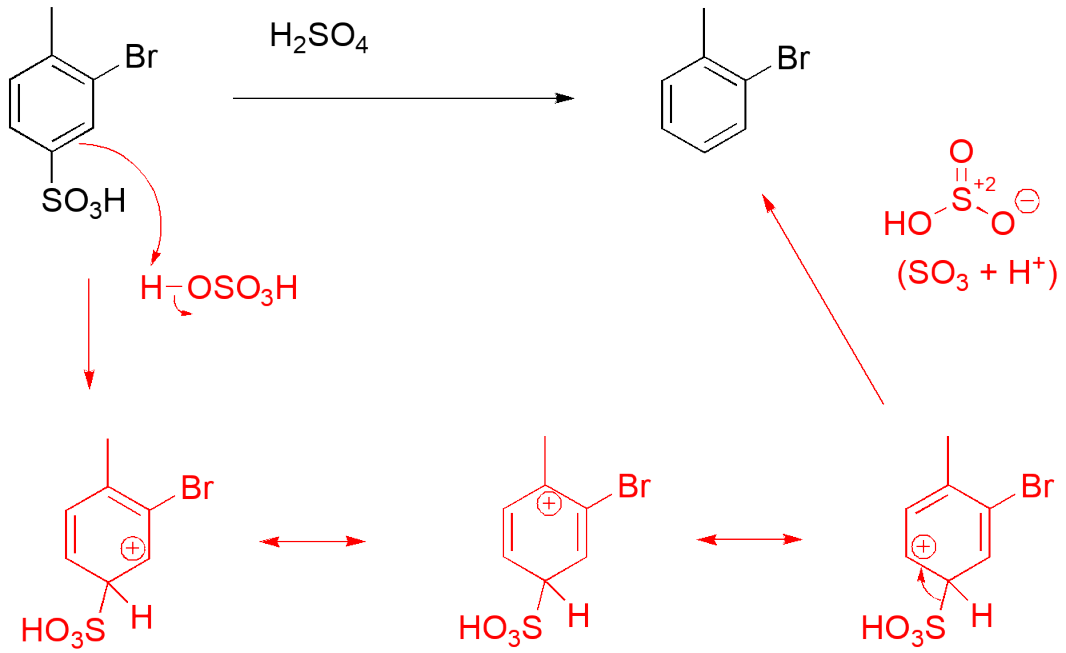
E. 

3. (20 points) Write multistep mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations. Be sure to draw resonance structures for any intermediate so stabilized.

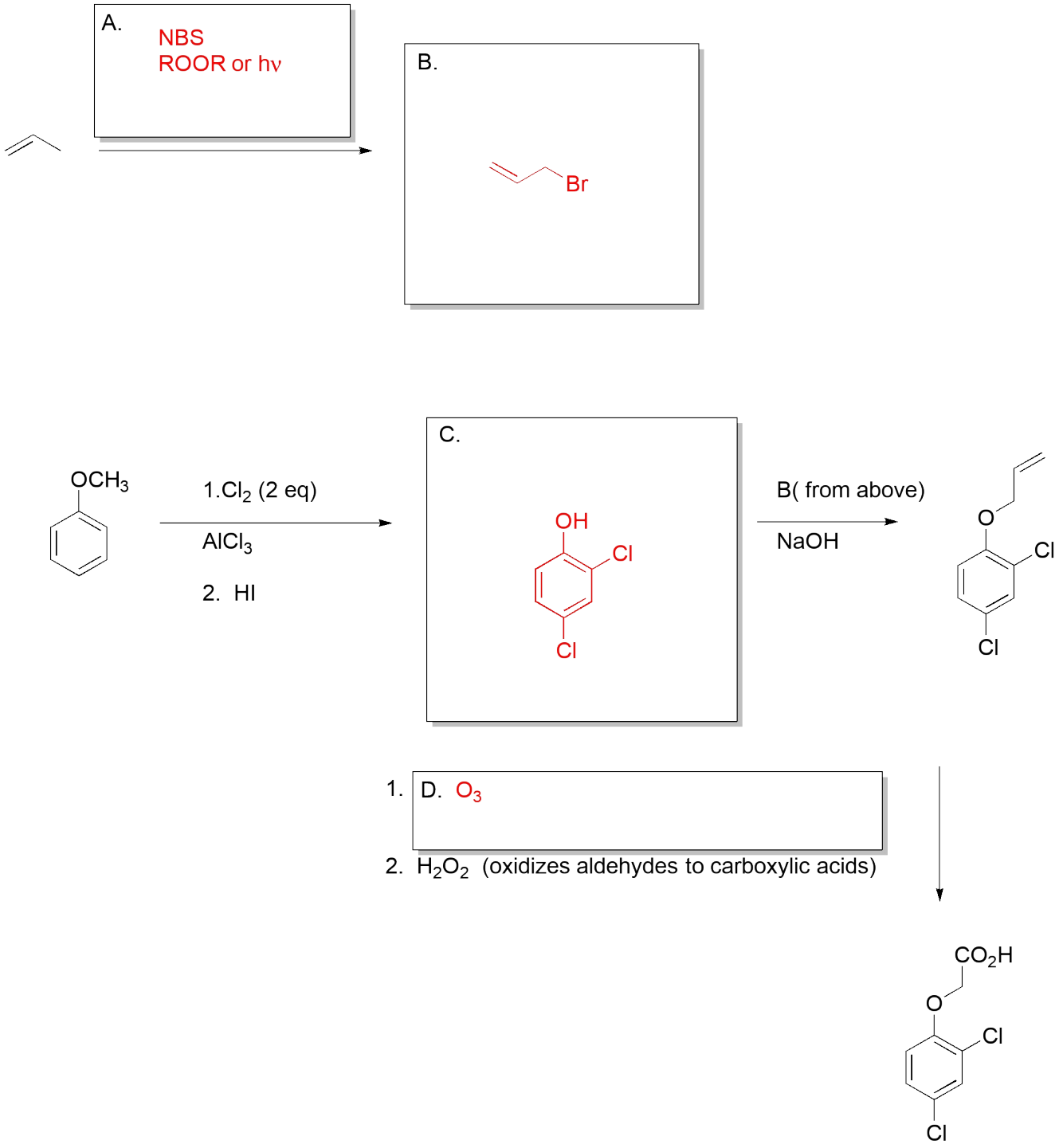
A.



B.

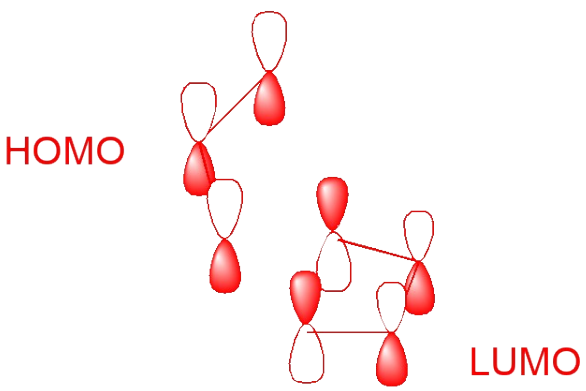


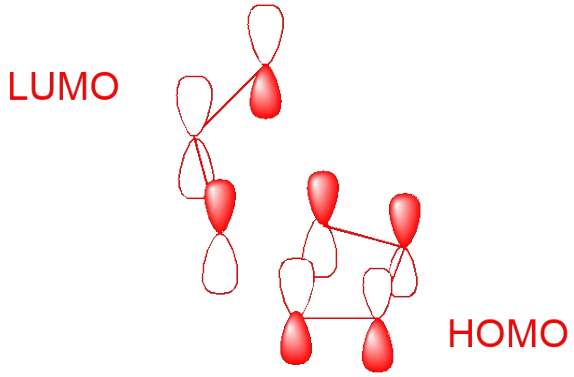
4. (16 points) Using multistep synthesis, show how to make 2,4-dichlorophenoxyacetic acid, sold commercially as the herbicide 2,4-D.



5. (9 points) Allyl cations will react with dienes in a concerted, pericyclic reaction very simular to the Diels-Alder reaction.

A. Sketch in the phase interactions in the two HOMO-LUMO interactions in this reaction. (If the particular p orbital is on a node, leave it completely blank.)

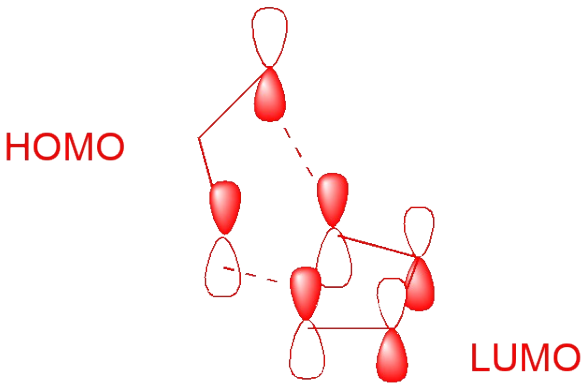


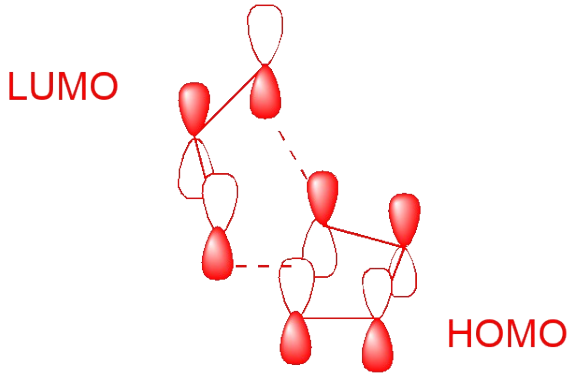


Note that in the allyl cation LUMO, the central p orbital lies on a node (and so does not really participate).

B. Explain why you think an allyl anion would or would not undergo the same reaction.

The allyl anion has two additional electrons. The LUMO of the cation becomes the HOMO of the anion; the LUMO of the anion is now the completely out-of-phase orbital. Since the MO phases don't match between the two molecules, the reaction cannot occur:



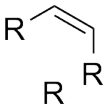


Bond strengths (kcal/mol):

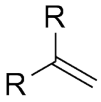
F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH_3-H	105
CH_3CH_2-H	101
$(CH_3)_2CH$-H	98.5
$(CH_3)_3C$-H	96.5
CH_3-F	110
CH_3-Cl	85
CH_3-Br	70
CH_3-I	57
CH_3CH_2-F	111
CH_3CH_2-Cl	84
CH_3CH_2-Br	70
CH_3CH_2-I	56
$(CH_3)_2CH$-F	111
$(CH_3)_2CH$-Cl	84
$(CH_3)_2CH$-Br	71
$(CH_3)_2CH$-I	56
$(CH_3)_3C$-F	110
$(CH_3)_3C$-Cl	85
$(CH_3)_3C$-Br	71
$(CH_3)_3C$-I	55

Typical Heats of Hydrogenation

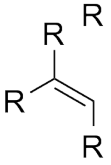
-30 kcal/mol



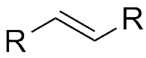
-28.2 kcal/mol



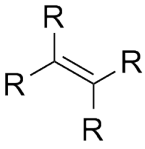
-27.9 kcal/mol



-26.5 kcal/mol



-27.4 kcal/mol



-26.3 kcal/mol