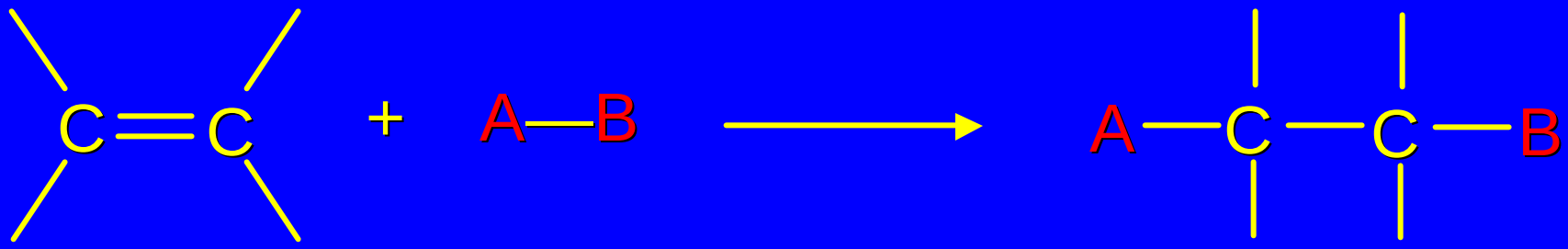
Chapter 6
Reactions of Alkenes:
Addition Reactions

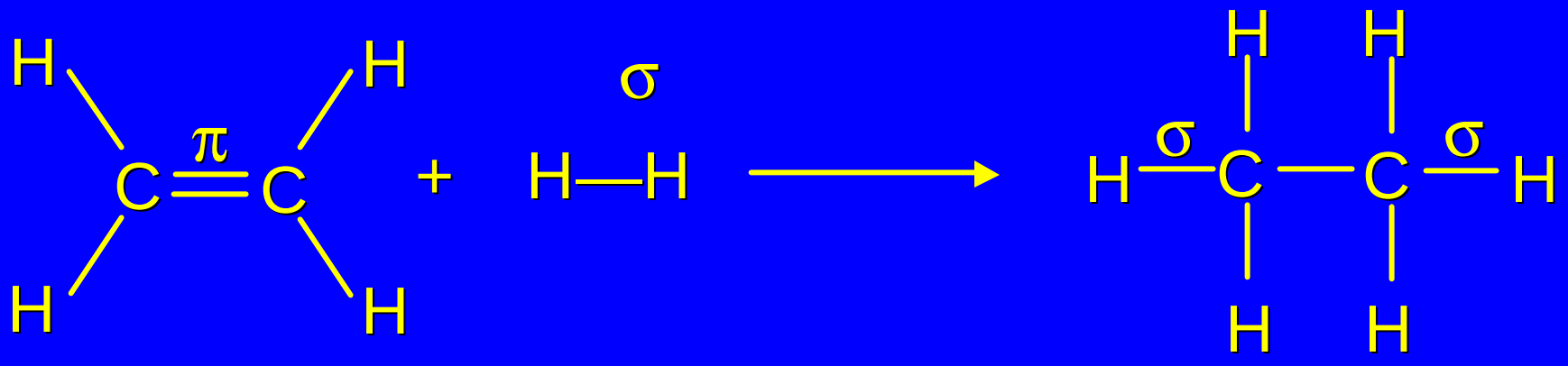
Reactions of Alkenes

The characteristic reaction of alkenes is addition to the double bond.



6.1
Hydrogenation of Alkenes

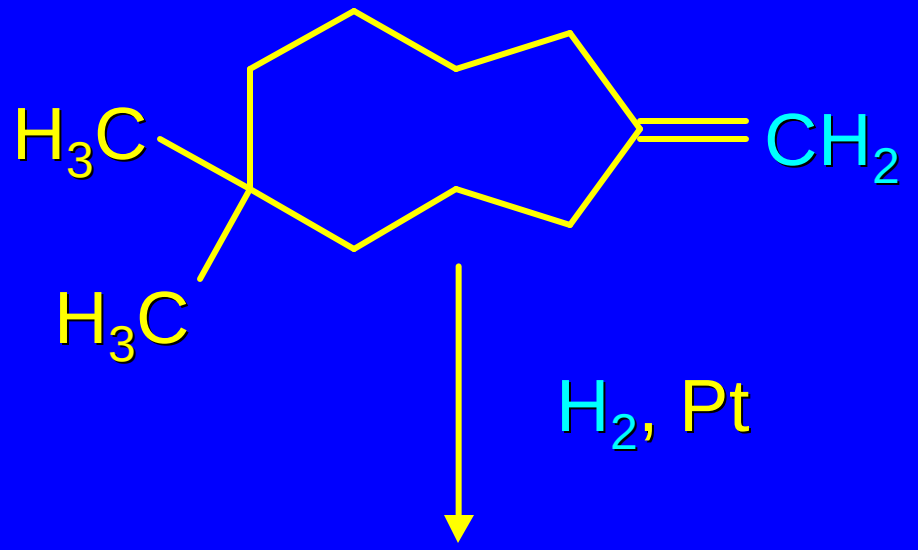
Hydrogenation of Ethylene

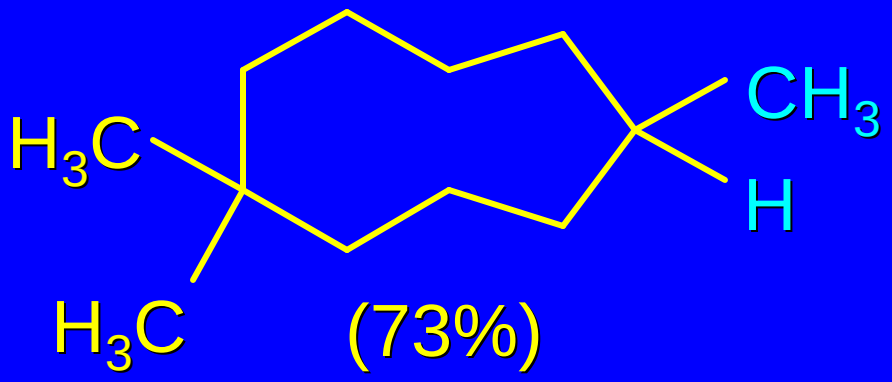


exothermic $\Delta H° = -136$ kJ/mol

catalyzed by finely divided Pt, Pd, Rh, Ni

Example

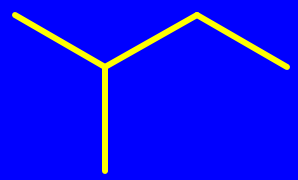




(73%)

Problem 6.1

What three alkenes yield 2-methylbutane on catalytic hydrogenation?



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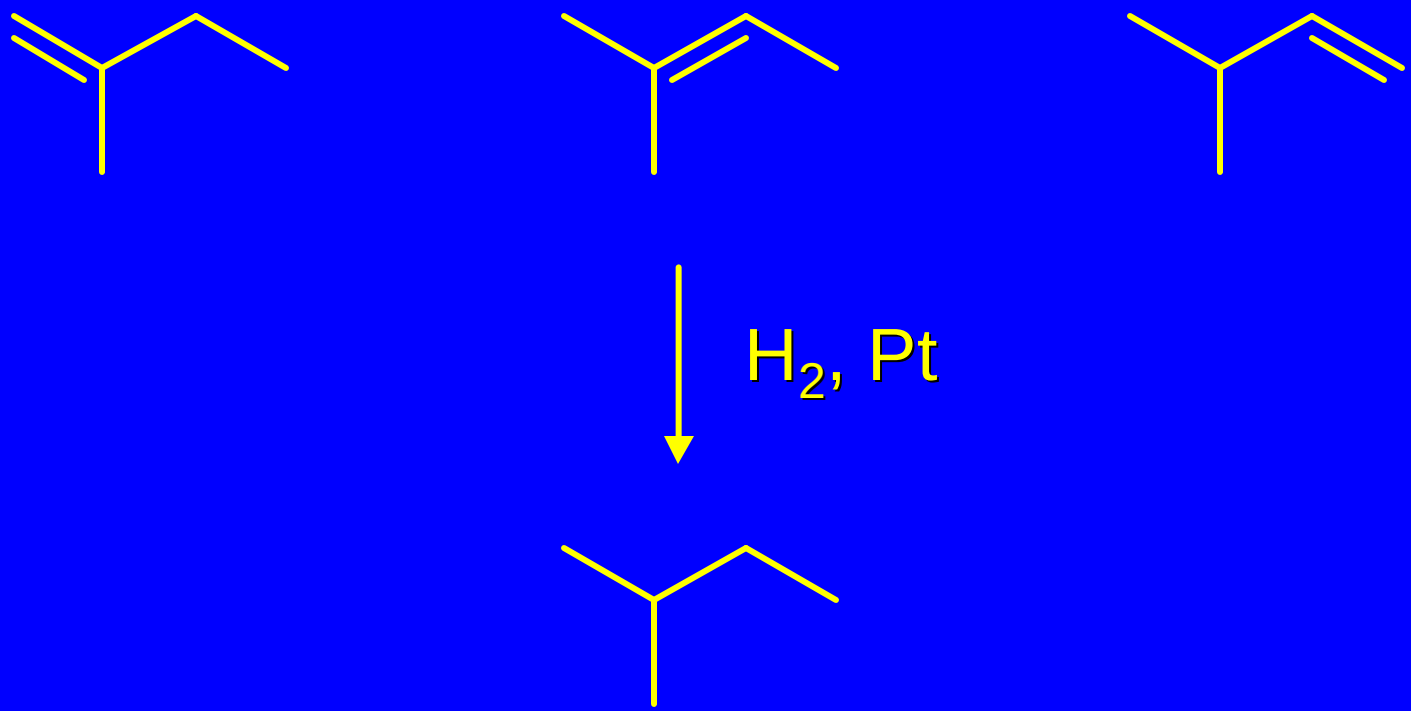
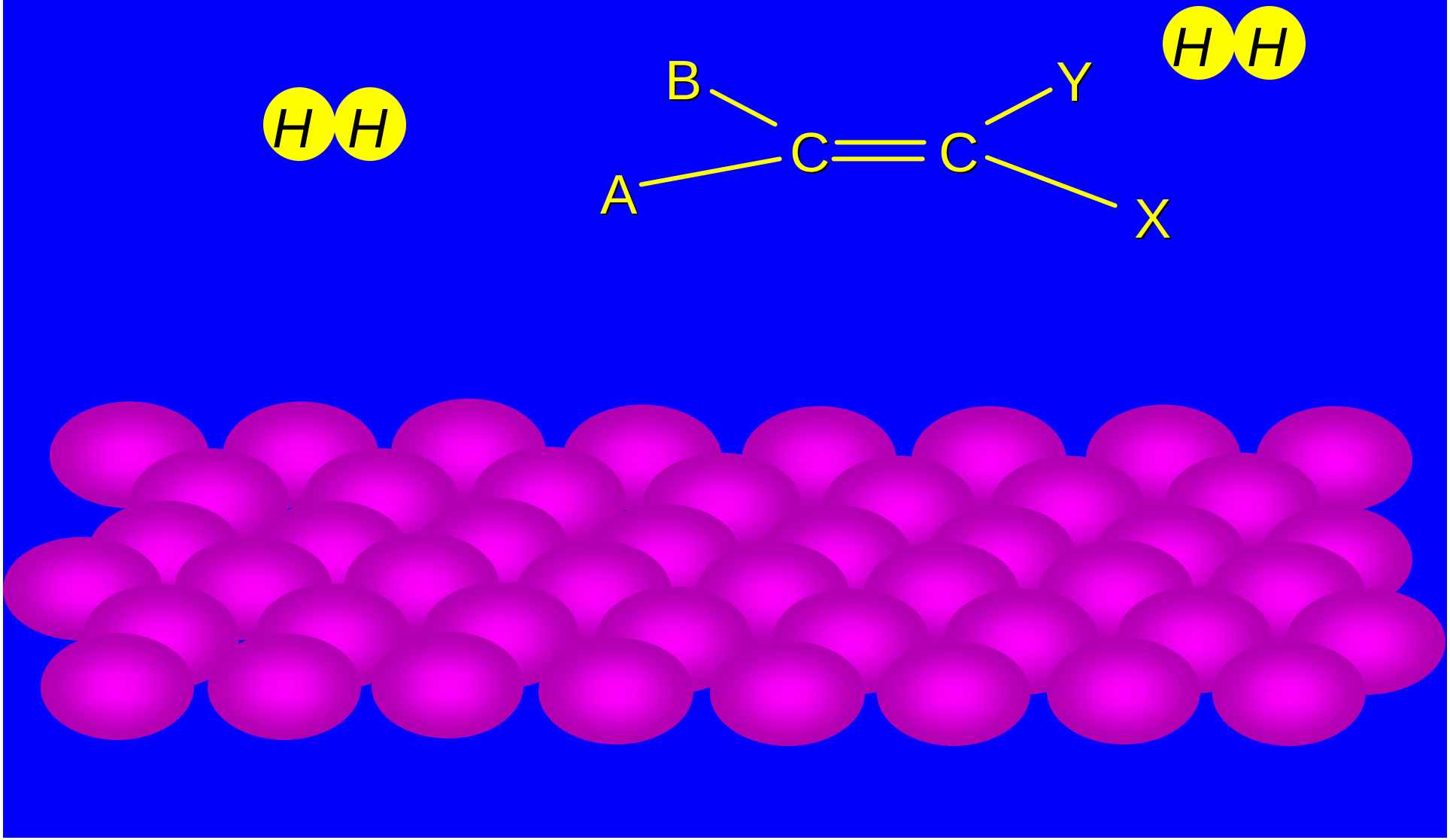
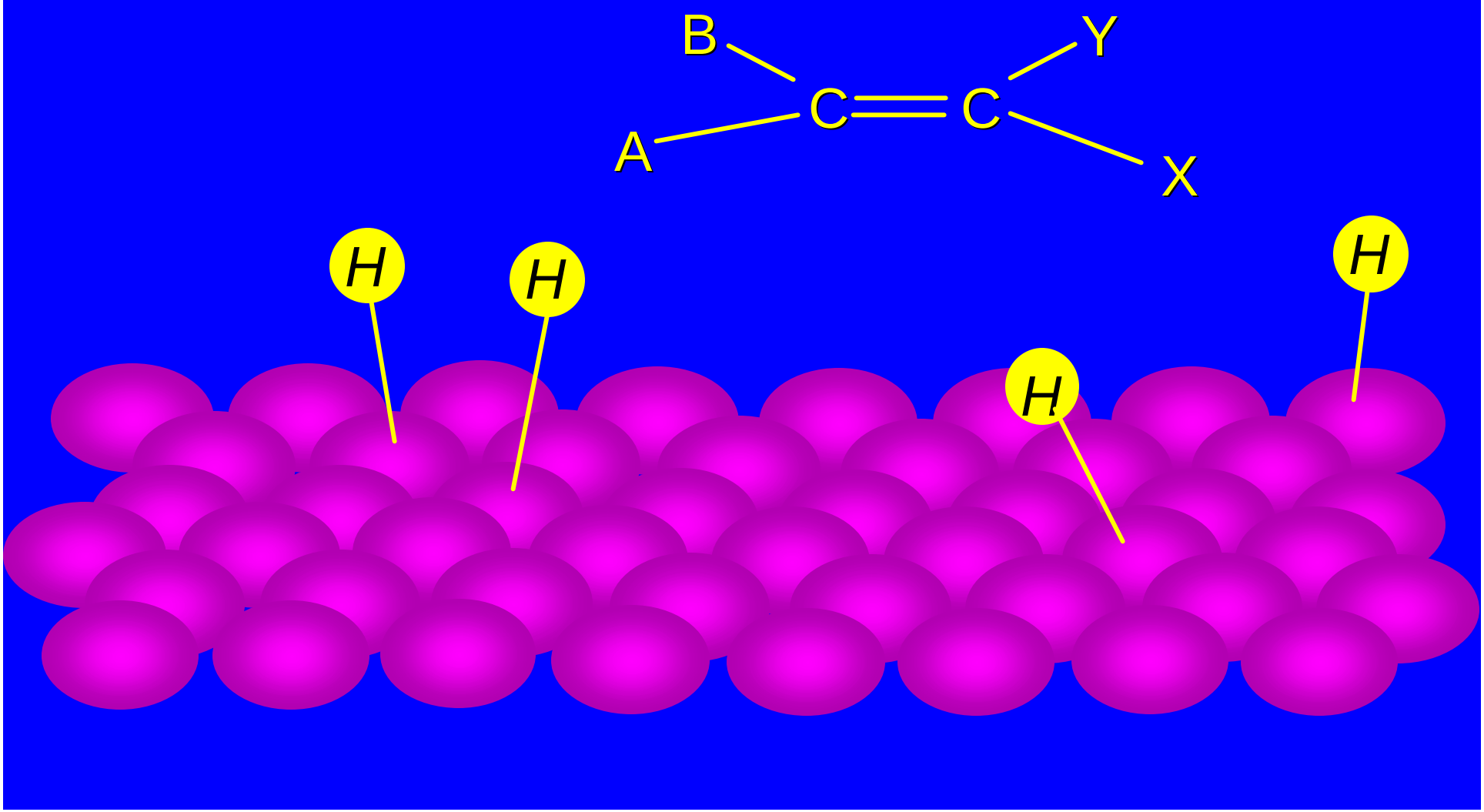


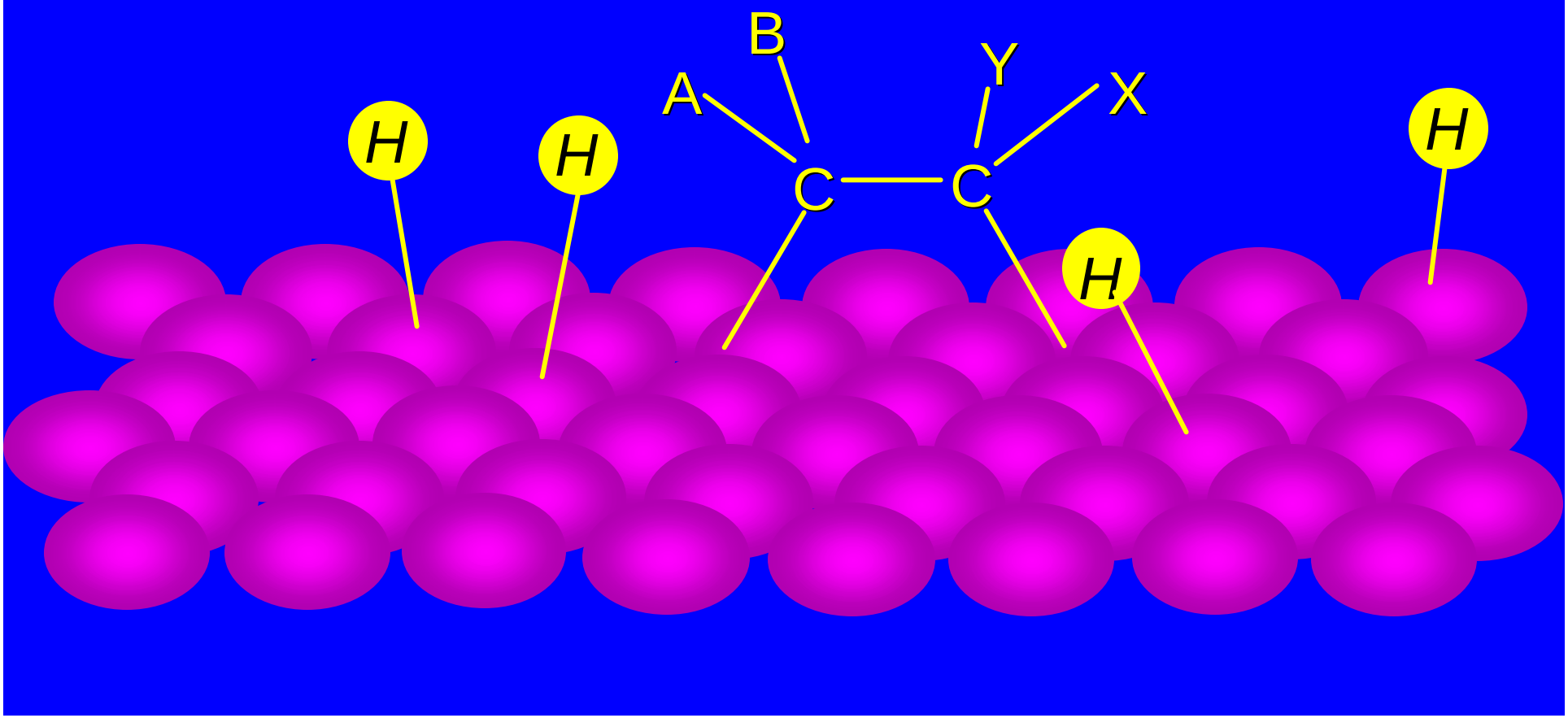
Mechanism of Catalytic Hydrogenation: Figure 6.1



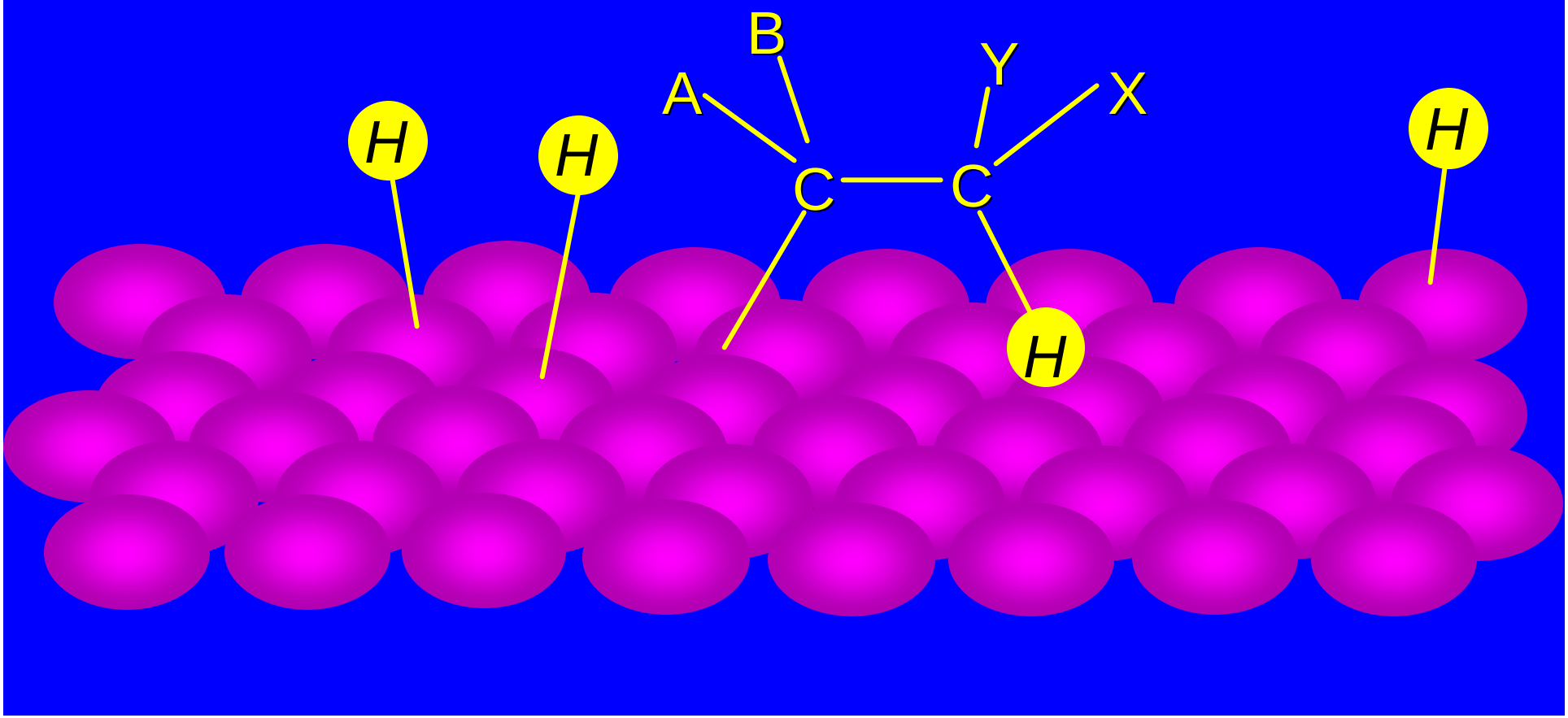
Mechanism of Catalytic Hydrogenation: Figure 6.1



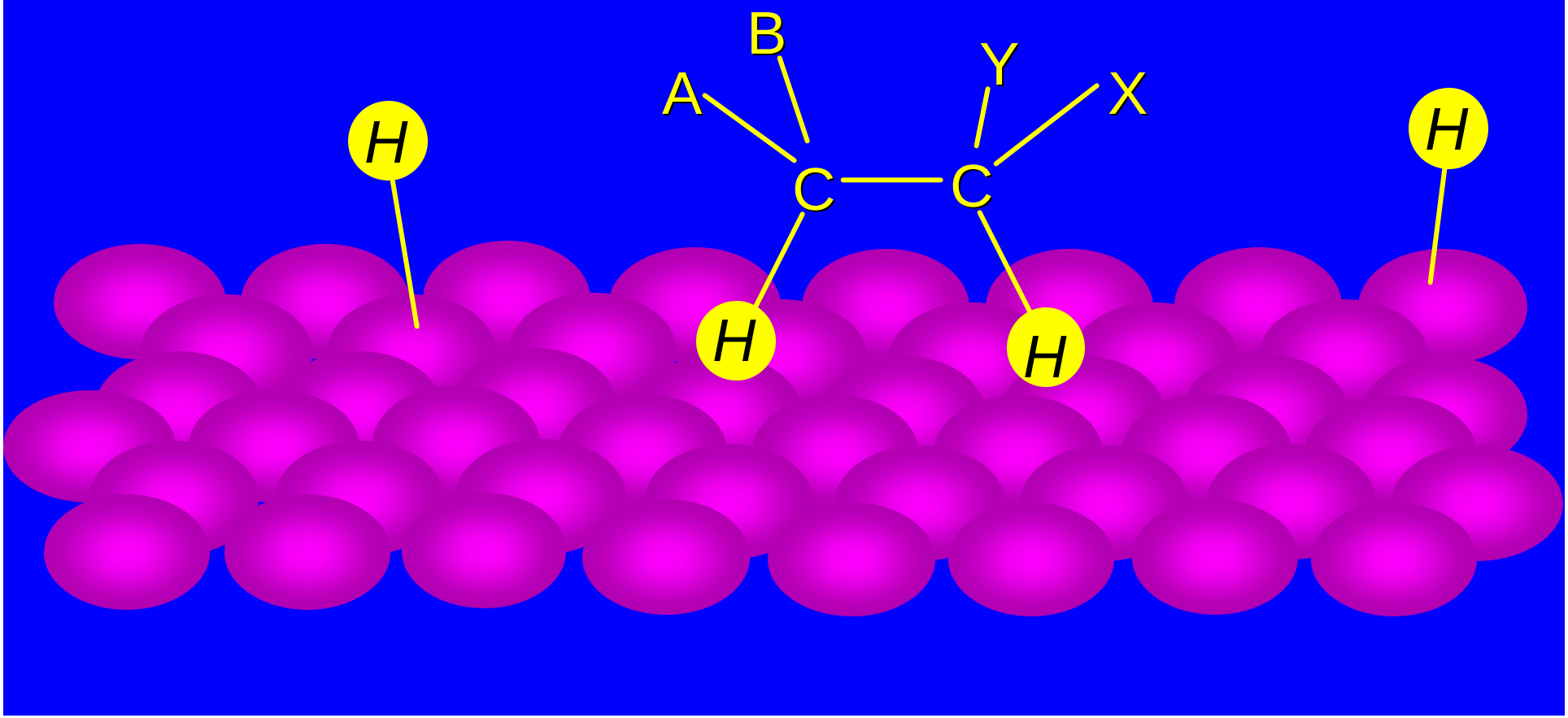
Mechanism of Catalytic Hydrogenation: Figure 6.1



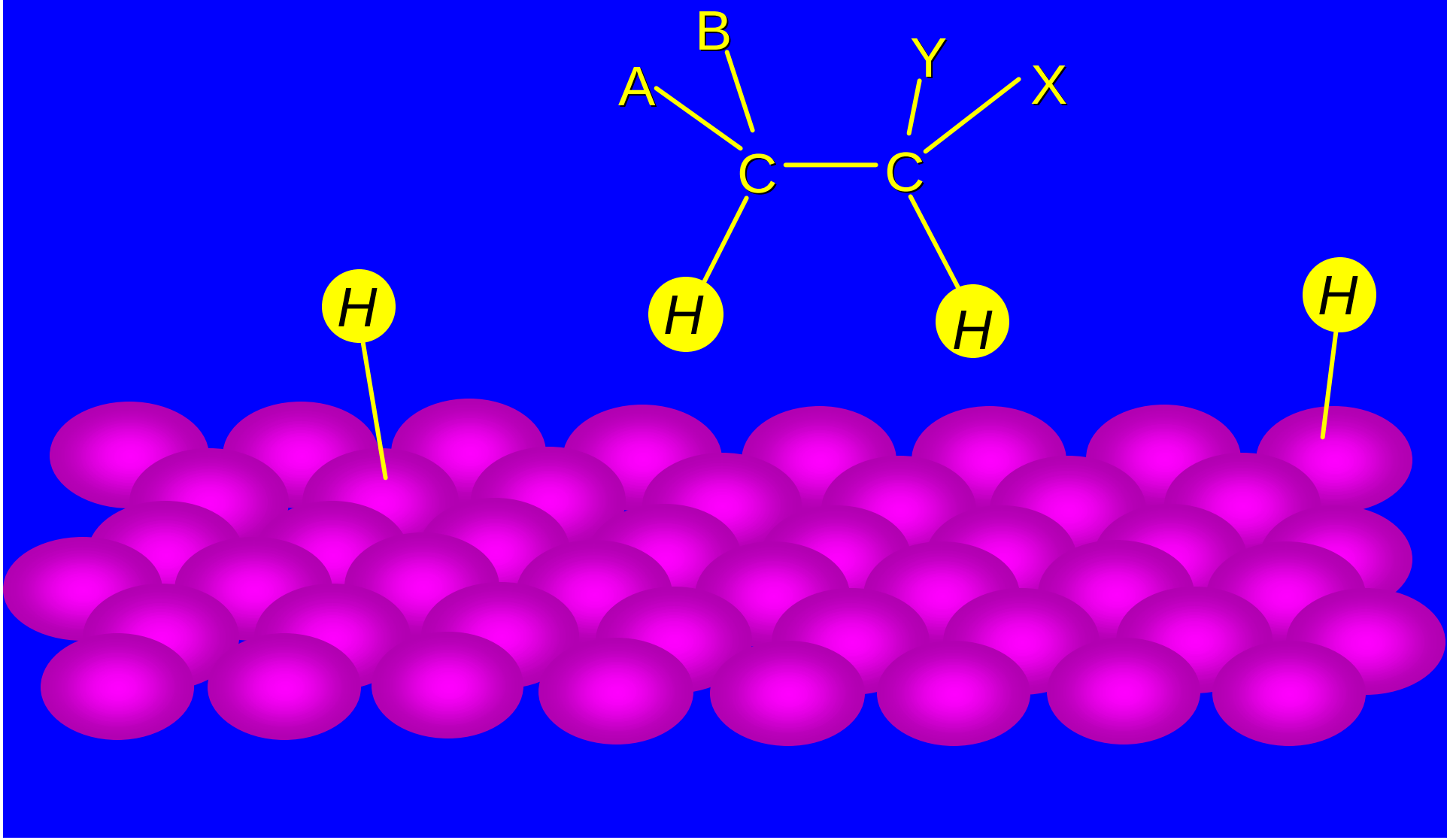
Mechanism of Catalytic Hydrogenation: Figure 6.1



Mechanism of Catalytic Hydrogenation: Figure 6.1



Mechanism of Catalytic Hydrogenation: Figure 6.1

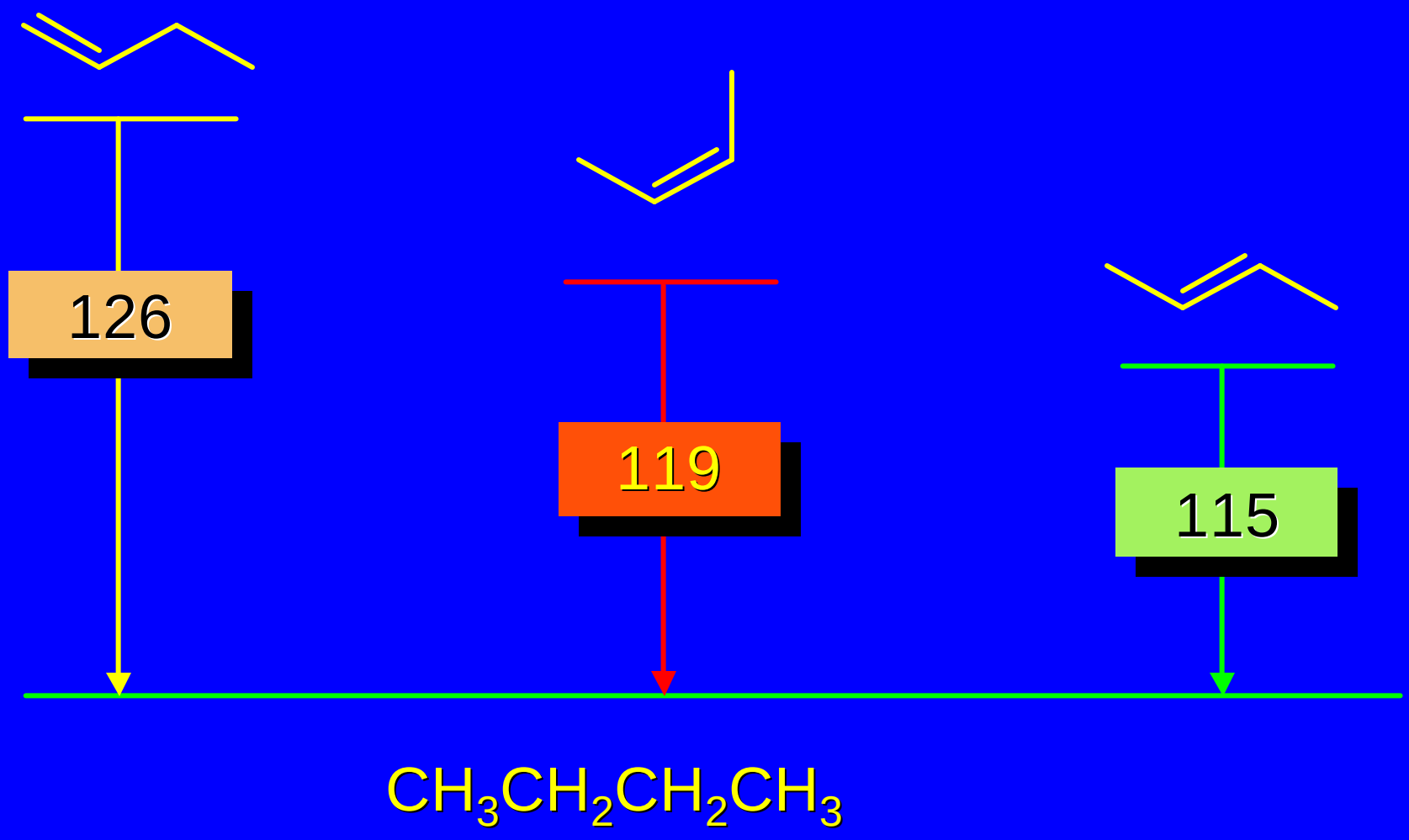


6.2
Heats of Hydrogenation

can be used to measure relative stability of isomeric alkenes

correlation with structure is same as when heats of combustion are measured

Heats of Hydrogenation of Isomers



Heats of Hydrogenation (kJ/mol)

Ethylene	136
Monosubstituted	125-126
cis-Disubstituted	117-119
trans-Disubstituted	114-115
Terminally disubstituted	116-117
Trisubstituted	112
Tetrasubstituted	110

Problem 6.2

Match each alkene of Problem 6.1 with its correct heat of hydrogenation.

126 kJ/mol

118 kJ/mol

112 kJ/mol

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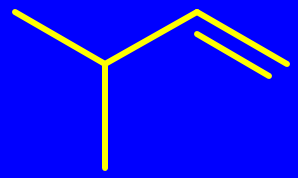
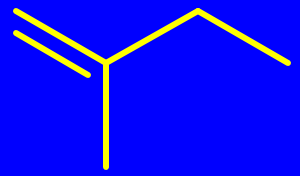
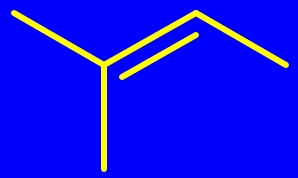


highest heat of hydrogenation; least stable isomer

118 kJ/mol



112 kJ/mol



lowest heat of hydrogenation; most stable isomer

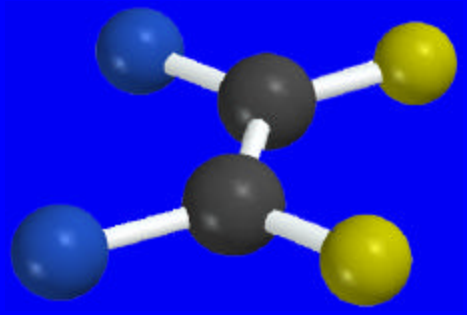
6.3
Stereochemistry of Alkene Hydrogenation

Two spatial (stereochemical) aspects of alkene hydrogenation:

syn addition of both H atoms to double bond

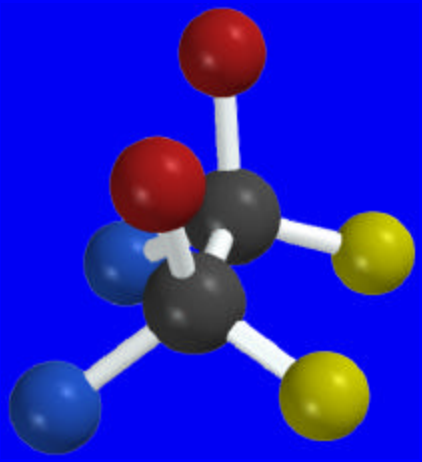
hydrogenation is stereoselective, corresponding to addition to less crowded face of double bond

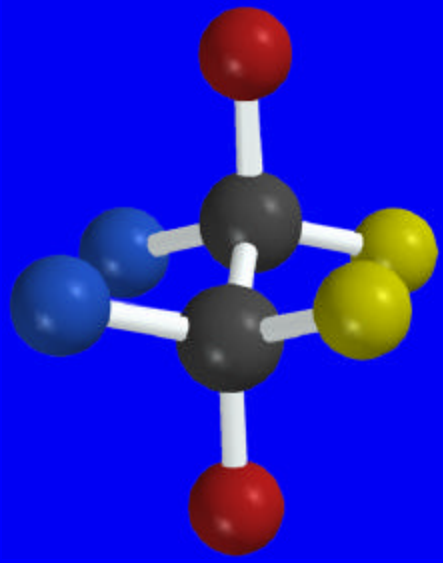
syn-Additon versus anti-Addition



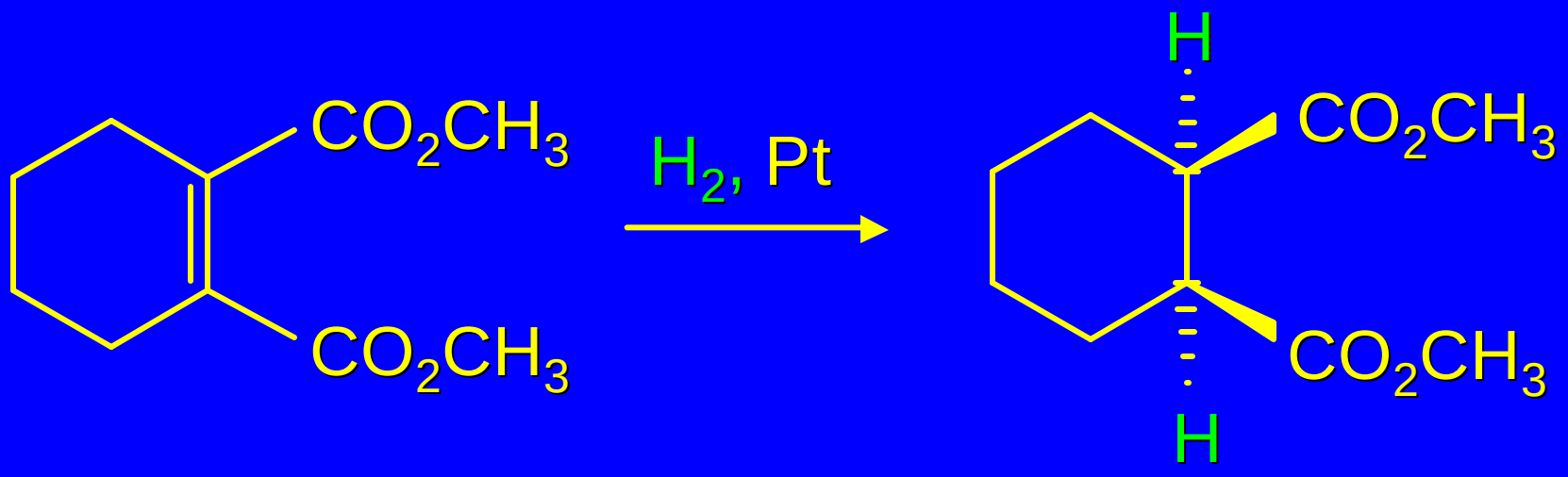
syn addition

anti addition





Example of Syn Addition

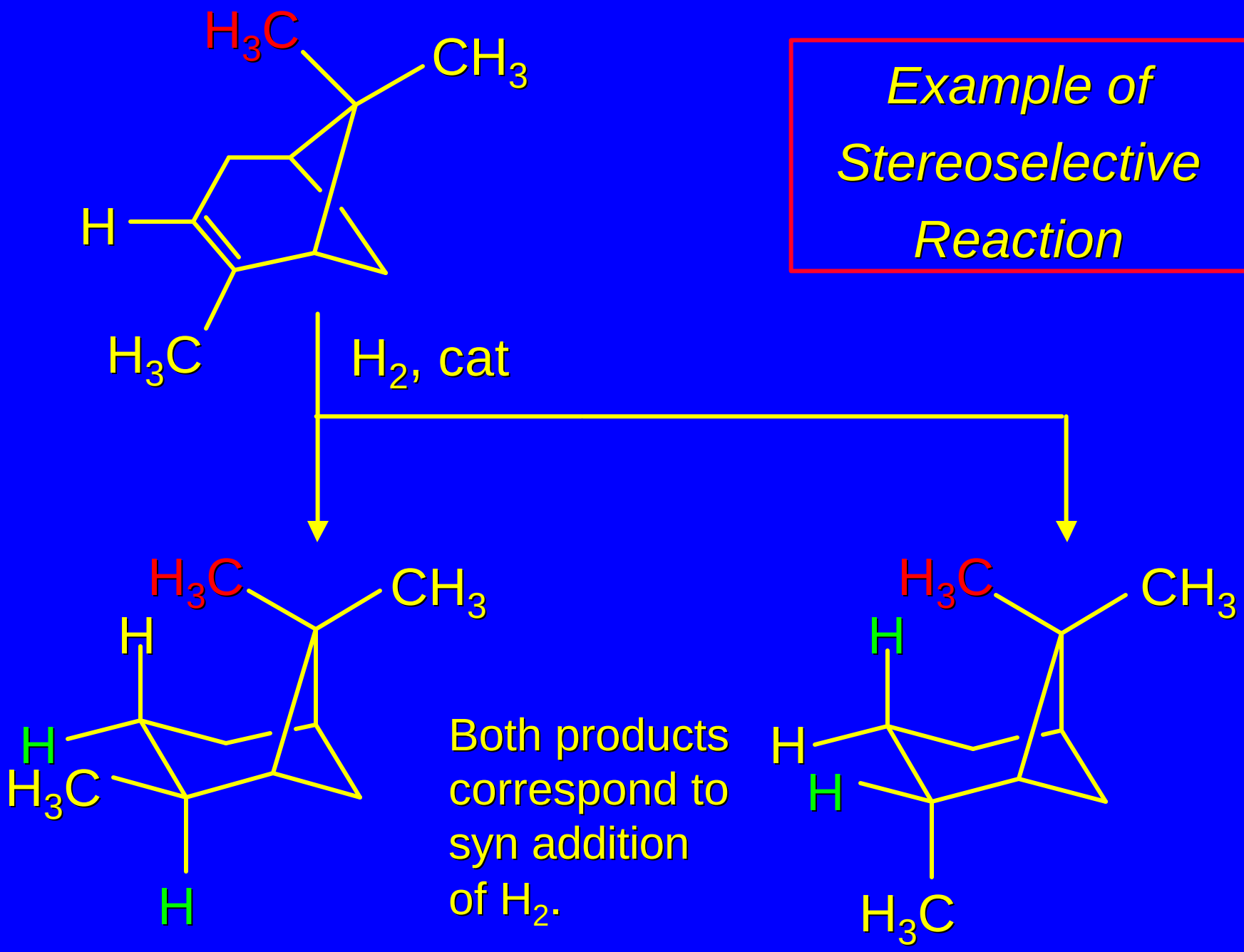


(100%)

Stereoselectivity

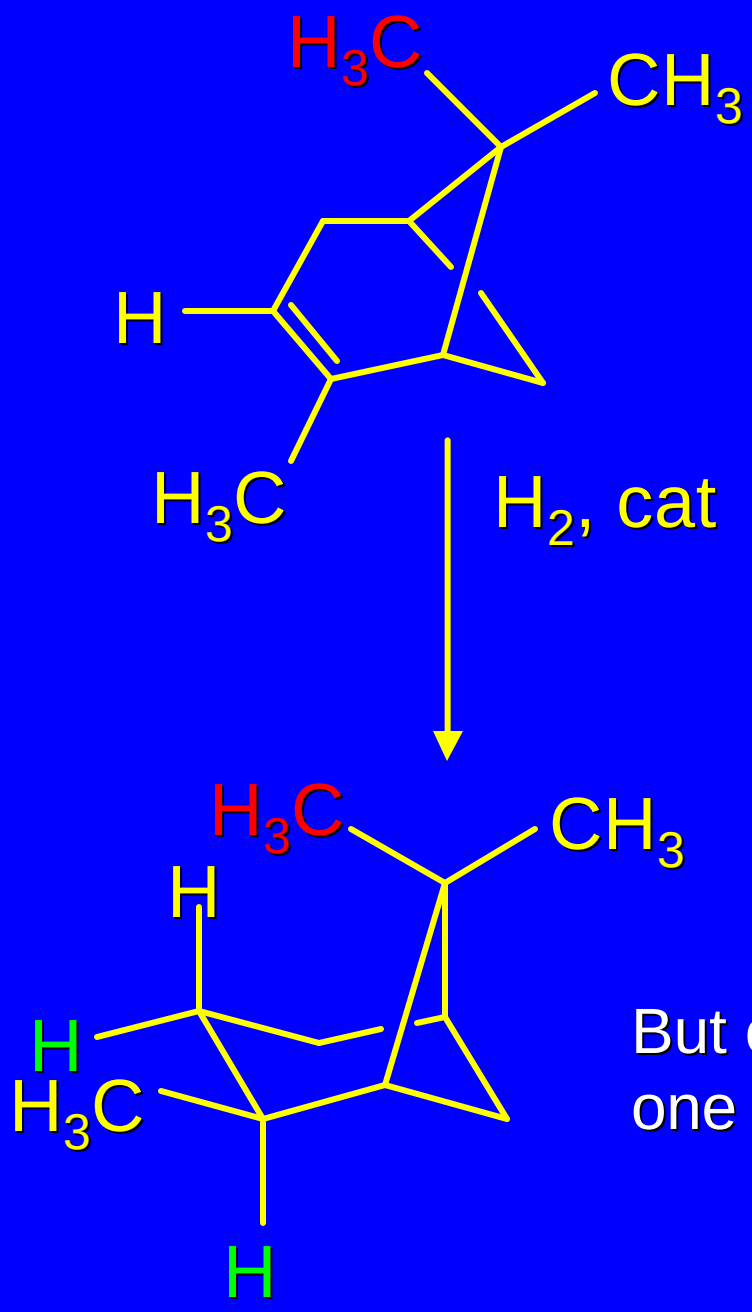
A reaction in which a single starting material can give two or more stereoisomeric products but yields one of them in greater amounts than the other (or even to the exclusion of the other) is said to be stereoselective.

Example of Stereoselective Reaction



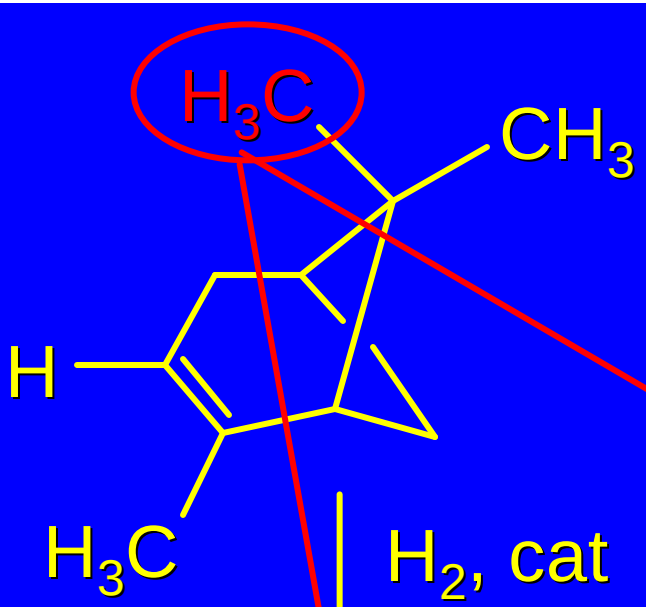
Both products correspond to syn addition of H_2.

Example of Stereoselective Reaction



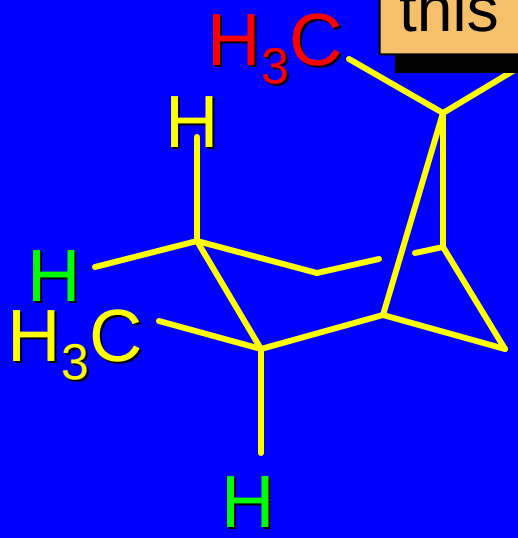
But only this one is formed.

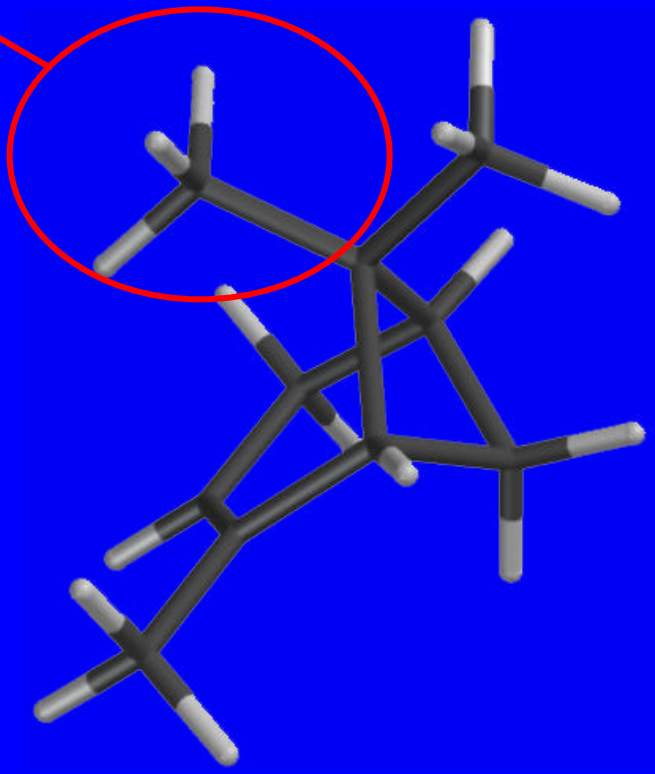
Example of Stereoselective Reaction



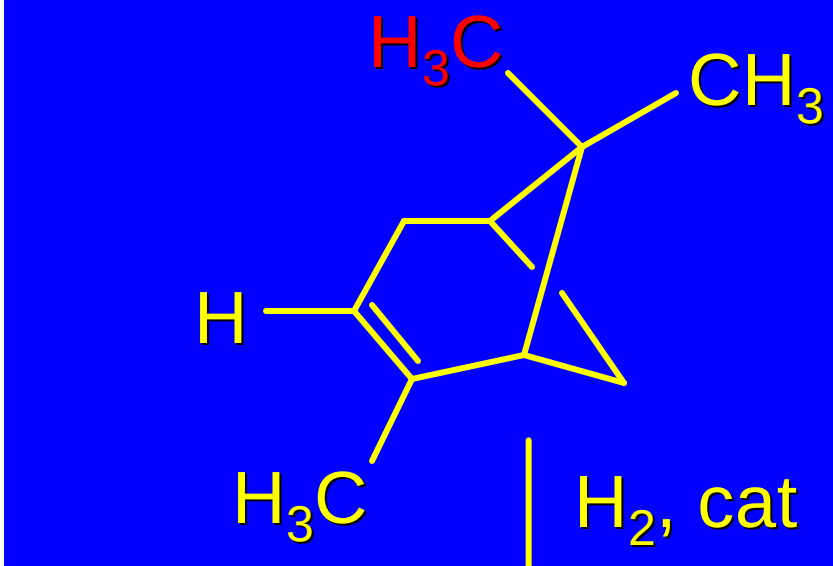
H_2, cat

Top face of double bond blocked by this methyl group

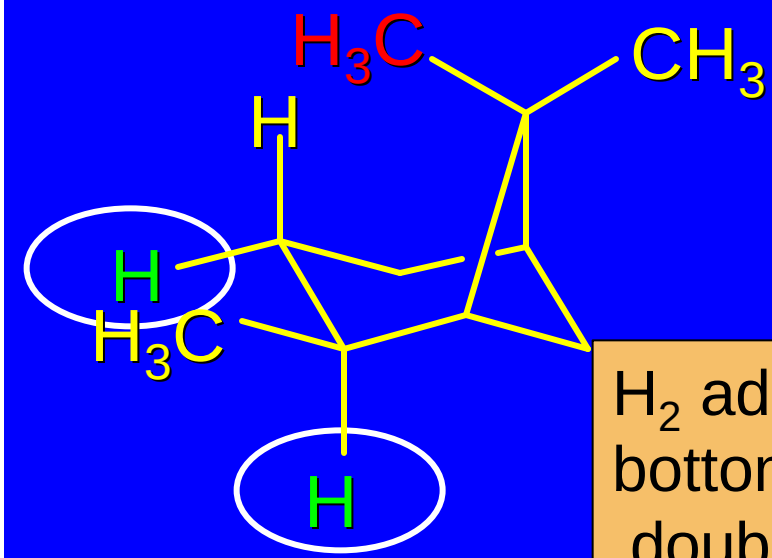




Example of Stereoselective Reaction



H_2, cat



H_2 adds to bottom face of double bond.