



Electrophilic Addition of Hydrogen Halides to Alkenes

Lecture in Organic chemistry

By

Doctoral student

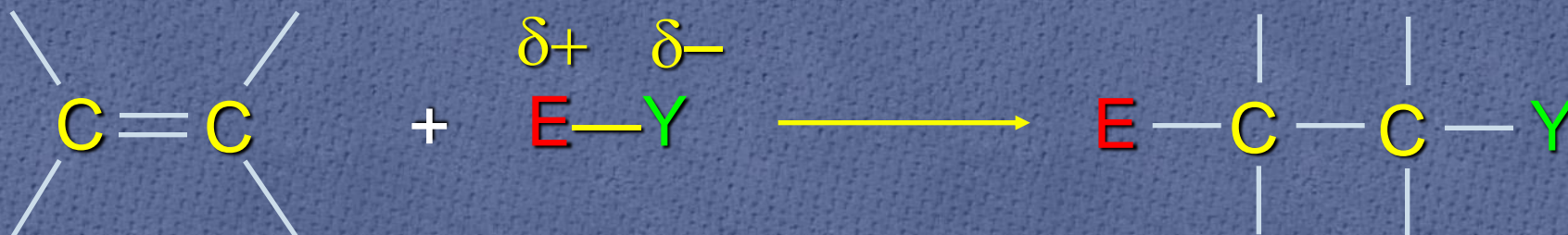
Sukaena H. Rashed

Supervised by : Prof. Hanaa Kaain Salih

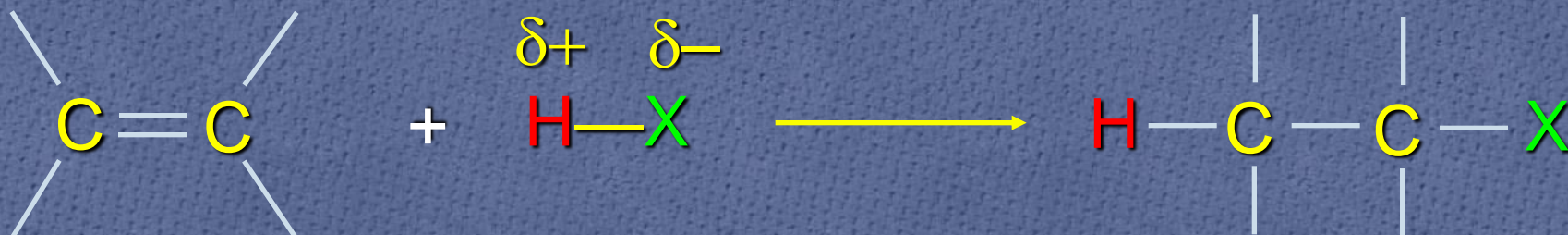
Tikrit University

Department of chemistry

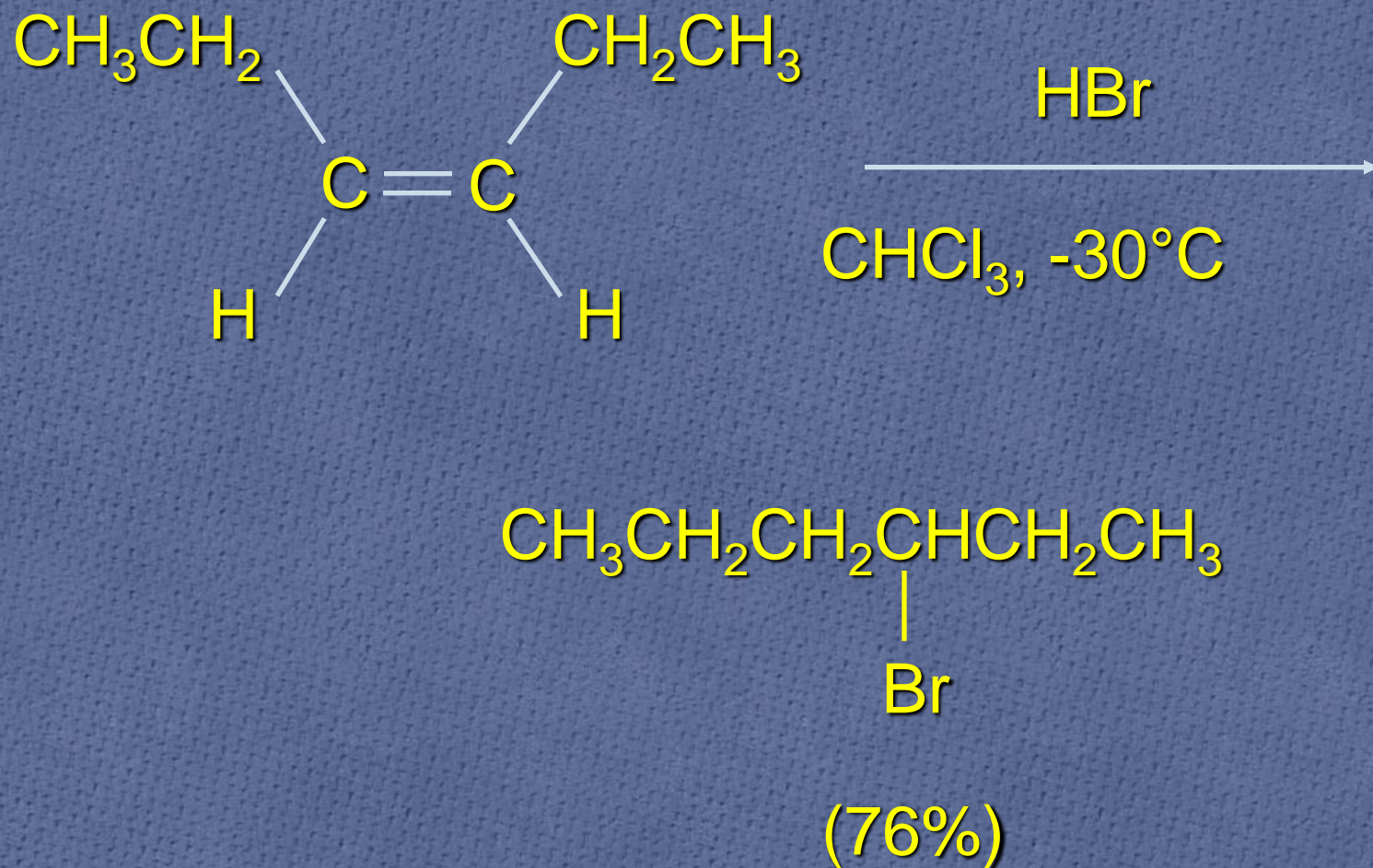
General equation for electrophilic addition



When EY is a hydrogen halide



Example

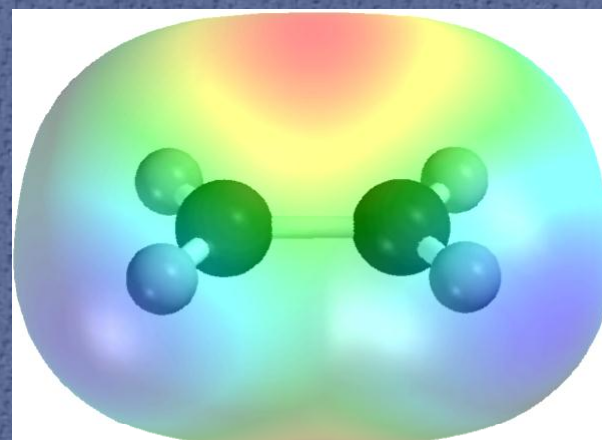
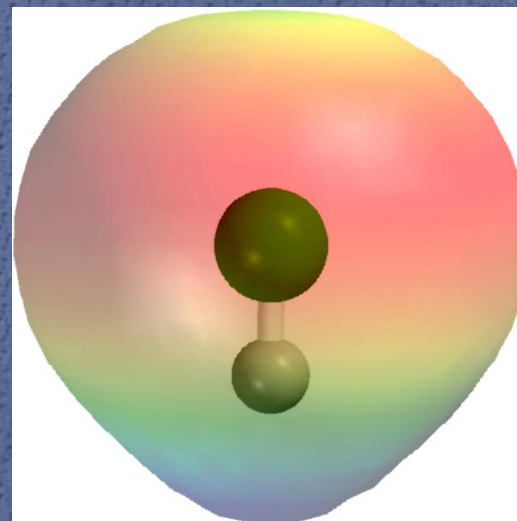


Mechanism

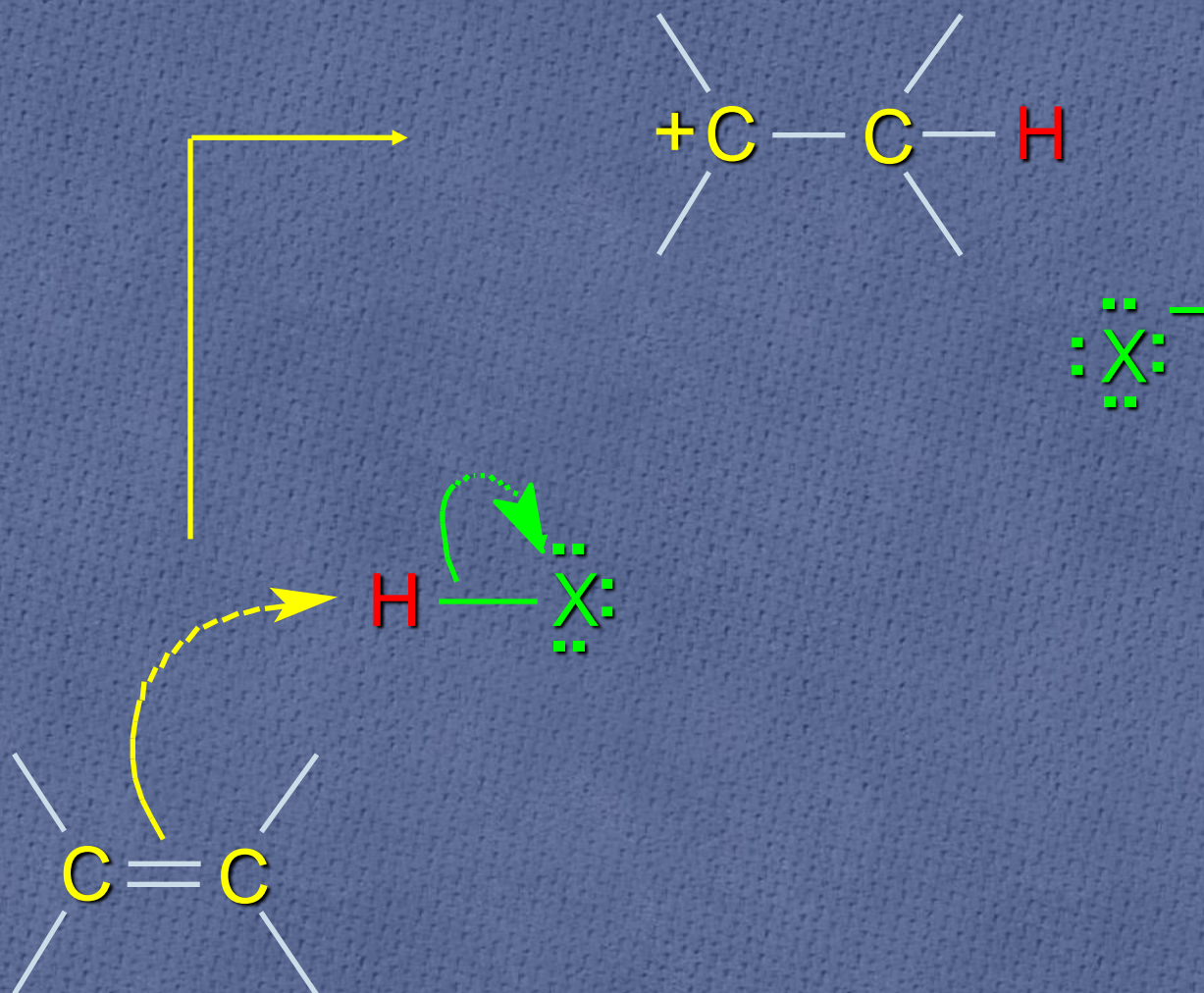
Electrophilic addition of hydrogen halides to alkenes proceeds by rate-determining formation of a carbocation intermediate.

Mechanism

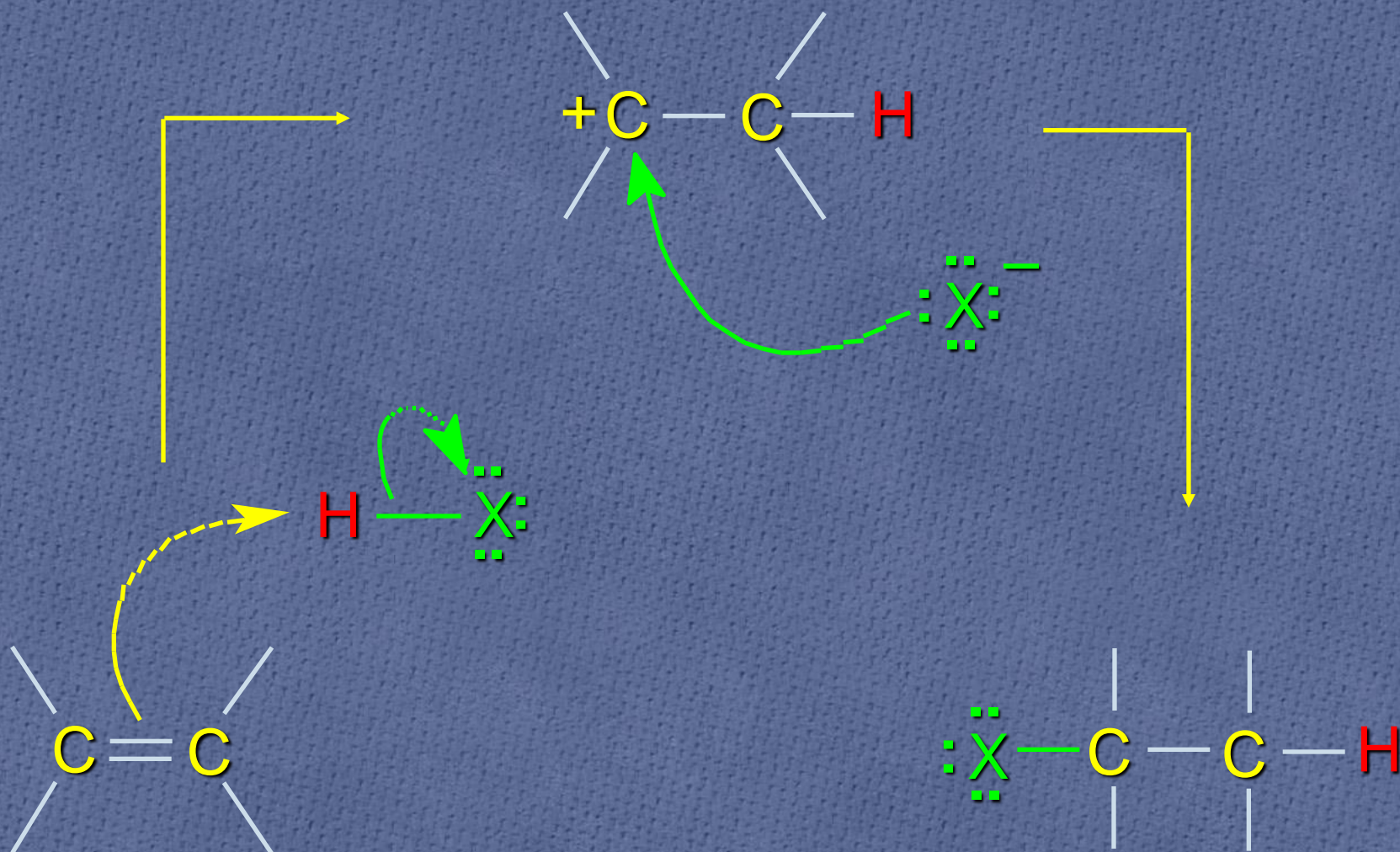
Electrons flow from the π system of the alkene (electron rich) toward the positively polarized proton of the hydrogen halide.



Mechanism



Mechanism

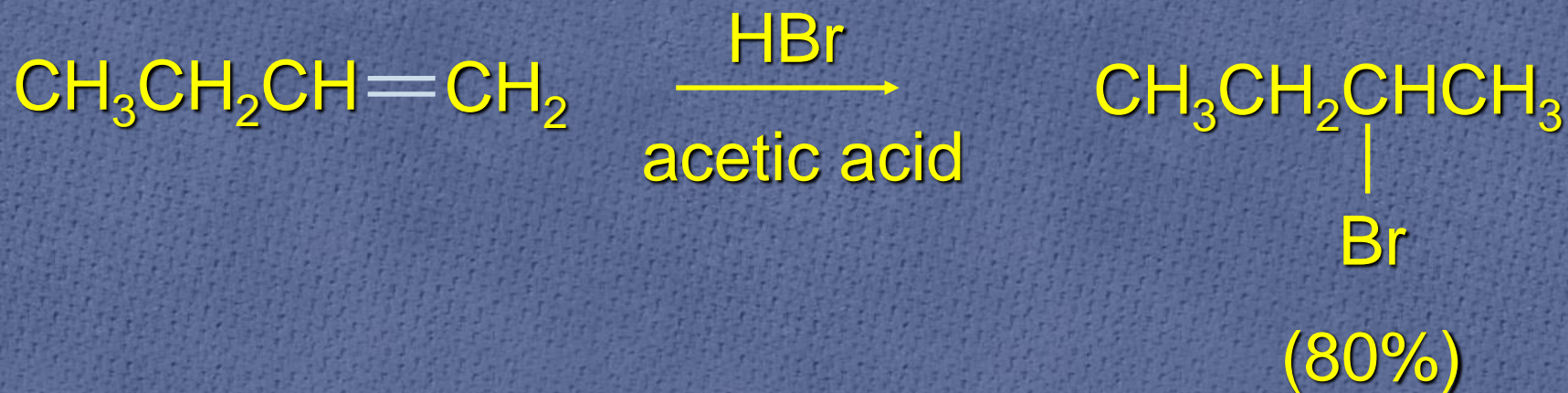


Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule

Markovnikov's Rule

When an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogen substituents, and the halogen adds to the carbon that has the fewer hydrogen substituents.

Markovnikov's Rule



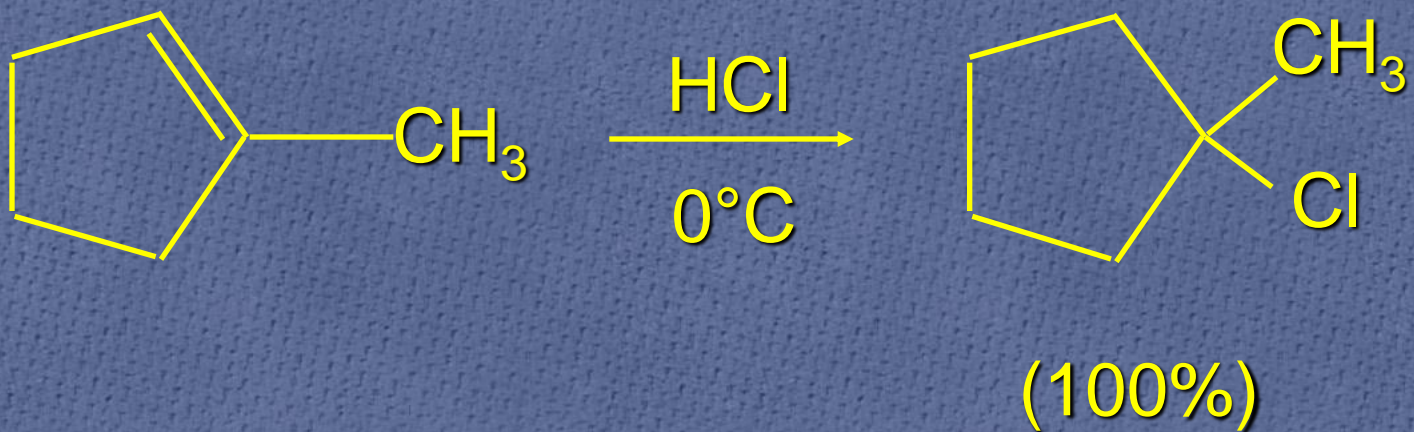
Example 1

Markovnikov's Rule



Example 2

Markovnikov's Rule

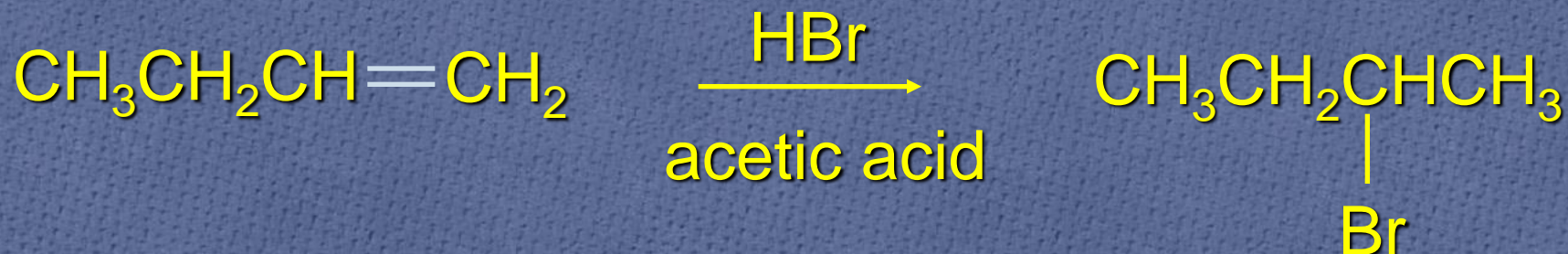


Example 3

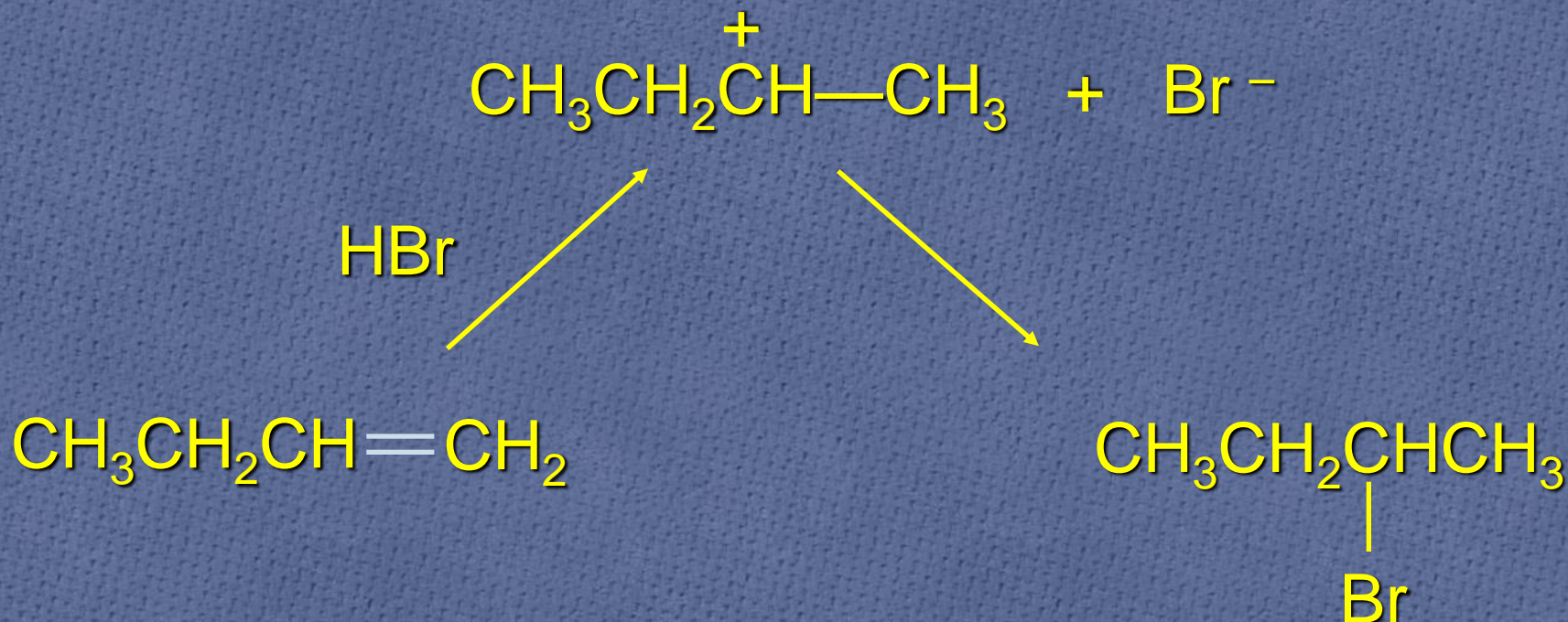
Mechanistic Basis for Markovnikov's Rule

Protonation of double bond occurs in direction that gives more stable of two possible carbocations.

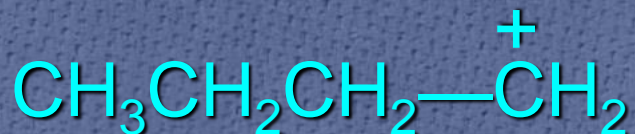
Mechanistic Basis for Markovnikov's Rule: Example 1



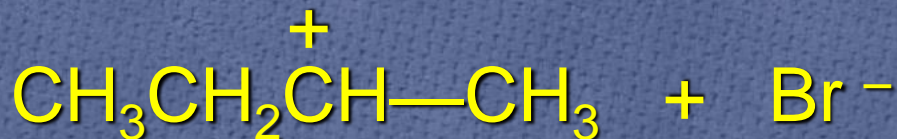
Mechanistic Basis for Markovnikov's Rule: Example 1



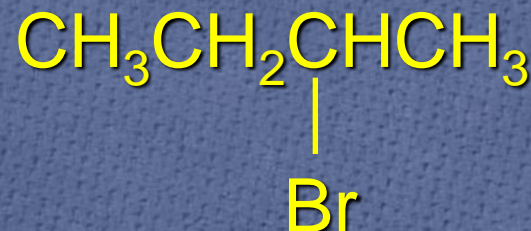
Mechanistic Basis for Markovnikov's Rule: Example 1



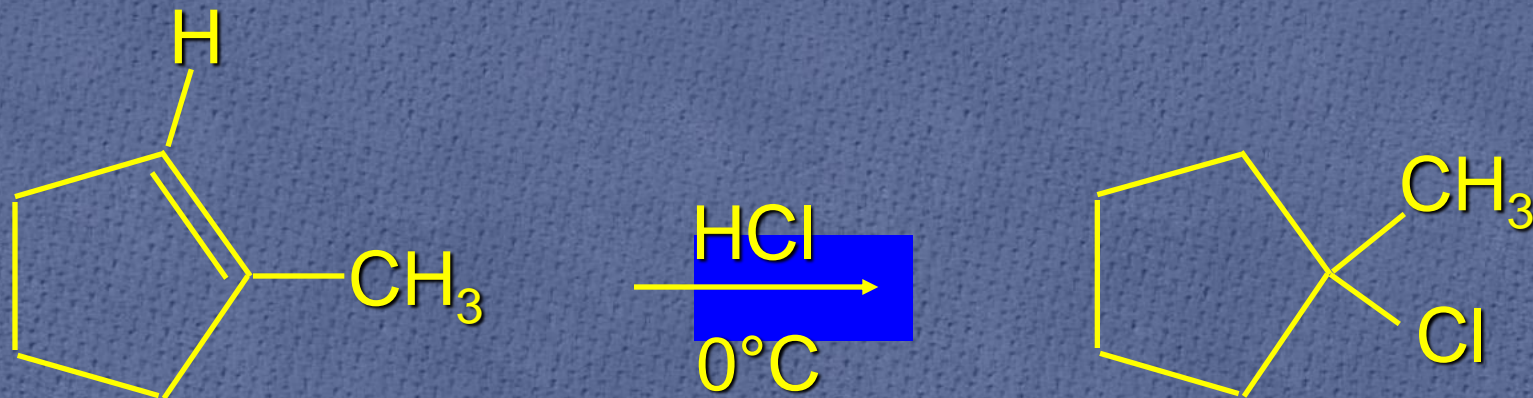
primary carbocation is less stable: not formed



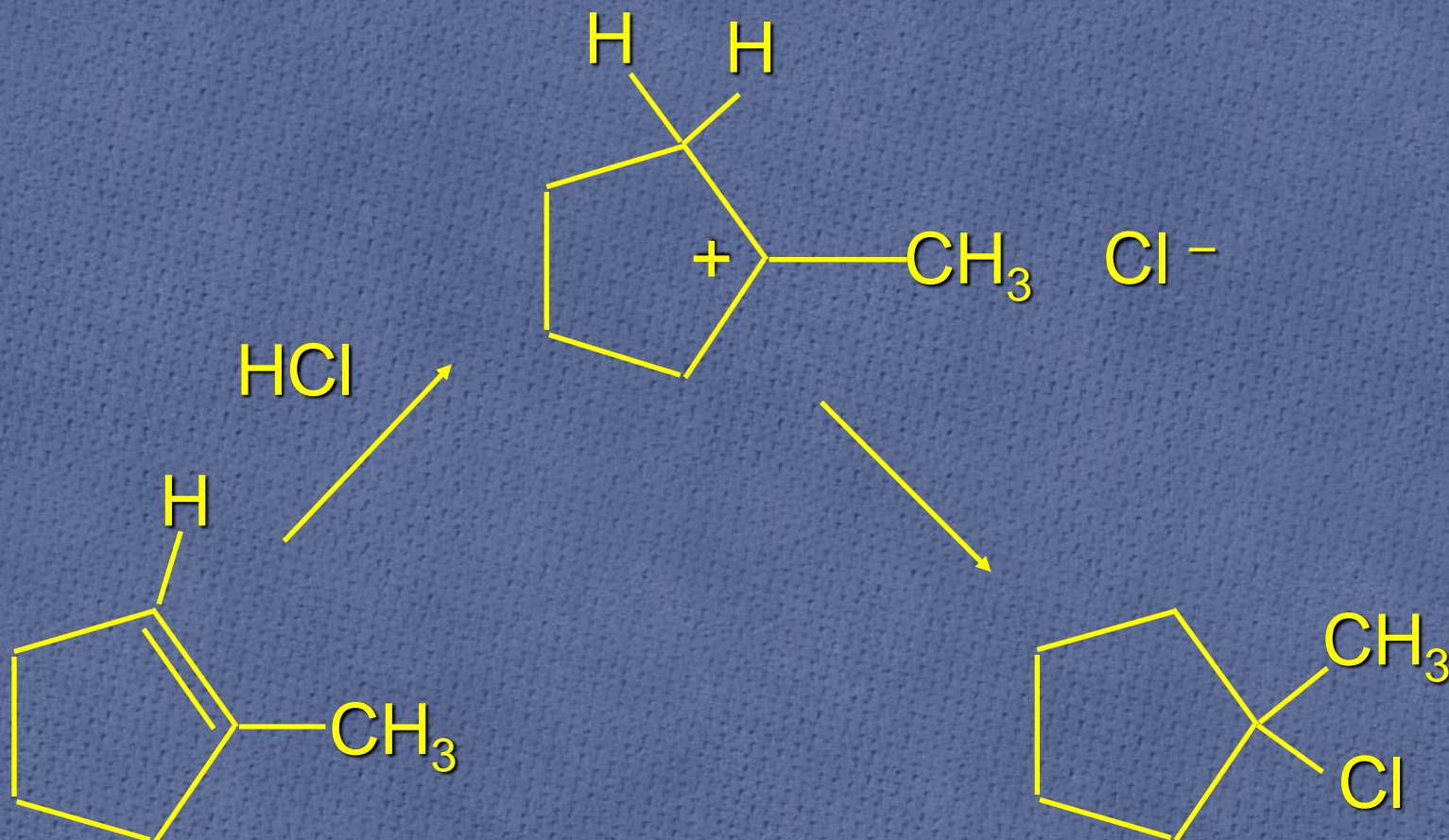
HBr



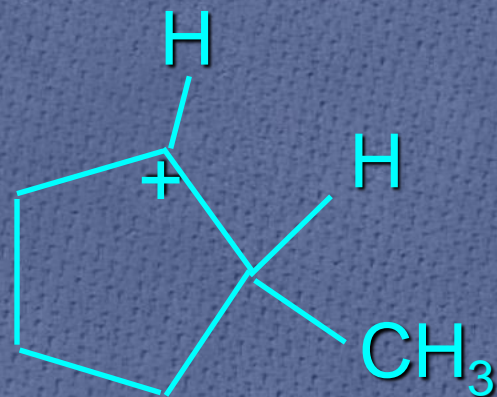
Mechanistic Basis for Markovnikov's Rule: Example 3



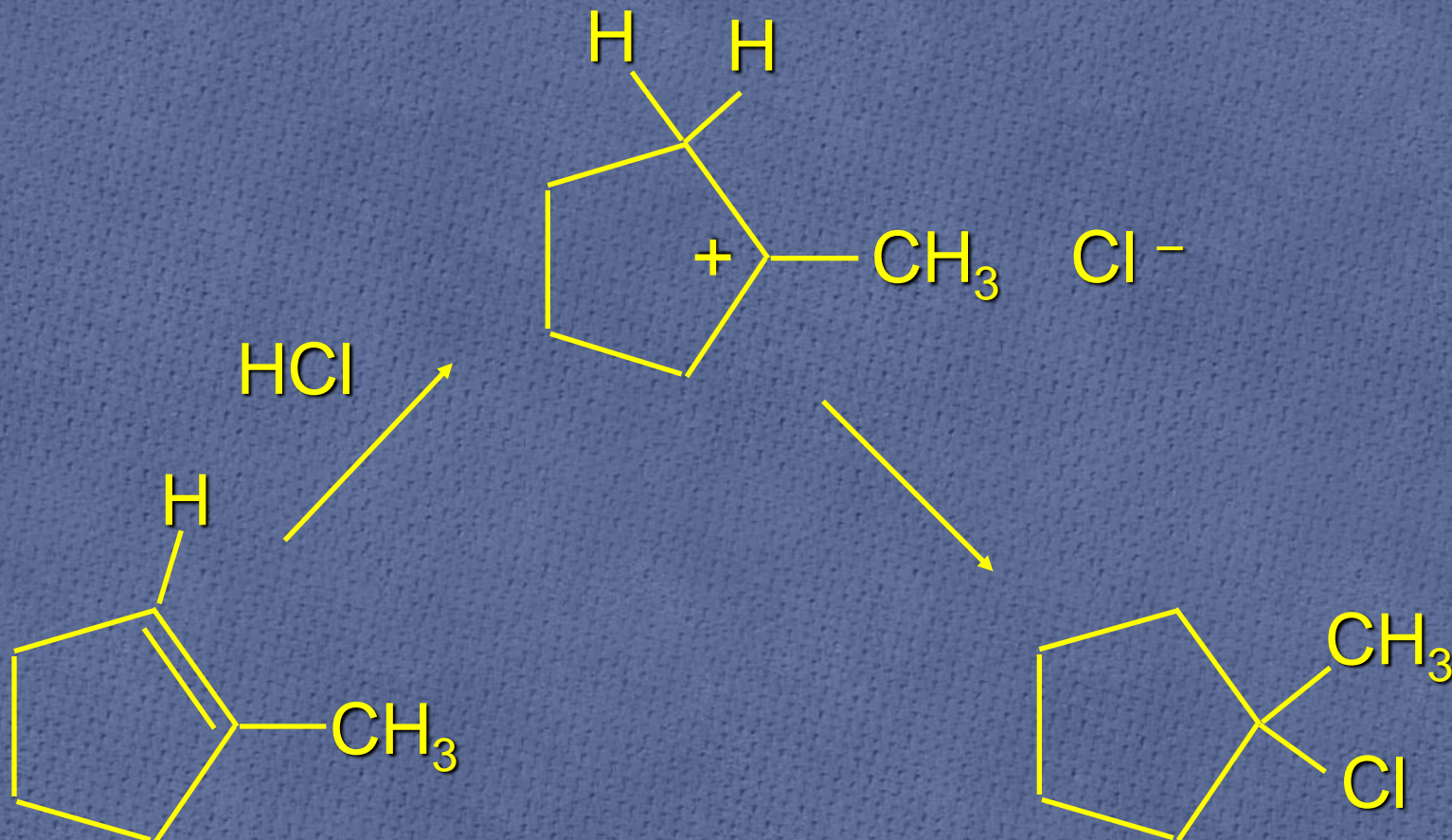
Mechanistic Basis for Markovnikov's Rule: Example 3



secondary
carbocation is
less stable:
not formed

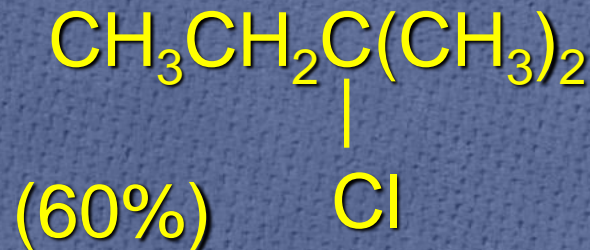
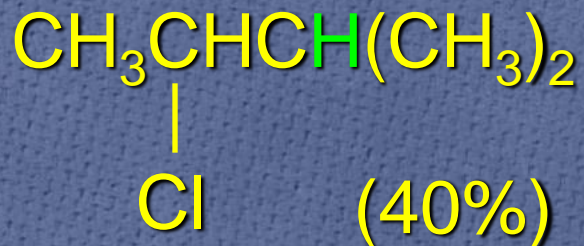
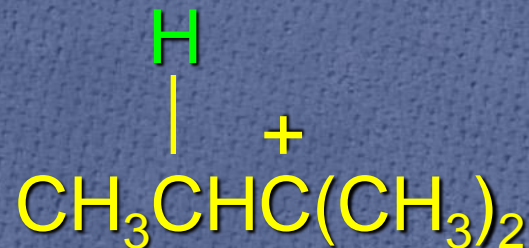
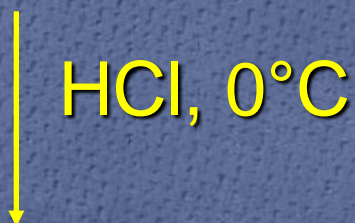


Mechanistic Basis for Markovnikov's Rule: Example 3



Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes

Rearrangements sometimes occur



References

- 1- Solomons, T.W. Graham; Fryhle, Craig B. (2003), Organic Chemistry (8th ed.).
- 2- Smith, Janice G. (2007), Organic Chemistry (2nd ed.), McGraw-Hill.
- 3- P.J. Kropp; K.A. Dans; S.D. Crawford; M.W. Tubergen; K.D. Kepler; S.L. Craig; V.P. Wilson (1990), "Surface-mediated reactions. 1. Hydrohalogenation of alkenes and alkynes", J. Am. Chem. Soc., 112 (112): 7433–7434.
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- 5- March Jerry; (1985). Advanced Organic Chemistry reactions, mechanisms and structure (3rd ed.). New York.
- 6- Dagani, M. J.; Barda, H. J.; Benya, T. J.; Sanders, D. C. (2012), "Bromine Compounds", Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH, doi:10.1002/14356007.404_405.

THANK YOU

