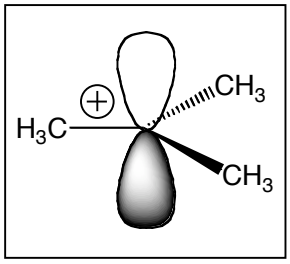
Massachusetts Institute of Technology

5.13: Organic Chemistry II ***Fall 2006***

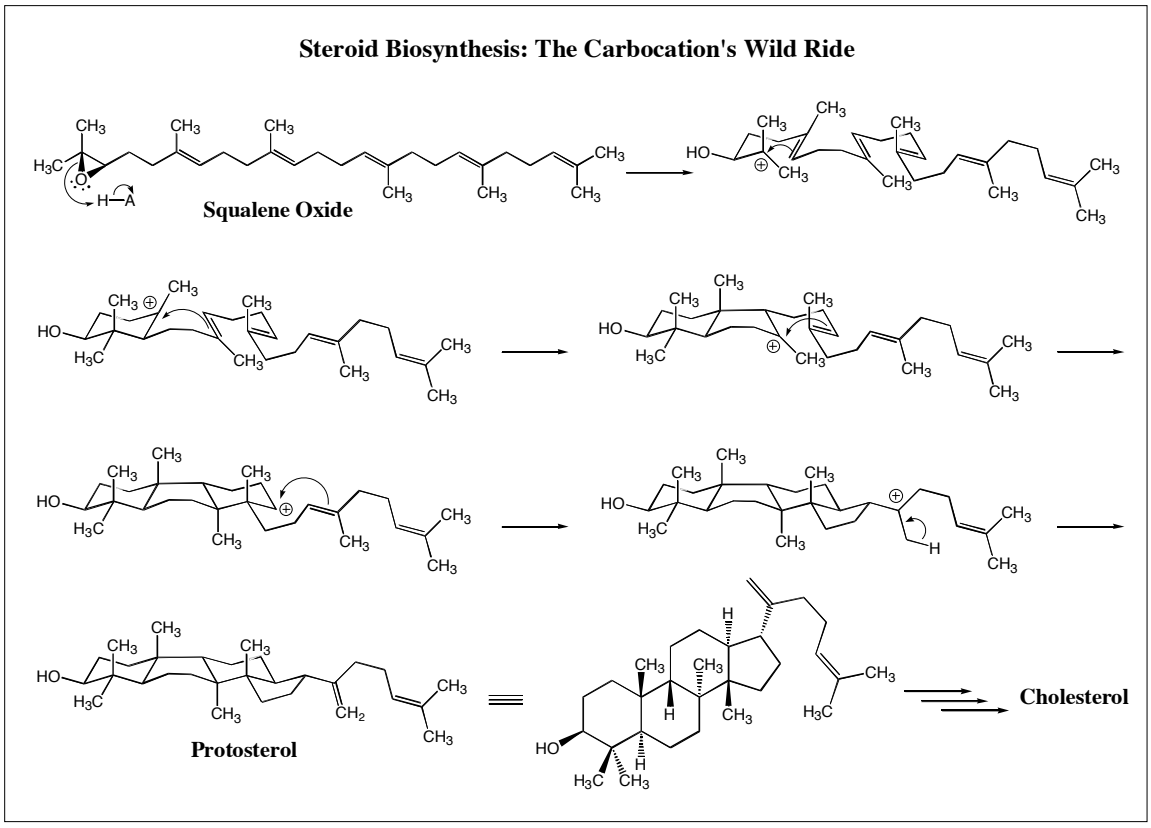
Outline & Study Guide for Unit VII. Carbocations

"Every generation of scientific men (i.e. scientists) starts where the previous generation left off; and the most advanced discoveries of one age constitute elementary axioms of the next." **–Aldous Huxley**

Carbocationic species are intermediates in many chemical reactions carried out in the laboratory, as well as numerous reactions that take place in nature. Carbocations are so important, in fact, that Professor George A. Olah of The University of Southern California was awarded the 1994 Nobel Prize in Chemistry for "his contribution to carbocation chemistry."



One famous example of a carbocationic cascade reaction is the biosynthesis of cholesterol from squalene oxide. Conversion of the linear polyene to the four-ring steroid nucleus happens through a series of carbocation rearrangements. Elucidation of this extraordinary biosynthetic pathway, one of the most complex known, was accomplished by Konrad Bloch, Feodor Lynen, John Cornforth, and George Popjak in the late 1950s. Interestingly, Bloch and Lynen were awarded the 1994 Nobel Prize in Physiology or Medicine for their work. In the course of the next few lectures, you will learn how you can harness the power of the carbocation in a number of useful synthetic transformations.



VIII. Carbocations

A. Introduction
    1. Structure
    2. Stabilization
        a. Alkyl groups
        b. Hybridization
        c. Aromaticity
        d. Resonance
            i. π bond
            ii. π-heteroatom

B. Generation of Carbocations
    1. Ionization of C-X
    2. Lone pair bonds with Lewis acid
    3. Addition of E^+ to π bond

C. Reactions of Carbocations
    1. Elimination
    2. Combination with Nucleophile
        a. n
        b. aromatic ring
        c. π bond
    3. Rearrangements and Fragmentations
        a. 1,2-Migration
            i. How
            ii. Why
        b. Solvent effects
        c. Reaction Examples
            i. Dienone-Phenol Rearrangement
            ii. Epoxides to Aldehydes
            iii. Pinacol Rearrangement
            iv. Tiffeneau–Demjanov Rearrangement
            v. Baeyer–Villiger Oxidation
            vi. Beckmann Rearrangement
    4. Neighboring Group Participation (Anchimeric Assistance)