

Third Edition

ORGANIC
CHEMISTRY

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ALLYN AND BACON, INC.

BOSTON
LONDON
SYDNEY
TORONTO

Illumina Ex. 1114
IPR Petition - USP 10,435,742

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ISBN 0-205-03239-7



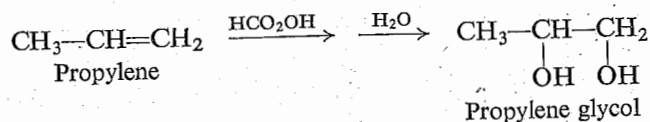
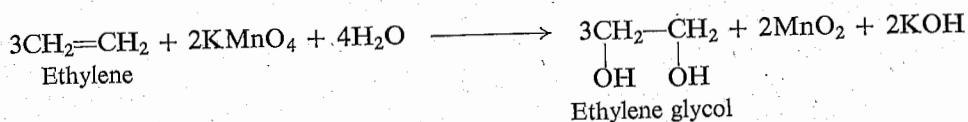
Tenth printing July, 1976

PRINTED IN THE UNITED STATES OF AMERICA

Hydroxylation with permanganate is carried out by stirring together at room temperature the alkene and the aqueous permanganate solution: either neutral—the reaction produces OH^- —or, better, slightly alkaline. Heat and the addition of acid are avoided, since these more vigorous conditions promote further oxidation of the glycol, with cleavage of the carbon-carbon double bond (Sec. 6.29).

Hydroxylation with peroxyformic acid is carried out by allowing the alkene to stand with a mixture of hydrogen peroxide and formic acid, HCOOH , for a few hours, and then heating the product with water to hydrolyze certain intermediate compounds.

A glycol is frequently named by adding the word *glycol* to the name of the alkene from which it is formed. For example:



Hydroxylation of alkenes is the most important method for the synthesis of glycols. Moreover, oxidation by permanganate is the basis of a very useful analytical test known as the **Baeyer test** (Sec. 6.30).

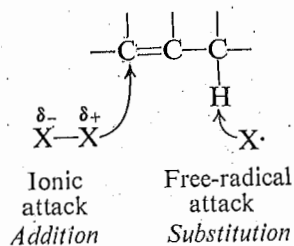
(We shall discuss the stereochemistry and mechanism of glycol formation in Sec. 17.12.)

6.21 Substitution by halogen. Allylic hydrogen

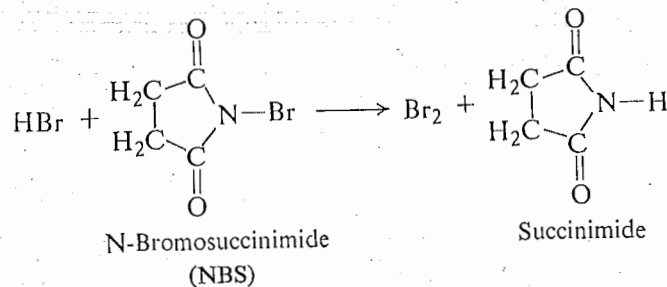
So far in our discussion of alkenes, we have concentrated on the carbon-carbon double bond, and on the addition reactions that take place there. Now let us turn to the alkyl groups that are present in most alkene molecules.

Since these alkyl groups have the alkane structure, they should undergo alkane reactions, for example, substitution by halogen. But an alkene molecule presents *two* sites where halogen can attack, the double bond and the alkyl groups. Can we direct the attack to just one of these sites? The answer is yes, *by our choice of experimental conditions*.

We know that alkanes undergo substitution by halogen at high temperatures or under the influence of ultraviolet light, and generally in the gas phase: conditions that favor formation of free radicals. We know that alkenes undergo addition of halogen at low temperatures and in the absence of light, and generally in the liquid phase: conditions that favor ionic reactions, or at least do not aid formation of radicals.



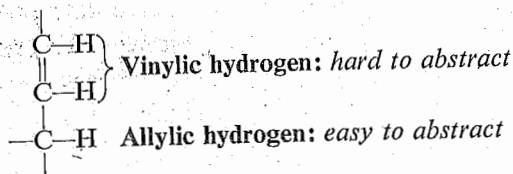
providing a constant, low concentration of bromine. As each molecule of HBr is formed by the halogenation, NBS converts it into a molecule of Br₂.



6.22 Orientation and reactivity in substitution

Thus alkenes undergo substitution by halogen in exactly the same way as do alkanes. Furthermore, just as the alkyl groups affect the reactivity of the double bond toward addition, so the double bond affects the reactivity of the alkyl groups toward substitution.

Halogenation of many alkenes has shown that: (a) hydrogens attached to doubly-bonded carbons undergo very little substitution; and (b) hydrogens attached to carbons adjacent to doubly-bonded carbons are particularly reactive toward substitution. Examination of reactions which involve attack not only by halogen atoms but by other free radicals as well has shown that this is a general rule: hydrogens attached to doubly-bonded carbons, known as **vinyl** hydrogens, are harder to abstract than ordinary primary hydrogens; hydrogens attached to a carbon atom adjacent to a double bond, known as **allylic** hydrogens, are even easier to abstract than tertiary hydrogens.

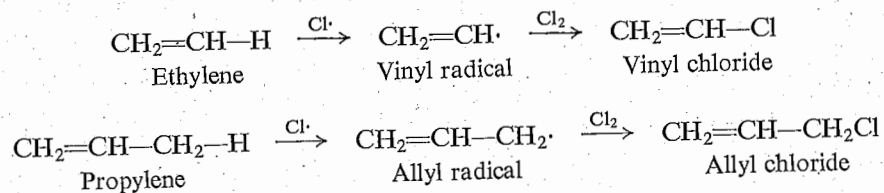


We can now expand the reactivity sequence of Sec. 3.23.

Ease of abstraction
of hydrogen atoms

allylic > 3° > 2° > 1° > CH₄, vinyl

Substitution in alkenes seems to proceed by the same mechanism as substitution in alkanes. For example:



Evidently the vinyl radical is formed very slowly and the allyl radical is formed very rapidly. We can now expand the sequence of Sec. 3.25.