

Third Edition

ORGANIC CHEMISTRY

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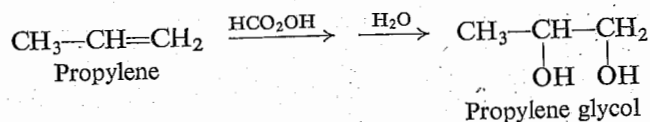
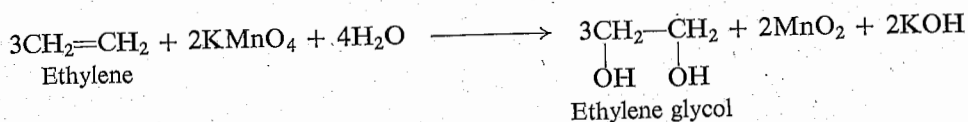
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Hydroxylation with permanganate is carried out by stirring together at room temperature the alkene and the aqueous permanganate solution: either neutral—the reaction produces OH^- —or, better, slightly alkaline. Heat and the addition of acid are avoided, 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).

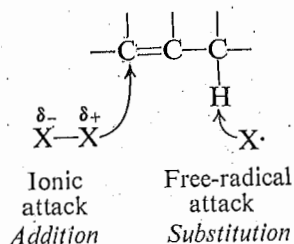
(We shall discuss the stereochemistry and mechanism of glycol formation in Sec. 17.12.)

6.21 Substitution by halogen. Allylic hydrogen

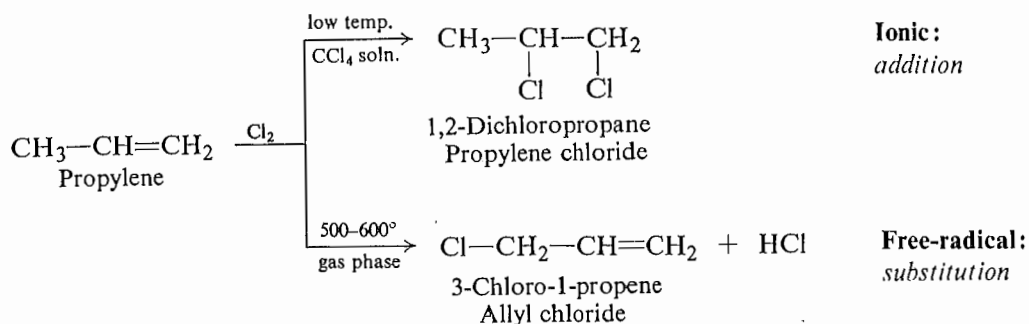
So far in our discussion of alkenes, we have concentrated on the carbon-carbon double bond, and on the addition reactions that take place there. Now let us turn to the alkyl groups that are present in most alkene molecules.

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*.

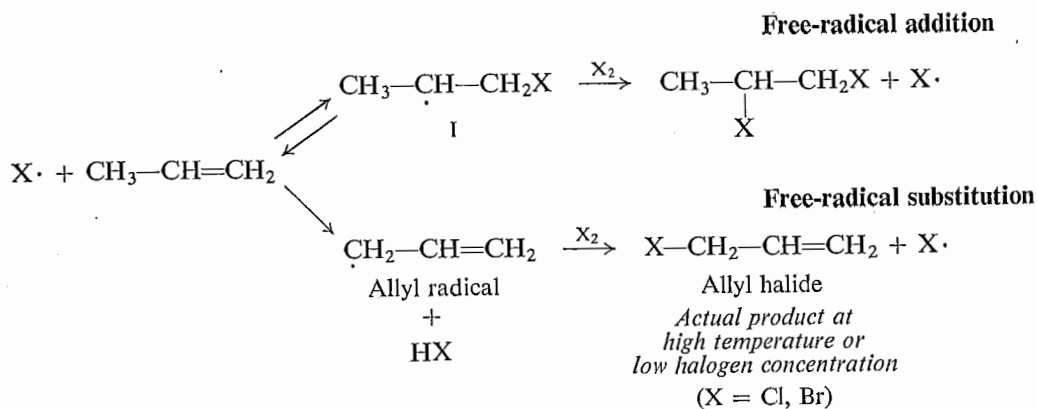
We know that alkanes undergo substitution by halogen at high temperatures or under the influence of ultraviolet light, and generally in the gas phase: conditions that favor formation of free radicals. We know that alkenes undergo addition of halogen at low temperatures and in the absence of light, and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



If we wish to direct the attack of halogen to the alkyl portion of an alkene molecule, then, we choose conditions that are favorable for the free-radical reaction and unfavorable for the ionic reaction. Chemists of the Shell Development Company found that, at a temperature of 500–600°, a mixture of gaseous propylene and chlorine yields chiefly the substitution product, 3-chloro-1-propene, known as *allyl chloride* ($\text{CH}_2=\text{CH}-\text{CH}_2-$ = **allyl**). Bromine behaves similarly.



In view of Secs. 6.17–6.18, we might wonder why a halogen atom does not add to a double bond, instead of abstracting a hydrogen atom. H. C. Brown (of Purdue University) has suggested that the halogen atom *does* add but, at high temperatures, is expelled before the second step of free-radical addition can occur.

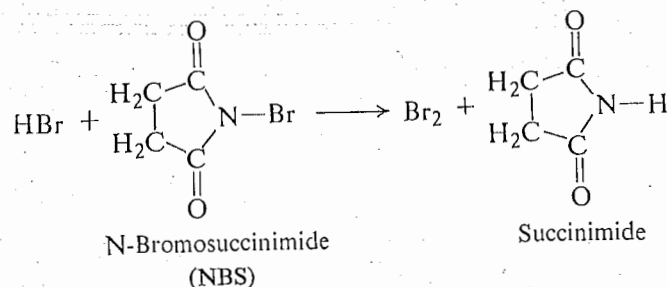


Consistent with Brown's explanation is the finding that *low concentration* of halogen can be used instead of high temperature to favor substitution over (free-radical) addition. Addition of the halogen atom gives radical I, which falls apart (to regenerate the starting material) if the temperature is high or if it does not soon encounter a halogen molecule to complete the addition. The allyl radical, on the other hand, once formed, has little option but to wait for a halogen molecule, whatever the temperature or however low the halogen concentration.

Problem 6.12 (a) What would the allyl radical have to do to return to the starting material? (b) From bond dissociation energies, calculate the minimum E_{act} for this reaction.

The compound **N-bromosuccinimide (NBS)** is a reagent used *for the specific purpose of brominating alkenes at the allylic position*; NBS functions simply by

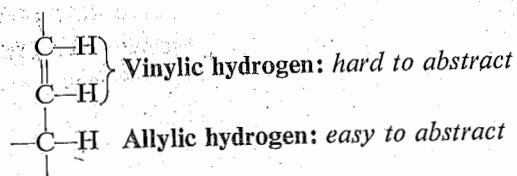
providing a constant, low concentration of bromine. As each molecule of HBr is formed by the halogenation, NBS converts it into a molecule of Br₂.



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.

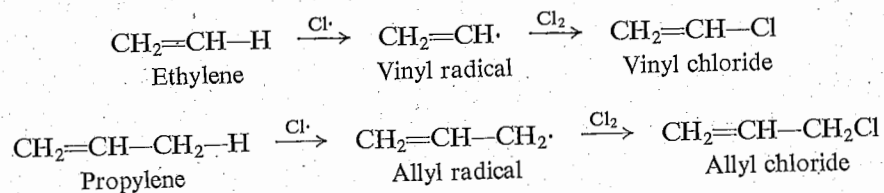


We can now expand the reactivity sequence of Sec. 3.23.

Ease of abstraction
of hydrogen atoms

allylic > 3° > 2° > 1° > CH₄, vinylic

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.