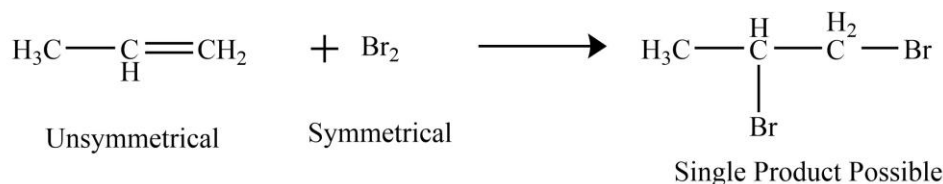
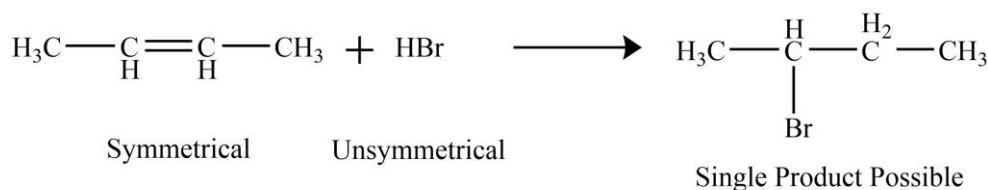


❖ Regio- and Chemoselectivity: Orientation and Reactivity

In this section, we will study the orientation (or regio-selectivity) and reactivity (chemo-selectivity) of addition to carbon-carbon multiple bonds.

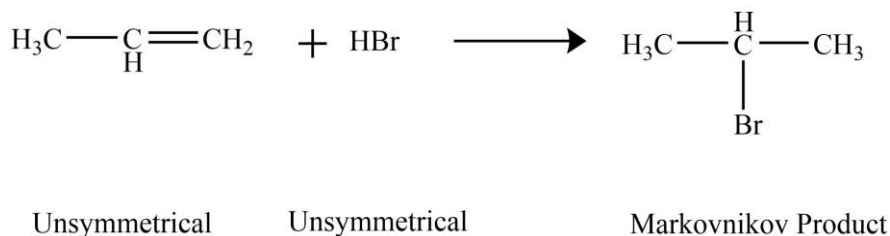
➤ Orientation of Addition to Carbon-Carbon Multiple Bonds

The structural orientation will not affect the final product if either the reagent or the alkene is symmetrical in nature. On the other hand, if the alkene and attacking reagent both are unsymmetrical, two different products can be obtained as shown below.



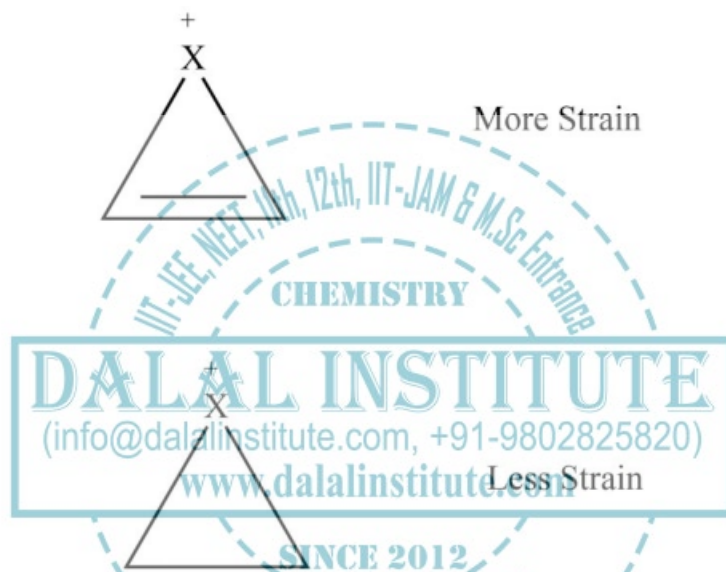
In such a case, one of the products will be major and the other one will be minor depending upon their relative yield. In other words, the structural orientation is nothing but the preference that the double gives during its shift to decide which carbon to bind electrophile and which one to the nucleophile. The regioselectivity of electrophilic addition can be rationalized via two different rules as given below.

1. Markovnikov's Rule: The problem of structural orientation or regioselectivity in electrophilic addition was solved by a Russian chemist, Vladimir Markovnikov, in 1870 by giving an empirical rule called Markovnikov's rule. This rule states that when a polar reagent (like protic acid HX) is added to unsymmetrical alkenes, the electronegative part (i.e., halide) binds to the carbon with more alkyl groups; whereas the electropositive part (i.e., hydrogen) binds to the carbon with more hydrogens.



The theoretical basis for Markovnikov's Rule is the creation of a stable carbocation in the course of addition. The addition of the H^+ to one of the carbons in alkene gives rise to a positive charge on another carbon, yielding an intermediate carbocation.

The higher susceptibility of triple bonds to nucleophilic attack can be attributed to the firm attachment of electrons in the triple bond due to smaller carbon-carbon bond length, which in turn make the electron density less available for any such attack. Alternatively, the lower susceptibility of triple bonds to electrophilic attack can be explained in terms of the accessibility of the empty orbital in the alkyne. In other words, it has been shown theoretically that bent alkynes have a π^* orbital of lower energy than the π^* orbital of simple alkenes; and therefore, linear alkynes can get a bent during transition states (electrophile addition) but alkene cannot. Also, bridged-ion intermediates arising from electrophilic addition to triple bonds will be more strained than their double bond counterparts; and therefore, slowing the rate of electrophilic addition. Nevertheless, triple bonds conjugated to the Z group favor the nucleophilic addition more aggressively.



As expected, the attachment of alkyl groups typically increases the electrophilic addition's rates because of increased electron density; though the order might change depending upon whether the intermediate formed is an open carbocation or a cyclic cation. If the first step is slowest (rate-determining) in electrophilic additions, like in the case of brominations, the rates for different substituted alkenes are dictated by the corresponding ionization potentials only and steric effects play little to no role.

No special types of substrates are required for free radical additions and the presence of a reactive free radical species predominantly dictates the overall rate. In the absence of initiator, reagents HBr or RSH prefer to attack via ionic pathway; however, the mechanism changes to free radical addition as the radical initiator is mixed. Nucleophilic and electrophilic radicals behave more or less like nucleophiles and electrophiles, respectively; and the rate is affected accordingly. Nevertheless, it isn't expected but the rate of reaction of nucleophilic radical attack is faster with alkenes than with alkynes. Finally, it is also worthy to note that the steric effect might get an important role in some particular cases like catalytic hydrogenation where substitution decreases the reaction rate due to adsorption on the catalyst surface.

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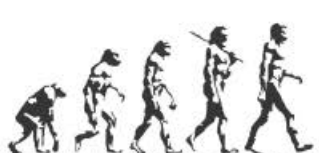
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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