10.11: Stereochemistry of Electrophilic Addition of HX

As illustrated in the drawing below, the pi-bond fixes the carbon-carbon double bond in a planar configuration, and does not permit free rotation about the double bond itself. We see then that addition reactions to this function might occur in three different ways, depending on the relative orientation of the atoms or groups that add to the carbons of the double bond: (i) they may bond from the same side, (ii) they may bond from opposite sides, or (iii) they may bond randomly from both sides. The first two possibilities are examples of stereoselectivity, the first being termed **syn-addition**, and the second **anti-addition**. Since initial electrophilic attack on the double bond may occur equally well from either side, it is in the second step (or stage) of the reaction (bonding of the nucleophile) that stereoselectivity may be imposed.

If the two-step mechanism described above is correct, and if the carbocation intermediate is sufficiently long-lived to freely-rotate about the sigma-bond component of the original double bond, we would expect to find random or non-stereoselective addition in the products. On the other hand, if the intermediate is short-lived and factors such as steric hindrance or neighboring group interactions favor one side in the second step, then stereoselectivity in product formation is likely. The following table summarizes the results obtained from many studies, the formula HX refers to all the strong Brønsted acids. The interesting differences in stereoselectivity noted here provide further insight into the mechanisms of these addition reactions.

Reagent	H–X	X_2	HO–X	RS–Cl	$Hg(OAc)_2$	BH_3
Stereoselectivity	mixed	anti	anti	anti	anti	syn

Contributors

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