

IV. Halogenation

Regioselectively replacing a particular hydrogen atom in a carbohydrate with a halogen atom depends upon a radical abstracting one hydrogen atom from among the many present in a typical molecule. When this type of selectivity occurs, it sometimes is linked to radical philicity; that is, a hydrogen atom that is more electron rich than others in a molecule can be abstracted preferentially by a highly electrophilic radical. This regioselectivity caused by radical philicity only occurs when the transition state is early in a reaction. When the transition state is late, selective reaction also can take place, but in this case selectivity exists because abstraction of a particular hydrogen atom produces a carbon-centered radical that is much more stable than radicals formed by abstraction of other hydrogen atoms. Since there are relatively few carbohydrates where highly selective hydrogen-atom abstraction occurs and since hydrogen-atom abstraction typically is the first step in halogenation, regioselective, free-radical halogenation reactions are limited in number.

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