

VIII. Summary

The free-radical bromination of a benzylidene acetal is a standard procedure in carbohydrate chemistry for ring opening that results in the formation of bromodeoxy sugars. Ring opening in the absence of bromine occurs when 4,6-*O*-benzylidene acetals react with peroxides in the presence of a thiol catalyst. Hydrogen-atom abstraction by an electrophilic, thiyl radical is the first step in this reaction. This is also the first step in reactions of other acetals leading to epimerization and deoxygenation.

Ethers, like acetals, serve as protecting groups during carbohydrate synthesis, but this protection is not total because both ethers and acetals undergo hydrogen-atom abstraction in the presence of reactive, electrophilic radicals. These radicals can be sulfur-, oxygen-, or bromine-centered. When hydrogen-atom abstraction by an alkoxy radical is intramolecular, it typically is highly regioselective and can lead to formation of a new ring system.

Acetals and ethers, including silyl ethers, have a connective role in radical cyclization reactions. The radical center and the multiple bond involved in a cyclization reaction are often joined together by an acetal or ether linkage.

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