β-Fragmentation is an elementary reaction that exhibits regioselectivity in ring opening and in radical expulsion. Regioselective ring opening occurs when a radical centered on an atom attached to a ring preferentially fragments one of the ring bonds. Regioselective radical expulsion takes place when one of the bonds to an atom β-related to a radical center preferentially cleaves to generate two fragments, one a new radical and the other an unsaturated compound.

A. Ring-Opening Reactions

1. Oxygen-Centered Radicals

Oxygen-centered radicals derived from carbohydrates usually have the radical-bearing oxygen atom bonded to a ring carbon atom; thus, β-fragmentation is likely to result in opening the ring. For the oxygen-centered radical 28, ring opening in either direction (i.e., producing either 29 or 30) stabilizes the developing radical by forming a carbonyl group, but the opening to give 29 passes through a more stable transition state because the radical center is shifting to a carbon atom, one with a radical-stabilizing chlorine atom attached (Scheme 17). The difference in stability of the developing, ring-open radicals 29 and 30 is sufficiently large at the transitions states for their formation that regiospecific ring opening takes place.

2. Carbon-Centered Radicals

Hydrogen-atom abstraction from a benzylidene acetal produces a carbon-centered radical that undergoes ring opening. This ring opening usually follows the pattern of producing the more stable intermediate radical; thus, the major product in the reaction shown in Scheme 18 arises from a secondary, rather than a primary, radical.
It is initially surprising to find that the radical 32, derived from the benzylidene acetal 31, undergoes ring opening regioselectively to form a product that comes from an intermediate, primary radical (Scheme 19). The contra-thermodynamic regioselectivity in this reaction (Scheme 19) is due to the difference in the amount of strain developed in the transition states leading to the radicals 33 and 34. Molecular mechanics calculations show that the transition state for producing the secondary radical 34 is significantly more strained than that leading to the primary radical 33. This strain is a more important factor to regioselective ring opening of 32 with its trans-fused ring system than the presumably greater thermodynamic stabilization of the developing radical 34. (A cautionary note is sounded in ref 48a about assuming that a secondary radical is necessarily more stable than an isomeric primary radical.)
A cis-fused ring system in a benzylidene acetal is more flexible than one that is trans-fused; consequently, less angle strain develops at the transition state for ring opening of a radical derived from a cis-fused benzylidene acetal. This reduction in strain is enough to make thermodynamic stability a more important factor in ring opening; thus, the major product in the reaction shown in eq 20 arises from formation of a secondary, rather than a primary, radical.\textsuperscript{48,49}

Reaction of a cyclic thionocarbonate represents a different approach to generating a carbon-centered radical that has ring-opening options similar to those available to a radical produced by hydrogen-atom abstraction from a benzylidene acetal. Addition of the tris(trimethylsilyl)silyl radical to the cyclic thionocarbonate 37 produces the radical 38, which undergoes ring opening with a contra-thermodynamic regioselectivity (Scheme 20) similar to that observed from the radical 32.\textsuperscript{49}
B. Radical Expulsion

In the reaction pictured in Scheme 21 ring-opening of the radical 41 to produce the highly energetic, oxygen-centered radical 42 cannot compete with radical expulsion.\(^{50}\) Even fragmentation that keeps the ring intact and gives the carbon-centered radical 43 is unable to match reactions that cause C–I, C–Br, C–Cl, and C–SR bonds to break and to produce I·, Br·, Cl·, and RS·, respectively. When loss of a radical from 41 would require breaking a stronger bond and producing a less stable radical (i.e., X = F, OTs, or OMs), β-fragmentation is too slow to compete with hydrogen abstraction.
Some reactions combine regioselective addition with regioselective β-fragmentation. This combination can cause the double bond in a molecule to relocate to a new position, as it does in the reaction shown in Scheme 22, or it can lead to the multiple bond remaining between the original two carbon atoms, as happens in the reaction shown in Scheme 23.

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