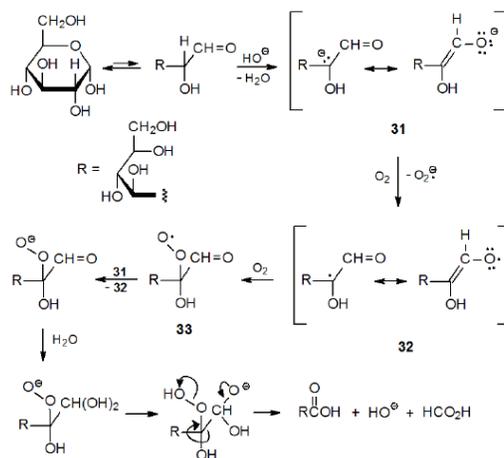


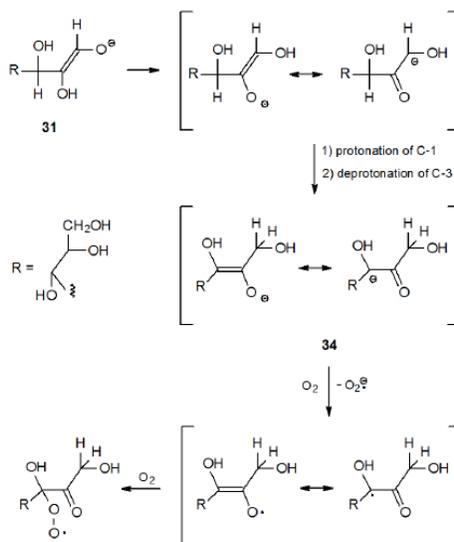
VI. Oxidative Degradation of Carbohydrates

The oxidative degradation of carbohydrates in the presence of base is another reaction that involves radical intermediates. Such reaction of D-glucose begins with ring opening and deprotonation to give the enediolate anion **31** (Scheme 9).^{31,32} Oxidation of this anion with O₂ produces the resonance stabilized radical **32**, which then is converted to the peroxy radical **33** by addition of O₂. Subsequent reduction of **33** gives an anion that ultimately fragments the C₁–C₂ bond to give a five-carbon aldonic acid (Scheme 9). Fragmentation of other carbon–carbon bonds also takes place because base-catalyzed isomerization of the 1,2-enediolate anion **31** produces the 2,3-enediolate anion **34** (Scheme 10). Reaction of **34** with O₂ and fragmentation analogous to that shown in Scheme 9 cleaves the D-glucose structure into two-carbon-atom and four-carbon-atom carboxylic acids. Continued isomerization of this type (**31** to **34**) produces other enediolates that undergo similar fragmentation reactions.³²

Scheme 9



Scheme 10



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