

III. Reactions with Redox Couples

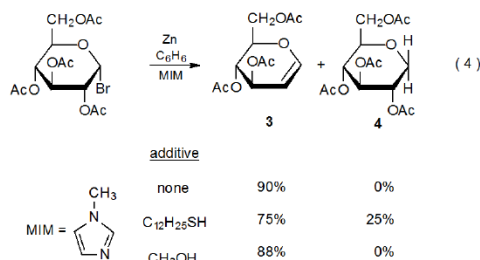
A. Addition Reactions

The total number of reactions of carbohydrate derivatives with redox couples is modest; among these addition reactions are reported more often than any other type.^{2,3,5-9} Addition processes often involve a couple formed by combining zinc metal with a copper salt.^{2,6,7,9} Such a reaction is illustrated in eq 1, where a zinc-copper couple participates in the addition of a halogenated carbohydrate to a compound with an electron-deficient double bond.

Since reaction between a zinc-copper couple and a carbohydrate is a heterogeneous process that takes place on the surface of finely divided zinc, efficient mixing during reaction is essential. Sonication, which often is used during redox-couple preparation and reaction, is believed to aid electron transfer indirectly by increasing mixing and improving metal-surface cleaning and directly by promoting electron transfer through the influence of ultrasonic waves.¹⁰

B. Elimination and Hydrogen-atom abstraction Reactions

The idea that a copper ion is not directly involved in electron transfer from a zinc-copper couple garners some support from the reaction shown in eq 4, where zinc metal alone is able to act as the electron source in generating a pyranos-1-yl radical.¹¹ After formation, this radical undergoes further reaction that leads to the D-glucal **3**. Support for the intermediacy of a pyranos-1-yl radical in this reaction comes from conducting reaction in the presence of 1-dodecanethiol ($C_{12}H_{25}SH$), an excellent hydrogen-atom transfer. When this thiol is present, a substantial amount of hydrogen-atom abstraction by the pyranos-1-yl radical takes place to produce the simple-reduction product **4**. Proton transfer (the competing, nonradical possibility) does not appear to be involved in formation of **4** because when methanol replaces 1-dodecanethiol in the reaction mixture, none of this simple-reduction product is formed (eq 4).¹¹



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