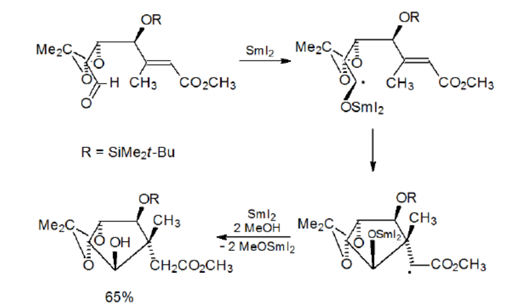
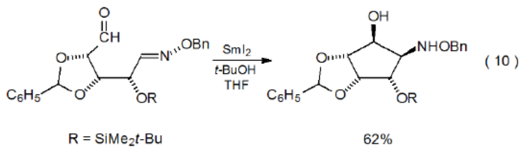
V. Reaction of Samarium(II) Iodide with Aldehydes and Ketones

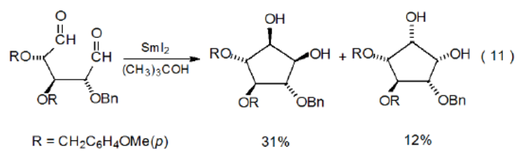
Reaction of an aldehyde or ketone with samarium(II) iodide produces a samarium ketyl.[26–39] These ketyls add intramolecularly to appropriately positioned carbon–carbon[25–33] (Scheme 10)[26] and carbon–nitrogen[34–37] (eq 10)[34] double bonds. Such reactions are reminiscent of the addition of typical carbon-centered radicals to multiple bonds.

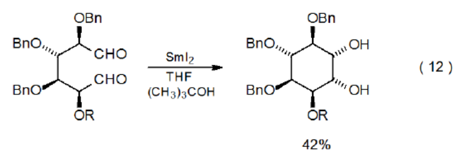
Scheme 10

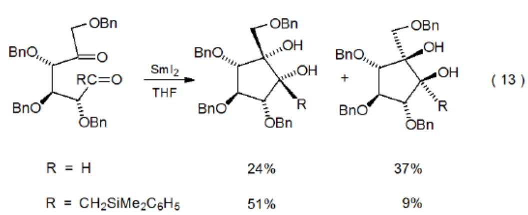




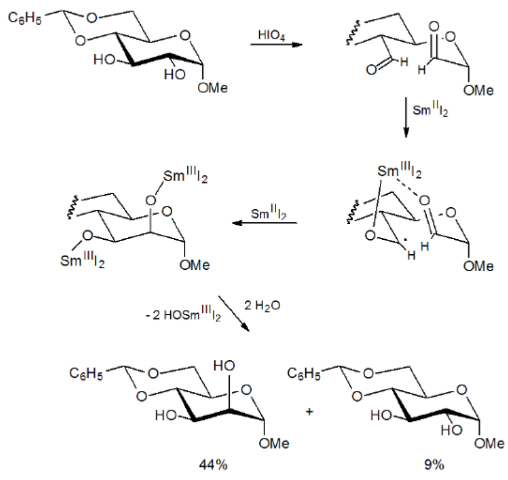
When samarium(II) iodide reacts with compounds containing two aldehydo groups, the first is converted into a samarium ketyl that then adds to the second. This addition depends upon proper separation between the reacting groups;[40–53] accordingly, pinacols with five-membered[40,49-53] (eq 11)[40] and six-membered[41–48] (eq 12)[41] rings form easily. It is not necessary for both interacting groups in a molecule to be aldehydo groups; pinacols also arise when one[49–52] (eq 13, R = H)[49] or both (eq 13, R = $CH_2SiMe_2C_6H_5$)[53] are keto groups. Complexation of the ketyl and carbonyl oxygen atoms with SmI_2 forces a cis relation between the hydroxyl groups in the products (Scheme 11).[42] Pinacol formation and other reactions of aldehydes and ketones with samarium(II) iodide is revisited in Chapter 20, where a broader discussion of the interaction of SmI_2 with carbohydrate derivatives takes place.







Scheme 11



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