

III. Summary

Alcohols are converted indirectly into alkoxy radicals through intermediate hypoiodites, nitrates, and phthalimides. A common reaction of alkoxy radicals is hydrogen-atom abstraction. This reaction becomes synthetically useful when the abstraction is internal because regioselective formation of a carbon-centered radical takes place. This selectivity depends on a combination of factors that include transition-state ring size, stability of the developing radical, and polarity matching between reacting atoms. Alkoxy radicals also can undergo carbon–carbon bond fragmentation that produces a carbonyl group and a carbon-centered radical. No matter which pathway is taken by the alkoxy radical (hydrogen-atom abstraction or β fragmentation), the resulting carbon-centered radical can undergo new ring formation, epimerization at a chiral center, ring opening, and other reactions characteristic of this radical intermediate.

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