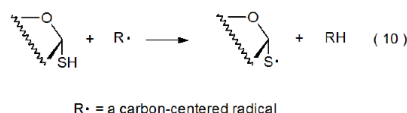
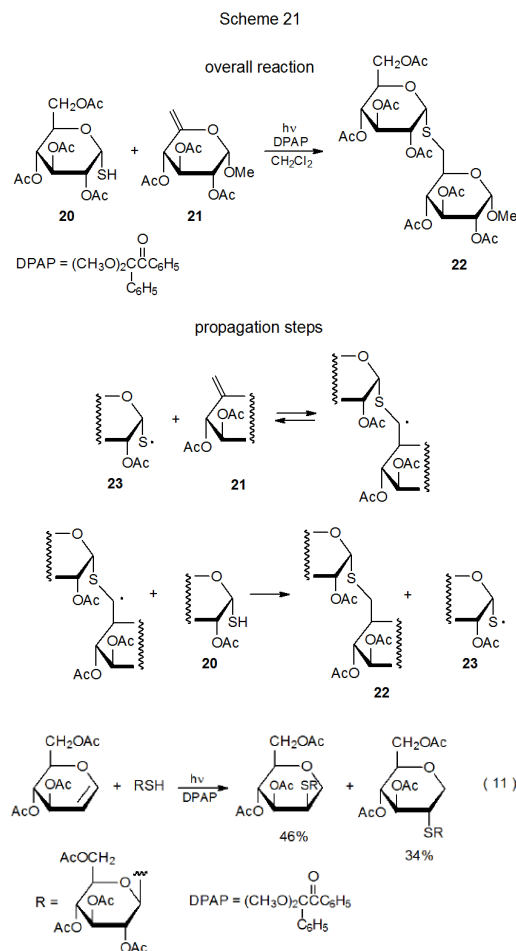


VIII. Thiols and Thiyl Radicals

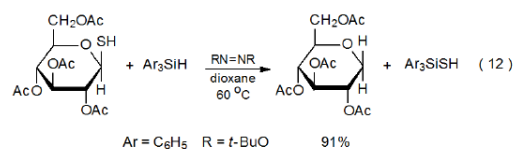
In compounds with an H-S bond, hydrogen-atom abstraction to produce a sulfur-centered radical (eq 10) is a significant (sometimes the exclusive) reaction pathway. Such reactivity exists because thiols are among the most effective hydrogen-atom transfers in organic chemistry. Rate constants for hydrogen-atom abstraction by primary, secondary, and tertiary, carbon-centered radicals from thiophenol range from 0.8×10^8 to $1.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ at 25°C .⁷⁰



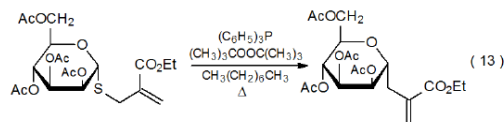
A characteristic reaction of a thiyl radical is addition to a carbon-carbon multiple bond.⁷¹⁻⁸⁵ In the reaction shown in Scheme 21, for example, addition of the thiyl radical **23** to the unsaturated carbohydrate **21** leads to formation of the *S*-disaccharide **22**.⁷⁷ This reaction is not only regiospecific but hydrogen-atom abstraction from **20** is so much faster than reaction with the molecular oxygen dissolved in the mixture that an inert atmosphere is not required for successful *S*-disaccharide formation. Similar radical addition takes place between the thiol **20** and various D-glycals, including the D-glucal **24** (eq 11).⁷⁸



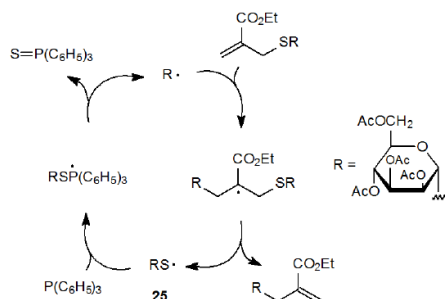
Even though the most common radical reaction of a compound with an H-S bond is hydrogen-atom abstraction, under some conditions the HS group is replaced by a hydrogen atom (eq 12).⁸⁶



Although a carbohydrate containing a sulfur-centered radical typically is generated by hydrogen-atom abstraction from a thiol, the reaction shown in eq 13 forms a thiyl radical by the addition-elimination sequence pictured in Scheme 22.⁸⁷ Critical to chain propagation in this reaction is the removal of the sulfur atom from **25** by reaction with triphenylphosphine.



Scheme 22



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