

III. Group Replacement Reactions

Since the reaction pictured in Scheme 1 depends upon $R\cdot$ adding to a molecule of the starting ester, one way to change the course of this reaction is to introduce a compound that will react more rapidly with $R\cdot$ than does the ester. Thiols meet this requirement.^{8,19–25} Hydrogen-atom abstraction by a carbon-centered radical from a thiol is rapid enough ($k_H = 1.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ at 25 °C for abstraction from $\text{C}_6\text{H}_5\text{SH}$ by $\text{Bu}\cdot$)²⁶ to occur in preference to radical reaction with the starting ester.

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