III. Group Replacement Reactions

Since the reaction pictured in Scheme 1 depends upon R· 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· 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 x 10^8 $M^{-1}s^{-1}$ at 25 °C for abstraction from C_6H_5SH by Bu·)[26] to occur in preference to radical reaction with the starting ester.