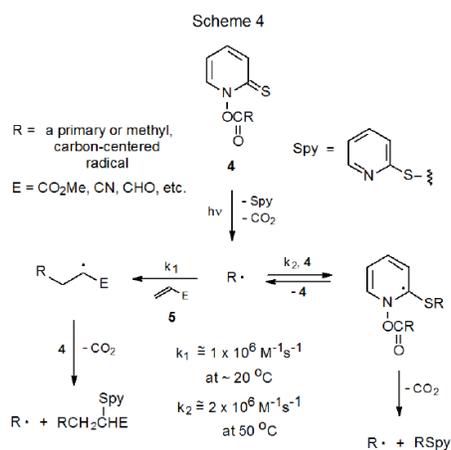


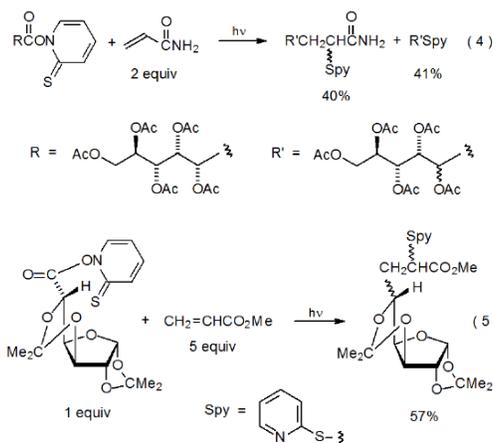
IV. Addition Reactions

A. A Competition Always Present

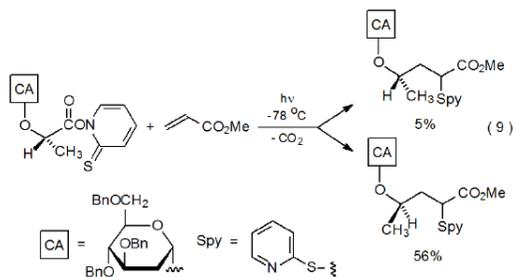
The rate constant for addition of a typical carbon-centered radical to an ester of *N*-hydroxypyridine-2-thione ($k_r \cong 2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ at 50°C)^{29,30} is large enough that competing addition of such a radical to a reactant with a carbon-carbon multiple bond occurs only for compounds with the most reactive bonds (i.e., those with electron-withdrawing substituents attached.) (The rate constants for addition to these unsaturated reactants are approximately $1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ at 20°C)³¹) In practice this means that unless the multiple bond has an electron-withdrawing substituent, the rate of addition of a carbon-centered radical will be too slow to compete effectively with addition to a Barton ester. As is emphasized in Scheme 4, a similarity in rate constants means that the competition between addition of a radical to the unsaturated compound **5**, as opposed to addition to a second molecule of the Barton ester **4**, depends heavily upon the relative concentrations of these two reactants (**4** and **5**).



Examples of the competition between radical addition to a molecule with an electron deficient double bond or to a molecule of unreacted starting ester are found in the reactions shown in equations 4-7. In the first of these (eq 4) acrylamide is present in two-fold excess; yet, products from addition of $R\cdot$ to the amide and to the starting ester are formed in essentially equal amounts.³² In the second reaction (eq 5) a good yield of the product from radical addition to methyl acrylate requires a five-fold excess of the unsaturated ester.³³ In the reaction shown in eq 6 even a six-fold excess of phenyl vinyl sulfone does not suppress completely addition to the starting ester of some of the carbohydrate radicals.³⁴ Radical addition to 2-nitropropene is similar to addition to other unsaturated compounds (eq 7).^{35,36}



process.³⁵ Selectivity in this case results primarily from steric interactions between methyl acrylate and the C-6 substituent in the reactant sugar.³⁵



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