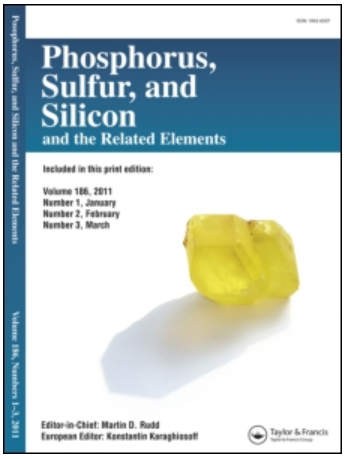

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Regioselective Michael Addition of Thiols to Unsymmetrical Fumaric Diesters or Esteramides

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INTRODUCTION

Fumaric derivatives are recognizade as useful C4 building blocks in organic synthesis. To avoid unnecesary regioisomeric problems, symmetrically substituted fumaric derivatives are usually used. It is not easy to differentiate and activate one of the two carbonyl groups that have different substituents. In this paper, we disclose conjugate addition of thiols to unsymmetrical fumaric derivatives takes place in a highly regioselective manner and both of the regioisomers are prepared as a single isomer.

RESULTS

Treatment of fumaric ethyl *tert*-butyl ester with thiophenol in the presence of catalytic amounts of lithium thiolate resulted in the selective formation of **1A**, in which thiolate attacked the carbon near to *tert*-butyl ester.[1] The best selectivity reached 41:1, which was observed when *o*-thiocresol was used as the nucleophile. Asymmeric fumaric amide esters underwent the addition of thiolate in the presence of catalytic amounts of base to give **2B** over 90/10 selectivity. To our surprise, the addition occurred in the absence of base and gave the adduct **2A** exclusively. This change of selectivity was observed with various kinds of fumaric amide esters and the two regioisomers A and B were prepared in good yields with excellent selectivity.[2]

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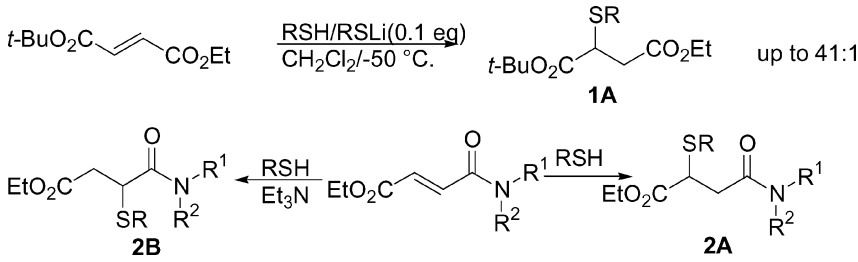
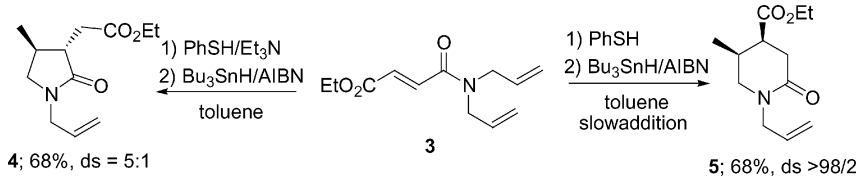


The adducts served as a precursors of radical cyclization upon treatment with Bu_3SnH. For example, base-catalyzed Michael addition of amide ester **3** followed by radical cyclization furnished pyrroridinone **4** in good yield, while nonbasic addition and radical cyclization converted **3** into piperidinone **5** stereoselectively.[3]



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