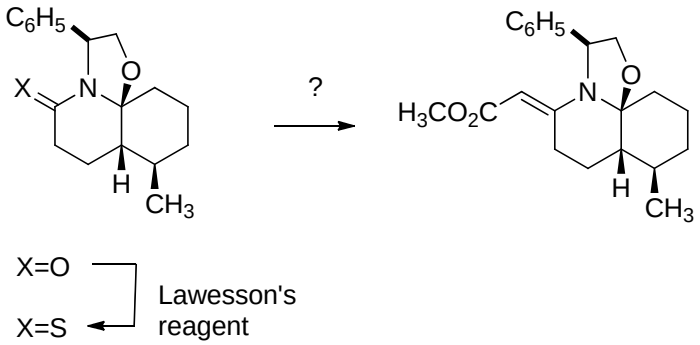
Written Qualifying Examinations
June 2010
Organic Chemistry

These questions are based on the following article:
Amat, Mercedes et al. "Biomimetic Construction of the Hydroquinoline Ring System. Diastereodivergent Enantioselective Synthesis of 2,5-Disubstituted cis-Decahydroquinolines" *J. Org. Chem.*, **2010**, 75 (11), pp 3797–3805.

1. (3 points) The paper describes a "biomimetic diastereodivergent enantioselective" synthesis. Define each of these terms clearly.

2. (4 points) An important synthetic step is the conversion of a lactam to a thioamide using Lawesson's reagent, and then to a β-enamino ester using the Eschenmoser sulfide contraction. (See illustration below.)



   a. What is Lawesson's reagent?
   b. What are the conditions for the Eschenmoser sulfide contraction?
   c. Propose a reasonable mechanism for the sulfide contraction.

3. (3 points) Interestingly, reversing the order of the catalytic hydrogenation (which precedes the steps shown above) and the Eschenmoster contraction had a dramatic effect. What was this effect, and what is the explanation for its occurrence?

<u>Green Chemistry Question (2 points):</u>
One of the later synthetic steps involves first debenzylation of the nitrogen and then addition of a Boc protecting group, which is removed three steps later. Comment on the overall "greenness" of protecting groups in terms of waste, atom economy, and any other factors that you feel are relevant. Also discuss the need to convert one group (the substituted benzyl moiety) into another (the Boc group).