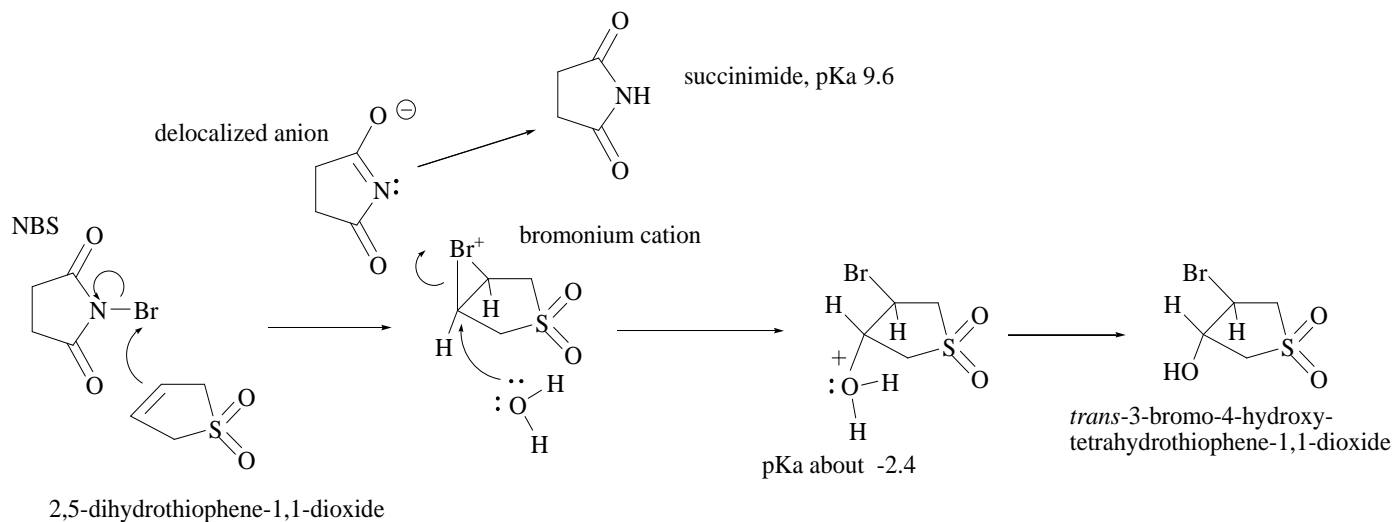


Title: Synthesis of *trans*-3-Bromo-4-hydroxytetrahydrothiophene-1,1-dioxide*Instrument operation:* FT-IR spectrometer, Fischer-Johns melting point apparatus*Introduction:*

Preparation of the title compound involves the addition of the elements of HOBr across the carbon-carbon double bond of 2,5-dihydrothiophene-1,1-dioxide. Rather than using HOBr itself, which is rather difficult to handle, the reagent used is *N*-bromosuccinimide (pronounced EN-bro-mo-SUK-sin-IM-id and abbreviated NBS). In NBS the nitrogen-bromine bond is polarized toward the nitrogen atom due to the greater electronegativity of nitrogen and the electron withdrawal of the two adjacent carbonyl (C=O) groups. This leaves the bromine atom with a slight positive charge, and in a polar medium such as water, NBS can react *as though* it were Br⁺. (We say that NBS is a “bromine cation equivalent.”)

Although the reaction occurs in a single process step, three mechanistic steps are thought to be involved. In the initial mechanistic step, the π electrons of the carbon-carbon double bond interact with the electrophilic bromine of NBS. Note that the other product of this bond breaking is a delocalized anion that is resonance stabilized. Resonance stabilization lowers the activation energy for breaking of the nitrogen-bromine bond and also reduces the chances of the anion itself reacting in the second step. The intermediate formed in this first reaction is a cyclic bromonium cation. In the second step, the oxygen atom of water displaces bromine and picks up the formal positive charge. In a third mechanistic step, a proton is lost to solvent H₂O (not shown here), leaving a bromine atom and hydroxyl group *trans* to each other across the ring. Ultimately the delocalized anion is protonated by H₃O⁺ or some weaker acid in solution to produce the neutral compound succinimide (pronounced SUK-sin-IM-id) as a coproduct of the process.

*Green aspects:*

This reaction avoids the use of the very toxic and difficult to handle molecular bromine, Br₂. The solvent for both the reaction and recrystallization is water.

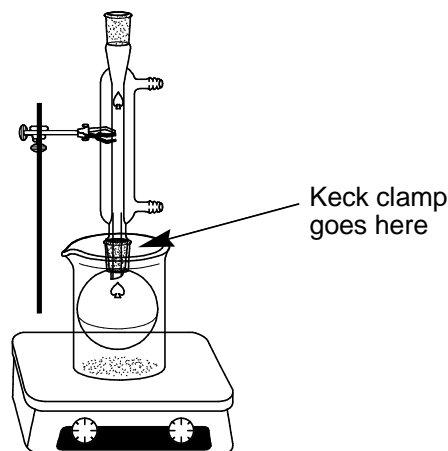
Procedure:

Place 1.2 g of 2,5-dihydrothiophene-1,1-dioxide and 1.8 g of *N*-bromosuccinimide in a 25-mL round-bottom flask along with 2 mL of H₂O. Add a stirbar and assemble the apparatus pictured on the right, consisting of the flask attached to a condenser using a Keck clamp and supported by clamp on a stand so that it can be suspended above a 250-mL beaker on a hot plate. Add enough water to the beaker to provide a bath around the mixture, but not so much as to cover the Keck clamp.

Turn on the magnetic stirrer, bring the water bath to a boil, and continue boiling for 1 hr, taking care to add water as necessary to the bath if it starts to evaporate. After the hour, raise the flask, remove the hotplate and water bath, and allow the apparatus to cool to room temperature. Collect the resulting crystals by suction filtration and wash them with ice-cold water. Recrystallize your crude product from a minimum amount of hot water. Allow the recrystallization process to continue until the next laboratory period. Once crystals have formed, cool the flask in an ice-bath, and collect the crystals by suction filtration, washing your purified product with ice-cold H₂O. Allow the crystals to dry over several layers of filter paper.

Determine the yield of your product and obtain its melting point (189-191°C reported in the literature) and its infrared spectrum (mineral oil mull).

*2,5-Dihydrothiophene -1,1-dioxide is an irritant.
N-Bromosuccinimide is an oxidant and an irritant.*



Keck clamps – the narrower side attaches to the condenser, and the wider side attaches to the flask.

PRE-LAB QUESTIONS:

1. Prepare a Green Process Analysis Report for this synthesis. As always, be sure to copy the reactant table into your notebook. Why is the atom economy so low?
2. Is the acid/base reaction of the delocalized anion with H₂O favorable? Explain why or why not.
3. If the product did not precipitate, describe a procedure by which you could separate the desired product from the coproduct (succinimide) using water, diethyl ether, 10% HCl, and/or 10% NaOH solutions.

ANALYSIS AND CONCLUSIONS

What was your percent yield? What evidence do you have that you made the desired product?