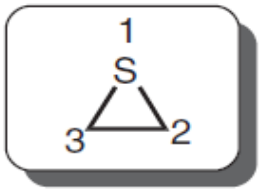
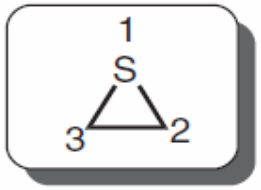
**Thiirane**



Thiiranes are also known as *episulfides*.

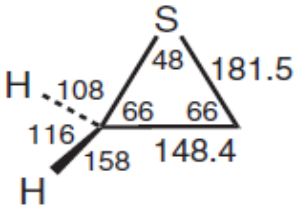



The thermochemically determined strain enthalpy of thiirane (83 kJ $mol^{-1}$) is less than hat of oxirane. The ionization potential amounts to 9.05 eV, the dipole moment to 1.66 D.

**Thiirane** (ethylene sulfide) is a colorless liquid, sparingly soluble in water, and of bp 55 °C.

The chemical shifts in the NMR spectra are $\delta_H = 2.27$, $\delta_C = 18.1$.

Structure of thiirane




(bond lengths in pm, bond angles in degrees).

# Chemical properties of Thiirane

The properties of the thiiranes are primarily due to ring strain. In spite of the smaller strain enthalpy, thiirane is thermally less stable than oxirane. Even at room temperature, linear macromolecules are formed because of polymerization of ring-opened products. Substituted thiiranes are thermally more stable. The following reactions are typical for thiiranes [32].

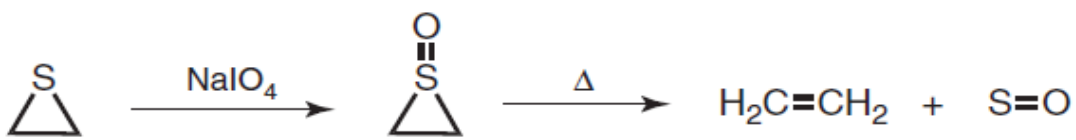
## Ring-opening by nucleophiles

Ammonia, or primary or secondary amines, react with thiiranes to give β-amino thiols:

The mechanism is the same as that described on p. 18 for oxiranes. However, the yields are lower, due to competing polymerization. Concentrated hydrochloric acid reacts with thiiranes to give β-chlorothiols (protonation on the S-atom and nucleophilic ring-opening by the chloride ion).

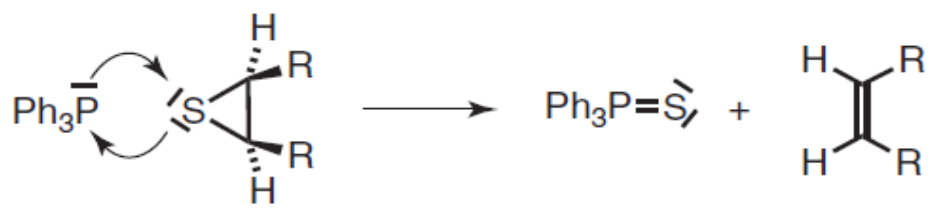
## Oxidation

Thiiranes are oxidized by sodium periodate or peroxy acids to give thiirane oxides. These undergo fragmentation at higher temperature to give alkenes and sulfur monoxide:



## Desulfurization to alkenes

Triphenylphosphane, as well as trialkyl phosphites, have proved to be reliable reagents for this purpose. The reaction is stereospecific. *cis*-Thiiranes yield (*Z*)-olefins and *trans*-thiiranes yield (*E*)-olefins. The electrophilic attack of the trivalent phosphorus on the heteroatom is different from that described on p. 20.



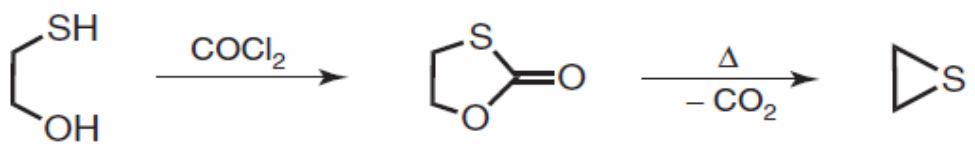

Organometallics, for example, *n*-butyllithium, also bring about a stereospecific desulfurization of thiiranes.

# Synthesis of Thiirane

The synthesis of thiiranes starts either from β-substituted thiols or from oxiranes and can be achieved as follows.

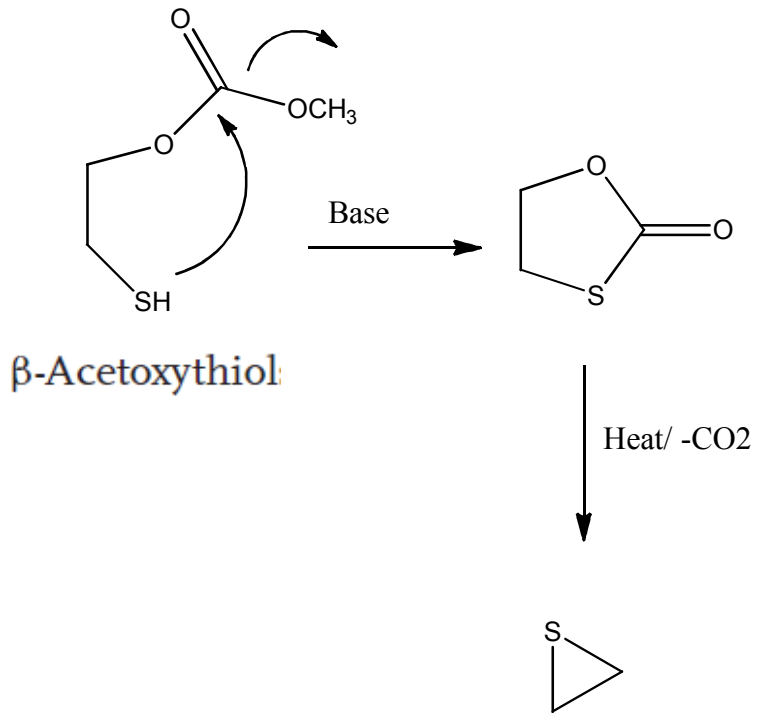
## Cyclization of β-substituted thioles

By analogy with the oxirane synthesis described on p. 21, halo thiols react with bases to give thiiranes. β-Acetoxythiols also yield thiiranes under similar conditions. 2-Sulfanylethanol reacts with phosgene in the presence of pyridine to give 1,3-oxathiolan-2-one, which on heating to 200 °C decarboxylates to give $CO_2$ and thiirane.




1,3-oxathiolane-2-one

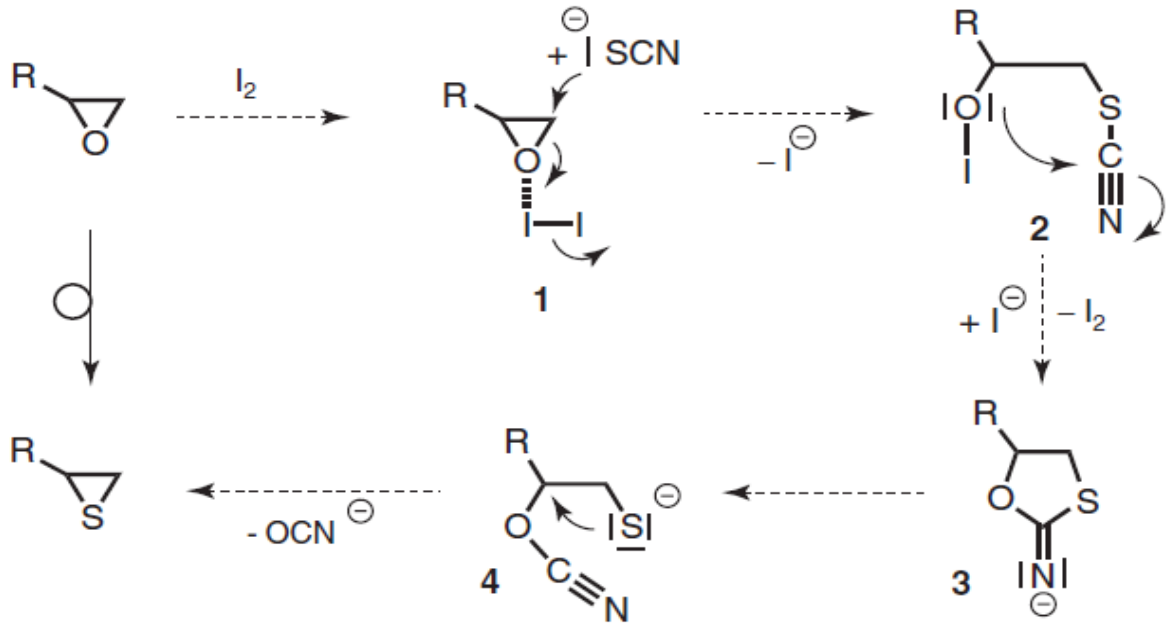
Example:




β-Acetoxythiol

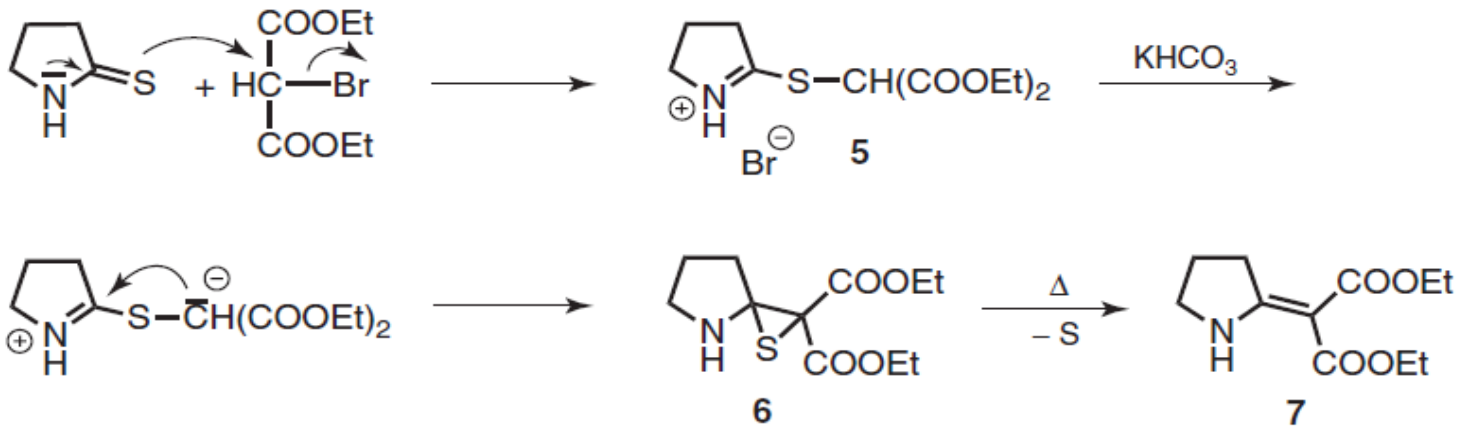
## Ring transformation of oxiranes

Oxiranes react with thiocyanates to give thiiranes, preferentially with $[NH_4]SCN$ in acetonitrile in the presence of iodine as catalyst [33]:



Application in synthesis:

A method for C–C coupling which is based on closing a thiirane ring and opening it by desulfurization is known as *sulfide contraction* according to ESCHENMOSER, for example:




1) Hydrolysis
2) Heat/-$CO_2$
3) Acid

The structure of latest product?