

PREPARATION OF OLEFINS BY REDUCTIVE ELIMINATION OF β -HYDROXYSULFIDES
USING 2-FLUOROPYRIDINIUM SALT AND LITHIUM IODIDE

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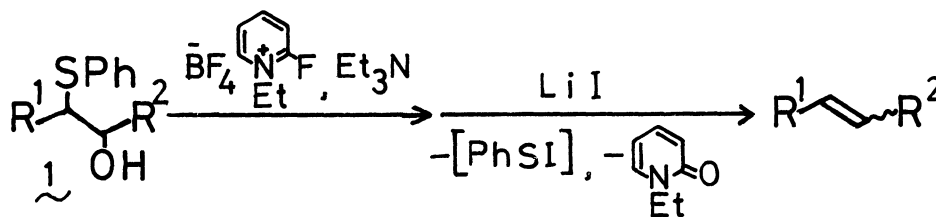
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Various olefins were prepared in good yields by reductive elimination of β -hydroxysulfides (1) with 1-ethyl-2-fluoropyridinium tetrafluoroborate (2) and lithium iodide.

Reductive elimination of β -hydroxysulfides provides a useful method for the preparation of olefins, and recently several works have been reported.¹⁾ However, these reductions are carried out under relatively drastic conditions using strong base or basic media except in the case of using low valent titanium compound as a reducing agent.²⁾

In the present communication, we wish to report a new method for the preparation of olefins by reductive elimination of β -hydroxysulfides 1 utilizing 2-fluoropyridinium salt 2³⁾ and lithium iodide under mild conditions.



A typical procedure is described for the preparation of trans-cyclododecene (4); to an acetone (1 ml) solution of 2 (179 mg, 0.84 mmol) was added a mixture of erythro-2-(phenylthio)cyclododecanol (3) (204 mg, 0.70 mmol) and triethylamine (85 mg, 0.84 mmol) in acetone (2.5 ml) at -3°C under an argon atmosphere, and the reaction mixture was stirred for 2 h. Lithium iodide (115 mg, 0.86 mmol) was then added in one portion, and the reaction mixture was refluxed for 2 h. After evaporation of the solvent under reduced pressure, the residue was directly subjected to thin layer chromatography on silica gel, and trans-cyclododecene 4 was isolated in 85% yield.

In a similar manner, various β -hydroxysulfides were converted to the corresponding olefins in good yields as summarized in the following Table.

Table. Reductive Elimination of β -Hydroxysulfides.

| Entry | β -Hydroxysulfide | Olefin | Yield(%) ^{a)} |
|-------|-------------------------|--------|--|
| 1 | | | 81 ^{b) c)} (cis/trans \approx 1) ^{d)} |
| 2 | | | 91 ^{b) c)} |
| 3 | | | 69 ^{b)} |
| 4 | | | 85 ^{e)} |
| 5 | | | 76 ^{e)} |
| 6 | | | 70 ^{b)} |
| 7 | | | 71 ^{b)} |

a) All of the products gave satisfactory IR and NMR data for assigned structures.

b) Refluxed for 1 h.

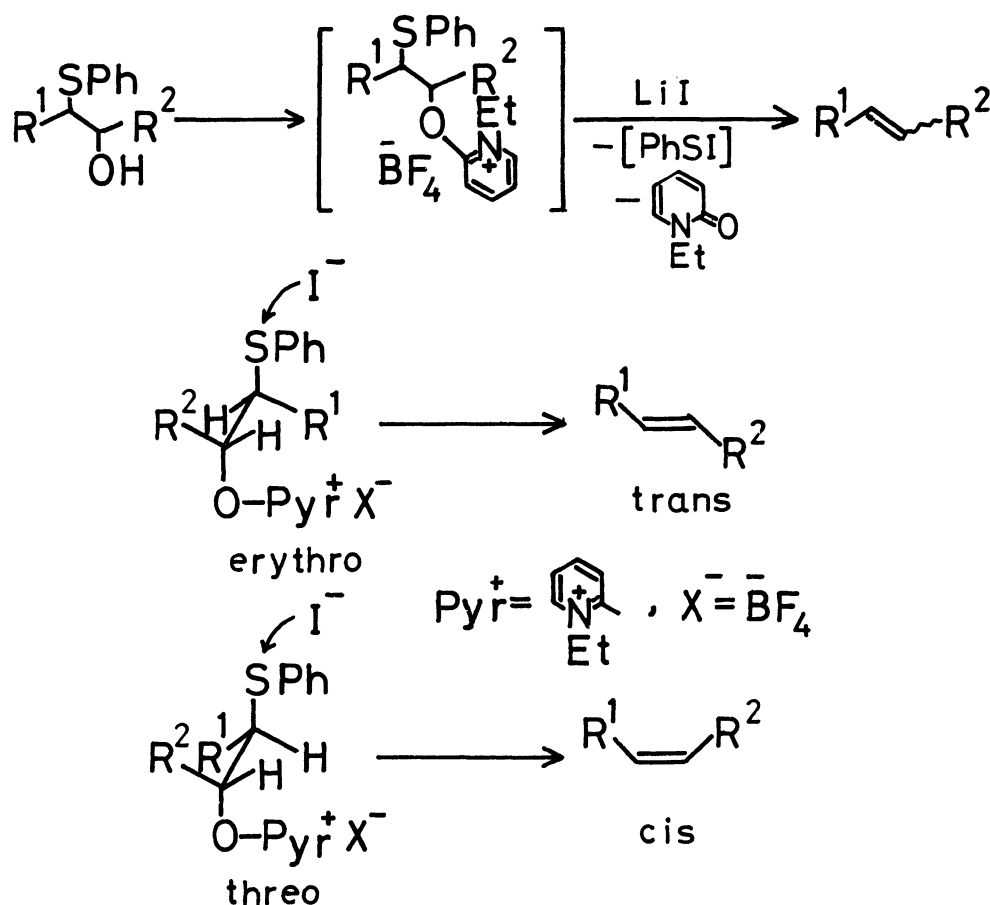
c) The chromatographed olefin contaminated by diphenyl disulfide was purified by treating with LiAlH_4 .

d) The ratio was determined by the integral ratio of NMR spectrum.

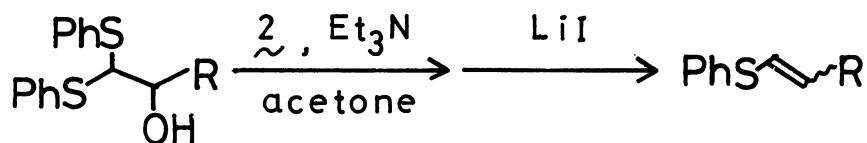
e) These products were assured to be pure by GLPC analysis on PEG 20M column.

There are alternative pathways of the attack by iodide ion on β -hydroxysulfides, that is, (i) the attack at sulfur atom to afford olefins with synchronous elimination of sulfenyl iodide and 1-ethyl-2-pyridone, and (ii) the attack at β -carbon of sulfide to afford S_N2 displacement products.⁴⁾ The results listed in the Table indicate that the former reaction takes place so much faster than the latter leading to the exclusive formation of olefins. Sulfenyl iodide thus formed disproportionated readily to result in the formation of diphenyl disulfide and iodine.

And as shown in the Table, erythro and threo form of 1 gave exclusively trans and cis olefins, respectively (See entry 4 and 5). This results indicate that the present reductive elimination reaction proceeds with perfect stereospecificity. Thus, the following trans elimination mechanism involving the direct attack of iodide ion at sulfur atom of β -hydroxysulfides is suggested as sketched below.



In addition, it was found that 2-hydroxythioacetals, instead of β -hydroxysulfide, gave the corresponding vinyl sulfides in moderate yields (See entry 6 and 7).



It is noted that β -hydroxysulfides, easily prepared from the reaction of carbonyl compounds with α -lithiosulfides, are converted to olefins by reductive elimination under mild conditions with perfect stereospecificity.

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