

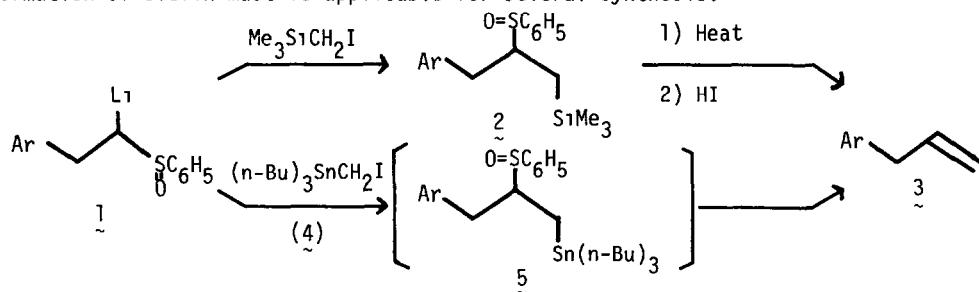
A NEW SYNTHESIS OF 1,3-DIENES FROM ALLYL SULFIDES
 AND ALLYL SULFONES USING TRI-*n*-BUTYLSTANNYLMETHYL IODIDE

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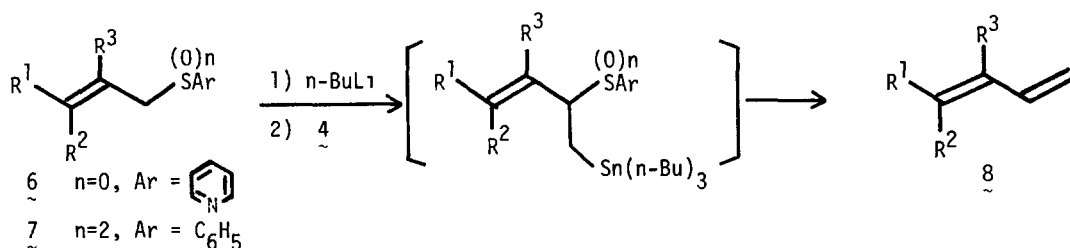
Summary Allyl 2-pyridyl sulfide 6 or allyl phenyl sulfone 7 on treatment with *n*-butyllithium in tetrahydrofuran followed by tri-*n*-butylstannylmethyl iodide (4) afforded directly the 1,3-diene 8 in good yield.

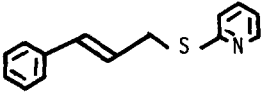
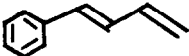
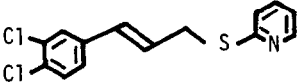
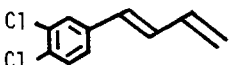
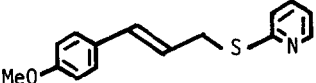
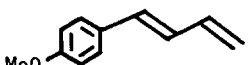
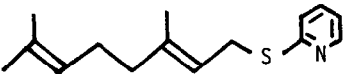
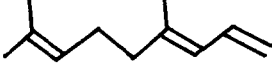
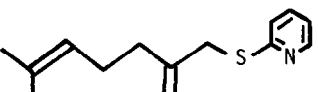
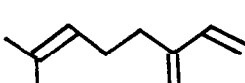
In a previous paper,¹ we reported the silicon-directed sulfenic acid elimination reaction of β -trimethylsilyl sulfoxide 2 followed by protodesilylation giving olefin 3 in a complete regioselective manner. Then we planned to prepare the β -stannyl sulfoxide 5, in order to compare the effect of silicon and tin atoms for the elimination reaction of sulfoxides. Thus lithio compound 1 (Ar=*p*-MeC₆H₄) was treated with tri-*n*-butylstannylmethyl iodide² (4) in tetrahydrofuran (THF). The product was not 5, but olefin 3 (46% yield), unexpectedly. This easy formation of olefin must be applicable for several syntheses.



First, we developed a general method for the single step synthesis of 1,3-diene 8 starting from allyl 2-pyridyl sulfide 6 or allyl phenyl sulfone 7.

2-Pyridyl sulfide 6 was expected to be a suitable material for this diene synthesis, because of the high regioselectivity for the alkylation of its ambident carbanion³ and of the superiority of pyridine-2-thio group as a leaving group. A typical procedure using 6a (6 R¹=ph, R²=R³=H) for the synthesis of 1-phenylbutadiene 8a is as follows: *n*-butyllithium (1.05

Table I Synthesis of Diene 8 from Allyl 2-Pyridyl Sulfide 6

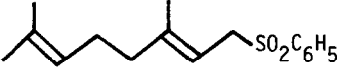
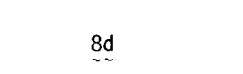
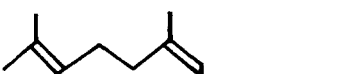
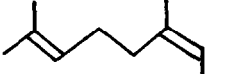
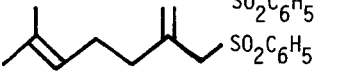
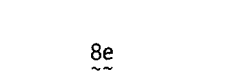
Allyl sulfide 6^a	Product 8	Yield ^b %
 6a	 8a	73 (89)
 6b	 8b	71
 6c	 8c	86
 6d	 8d	47 (58)
 6e	 8e	(42)

a) Allyl sulfide 6 was prepared from the corresponding allyl chlorides by treatment with sodium salt of 2-mercaptopyridine 4 b) Isolated yield (GLC yield)

equivalent) in hexane was added to a solution of sulfide 6a in tetrahydrofuran at -78° and the solution was stirred for 30 min. To the resulting red solution was added a solution of 4 (1 equivalent) in tetrahydrofuran very slowly. The color of the solution turned to pale yellow. The temperature must be kept at -78° during the whole operations described above. After stirring for 20 min at the same temperature and for 1.5h at 0° , the reaction mixture was quenched with aqueous ammonium chloride solution. Extraction with *n*-pentane-ether, drying, evaporation, and then purification of the resulting residue by preparative TLC afforded 1,3-diene 8a in 73% yield. The rate of addition of 4 must be very slow, otherwise the yield of diene 8a drops markedly.

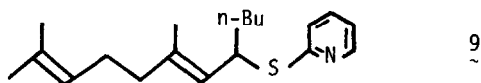
The results of diene synthesis from a variety of allyl 2-pyridyl sulfides (6) are summarized in Table I.

Table II Synthesis of Diene 8 from Allyl Sulfone 7

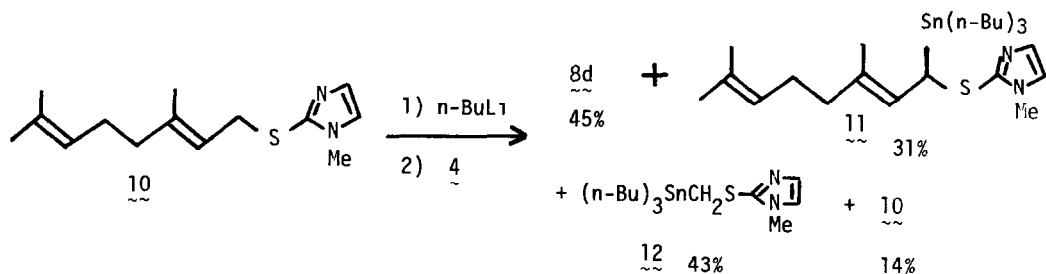
Allyl sulfone 7 ^a	Product 8	Yield ^b %
 7a	 8d	78 (94)
 7b	 8f	75
 7c	 8e	(46) ^c

a) Allyl sulfone 7 was prepared from the allyl chloride by treatment with sodium benzenesulfinate dihydrate and tetrabutylammonium bromide according to the slightly modified procedure of Vennstra and Zwanenburg.⁹ b) Isolated yield (GLC yield) c) Nineteen % of allyl sulfone 7c was recovered.

In the use of excess amounts of *n*-butyllithium, a side reaction was observed when geranyl 2-pyridyl sulfide 6d was treated with 2 equivalents of *n*-butyllithium followed by 4, the major product was shown to be sulfide 9 (62% yield)⁵ and diene 8d was obtained only in a trace amount. The compound 9 may be produced from 6d by the alkylation with *n*-butyl iodide which must be produced *in situ* by a rapid reaction of excess *n*-butyllithium with 4.⁶

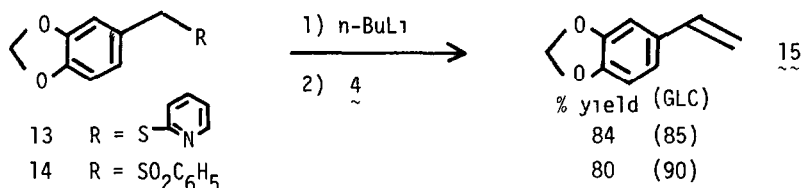


The reaction with *N*-methyl-2-imidazolyl sulfide 10⁷ gave no improvement of the yield of diene 8d, considerable amounts of stannylation product 11 and stannylmethyl sulfide 12 were produced.⁸ The formation of these undesirable products was considerably suppressed by the use of phenyl sulfone derivative. Thus geranyl phenyl sulfone 7a on treatment with *n*-butyllithium



at -78° followed by iodide 4 at -78° for 1h resulted in the formation of 8d in 78% yield. Neryl phenyl sulfone 7b afforded the Z-isomer 8f (Table II).

The reaction was found to be applicable to the synthesis of styrene derivative. Both piperonyl 2-pyridyl sulfide (13) and piperonyl phenyl sulfone (14) produced the styrene derivative 15 in good yields.



The detailed reaction mechanism is unknown.¹⁰ But the stability of allyl carbanions as well as the regioselectivity toward α -alkylation of allyl anions seem to be the most important factors controlling the synthesis of 1,3-dienes.

References and Notes

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8. The structures of 11 and 12 were confirmed by the comparison with their authentic samples, respectively
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