THE REACTION OF β -phenylsulfinyl β , γ -UNSATURATED ETHERS WITH TRIBUTYLSTANNYLLITHIUM. A NEW ROUTE TO SUBSTITUTED ALLENES

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Substituted allenes were prepared in good yields by the reaction of β -phenylsulfingl β , γ -unsaturated ethers with tributylstan-nyllithium.

The properties and reactions of substituted allenes have been extensively studied.¹⁾ Although various methods of allene synthesis including nucleophilic addition to propargyl halides,²⁾ acetates,³⁾ and 2-propargyloxypyridinium salts,⁴⁾ and the reaction of titanacyclobutanes with carbonyl compounds⁵⁾ were reported, it is still difficult to prepare substituted allenes.

Recently, we reported that β -phenylthio β , τ -unsaturated alcohols (<u>1</u>) were easily obtained by reaction of aldehydes or ketones with 1-(phenylthio)vinyllithium reagents prepared by reaction of 2-methoxyalkyl sulfides with two equivalents of butyllithium.⁶) In this communication, we wish to report a useful procedure for the conversion of <u>1</u> to substituted allenes (<u>3</u>) using tributylstannyllithium as a reducing agent. Chan et al. reported a similar approach using \varkappa -silylvinyl carbanion⁷) and Posner et al. also reported that the treatment of some alkenyl sulfoxides with lithium 2,2,6,6,-tetramethylpiperidide gave allenes.⁸) However, these methods are available only for the terminal allene synthesis.



 β -Phenylthio β,γ -unsaturated alcohol (<u>1</u>) was treated with sodium hydride and methyl iodide successively in THF at 0 °C to room temperature to give the corresponding methyl ether. Then the methyl ether was oxidized with an equimolar amount of MCPBA in CH₂Cl₂ at -23 °C and alkenyl sulfoxide (<u>2</u>) was obtained in good yields (<u>2a</u>; 68%, <u>2b</u>; 74%, <u>2c</u>; 67%, <u>2d</u>; 89%, <u>2e</u>; 90%, <u>2f</u>; 80%, <u>2g</u>; 51%).⁹⁾ The conversion of <u>2</u> to substituted allene (<u>3</u>) was easily carried out by the simple treatment of <u>2</u> with tributylstannyllithium in THF. The following experimental procedure is representative; to a THF (6 ml) solution of 5methoxy-l-phenyl-4-phenylsulfinyl-3-dodecene (399 mg, 1 mmol) was added a THF solution of tributylstannyllithium (2 mmol)¹⁰⁾ at -17 °C. After stirring for 2 h, the reaction was quenched by addition of 1 M NaOH aqueous solution. The organic material was extracted with AcOEt and the extract was dried over Na₂SO₄. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane) and 1-phenyl-3,4-dodecadiene (192 mg) was isolated in 79% yield.

In a similar manner, various substituted allenes (3) were obtained in good yields (Table 1).

> Rl _R² Yield/%^{a)} R³ 2a Ph(CH₂)₂ Ph(CH₂)₂ 84 H 2b Ph(CH₂)₂ (CH₃)₂CHCH₂ H 84 Ph(CH₂)₂ 2c CH3(CH2)6 Н 79 2đ CH₃(CH₂)₆ H (CH₃)₂CHCH₂ 70 CH₃(CH₂)6 70 <u>2e</u> H CH₃(CH₂)₆ SnBu -(CH₂)₅ Ph(CH₂)₂ 2f 72 $Ph(CH_2)_2 CH_3(CH_2)_6$ $Ph(CH_2)_2$ 75 2g 4

Table 1. Synthesis of substituted allenes (3)

a) All products were identified by IR and NMR spectra.

Fujita et al. reported that the β -tributylstannyl sulfone is produced by the reaction of alkenyl sulfone with tributylstannyllithium.¹¹⁾ It is reasonable to assume that the present reaction proceeds via a similar intermediate (4). The fact that the treatment of 1,5-diphenyl-2-phenylsulfinyl-2-pentene with tributylstannyllithium in THF at -17 °C for 2 h gave the corresponding olefin in 78% yield would support the above assumption.

Since 2-methoxyalkyl phenyl sulfides were easily prepared from the corresponding aldehydes (R³CHO) in good yields,^{6b)} it should be noted that a new route to substituted allenes (3) utilizing two different carbonyl compounds $(R^{1}R^{2}C=0 \text{ and } R^{3}CHO)$ was established by the present study.

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