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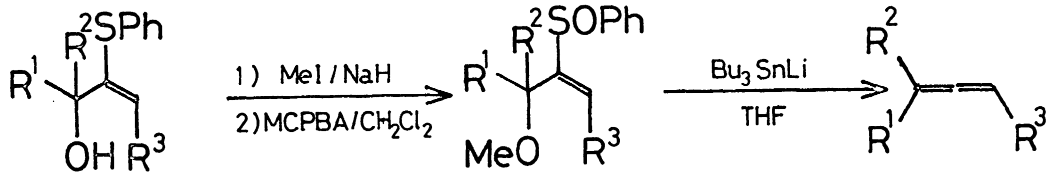
# THE REACTION OF β-PHENYLSULFINYL β,γ-UNSATURATED ETHERS WITH TRIBUTYLSTANNYLLITHIUM. A NEW ROUTE TO SUBSTITUTED ALLENES

Takeshi TAKEDA,* Koichi SUZUKI, Hiroyuki OHSHIMA, and Tooru FUJIWARA
Department of Industrial Chemistry, Faculty of Technology, Tokyo
University of Agriculture and Technology, Koganei, Tokyo 184

Substituted allenes were prepared in good yields by the reaction of β-phenylsulfinyl β,γ-unsaturated ethers with tributylstannyllithium.

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,γ-unsaturated alcohols (1) 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 1 to substituted allenes (3) using tributylstannyllithium as a reducing agent. Chan et al. reported a similar approach using α-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.



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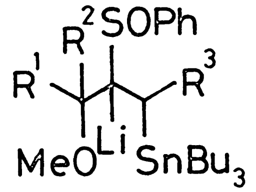
β-Phenylthio β,γ-unsaturated alcohol (1) was treated with sodium hydride and methyl iodide successively in THF at 0 °C to room temperature to give the corresponding methyl ether. Then the methyl ether was oxidized with an equimolar amount of MCPBA in $CH_2Cl_2$ at -23 °C and alkenyl sulfoxide (2) was obtained in good yields (2a; 68%, 2b; 74%, 2c; 67%, 2d; 89%, 2e; 90%, 2f; 80%, 2g; 51%).9) The conversion of 2 to substituted allene (3) was easily carried out by the simple treatment of 2 with tributylstannyllithium in THF. The following experimental procedure is representative; to a THF (6 ml) solution of 5-methoxy-1-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 $Na_2SO_4$. 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).

Table 1. Synthesis of substituted allenes (3)

| | $R^1$ | $R^2$ | $R^3$ | Yield/%[a)] |
|---|---|---|---|---|
| 2a | $Ph(CH_2)_2$ | H | $Ph(CH_2)_2$ | 84 |
| 2b | $Ph(CH_2)_2$ | H | $(CH_3)_2CHCH_2$ | 84 |
| 2c | $CH_3(CH_2)_6$ | H | $Ph(CH_2)_2$ | 79 |
| 2d | $CH_3(CH_2)_6$ | H | $(CH_3)_2CHCH_2$ | 70 |
| 2e | $CH_3(CH_2)_6$ | H | $CH_3(CH_2)_6$ | 70 |
| 2f | $-(CH_2)_5-$ | | $Ph(CH_2)_2$ | 72 |
| 2g | $Ph(CH_2)_2$ | $Ph(CH_2)_2$ | $CH_3(CH_2)_6$ | 75 |

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



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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 ($R^3CHO$) in good yields,[6b)] it should be noted that a new route to substituted allenes (3) utilizing two different carbonyl compounds ($R^1R^2C=O$ and $R^3CHO$) was established by the present study.

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