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SILA-PUMMERER REARRANGEMENTS AT SP^2-HYBRIDIZED CARBON

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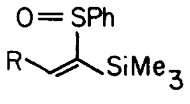
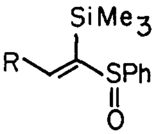
Summary: α-Trimethylsilylvinyl sulfoxides undergo sila-Pummerer rearrangements upon warming in benzene. Alkynes, vinylsulfoxides, and ketene S,O-acetals are obtained as products.

A number of molecular rearrangements involving migration of a silyl group from sp^3-hybridized carbon to oxygen have been reported.[3] The sila-Pummerer reaction, one member of this family of rearrangements, involves the thermal conversion of α-silyl sulfoxides to S,O-acetals.[4] During the course of studies in the area of alkaloid synthesis, we discovered that α-silylvinyl sulfoxides undergo a related rearrangement. This report describes our initial observations and documents the first examples of sila-Pummerer rearrangements at sp^2-hybridized carbon.[5,6]

Warming of a 0.064M solution of sulfoxide **1a**[7] in benzene under reflux for 30h followed by removal of solvent and chromatography over silica gel afforded sulfoxide **3a** (19%),[8] alkyne **4a** (37%), and ketene S,O-acetal **5a** (32%).[9] The structures of **3a** and **4a** were proven by comparison with authentic samples prepared via alternate routes.[10,11] The structure of **5a** was based on spectral data and its conversion to thioester **6a** (91%) upon treatment with 1-3 mol% p-toluenesulfonic acid in methanol (room temperature, 40 min). In addition,



1



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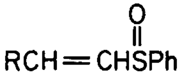
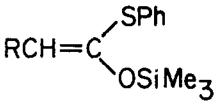


$RCH{=}CH\overset{\overset{O}{\|}}{S}Ph$

3

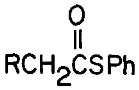
$R{-}C{\equiv}C{-}SPh$

4



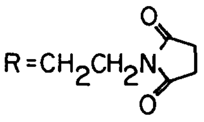
$RCH{=}C(SPh)(OSiMe_3)$

5



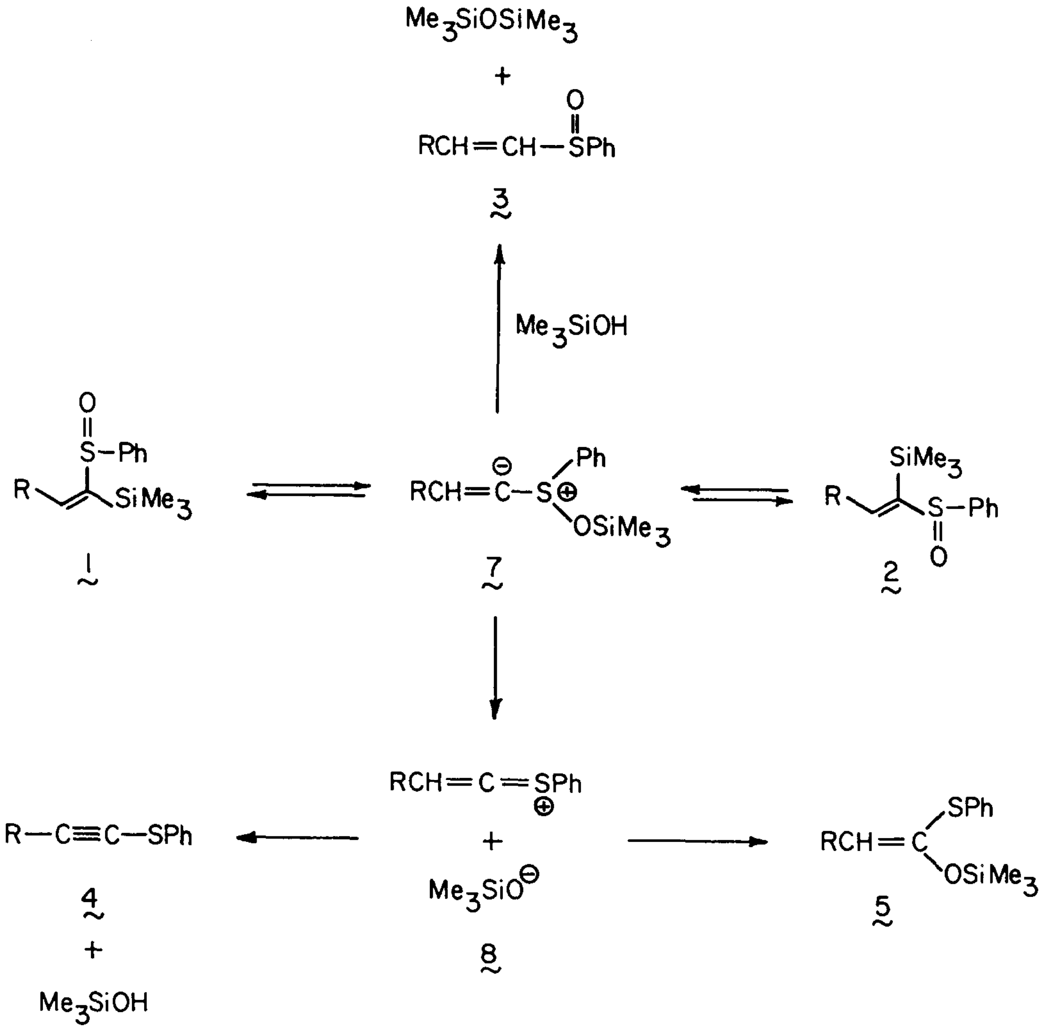
$RCH_2\overset{\overset{O}{\|}}{C}SPh$

6

a 

b $R{=}CH_2CH_2OAc$ **c** $R = n\text{-}C_7H_{15}$

it was noticed that at early stages of the reaction, sulfoxide 1a had isomerized in part to sulfoxide 2a. These observations can be accommodated by the mechanism outlined in Scheme I. Thus, reversible 1,3-silicon to oxygen migration could effect sulfoxide isomerization via the intermediacy of ylid 7. Ionization of 7 might afford ion pair 8 which could collapse to ketene S,O-acetal 5 or lose a proton to give alkyne 4. Finally, reaction between 7 and a proton donor-nucleophile pair would yield vinyl sulfoxide 3.[12]



The generality of this reaction is underscored by the additional examples shown in Table I. In each case, rapid sulfoxide isomerization ($1 \rightleftharpoons 2$) was observed. Furthermore, although ketene S,O-acetals 5b and 5c were not isolated, their presence was detected by thin layer chromatography prior to treatment of the rearrangement mixtures with *p*-toluenesulfonic acid in methanol.

Table I: Thermal Rearrangement of α-Trimethylsilylvinyl Sulfoxides

$$\mathbf{1}\ (\mathbf{2}) \xrightarrow[\text{2. MeOH, TsOH (cat.)}]{\text{1. Benzene, reflux}} \mathbf{3} + \mathbf{4} + \mathbf{6}$$

Sulfoxide	Conditions[a,b]	%**3**[c,d]	%**4**[c,d]	%**6**[c]
1a	30h	20	36	32
1b	12h	15	41	35
2b	10h	12	40	33
1c	4.5h	5	38	48
2c	10h	6	46	36

(a) All rearrangements were run 0.064 *M* in benzene under reflux for the indicated time periods. Hydrolyses were performed in methanol (3.5 mL of MeOH per mmol **1** or **2**) containing 1-3 mol% *p*-toluenesulfonic acid for 15-60 min. (b) Reactions were monitored by TLC and reaction times reflect the time required for the disappearance of **1** (**2**). (c) Isolated yield. (d) Compounds **3** and **4** were stable to the methanolic *p*-toluenesulfonic acid.

In summary, α-trimethylsilylvinyl sulfoxides undergo thermal rearrangements in benzene to give mixtures of vinyl sulfoxides, acetylenic sulfides, and ketene S,O-acetals. Experiments directed toward understanding the mechanism of these transformations and developing their synthetic potential are under investigation.

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