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1-PHENYLTHIO-1-(TRIMETHYLSILOXY)CYCLOPROPANES VIA THE SILA-PUMMERER REARRANGEMENT

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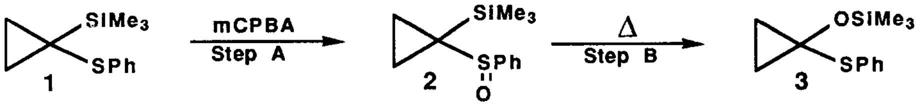
Abstract*: This first study of the sila-Pummerer rearrangement in a cyclopropane system reveals that several 1-trimethylsiloxy-1-(phenylthio)cyclopropanes can be prepared stereoselectively through putative sulfur-stabilized carbocationic intermediates.*

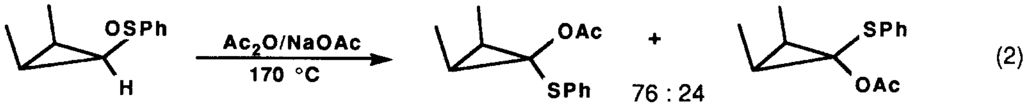
Continuing our efforts on the synthesis of suitable precursors for the preparation of cyclobutanones[1] *via* reductive lithiation by radical anions, we have investigated the synthesis of the title compounds, which we hoped would serve the function of the corresponding 1-methoxy-1-(phenylthio)cyclopropanes. We harnessed the ready availability, via efficient procedures recently developed in our laboratory,[2] of 1-phenylthio-1-(trimethylsilyl)cyclopropanes to prepare the title compounds via the sila-Pummerer rearrangement[3,4,5] as shown in equation 1. Although the original impetus for the study was foreclosed by the Brook rearrangement[6] of the 1-lithio-1-siloxycyclopropanes produced by reductive lithiation of compounds such as **3**, the study did reveal interesting mechanistic information since the sila-Pummerer rearrangement has never been applied to cyclopropyl systems and the stereochemistry of the siloxy transfer has never been established; it was found to provide excellent yields of the desired siloxy compounds which are currently unavailable and which should be useful as masked cyclopropanones (see below). The results of the rearrangements, which were performed in refluxing benzene, are summarized in Table I.[7]



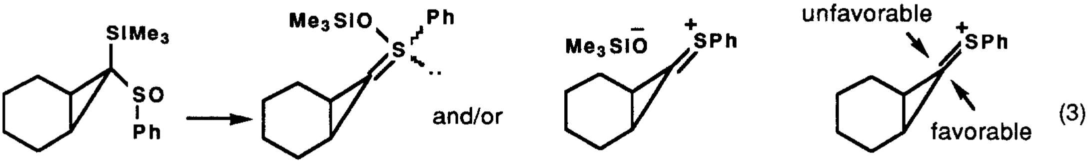
(1)

We observed that the bicyclic cyclopropanes **6** and **7** rearranged much faster than the parent system **2** and that **7** rearranged faster than **6** and was indeed unstable at room temperature. The transfer of the trimethylsilyl group to oxygen[3,4,8] should relieve steric compression between the endo substituent and the cyclohexane ring, an interaction which is absent in the monocyclic system **2** and which would be more serious in **7**, because of the bulk of the *endo*-trimethylsilyl group,[9] than in **6**.

The stereochemical course of the reaction is completely different from that of the only other Pummerer rearrangement that has been studied in a cyclopropyl system. Oae *et al.*[10] have studied the Pummerer rearrangement of the cyclopropane shown in equation 2. They observed the reaction to proceed mainly with inversion of configuration; the isomer which is epimeric about the sulfur-bearing carbon atom underwent the rearrangement with complete inversion of configuration.



We observed that **6** gives the *exo*-siloxy isomer **8** as the only product and **7** gives the same isomer as the major product. The preferential formation of **8** is readily explained by the attack of the trimethylsiloxy anion on the sterically least hindered *exo*-face of the sulfur stabilized carbocation **12**.[11] If the rearrangements of both **6** and **7** pass through the same intermediate (**12**), then the product ratio must be the same in both cases. The fact that **9** (*endo*-siloxy isomer) is formed only from the *endo*-trimethylsilyl substrate, **7** but not from the *exo*-trimethylsilyl substrate **6**, suggests that, to some extent, a contact ion pair (**11**) or an intramolecular rearrangement of the siloxy group in the ylide **10** might be involved.



7 **10** **11** **12**

Since the siloxy compounds such as **3** were not suitable for the synthesis of cyclobutanones, we returned our attention to methoxy compounds such as **13**. The intermediacy of **12** in the sila-Pummerer rearrangement suggested that if methanol were used as the solvent, it (or methoxide) could compete with the trimethylsiloxy anion for **12**. We carried out the rearrangement of a few silyl sulfoxides in refluxing methanol and the results are shown in Table II. The rearrangements were far slower in methanol than in benzene, presumably because of hydrogen bonding of the solvent to the sulfoxide group. The results are completely consistent with the intermediacy of species such as **12** which undergo attack largely by methanol or its conjugate base rather than by trimethylsiloxide, again from the least hindered face of **12**. It is especially significant that **15** yields a large amount of 6-membered cyclic allylic ethers, undoubtedly the result of ring opening of the cation analogous to **12**; cyclopropyl cations which are fused to 5-membered rings open to allyl cations far more rapidly than those fused to 6-member rings[12] and it is also known that **10** is rather stable to ring opening.[13]

These results with the sila-Pummerer reaction are similar to those that we observed in the Pummerer reaction of methoxy(phenyl)sulfonium salts in the same systems,[14] a type of reaction for which Johnson[15] has provided convincing evidence for carbocation intermediates. We can speculate that the sharp differences between these results and those of Oae[10] (see above) is due to the conformation of the acetoxy group at the time of proton removal being appropriate for a [2,3]-sigmatropic acetoxy migration (eq. 4) and is thus extremely facile, occurring before substantial ionization; some evidence for such a rearrangement mechanism is available from studies of chirality transfer and ^{18}O labeling.[16,17]

The 1-phenylthio-1-(trimethylsiloxy)cyclopropane products will almost certainly be useful as masked cyclopropanones.[18] Treatment of **8** with tetrabutylammonium fluoride yields the hemi-thioacetal 7-phenylthio-7-norcaranol, the formal addition product of thiophenol and 7-norcaranone.

Table I: Synthesis and the Sila-Pummerer Rearrangements of Sulfoxides in Benzene

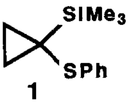
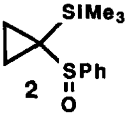
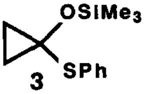
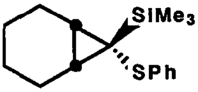
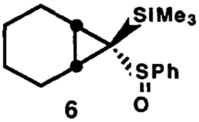
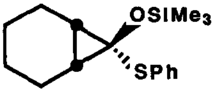
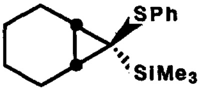
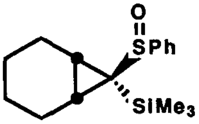
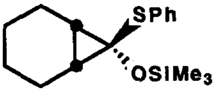
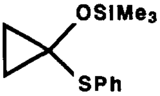
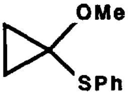
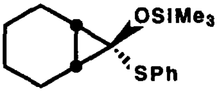
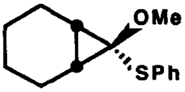
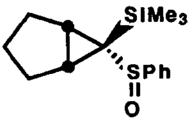
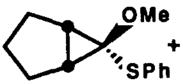
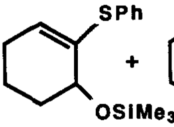
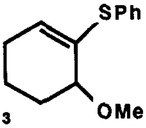
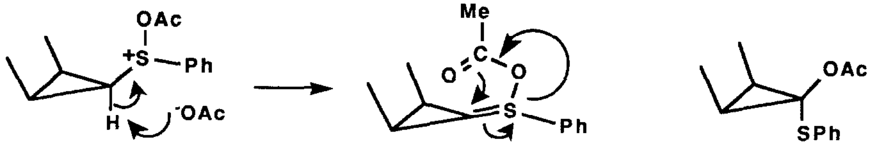
Sulfide	Sulfoxide	%Yield Step A	Siloxy Product	Reaction Time (%Yield) Step B
 **1**	 **2**	96	 **3**	22 h (75)
 **4**	 **6**	95	 **8**	30 m (86)
 **5**	 **7**	98	**8** +  **9** (84 : 16)	15 m (69)

Table II: Sila-Pummerer Rearrangements in Methanol

Sulfoxide	Reaction Time	Products (%Yield)
2	14 d	 **3** (3) +  **13** (42)
6	17 h	 **8** (15) +  **14** (68)
 **15**	5 h	 **16** (12) +  **17** (29) +  **18** (15) +  **19** (43)



(4)

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References and Notes

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[11] An alternative explanation that the starting materials are interconverted by reversibility of the silyl transfer is unlikely. Conversion of **7** to **6** before the Pummerer rearrangement can be ruled out since **6** rearranges far slower than **7**. Conversion of **6** to **7** would produce the ylide intermediate **12** which would be expected to yield **9** which is produced in only very minor amounts and then only from **6**.

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[17] Although we accept Oae's other arguments against a carbocation intermediate in this reaction, we do not agree that the lack of ring opening is evidence against such an intermediate.[10] There is ample evidence in the present paper and elsewhere that sulfur-stabilized cyclopropyl cations are sometimes stable to ring opening. Jorritsma, R., Ph. D. thesis University of Amsterdam, **1979**.

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