Tetrahedron Letters No. 24, pp 2017 - 2020, 1975. Pergamon Press. Printed in Great Britain.

SILICON-PUMMERER REARRANGEMENTS; STEREOSELECTIVE SULFINYLCARBANION SILYATION*

E. Vedejs and M. Mullins
Department of Chemistry, University of Wisconsin,
Madison, Wisconsin 53706

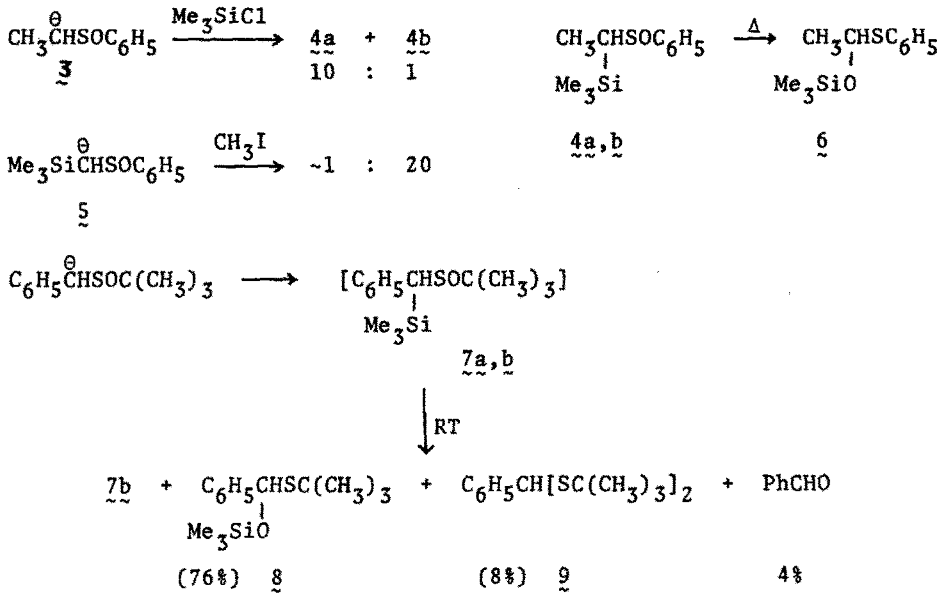
(Received in U.S.A. 20 March 1975; received in UK for publication 1 May 1975)

In connection with a synthetic project we required a mild method for Pummerer rearrangement of dialkyl sulfoxides. A potential solution was suggested by the work of Brook and Anderson who discovered that α-trimethylsilyl sulfoxide 1 rearranges at 60° into the hemithioacetal trimethylsilyl ether 2.[1] This reaction appeared to meet our requirements, provided that α-sulfinyl carbanions could be silylated efficiently. Other workers have encountered difficulties with the silylation step,[1,2] but we find that good results can be achieved by an inverse addition procedure. Thus, treatment of methyl phenyl sulfoxide in tetrahydrofuran with lithium diisopropylamide (LDA) at -78° (1 hr) followed by dropwise addition of the anion to excess chlorotrimethylsilane at -78° results in a 90-95% yield of 1, identical to material prepared previously by an alternate route.[1] Thermolysis of 1 (60°) affords 2 in 72% isolated overall yield after distillation together with 10% recovered methyl phenyl sulfoxide. The mechanism of this reaction as proposed by Brook and Anderson involves initial silicon migration from carbon to oxygen to give a siloxysulfonium ylid which then rearranges by the usual Pummerer pathway.

FIGURE 1

$$\begin{tikzcd}
CH_3SOC_6H_5 \arrow[r, "1)\,LDA", "2)\,Me_3SiCl"'] & \underset{\textstyle 1}{Me_3SiCH_2SOC_6H_5} \arrow[r, "60^\circ"] & {[CH_2{=}S(OSiMe_3)C_6H_5]} \arrow[d] \\
 & & \underset{\textstyle 2}{Me_3SiOCH_2SC_6H_5}
\end{tikzcd}$$

*This work was supported by the National Science Foundation.



$$CH_3\overset{\ominus}{C}HSOC_6H_5 \xrightarrow{Me_3SiCl} \underset{10}{4a} \; + \; \underset{1}{4b}$$

3

$$Me_3Si\overset{\ominus}{C}HSOC_6H_5 \xrightarrow{CH_3I} \sim 1 \; : \; 20$$

5

$$CH_3\underset{Me_3Si}{CH}SOC_6H_5 \xrightarrow{\Delta} CH_3\underset{Me_3SiO}{CH}SC_6H_5$$

4a,b 6

$$C_6H_5\overset{\ominus}{C}HSOC(CH_3)_3 \longrightarrow [C_6H_5\underset{Me_3Si}{CH}SOC(CH_3)_3]$$

7a,b

$$\downarrow RT$$

$$7b + C_6H_5\underset{Me_3SiO}{CH}SC(CH_3)_3 + C_6H_5CH[SC(CH_3)_3]_2 + PhCHO$$

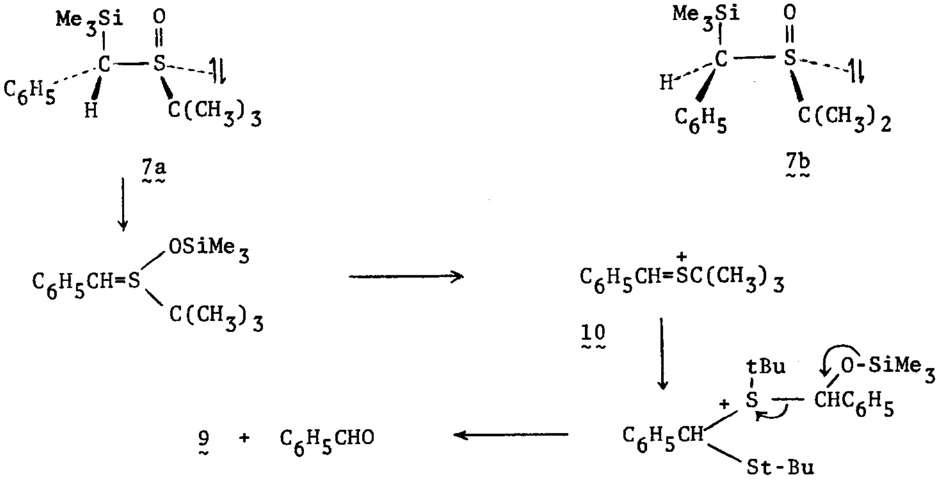
(76%) 8 (8%) 9 4%

Silylation of ethyl phenyl sulfoxide by the same procedure gives a 10:1 mixture of diastereomers 4a and 4b (85%). The major isomer 4a is characterized by methine and methyl chemical shifts at 2.25δ (q,J=7Hz) and 1.02δ (d,J=7Hz). The minor isomer 4b is identical to a substance obtained by Carey and Hernandez by methylation of the anion 5.[2] We have reexamined the latter reaction and find that both diastereomers are formed in a ratio of 4a:4b of ca. 1:20 by nmr analysis of the C-methyl region. Upon thermolysis, the major isomer from silylation (4a) is completely converted to 6 within an hour at 60° while only 7% of 4b reacts under the same conditions. At 80°, the rearrangement of 4b to 6 is complete after 2 hours, in agreement with an earlier observation by Carey and Hernandez.[2]

Silylation of benzyl tert-butyl sulfoxide anion[3] also affords a mixture of diastereomers at -78°. In this case, the major diastereomer 7a cannot be isolated at room temperature due to its facile rearrangement to 8 (76%). Small amounts of benzaldehyde and the dithioacetal 9 are also present in the crude reaction product, together with 7b (6-7% by nmr analysis). Examination of crude silylation mixtures by low temperature nmr reveals a weak methine singlet at 6.08δ due to 8. This signal increases considerably in intensity between 0-10°, indicating that unrearranged 7a must be present at lower temperatures. In contrast, the minor isomer 7b is quite stable at room temperature and can be purified by chromatography. Upon thermolysis at 68°, 7b rearranges to 8 (20%), benzaldehyde (35%), and 9 (30%). These sideproducts are not formed from purified 8 under the same conditions, and are best explained by intermolecular S-alkylation of 8 by the ionic intermediate 10 as shown in Figure 2.

The dramatic reactivity difference between 7a and 7b can be rationalized by Brook's mechanism[1] if silicon migration from carbon to oxygen is an intramolecular 4-center process.[4] The more reactive diastereomer 7a would then be assigned the relative stereochemistry which minimizes phenyl-tert-butyl interactions in the 4-center transition state (eclipsed C-Si and S=O bonds, Fig. 2) Similar reasoning can be used to assign the stereochemistry of 4a and 4b, but the reactivity difference is smaller and the argument is correspondingly weaker. It is significant that 7a corresponds to silylation of the anion with opposite stereoselectivity compared to protonation as observed by Durst and Viau.[3] Furthermore, the preferential formation of a different diastereomer from silylation of 3 compared to methylation of 5 is consistent with the same stereochemistry for silylation as for methylation, provided that 3 and 5 have similar geometry.[5]

Figure 2



The synthetic potential of the silicon Pummerer rearrangement is illustrated by several dialkyl sulfoxide silylations (Table 1). In general, the intermediate α-trimethylsilyl sulfoxides rearrange below room temperature. This enhanced reactivity compared to 2 and 4a,b suggests that silicon migration is favored by greater electron density at oxygen in dialkylsulfoxides compared to alkylaryl-sulfoxides. Substantial yields of vinyl thioethers are also obtained, presumably by deprotonation of intermediate sulfonium ions. Although the yields of Pummerer products are modest, we note that di-n-butyl sulfoxide and certain other alkyl sulfoxides give only the vinyl thioethers under standard Pummerer conditions.[6]

Table 1. (Silylation at -78°, workup at 20°)

$$(n\text{-}C_4H_9)_2SO \xrightarrow[2)ClSiMe_3]{1)LDA} \underset{45\%}{C_4H_9SCH(OTMS)C_3H_7} + \underset{30\%}{C_4H_9SCH{=}CHC_2H_5} + \underset{13\%}{(C_4H_9S)_2CHC_3H_7}$$

$$t\text{-}C_4H_9SO\text{-}n\text{-}C_4H_9 \xrightarrow{etc.} \underset{44\%}{t\text{-}C_4H_9SCH(OTMS)C_3H_7} + \underset{41\%}{t\text{-}C_4H_9SCH{=}CHC_2H_5}$$

$$PhCH_2SOCH_3 \longrightarrow \underset{34\%}{PhCH(OTMS)SCH_3} + \underset{32\%}{PhCH(SCH_3)_2} + \underset{34\%}{PhCHO}$$

$$PhCH_2CH(SCH_3)SOCH_3 \longrightarrow \underset{86\%}{PhCH{=}C(SCH_3)_2}$$

References

1. A. G. Brook and D. G. Anderson, Can. J. Chem., 46, 2115 (1968).

2. F. A. Carey and O. Hernandez, J. Org. Chem., 38, 2670 (1973).

3. R. Viau and T. Durst, J. Amer. Chem. Soc., 95, 1346 (1973).

4. A number of related thermal 1,2 and 1,3 silicon migrations are known. All studied cases are intramolecular: A. G. Brook, Accts. Chem. Res., 7, 77 (1974) and references therein.

5. In some cases, alkylation of sulfinyl carbanions occurs with opposite stereochemistry compared to protonation: T. Durst, R. Viau, and M. R. McClory, J. Amer. Chem. Soc., 93, 3077 (1971); D. A. Evans, T. C. Crawford, T. T. Fujimoto, and R. C. Thomas, J. Org. Chem., 39, 3177 (1974). However, the results may be affected considerably by reaction conditions: J. F. Biellmann and J. J. Vicens, Tetrahedron Lett., 2915 (1974); T. Durst and M. Molin, ibid., 63 (1975).

6. L. Horner and P. Kaiser, Justus Liebigs Ann. Chem., 626, 19 (1959); W. E. Parham, L. Christensen, S. H. Groven, and R. M. Dodson, J. Org. Chem., 29, 2211 (1964).