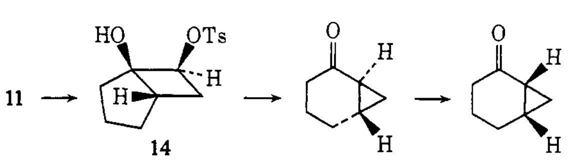
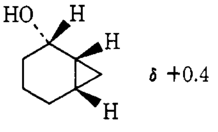
With **11** on hand we proposed to take advantage of the stereospecificity of the glycol monotosylate rearrangement to form the desired product **2**. The stereospecificity of such rearrangements has been well established in the synthesis of many bicyclic systems[22–24] including *trans*-bicyclo[7.1.0]decan-2-one.[1] The most important feature for our choice was that the rearrangement could be run under very mild conditions.[1,22] Thus, treatment of **11** with tosyl chloride in pyridine and rearrangement of the monotosylate **14** with 1 equiv of potassium *tert*-butoxide in THF for 10 min gave a product in 83% yield which we assigned as **2**. Molecular distillation gave a pure product which exhibited $\nu_{\max}^{\mathrm{CCl_4}}$ 3010 and 1703 cm^{-1} and δ (CCl_4) +0.4 ppm (1 H, m, cyclopropyl and no resonances below 2.5 ppm).[18] When the reaction was allowed to proceed for 19 hr and with 2 equiv of potassium *tert*-butoxide, a different product was isolated in 73% yield. This product, **15**, was identical in all respects with *cis*-bicyclo[4.1.0]heptan-2-one prepared by a known route:[25] $\nu_{\max}^{\mathrm{CCl_4}}$ 1690 cm^{-1} and δ (CCl_4) 1.0 ppm (highest field multiplet). The isolation of **15** is consistent with the initial formation of **2** followed by isomerization to **15**. When the rearrangement was run in *tert*-butyl alcohol-*d* the product contained less than 33 mol % deuterium[26] indicating that the rearrangement proceeds primarily without enolization of any kind.



14 **2** **15**

If the rearrangement of **14** is done in the presence of a reducing agent, such as potassium tri-*tert*-butoxyaluminum hydride, the ketone **2** can be reduced to a mixture of alcohols **3** and **4** in a ratio of 2:1, respectively. Comparison of the nmr and infrared spectra of **3** and **4** and the known *cis*-bicyclo[4.1.0]heptan-*cis*- and -*trans*-2-ols[25] (**16** and **17**) indicated that the compounds were not the same. The presence of the complex multiplets in the nmr spectrum of **3** at δ (CCl_4) -0.5 ppm and for **4** at 0.2 ppm clearly indicated the presence of cyclopropyl in **3** and **4**. On the basis of the chemical shifts of **16** and **17** and the possible conformations for **3** and **4** one can tentatively assign the structure of the two alcohols as *trans*-bicyclo[4.1.0]heptan-*trans*-2-ol for **3** and *trans*-bicyclo[4.1.0]heptan-*cis*-2-ol for **4**.[14] The alcohols are not stable to glpc but can be purified by trap-to-trap distillation (54% yield). Acetates and other derivatives of **3** and **4** can be formed by standard methods without undue difficulty.



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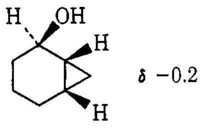

17

We are examining the reaction of the ketone **2**, the alcohols **3** and **4**, and the derivatives of **3** and **4** to determine the reactivity of *trans*-bicyclo[4.1.0]heptanes. We have also synthesized by similar methods *cis*- and *trans*-bicyclo[5.1.0]octanes and *cis*- and *trans*-bicyclo[6.1.0]nonanes and are examining their reactivity toward a variety of reagents.

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[22] G. Buchi, W. Hofheiz, and J. V. Paukstelis, *J. Amer. Chem. Soc.*, **91**, 6473 (1969).

[23] M. Nussim and Y. Mazur, *Tetrahedron*, **24**, 5337 (1968), and references therein.

[24] D. Redmore and C. D. Gutsche, *Advan. Alicycl. Chem.*, **3**, 1 (1971), and references therein.

[25] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963).

[26] The mass spectral analysis indicated 67% *O-d*, 17% *1-d*, 14% *2-d*, and 2% *3-d*.

New Anionic Rearrangements. XVI. 1,2-Anionic Rearrangement from Sulfur to Carbon in Benzylthiotrimethylsilane[1–3]

Sir:

Many organic ethers may be converted to isomeric alcohols in the presence of excess organolithium reagent by the classical Wittig rearrangement.[4] The analogous rearrangement of organic sulfides to mercaptans has not previously been observed.[5] Generally, metalation of the rather acidic proton α to sulfur in sulfides,[6] sulfoxides,[10] and sulfones[11] produces stable carbanions which do not rearrange.

We now find that benzylthiotrimethylsilane (**1**) rearranges rapidly and in high yield[12,14] to α-trimethylsilylbenzylmercaptan (**2**) in the presence of excess *tert*-butyllithium.[17] This is apparently the first example

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[1] Previous paper in this series: R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, in press.

[2] For a review of silylanionic rearrangements see R. West, *Pure Appl. Chem.*, **19**, 291 (1969).

[3] Research sponsored by Air Force Office of Scientific Research (SRC)-O.A.R., USAF, Grant No. AF-AFOSR 70-1904.

[4] (a) G. Wittig and L. Löhmann, *Justus Liebigs Ann. Chem.*, **550**, 260 (1942); (b) D. L. Dalrymple, T. L. Kruger, and W. N. White in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, New York, N. Y., 1967, p 617; (c) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

[5] A Wittig-like mechanism has been used to explain the formation of stilbene from benzyl sulfide and strong base. See T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1271 (1965).

[6] For example: CH_3SCH_2Li;[7] $PhSCH_2Li$;[8] lithiated 1,3-dithianes.[9]

[7] D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967).

[8] H. Gilman and F. J. Webb, *J. Amer. Chem. Soc.*, **71**, 4062 (1949).

[9] E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075 (1965).

[10] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

[11] B. S. Thyagarajan, *Mech. React. Sulfur Compounds*, **4**, 115 (1969).

[12] Recently we reported the almost quantitative Wittig-type rearrangement of triethylbenzyloxysilane to phenyltriethylsilylcarbinol in the presence of excess *tert*-butyllithium.[13]

[13] R. West, R. Lowe, H. F. Stewart, and A. Wright, *J. Amer. Chem. Soc.*, **93**, 282 (1971).

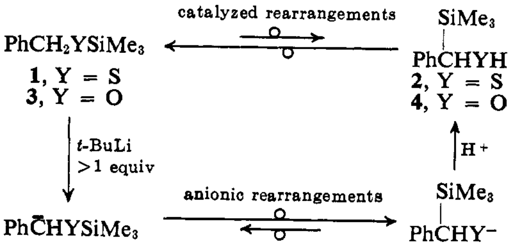
[14] The migratory aptitude of silicon in 1,2 anionic rearrangements is remarkable.[2,13] When carbon migrates, as in the Wittig rearrangement, a simple 1,2 sigmatropic suprafacial shift is disallowed by the Woodward–Hoffmann rules[4c,15] with the result that rearrangements proceed slowly, often in low yield, and apparently by a cleavage–recombination mechanism. Silicon probably migrates *via* a pentacoordinate transition state without the above symmetry restrictions.[16]

[15] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

[16] A. G. Brook, G. E. LeGrow, and D. M. MacRae, *Can. J. Chem.*, **45**, 239 (1967).

[17] The remote rearrangement $LiC_6H_4SSiMe_3 \rightarrow Me_3SiC_6H_4SLi$ has been reported: see A. R. Bassindale and D. R. M. Walton, *J. Organometal. Chem.*, **25**, 389 (1970).

of a Wittig-type rearrangement involving migration from sulfur to negatively charged carbon. **2** undergoes quantitative rearrangement back to **1** in the presence of a radical catalyst, or upon heating, but not in the presence of catalytic amounts of base. In these respects **2** differs sharply from phenyltrimethylsilylcarbinol (**4**) which rearranges to the alkoxysilane **3** thermally only in poor yield and at high temperature, but undergoes the rapid Brook rearrangement[16] to **3** in the presence of catalytic quantities of base.



1, bp 130° (14 Torr), $n^{20}D$ 1.5305, was prepared in 86% yield by silylating benzylmercaptan with excess hexamethyldisilazane in refluxing toluene. *tert*-Butyllithium (0.33 mol; 1.24 *M* in pentane) was added to 59.0 g (0.30 mol) of **1** in 266 ml of dry tetrahydrofuran at −78°. A homogeneous solution resulted, showing in its pmr spectrum only one trimethylsilyl resonance and the removal of one benzylic proton. A peak at τ 12.15, corresponding to the $SiCH_2Li$ moiety,[18] indicated 10% metalation of the trimethylsilyl group (*vide infra*).

The anion solution was warmed to −22° and 150 ml of 2.2 *M* aqueous $MgCl_2$ was injected into the agitated solution. The mixture was warmed to 25°, the organic layer separated from the aqueous layer, and solvent evaporated. Vacuum distillation yielded 53 g of a clear oil which contained 0.4% $PhCH_2SH$ and 99.6% **2**. **2** was obtained almost quantitatively even if the anion, once formed, was heated to 180° followed by protonation at 100°.

Structure **2** was assigned from the proton nmr (CCl_4, C_6H_{12}) which showed a singlet at τ 9.96 ($SiMe_3$), a doublet at 8.38 (SH), a doublet at 6.73 (CH), and a singlet at 2.86 (C_6H_5), with relative intensities 9.0:1.0:1.0:5.2. The ir spectrum (neat) shows a weak SH stretch at 2570 cm^{-1}.

The rearrangement was repeated with the anionic species being trapped in turn with methyl iodide, dimethyl sulfate, and triethylchlorosilane by injecting the derivatizing agent into samples of anion at −78°. The resulting solutions were evaporated of solvent, totally distilled under vacuum, and separated into individual compounds by preparative glc. That both methylations occurred only at sulfur rather than at the carbon is proven unequivocally by the nmr which shows a single methyl resonance at τ 8.15 in the isolated product. Silylation also occurred at sulfur since acid hydrolysis of this product gave only hexaethyldisiloxane and **2**. Minor products arise from cleavage of **1** by *tert*-butyllithium and trapping of $PhCH(SiMe_2CH_2Li)SLi$, the species responsible for the high-field resonance in the anion nmr. No **1** was recovered, even when methyl iodide injection followed *tert*-butyllithium addition by as little as 10 sec (see Table I).

Table I. Products from Derivatization of Anion of **1**, %

	Trapping agent			
	H_2O	CH_3I	Me_2SO_4	Et_3SiCl
	R =			
	H	CH_3	CH_3	Et_3Si
$PhCHRSSiMe_3$	0	0	0	0
$PhCH(SiMe_3)SR$	89.9	93.2	94.3	90.4
$PhCH(SiMe_2CH_2R)SR$	9.7	6.7	4.1	9.6
$PhCH_2SR$	0.4	0.1	1.6	0

The rearrangement of **3** to **4** under the above conditions occurs rapidly in 95% yield at −78°, 79% at 0°,[19] with the interesting difference that the alkylating derivatizing agents trap metalated **3** predominantly in the *unrearranged* form as $PhCHMeOSiMe_3$.

Pitt has reported the radical-catalyzed quantitative 1,2 migration of the trimethylsilyl group from silicon to sulfur in $(Me_3Si)_2Si(SH)Me$.[20] We now report the first example of a radical-catalyzed 1,2 migration of a trimethylsilyl group from carbon to sulfur. Thus 250 mg of **2** heated to 100° in heptane in the presence of 17 mg of azobisisobutyronitrile yielded 92% **1** and 8% recovered **2** after 37 min. Negligible rearrangement of **2** to **1** occurred in the absence of the radical initiator, or in the presence of the nonradical products of previously decomposed initiator.

Heating **2** to 195° neat for 30 min gave quantitative first-order thermal rearrangement to **1**, $k = 0.97 \times 10^{-3}$ sec^{-1}. In contrast, **4** rearranged to **3** only at 275° and then slowly with formation of several side products. However, **4** *does* undergo the silyl anti-Wittig rearrangement[15] in tetrahydrofuran–pentane solution to give **3** in 85–90% yield, when treated 3 min with 0.085 equiv of liquid sodium–potassium alloy at 0°, or when treated 25 hr with 0.10 equiv of *n*-butyllithium at 25°. The alloy is not observed to be consumed nor is hydrogen evolved. **1** and **3** are thus clearly the thermodynamically favored products, formed when the *neutral* species are equilibrated.

Curiously **2** does not rearrange to **1**, nor **1** to **2**, either in the presence of sodium–potassium alloy or under any other conditions commonly used in the catalytic silyl anti-Wittig rearrangement. Sodium–potassium alloy rapidly liberates hydrogen from **2**. The thermal rearrangement of **2** to **1** is accelerated only slightly at 195° in the presence of small amounts of base.

The 1,2 sulfur–carbon silylanionic rearrangement should have considerable synthetic utility in generating carbon-functional organosilanes as exemplified by the rearrangement of sulfide **5** to mercaptan **6**.

$$\underset{\mathbf{5}}{CH_3SSiMe_2\text{-}t\text{-}Bu} \xrightarrow[2.\ H^+]{1.\ t\text{-BuLi}} \underset{\mathbf{6}}{t\text{-}BuMe_2SiCH_2SH}$$

5 treated with excess *tert*-butyllithium in 1:1 tetrahydrofuran–pentane solution for 16 hr at −45°, followed by aqueous protonation, yielded **6**, 35%, and recovered **5**, 65%. **6** was isolated by preparative glc and identified by 100-MHz pmr and mass spectroscopy.

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